

# Passive In-situ Remediation of Acidic Mine / Industrial Drainage (PIRAMID)

A Research Project of the European Commission Fifth Framework Programme  
(Key Action 1: Sustainable Management and Quality of Water)  
Contract Number EVK1-CT-1999-000021

## FINAL REPORT

\* PUBLIC EDITION \*

"The past ...



mine water pollution

... we inherit ...



remediation

passive in situ

... the future ...



... we build"

June 2003

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## Executive Summary

<b>Contract No.</b>	EVK1-CT1999-00021	<b>Reporting Period</b>	3 years to 3/03
<b>Title</b>	Passive In Situ Remediation of Acidic Mine/ Industrial Drainage (PIRAMID)		
<p><b>Objectives:</b> The aim of the PIRAMID project was to achieve the following:</p> <ul style="list-style-type: none"> <li>- Completion of a database of existing passive <i>in-situ</i> remediation (PIR) systems for acidic / ferruginous mine waters in Europe (freely available for download at <a href="http://www.piramid.org">www.piramid.org</a>) (WP1)</li> <li>- Develop process-based models of PIR systems (WP2)</li> <li>- Evaluate PIR applicability for countries in central and eastern Europe which were lacking the technology in 1999 (WP3)</li> <li>- Experimentally evaluate, in the field and the lab, novel reactive substrates for PIR systems (WP4)</li> <li>- To produce and disseminate engineering guidelines for the future design, construction and operation of PIR systems (WP5)</li> </ul> <p><b>Scientific achievements:</b> The scientific research completed as part of the PIRAMID project has been extremely successful, producing an abundance of information which provide many possibilities for the application of passive in-situ remediation to a wide range of pollution problems. In particular:</p> <ul style="list-style-type: none"> <li>- the critical importance of macrophytes in achieving low residual Fe concentrations in aerobic wetland systems was demonstrated, together with fundamental insights into the effects of elevated proton and metal activities on wetland plant growth</li> <li>- low-cost substrates for treatment of acidic waters have been investigated (including synthetic zeolites made from PFA, caustic magnesia, and organic matter promoting dissimilatory bacterial sulphate reduction, in particular green waste composts and farmyard manures)</li> <li>- the use of oxidative and reductive systems for the treatment of arsenic-rich mine drainage has been investigated, with the kinetics of oxidative systems proving the more favourable of the two; arsenic-oxidising bacteria have been identified and isolated</li> <li>- the safe, passive destruction of residual cyanide leaching from gold mine tailings has been achieved using compost-based wetland-type passive systems (which also remove residual copper), thus complementing active cyanide-destruction techniques used while the mine remains operational</li> <li>- detailed field investigations of: (i) conventional wetland-type passive systems in the UK, France and Slovenia, removing Fe, As and U respectively from diverse mine waters (ii) a conventional permeable reactive barrier (PRB) within an aquifer at Aznalcóllar (Spain), treating highly acidic groundwaters associated with a base metal mine, and (iii) a novel, hybrid passive system at Shilbottle (UK) which intercepts extremely acidic colliery spoil leachates using a surficial PRB (with substrates including organic matter mixed with limestone and / or blast furnace slag, promoting inorganic and bacterial neutralisation processes), which releases its effluent into a series of oxidation ponds and aerobic wetlands downstream.</li> </ul> <p>Significant advances were also made in relation to natural and stimulated natural attenuation of acidity in mine pit lakes, and in the assessment of the sustainability of dry covers and water covers for tailings and waste rock piles, under both cold (sub-arctic) and warm (Mediterranean) climatic conditions.</p> <p>Modelling software has been developed allowing simulation of subsurface-flow passive treatment systems (RETRASO), wetland-type systems (NOAH2D) and the natural attenuation of mine water pollutants in flooded deep mines (RUMT3D).</p> <p>PIR was found to have considerable potential for application in many European countries, and offers potential solutions to pollution problems in most Newly-Associated States with significant past or present mining industries. Such developments, in these and other countries, will be greatly facilitated by the PIRAMID engineering guidelines.</p> <p><b>Socio-economic relevance and policy implications:</b> Working in partnership with another FP5 project (ERMITE; EVK1-CT-2000-00078) PIRAMID made significant contributions to the technical background invoked in drafting the June 2003 'Proposal for a Directive of The European Parliament and of the Council on the management of waste from the extractive industries' (COM(2003) 319 final; 2003/0107 (COD)). Through continued work with ERMITE, it is anticipated that the findings of PIRAMID will also make a significant contribution to the guidelines currently being prepared by the ERMITE project in relation to implementation of the Water Framework Directive (2000/60/EC) with respect to mining operations and abandoned mines.</p> <p><b>Conclusions:</b> The original objectives of PIRAMID have been successfully realised, providing a firm foundation for the further development and practical application of passive in-situ remediation technologies. PIRAMID has also led organically to the development of a network of scientific and engineering specialists with expertise in this form of remediation, which will have substantial positive implications for future training of technical specialists, and for integration of efforts across Europe in the remediation of contaminated mine sites.</p>			

## Foreword

This document is the public edition of the final report of the research and technological development project 'PIRAMID' (Passive In-situ Remediation of Acidic Mine / Industrial Drainage), which was funded under the European Commission's 5<sup>th</sup> Framework RTD Programme (contract number EVK1-CT-1999-000021), and which was active from March 2000 to February 2003.

This final report has been written by the entire PIRAMID Consortium, the leading members of whom are identified in the list of partner institutions below. Editing of the final report, and drafting of most of the sections involving narrative synthesis of results, was carried out jointly by Dr Lesley Batty and Professor Paul L Younger (the Coordinator of PIRAMID).

This report presents an overview of the key outcomes of PIRAMID. Details of individual experiments may be sought in the numerous publications of the project listed in the Appendix. (For copyright reasons, the interested reader is advised to seek copies of the individual papers through their library, as the PIRAMID Coordinator cannot supply copies of the papers directly).

The single most important outcome of PIRAMID are the 'Engineering Guidelines', the formal reference for which is as follows:

PIRAMID Consortium (2003) *Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters*. European Commission 5<sup>th</sup> Framework RTD Project no. EVK1-CT-1999-000021 "Passive in-situ remediation of acidic mine / industrial drainage" (PIRAMID). University of Newcastle Upon Tyne, Newcastle Upon Tyne UK. (ISBN 0-9543827-1-4). 166pp.

These guidelines may be down-loaded free of charge from the PIRAMID web-site ([www.piramid.org](http://www.piramid.org)); after the latter site ceases to function, they will remain available indefinitely (and with periodic updates) through [www.minewater.net](http://www.minewater.net).

Finally, although the funding provided by the European Commission is gratefully acknowledged, it is important to note that this report shall not be construed as representing the official policy or views of the European Commission, Parliament or Council.

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June 2003



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## 1. Background

Acidic drainage from mines and associated drainage is a major cause of ground and surface water pollution in the EU. A recent estimate suggests that as much as 4500km of European watercourses are currently polluted by contaminated drainage from abandoned mines (Younger 2002). The temporal evolution of the quality of mine site drainage is now known to typically follow a pattern in which the worst quality is encountered soon after recently-flooded underground workings first overspill to surface, followed by an initial improvement in water quality, the rate of which gradually reduces over time until a stable “asymptotic” level of pollution is reached, at which level the discharge will persist until mineral sources for the metals are finally depleted (Younger 1997, 2000a,c; Younger and Banwart 2002; Younger *et al.* 2002). Given the longevity of these problems therefore, the most sustainable solutions to ecological and socio-economic damage wrought by such discharges will be those which require a minimum of operating expenditure in the long-term, many decades after the industrial activity which gave rise to them has ceased. In many cases this will mean that water treatment will need to persist long after the economic viability of the mining companies themselves has ended. In theory, the key advantage of passive treatment over conventions (“active”) treatment is that the costs are concentrated into capital expenditure, rather than operating expenditure, so that concerns over long-term maintenance of treatment are minimised. In practice, a number of hurdles need to be overcome (such as the rates of consumption of substrate and of accumulation of solids within passive systems) before the technology will become an attractive option for the full range of polluted waters associated with the mining and metallurgical industries (past and present) in Europe. PIRAMID has addressed some of these ‘hurdles’ by means of focused internationally replicable experiments under lab and field conditions, coupled with innovative modelling. Some of the most promising technological developments in this context are the recent implementation of “passive treatment” systems, in which biogeochemical reactors (mostly configured as wetland systems) are placed in the path of the polluted drainage, which passes through them by gravity flow, undergoing a number of beneficial biogeochemical reactions. For acidic, metalliferous waters the most common reactions used in passive systems to date have been carbonate dissolution, dissimilatory bacterial sulphate reduction (with

concomitant precipitation of sulphides and/or hydroxide minerals which serve as sinks for the ecotoxic metals.

Developments in this field up to 1993 took place entirely in the USA. Subsequently, substantial further development of the technology has taken place in the UK (Younger 2000a,b), where more than a dozen full-scale passive systems are now working at abandoned mine sites. UK researchers have assisted the spread of the technology into Spain. Passive treatment technology is not restricted in application to acidic metalliferous waters. For instance in the USA and Canada, hydrogeologists have developed passive systems for the in-situ, subsurface treatment of ground water contaminated by man-made organic compounds. These systems are generally termed “permeable reactive barriers”. In the context of organic contaminants most field applications to date have used zero-valent iron as the reactive medium, which serve to reduce the organics to simpler, hydrogenated molecules which can disperse harmlessly in the environment. The number of successful applications of permeable barrier technology to organic pollutants has now grown to the point that practical guidelines on their design, construction and monitoring have been published. A team of Canadian hydrogeologists with extensive experience in the use of this technology have extended the approach to the treatments (at field-scale) of acidic, metalliferous ground water recharged by leachate leaking through the base of a redundant mine tailings dam. The reactive barrier described by these workers was based on many of the same principles as mine water treatment wetlands, yet was apparently developed in isolation from the earlier experiences of treatment wetland researchers. One of the principal objectives of PIRAMID has been to collate experiences with a variety of passive systems, embracing both surface and subsurface in situ solutions.

## 2. Scientific/technological and socio-economic objectives

The main scientific and technical objectives of PIRAMID were to:

1. Assemble a European database of experiences with passive in situ remediation (PIR) of acidic mine/industrial drainage, covering both surface and subsurface PIR systems
2. Develop process based models of PIR system performance to support improvement of future designs
3. Critically evaluate the potential application of PIR in areas of Europe which still do not have the technology
4. Test in lab and field novel approaches to PIR, for other specific contaminants and using novel substrates
5. Develop engineering guidelines for PIR application at new sites throughout the EU.

Objectives 3 and 5, though technical in content, may also be considered to be 'socio-economic' objectives, in that they explicitly address the uptake of this technology, and of course the realisation of its socio-economic benefits, in various parts of Europe, with a particular emphasis on EU accession countries and potential future accession countries.

Furthermore, as the project unfolded, opportunities arose for the findings from PIRAMID to be used in support of the development of EU policy, particularly in relation to the development of a proposed directive on the management of wastes from the extractive industry. The outcomes of these endeavours are briefly summarised in Section 4 below.

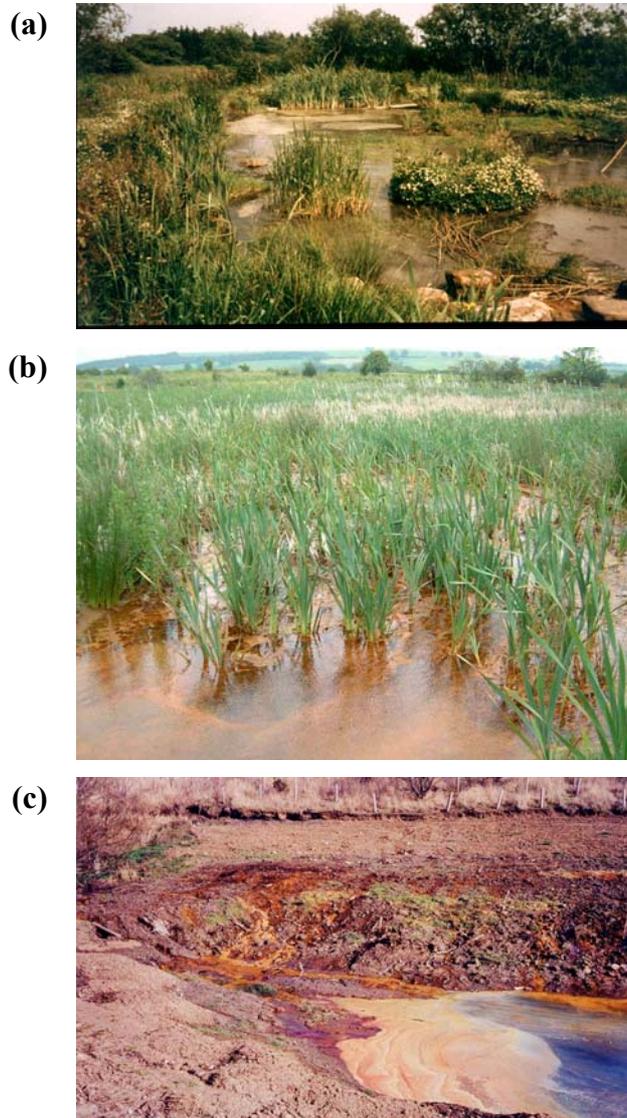
### **3. Applied methodology, scientific achievements and main deliverables**

#### **3.1. Applied methodology**

Within this overall framework more specific R&D methodology was developed within PIRAMID, most notably including:

- (i) A combination of field-based and lab-based studies, consciously spanning the 'scale-boundary' between these two typical levels of resolution in scientific research. Field investigations were undertaken on three types of field installation:
  - existing, full-scale passive systems, comprising several wetland-type treatment systems in the UK (Figure 1), several full-scale 'passive prevention' systems (dry covers and water covers) in Sweden, and a permeable reactive barrier (PRB) at Aznalcóllar in Spain (Figure 2)
  - naturally-occurring analogues of passive treatment systems, which had spontaneously developed as wetlands fed by mine waste leachates in Slovenia (uranium mine wastes at Žirovski vrh) and France (Pb-Zn wastes releasing acidic, As-rich leachates at Carnoulès)
  - purpose-built pilot passive systems in Sweden (a PRB at Adak), Spain (cyanide removal system at Rio Narcea Gold Mines; Figure 3) and France (for arsenic removal, at Carnoulès)
- (ii) The field and laboratory experiments were focused on the development and testing of low-cost reactive media suited to treatment of a variety of polluted waters using a wider variety of reaction mechanisms than had previously been tested. Bearing the 'sustainability' focus of the FP5 Work Programme in mind, a particular focus of this work was on exploring the potential use of waste streams from other industrial activities (e.g. caustic magnesia, PFA, blast furnace slag, farmyard manures etc) as the raw material for passive mine water treatment.

- (iii) Investigation of the applicability of existing and new passive treatment approaches to particularly challenging waters found on some mine sites, such as cyanide-rich leachates from gold mine tailings, arsenic-rich mine waters, and the radioactive waters associated with uranium mining/processing sites. The aim was to build upon previous theoretical and lab-scale work (and upon existing knowledge of the nature and extent of current and future uranium mine site effluents in southern and eastern Europe; e.g. Merkel *et al.* 2002) to develop a regulatorily-defensible strategy for the long-term deployment of passive systems in these challenging contexts.
- (iv) An assessment of the applicability of PIR in cold climates, drawing upon the experience and expertise associated with Sweden's MiMi research programme (MiMi 2002). Interaction with MiMi also afforded the opportunity to place passive *treatment* within the wider context of other measures (source control by means of dry covers / water covers, re-vegetation etc) which can be implemented at abandoned mine sites, thus fostering the development of a more integrated concept of passive *in-situ* remediation which embraces both treatment and prevention strategies (see Section 3.2 below).
- (v) Improved application of passive treatment concepts to groundwater systems, which requires the deployment of appropriate expertise in predicting and monitoring the permeability of the reactive media.
- (vi) The development of physico-chemically based models of passive system performance, which can aid in the interpretation of modelling data and used to anticipate changes in treatment efficiency.



**Figure 1. Full-scale passive treatment systems in north-east England used for PIRAMID field research. (a) compost wetland treating moderately acidic spoil leachate at Quaking Houses. (b) Aerobic reed-bed treating ferruginous overflow from abandoned underground coal workings at St Helen Auckland. (c) Part of the hybrid passive system at Shilbottle, comprising a surficial PRB (note seepage face) and oxidation ponds treating extremely acidic spoil leachates.**



**Figure 2. The Aznalcóllar Permeable Reactive Barrier (PRB), Spain, used as a major field study facility of PIRAMID. View looking east across the Río Agrio, along the long axis of the PRB. (Groundwater flows from left to right). The paired pipes in the centre of the picture are the casings of monitoring wells which access the interior of the barrier, and the other pipes visible at the left and right extremes of the field of view are up-gradient and down-gradient monitoring wells respectively.**



**Figure 3. The pilot system for passive destruction of cyanide at Río Narcea Gold Mines' El Valle Mine, Belmonte (Asturias, northern Spain), showing aeration cascade leading towards two parallel treatment streams, each comprising a compost wetland cell followed by an aerobic cell.**

### 3.2. Scientific achievements

The scientific research completed as part of the PIRAMID project has been extremely successful, producing an abundance of information which provide many possibilities for the application of passive in-situ remediation to a wide range of pollution problems. Some of the key findings are summarised below; further details may be pursued in the detailed experimental report (Section 3 of this document) and in the main published papers arising from the project (see list in Section 6 below).

#### i. Behaviour and role of macrophytes in aerobic mine water treatment wetlands.

The single most exciting finding from this aspect of the research was that where dissolved Fe concentrations in wetland waters are at or below 1 mg/l, direct uptake of Fe by plants occurs to such an extent at a sufficiently-rapid rate that it can account for 100% of iron removal (Batty and Younger 2002). This finding explains why aerobic reed-beds remove dissolved Fe at far greater rates than would be anticipated on the basis of the first-order kinetics of Fe<sup>2+</sup> oxidation. It was also found that the same 1 mg/l Fe threshold was also an optimum for healthy growth of *Phragmites australis*: at much greater concentrations, the plants are not as productive, while at lower concentrations they will be healthy but still not quite as vigorous as those growing in water with about 1 mg/l Fe.

The unique opportunity afforded by the presence of two otherwise identical wetlands on one site, one of which receives acidic drainage while the other receives clean surface runoff, afforded an opportunity to come to some preliminary conclusions about the effects of acidity and elevated metal concentrations on plant growth and metal uptake. Vegetative analysis revealed unequivocal reductions in shoot height and seed development in plants growing in the acidic wetland. Calcium concentrations in the tissues of plants from the acidic wetland were also lower than those in the uncontaminated wetland, despite higher concentrations of Ca in the surface waters of the former, possibly due to inhibition of Ca uptake by competition from other cations (notably Fe and H<sup>+</sup>). N concentrations in plants from the acidic wetland were below those normally considered to be adequate for growth.

It is possible that this was also due to the interference of nitrate uptake by the elevated concentrations of cations in the surrounding waters, but it is also postulated that ammonium concentrations were low in waters flowing into the wetland and as this is the preferred source of nitrogen for wetland plants, supply of nitrogen was inadequate.

These results have important implications in the growth of plants in constructed wetlands receiving waters containing elevated concentrations of metals. The poor growth of plants in some constructed wetlands may be due to one or more of the causes that have been proposed here. In particular the application of wetlands to treat waters which contain very high concentrations of Fe is not recommended, albeit the plants do show remarkable resilience under stress. The nutrient status of the inflowing waters should also be considered. Mine waters usually contain very low levels of nutrients such as nitrate and phosphate and this may not be adequate or in the correct form which is suitable for the growth of wetland plants.

A commonly-voiced criticism of wetland treatment is the perceived risk of seasonal release of contaminants during the winter, when wetland macrophytes die back. This theoretical risk was investigated experimentally by means of mesocosm experiments on plant litter collected from long-established mine water treatment wetlands in the UK. It was found that metals were not released from the plant litter even where pH dropped markedly. Neither did the decomposition of the plant litter increase as pH dropped. In fact, Fe concentrations in the litter actually increased after 6 months of decomposition, an observation which was attributed to the adsorption of Fe from the mine water onto the plant litter. This has important positive implications for the cycling of Fe within treatment wetland environments. It also corroborates the findings of all field studies undertaken within PIRAMID, in which wetland-type passive treatment seasons were net-sinks for contaminants (including As and U) all year round. (It should nevertheless be noted that seasonal re-mobilisation of Zn is commonly observed in aerobic wetlands receiving significant dissolved Zn; e.g. Kalin 1998; Younger *et al.* 2002).

## ii. Testing of alternative, low-cost substrates for treatment of acidic waters.

A number of alternative substrates for use in PIR systems were tested as part of PIRAMID with variable results. Those substrates which showed promising results were as follows:

- (i) Caustic magnesia. A laboratory assessment of the dissolution of caustic magnesia (an inexpensive industrial by-product) in acid waters was undertaken, using packed columns analogous to typical porous-medium reactors which might be deployed in the field. It was found that a 7 cm column containing a mixture of caustic magnesia (>40 wt.%) and quartz was able to remove the entire pollutant metal content from a flux of  $0.06 \text{ mL}\cdot\text{s}^{-1}$  of polluted mine water over a period of at least 10 months. Up-scaling calculations suggest that a passive system with a 2 m layer of caustic magnesia normal to flow direction could treat field-scale fluxes of mine water for more than 2 decades (Cortina *et al.* 2003). Caustic magnesium is far more efficient than neutralisation by means of bacterial sulphate reduction, which means that much smaller systems can be built than would be necessary to achieve the same amount of treatment in a sulphate-reducing bioreactor (cf Younger *et al.* 2002, pp. 375 - 383). Caustic magnesium is also less soluble and longer-lasting than lime, and it is commonly available in a range of grain sizes resulting in permeable packed beds. Moreover, the pH resulting from magnesium oxide dissolution (8 to 10) is closer to natural values, and is more efficient in precipitating most metals than the pH resulting from lime dissolution (12).
- (ii) Iron hydr(oxide) precipitates for the removal of other metals and metalloids. Secondary iron-containing solid phases are formed by oxidation of ferrous iron present in mine waste leachates at rates that are strongly pH dependent. Copper and Zn are strongly associated with the fresh precipitates. Uptake experiments with field samples of secondary iron precipitates indicate strong pH dependence for metal uptake. The long-suspected role of such ferric hydroxides as 'scavengers' for other metals is confirmed, and is especially important as pH approaches neutral. Ferric

hydroxides phases were also found to be critical to the removal of As from solution (see below).

- (iii) A mixture of composted green waste, cow slurry screenings and limestone for the amelioration of metal contaminated water in a permeable reactive barrier. While bacterial sulfate reduction did not prove as important as anticipated within the Aznalcóllar PRB (Figure 2), in which carbonate dissolution tended to predominate, it was extremely vigorous in the PRB at Shilbottle (Figure 1a). The difference between the two systems is almost certainly down to differences in inoculum, i.e. the presence of cysts of viable sulfate reducing bacteria in the materials used in the two barriers. Extremely rapid establishment of sulfate reduction was found for the Shilbottle reactive substrate (see Amos and Younger 2003), and H<sub>2</sub>S gas is invariably detected evolving from pumped borehole waters during sampling at the latter site. PH is consistently raised from around 2.8 to 6 within the Shilbottle PRB, all within a lateral flow path of less than 2m. Subsequent release of the reduced water to an oxidation pond gives rise to very rapid removal of metals from solution by means of oxidative hydrolysis.
- (iv) Organic wastes and natural rock material as sorptive substrates for U removal from mine waters. Laboratory batch tests showed a clear uranium absorbing capacity of all the tested sediments from natural wetlands which have developed around an abandoned uranium mine in Slovenia. The results show that, with an adequate wetland sediment, almost total clean-up of the uranium rich mine water can be achieved. The observed U<sub>3</sub>O<sub>8</sub> retention capacities of tested natural wetland sediments were in the range 1.4 - 63.5 µg U<sub>3</sub>O<sub>8</sub> per gram of material, with the highest values being displayed by a zeolitic tuff.

### iii. Passive removal options for arsenic-rich mine drainage.

Both compost-based (anaerobic) and aerobic options were investigated at the Carnoulès site in southern France, where extremely acidic, As-rich mine waste leachates severely contaminate the Reigous Creek. Although the experiments on the anaerobic system were curtailed prematurely due to a freak storm which caused extensive damage in the catchment, the findings of the experiments tended to favour the kinetics of the aerobic

option for full-scale passive system development (Casiot *et al.* 2003). Removal of As occurs by precipitation of various ferric arsenate compounds (Morin *et al.* 2003), forming vivid orange ochres with high As contents. Removal rates for As in the Carnoulès system were similar to those reported for Fe in aerobic wetlands receiving net-alkaline mine waters elsewhere, i.e. exceeding 10 g As/d/m<sup>2</sup> (cf. Younger *et al.* 2002, p.356).

As anticipated, bacterial catalysis proved to play a key role in the effective removal of As from contaminated mine waters. Investigations at Carnoulès revealed the existence of strains of the bacterial genus *Thiomonas* which specifically catalyse the oxidation of As(III) to As(V), thus promoting the formation of amorphous As(V) ferric hydroxides (Morin *et al.* 2003). Further studies of these bacteria might in future lead to more efficient design of bioreactors for As treatment.

#### iv. Passive destruction of residual cyanide in leachates of gold mine tailings.

While photolysis and volatilisation of cyanide compounds are well-established 'passive' means of removing cyanide from gold mine processing effluents, both processes are temperature- (and thus weather-) dependent. For mines situated in cooler, cloudier parts of the world alternative processes may well be necessary to achieve sufficiently low residual cyanide concentrations. While proprietary cyanide destruction processes are convenient to use during the life of the mine, less intensive means are desirable for the post-closure period. In this context various options have been explored in the laboratory and the field (see Figure 3), and it is concluded that one of the most appropriate options (in terms of minimising exposure risks etc) is the reductive hydrolysis of cyanide to formic acid and ammonium formate, which can be achieved in compost-based bioreactors similar to those used for the treatment of acidic drainage. Experiments to date suggest that WAD removal in such systems can be expected to average around 10.6 mg/m<sup>3</sup>/d, which equates to an area-adjusted removal rate of 4.2 g/m<sup>2</sup>/d for a substrate 0.5m in depth. This loading value may be a conservative starting point for the design of full-scale systems. Site-specific pilot testing is nevertheless advisable until a sufficiently large number of such systems exists to allow confident adoption of design cyanide removal rate values.

## v. Characterisation of field-scale PIR system performance.

Detailed investigations have been made a number of full-scale passive systems (and systems in which natural attenuation is occurring), including:

- (i) conventional wetland-type passive systems in the UK (removing Fe and acidity), France (As removal, see above) and Slovenia (U removal).
- (ii) conventional permeable reactive barriers (PRBs), one within an aquifer at Aznalcóllar (Spain) (Figure 2), the other in shallow soil at the Adak mine site in Sweden
- (iii) a novel, hybrid passive system at Shilbottle (UK) (Figure 3) treating the UK's most severely-polluted colliery spoil leachates.
- (iv) Natural attenuation in two mine pit lakes, and stimulated *in situ* attenuation using suspended bioreactors in two other pit lakes, all in Sweden
- (v) The well-established dry cover on the tailings at Adak mine in Sweden.

Arising from the detailed assessments of (i) through (iii) above (plus an exhaustive review of all available literature; Younger *et al.* 2002) a compilation has been made of area-adjusted removal rates in wetland-type passive treatment systems for a wide range of contaminants (Table 1). This table provides the basis for some of the recommendations in the PIRAMID engineering guidelines (PIRAMID Consortium 2003; see also Younger *et al.* 2002), and will also provide a starting point for future studies aiming to improve the certainty of these current estimates.

**Table 1. Summary of tentative areally-adjusted removal rates for some of the less common mine water contaminants in conventional, wetland-type passive systems, according to PIRAMID findings and re-interpretation of existing published data<sup>a</sup>.**

Pollutant	Type of system	Areally-adjusted removal rate (g/d/m <sup>2</sup> )	Comments
As	Aerobic reed-bed	18	Bacterially-catalysed under acidic conditions; value derived from PIRAMID Carnoulès data-set
Cd	Compost wetland	0.02	Cadmium can be immobilised as a sulphide (greenockite; CdS) within the anoxic substrate.
CN <sup>-</sup> (WAD)	Compost wetland	4	Preliminary result from PIRAMID studies in Asturias (Spain)
Cu	Aerobic reed-bed dominated by <i>Phragmites</i>	0.05	Value from a non-engineered wetland in which flow was not well-constrained; areas used to calculate removal rates likely over-estimated so that this is a minimum value.
Cu	Compost wetland	10	Cu removal likely to be as a carbonate phase, formed by reaction with CO <sub>2</sub> released by microbial respiration.
Mn	Aerobic reed-bed <sup>b</sup>	0.5	Higher rates achievable in warm climates with algal growth
Ni	Aerobic reed-bed	0.04	Preliminary findings.
Ni	Compost wetland	2	Nickel can be immobilised as a sulphide (millerite; NiS) within the anoxic substrate.
U	Aerobic reed-bed	0.1	Single value from PIRAMID study of volunteer wetland at Boršt (Slovenia)
Zn	Aerobic reed-bed dominated by <i>Phragmites</i> <sup>b</sup>	0.04	Subject to substantial seasonal fluctuations; remobilised from wetland on occasions during winter.
Zn	Aerobic reed-bed with floating algal mats <sup>b</sup>	7	Removal varies seasonally and will only be as high as indicated during the growing season; it may be negative in the winter.

<sup>a</sup> For literature sources and further discussion see PIRAMID Consortium (2003).

<sup>b</sup> emerging subsurface flow reactors provide much higher rates of removal.

In relation to natural attenuation in pit lakes ((iv) above), a study of two Swedish pit lakes found that one (Ravlidmyran pit lake) is permanently stratified and meromictic, while the other (Udden pit lake) is dimictic and overturns every spring and autumn. Due to the well-oxygenated water column in the Udden lake, sulfate reduction did not seem to occur. Trace metals appeared to be removed from the water column through adsorption and/or co-precipitation with newly formed Fe oxyhydroxides rather than by sulfate reduction and sulfide formation. Although the water column in the Ravlidmyran lake was more or less anoxic below the chemocline, geochemical modelling indicates that sulfate reduction and sulfide formation is not occurring there either, presumably due to the lack of a suitable carbon source and/or a lack of suitable attachment sites for sessile bacteria.

Four small-scale passive in-situ remediation test cells (each with a reactive zone of 0.15 m<sup>3</sup>) were suspended in the water columns of two pit lakes in order to study possible treatment by bacterial sulphate reduction. The reactors contained reactive substrates of two types: (a) a mixture of peat/compost/sewage sludge intended to promote bacterial sulfate reduction, and (b) zero-valent iron scrap, intended to promote vigorous reduction (with reductive removal of dissolved arsenic as the target). The reactors in one of the pit lakes (Adak) failed to yield any response indicative of remedial reactions within the test cell. However, the reactors in the Lindsköld pit-lake gave more promising results, with both of them consuming oxygen, and the reactor containing organic matter also showing an internal rise in pH (consistent with sulfate reduction).

Lysimetric studies were made of the dry (soil) cover at the Adak mine site in Sweden ((v) above). This cover was installed to prevent future weathering of about 6 million tonnes of sulfidic tailings. The cover comprises a basal layer of 0.5 m of compacted clay-rich till, overlain by 1.5 m of till of unspecified properties, upon which grass has been established. The site study concluded that the soil cover at Adak does give a significant reduction of the ingress of oxygen into the tailings under the climatic conditions normally expected. However, the measurements also show a significantly increased oxygen exposure during dry periods, demonstrating the need for caution where such covers are used in regions with long dry seasons.

vi. Modelling of PIR systems, and of pollutant release / natural attenuation in flooded uranium mine workings.

Modelling software has been developed allowing simulation of subsurface-flow passive treatment systems (RETRASO), wetland-type systems (NOAH2D) and the natural attenuation of mine water pollutants in flooded deep mines (RUMT3D).

NOAH2D simulates overland flow and solute transport through reed-beds, allowing for frictional resistance to flow offered by wetland vegetation, and also allows for exchange with (and hyporheic flow within) permeable wetland bed sediments. Geochemical capabilities are as yet limited to calls of RETRASO for bed sediment simulations, coupled to simpler mass-balance modelling of non-conservative transport within the overland flow domain. RETRASO has been successfully used to model reactive transport through PRBs in addition to wetland bed sediments. RUMT3D couples the porous-medium flow model MODFLOW to a pipe-flow simulation (representing major mine roadways etc), with reactions being handled by calls to PHREEQC, and transport modelled using MT3D.

As will be readily appreciated from the above summary descriptions, these three codes are research tools rather than software directly applicable to real-world problems. As such they produced very interesting results, indicating modal forms of solute transport and dominating geochemical reactions meriting further investigation. However, the complexity of these codes is such that they require very long run-times, and their full potential is only likely to be released at some point in the future when the speed of central processing units has increased still further.

### **3.3. Main deliverables**

Altogether, PIRAMID was predicated on the production of 10 deliverables. Some of these were essentially administrative (reports to the Commission) and some were working documents for use within the consortium. Of more interest to readers who were not intimately involved in the work are the major, publicly-available deliverables, of which there are essentially four of paramount importance:



(i) The PIRAMID database. This database had the ambition of collating and summarising all prior European experiences with the passive *in situ* remediation of polluted mine waters, and this was delivered in month 11 of the project (with annual updates thereafter) in the form of an MS-ACCESS database with details for some 59 systems. The reason for the early deadline for this deliverable was that the information provided by the database was to directly inform later work packages (in particular WP2 and WP4). A data collation template was prepared to facilitate the collection of data on existing treatment systems which included aerobic wetlands, SAPS, compost wetlands and permeable reactive barriers. Although most of the engineering details connected to each site were not generally amenable to database storage, plans of the systems were included where possible to facilitate the interpretation of data. The resulting file was then uploaded onto the PIRAMID website where it was (and continues to be) freely available to all users. Last updated in 2002, as the number of PIR systems in Europe is now increasingly rapidly, it is probably already too late to consider maintaining a comprehensive database covering all known systems. That this should be the case is in part a vindication of the disseminatory role of PIRAMID.

(ii) An extensive evaluation of the potential applicability of PIR in major mining fields of Europe. This involved a review of available literature and local knowledge regarding major mining areas in 20 countries, most of which are located in Eastern Europe. (The review excluded UK, Sweden and Spain, which already hosted the vast majority of PIR systems in Europe at the outset of the project). This reconnaissance phase was successfully completed and has identified many sites within Europe that have considerable PIR application potential in the future. It is envisaged that increased scientific understanding of PIR systems will facilitate and encourage the future uptake of PIR in these areas.

(iii) Experimental results. As described in Sections 3.1 and 3.2 above, much of the practical work in PIRAMID concerned laboratory and field investigations of processes responsible for passive remediation, as well as the nature and utility of potential novel reactive substrates for such systems. Section 3 of this report essentially comprises the finalised version of the experimental data report, which was first collated in full in December 2002 and updated slightly for this report. It is intended to make Section 3 of this report available in future on request to collaborating researchers.

(iv) Engineering guidelines. The results from the experimental work were combined with insights of experienced remediation engineers (principally at IMC Consulting Engineers Ltd and at the University of Newcastle) to produce practical guidelines for the effective engineering design and construction of PIR systems for acidic / metalliferous drainage. The guidelines are intended to provide practitioners who already possess some knowledge of mine water pollution and civil engineering with specific guidance on what approaches are most likely to be effective in developing remediation feasibility studies and outline designs for treatments scheme. Of course they cannot replace the deployment of specific engineering expertise, but they certainly will help the newcomer to the field to identify what kinds of help they will need. The guidelines are to be made freely available from [www.piramid.org](http://www.piramid.org) for all interested users to download.

## 4. Conclusions

### 4.1 *Scientific conclusions*

The scientific research completed as part of the PIRAMID project has been extremely successful, producing an abundance of information which provide many possibilities for the application of passive in-situ remediation to a wide range of pollution problems. In particular:

- ❖ the critical importance of macrophytes in achieving low residual Fe concentrations in aerobic wetland systems was demonstrated, together with fundamental insights into the effects of elevated proton and metal activities on wetland plant growth
- ❖ low-cost substrates for treatment of acidic waters have been investigated (including synthetic zeolites made from PFA, caustic magnesia, and organic matter promoting dissimilatory bacterial sulphate reduction, in particular green waste composts and farmyard manures)
- ❖ the use of oxidative and reductive systems for the treatment of arsenic-rich mine drainage has been investigated, with the kinetics of oxidative systems proving the more favourable of the two; arsenic-oxidising bacteria have been identified and isolated
- ❖ the safe, passive destruction of residual cyanide leaching from gold mine tailings has been achieved using compost-based wetland-type passive systems (which also remove

residual copper), thus complementing active cyanide-destruction techniques used while the mine remains operational

- ❖ detailed field investigations of: (i) conventional wetland-type passive systems in the UK, France and Slovenia, removing Fe, As and U respectively from diverse mine waters (ii) a conventional permeable reactive barrier (PRB) within an aquifer at Aznalcóllar (Spain), treating highly acidic groundwaters associated with a base metal mine, and (iii) a novel, hybrid passive system at Shilbottle (UK) which intercepts extremely acidic colliery spoil leachates using a surficial PRB (with substrates including organic matter mixed with limestone and / or blast furnace slag, promoting inorganic and bacterial neutralisation processes), which releases its effluent into a series of oxidation ponds and aerobic wetlands downstream.

Significant advances were also made in relation to natural and stimulated natural attenuation of acidity in mine pit lakes, and in the assessment of the sustainability of dry covers and water covers for tailings and waste rock piles, under both cold (sub-arctic) and warm (Mediterranean) climatic conditions.

Modelling software has been developed allowing simulation of subsurface-flow passive treatment systems (RETRASO), wetland-type systems (NOAH2D) and the natural attenuation of mine water pollutants in flooded deep mines (RUMT3D).

PIR was found to have considerable potential for application in many European countries, and offers potential solutions to pollution problems in most Newly-Associated States with significant past or present mining industries. Such developments, in these and other countries, will be greatly facilitated by the PIRAMID engineering guidelines.

#### **4.2 Socio-economic relevance**

As was mentioned in the introduction to this report (section 1 above) it is estimated that around 4500km of European watercourses are currently polluted by polluted drainage from abandoned mines. As the coal industry contracts further, most notably following recent coalfield closures in France, and projected coalfield closures over the next few decades in

Spain, Germany (with further closures in the more distant future in Poland, Romania and other countries), the total length of European watercourses affected by this form of pollution will certainly increase, and may eventually approach a grand total of around 10,000km.

Water pollution by abandoned mine discharges is a severe form of freshwater pollution. Although much of the literature focuses on 'acid mine drainage', it is important to realise that many alkaline coal mine water discharges are still sufficiently rich in iron to be highly contaminating. Indeed, biological studies have revealed that the damage caused to benthic invertebrate faunas by alkaline, ferruginous discharges is generally as severe as that caused by acidic mine water discharges. This is because the smothering of the benthos with iron hydroxide precipitates prevents photosynthesis, and therefore locally removes the foundations of the trophic web (i.e. the 'food chain').

PIRAMID has demonstrated the reliability of existing measures to passively counteract these problems. While 'passive prevention' certainly has an important role to play in relation to spoil heaps and redundant tailings dams, for large systems of underground mines typical of many European countries passive treatment will undoubtedly be the most important technology. PIRAMID has substantially extended the repertoire of passive treatment, allowing fairly confident design of low-cost, low-maintenance wetland-type systems to deal not only with Fe and acidity, but also with arsenic, cyanide and uranium. The socio-economic relevance of PIRAMID is thus extremely high in relation to this major form of post-industrial pollution.

PIRAMID has also demonstrated the feasibility of PRB treatment for shallow groundwater systems (<10m deep). However, the geology of Europe's major coalfields is such that *in situ* technologies capable of working to much greater depths may well be needed. For although most documented instances of aquatic pollution from abandoned mines relate to surface waters, it is important to realise that polluted mine waters can also migrate into adjoining, fresh water aquifers, jeopardising their utility as water resources. Examples of aquifer pollution by migration of mine water from abandoned coal mines are surprisingly sparse in the literature, probably due to a lack of open investigation. One of the few

documented examples comes from the southern Durham Coalfield of the UK (Younger 2002), where rebound of mine waters between 1975 and 1983 gave rise to a very extensive plume of SO<sub>4</sub>-contaminated water in the overlying public supply aquifer (Permian sandstones and dolomites) (Younger 2002). Twenty years later this plume is now poised to pollute public supply wells used to supply a large town. Similar eventualities will no doubt arise in future in areas of France, Germany, Belgium and the Netherlands where extensive bedrock aquifers overlie now-abandoned coalfields. Existing PRB technologies are neither capable of yielding wholesale removal of SO<sub>4</sub> to below the drinking water limit (250 mg/l), nor of being implemented in hard rock aquifers such as that in Durham, where it would be necessary to intercept waters at depths of up to 200m. At present, pump-and-treat solutions are the only intervention option available for such circumstances. There is clearly scope for further R&D on these and related issues.

### **4.3. Strategic aspects**

PIRAMID has led organically to the development of a network of scientific and engineering specialists with expertise in this form of remediation, which will have substantial positive implications for future training of technical specialists, and for integration of efforts across Europe in the remediation of contaminated mine sites. To bolster this organic development, it is important to take steps to ensure the formation of skilled professionals able to confidently apply the technology through design and construction. With this in mind, the PIRAMID Coordinator has developed a methodology for fostering the further training of European specialists able to take up this challenge. The Coordinator has formed a consortium with a number of site-owners and CL:AIRE (the UK's national 'clearing house' for dissemination of best practice in relation to contaminated site remediation) to establish a research facility called 'CoSTaR' (Coal mine Sites for Targeted Remediation Research), which comprises a 'constellation' of six established passive mine water remediation sites located in one small geographical area, which have been selected to provide at least one example of each of the principal types of passive systems currently used to treat polluted mine waters at numerous sites in North America and Europe. Three of the included systems were studied during PIRAMID, and benefit from the data generated during the project. Nowhere else in the world is such a complete array of passive treatment systems available within such a small geographical area.

CoSTaR provides an ideal platform for Use of the CoSTaR systems for user-specific research and training on passive *in situ* remediation technology for mine sites. About the application of this form of technology at full-scale. The European Commission has signalled its intention to provide around €470K over from 2004 - 2008 through its FP6 "Access to Research Infrastructure" programme to allow funded study periods by post-docs and established research professionals at the CoSTaR facilities. For the latest information on this initiative and the funding available, the interested reader is referred to the CoSTaR web-site:

<http://www.minewater.net/CoSTaR/CoSTaR.htm>

The Coordinator is also actively pursuing negotiations with INAP (the global 'international network on acid drainage prevention') concerning the establishment of a European corresponding association, based on the network established by PIRAMID and ERMITE, to act as a partner of INAP alongside Canada's MEND programme, the USA's ADTI programme and ACMER in Australia. In this manner the research initiated within PIRAMID will hopefully prove to have been the first step along a road leading to thorough integration of European initiatives with those originating in other industrialised continents.

#### **4.4. Policy implications**

Working in partnership with another FP5 project (ERMITE; EVK1-CT-2000-00078) PIRAMID has made substantial contributions to the technical background invoked in drafting the June 2003 'Proposal for a Directive of the European Parliament and of the Council on the management of waste from the extractive industries' (COM(2003) 319 final; 2003/0107 (COD)). Some of the background material to which PIRAMID contributed is summarised in the paper by Kroll *et al.* (2002). Beyond the life of PIRAMID, its findings will continue to be used by the participants in the ERMITE project as they continue to work with the Commission on the implementation of the Water Framework Directive (2000/60/EC) with respect to mining operations and abandoned mines.

## 5. Dissemination and exploitation of results

The PIRAMID website ([www.piramid.org](http://www.piramid.org)) has been the principal dissemination tool of the project, and has received almost 10,000 hits over the lifetime of the project. It is currently planned to maintain the site for at least another two years, after which PIRAMID deliverables will still be available for download via [www.minewater.net](http://www.minewater.net).

The user-friendly PIRAMID database is one of the most popular downloads from the PIRAMID web-site, though it is anticipated that the PIRAMID engineering guidelines will soon become even more popular after they are released via the site in summer 2003.

Beyond these core dissemination activities, PIRAMID has already been extraordinarily successful in publishing scientific papers in peer-reviewed international journals (see Appendix) with especially impressive success in relation to two journals with very high impact factors, i.e. *Environmental Science & Technology* and *Water Research*.

The detailed technological implementation plan produced for PIRAMID illustrates that further exploitation of the results of the project has already commenced, with enthusiastic uptake of the research findings by industrial collaborators, who have commissioned members of the PIRAMID consortium to help them develop pilot- and full-scale *in situ* remediation reactors in the UK, Spain, Sweden, France and Germany. The dissemination of the PIRAMID engineering guidelines is expected to increase the demand for this mode of converting new research results into practical applications.

## 6. Principal publications of the PIRAMID project

Amos, P.W., and Younger, P.L., 2003, Substrate characterisation for a subsurface reactive barrier to treat colliery spoil leachate. *Water Research* **37**: 108 - 120.

Batty, L.C. & Younger, P.L. 2002 Critical role of macrophytes in achieving low iron concentrations in mine water treatment wetlands. *Environmental Science and Technology* **36**: 3997-4002

Casiot, C., Morin, G., Bruneel, O., Personné, J.C., LeBlanc, M., Dusquesne, C., Bonnefoy, V. & Elbaz-Poulichet, F. 2003 Bacterial immobilisation and oxidation of arsenic in acid mine drainage (Carnoulés creek, France). Arsenic behaviour in the aqueous phase. *Water Research* (in press)

Cortina, J.L., Holtermann, I., de Pablo, J., Cama, J. & Ayora, C. 2003 Passive in-situ remediation of polluted water with caustic magnesia. *Environmental Science and Technology* (in press)

Kroll, A., Amezaga, J.M., Younger, P.L., and Wolkersdorfer, C., 2002, Regulation of mine waters in the European Union: the contribution of scientific research to policy development. *Mine Water and the Environment*, **21**: 193 - 200.

Moreno, N., Querol, X., Ayora, C., Fernandez-Pereira, C. & Janssen-Jurkovicova, M. 2001. Utilisation of zeolites synthesised from coal fly ash for the purification of acid mine waters. *Environmental Science and Technology* **35**: 3526-3524

Morin, G., Juillot, F., Casiot, C., LeBlanc, M., Ildefonse, P & Calas, G. 2003 Bacterial formation of tooeleite and mixed arsenic (V)/(II)-iron(III) gels in the Carnoulés AMD France. A combined XANES, XRD and SEM study. *Environmental Science and Technology* (in press)

PIRAMID Consortium (2003) *Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters*. University of Newcastle Upon Tyne, Newcastle Upon Tyne UK. (ISBN 0-9543827-1-4). 166pp.

Wolkersdorfer, C., and Younger, P.L., 2002. Passive Grubenwassereinigung als Alternative zu aktiven Systemen. *Grundwasser* **7**: 67 - 77.

Younger, P.L., 2002, Coalfield closure and the water environment in Europe. *Transactions of the Institution of Mining and Metallurgy (Section A: Mining Technology)*, **111**: A201 - A209.

Younger, P.L., Banwart, S.A. & Hedin, R.S. 2002 *Mine water: hydrology, pollution, remediation*. Kluwer Academic Publishers, Dordrecht (ISBN 1-4020-0137-1). 464pp.



## **Appendix: List of publications arising from the PIRAMID project**

Peer-reviewed articles

Authors	Date	Title	Journal	Reference
Alcolea A, Ayora C, Bernet O, Bolzicco J, Carrera J, Cortina JL, Coscera G, de Pablo J, Doménech C, Galache J, Gibert O, Knudby C, Mantecón R, Manzano M, Saaltink MW & Silgado A.	2001	Barrera geoquímica	Boletín Geológico y Minero	112, 229-256
Amos, P.W., and Younger, P.L.	2003	Substrate characterisation for a subsurface reactive barrier to treat colliery spoil leachate.	Water Research	37, pp. 108 - 120.
Ayora C, Baretino D, Doménech C, Fernández M, López-Pamo E, Olivella S, de Pablo J & Saaltink MW	2001	Meteorización de los lodos piriticos de Aznalcóllar	Boletín Geológico y Minero	112, 137-162
Ayora C, Bernet O, Bolzicco J, Carrera J, Cerón JC, Doménech C, Fernández M, Gómez P, Jaén M, Mantecón R, Manzano M, Martin-Machucha M, Mediavilla C, Navarrete P & Salvany JM	2001	Hidrogeología del valle del Guadamar y zonas colindantes. Funcionamiento del sistema acuifero.	Boletín Geológico y Minero	112, 69-92
Batty LC	2002	Wetland Plants-more than just a pretty face?	Proceedings of the National Conference: Mine Water Treatment: A Decade of Progress, Newcastle Uk 2002	
Batty LC	2003(in press)	Wetland plants-more than just a pretty face?	Journal of Land contamination and reclamation Sp Ed.	
Batty LC & Younger PL	2002	Critical Role of Macrophytes in Achieving Low Iron Concentrations in Mine Water Treatment Wetlands	Environmental Science and Technology	36, 3997-4002

Batty LC & Younger PL	2003 (in review)	Effects of external iron concentration upon seedling growth and uptake of Fe and phosphate by the common reed, <i>Phragmites australis</i> Trin. ex Steudel	Annals of Botany	
Batty LC & Younger PL	2003 (in review)	Use of waste materials in passive remediation of minewaters	Surveys in Geophysics	
Bolzicco J, Carrera J, Ayora C, Cerón JC, Fernández I	2001	Comportamiento y evolución de una barrera geoquímica experimental, Río Agrio, Aznalcollar, España.	En Ballester A. et al. (EDs.): "Investigación, gestión y recuperación de acuíferos contaminados", Murcia, Julio 2001.	
Bruneel O, Personne JC, Casiot C, LeBlanc M, Elbaz-Poulichet F, LeFleche A & Grimont PAD	2003 (in press)	<i>Thiomonas</i> sp. Mediated arsenic oxidation in acid mine drainage (Carnoulés Creek, France)	Journal of Applied Microbiology	
Cama J, Querol, X, Ayora C, Sanz E. & Ganor J.	2001	Dissolution of synthetic zeolites at low temperatures. Preliminary results	Water Rock Interaction WRI-10 (En R Cidu (Ed)), Vilaasimius, Italy	247-250
Carrera J, Ayora C, Bolzicco J, Alcolea A, Bernet O, Cortina JL, Coscera G, de Pablo J, Doménech C, Galache J, Gibert O, Knudby C, Mantecón R, Manzano M, Saaltink MW & Silgado A.	2001	Diseño, construcción y resultados preliminares de la barrera geoquímica de Aznalcóllar	Actas del VII Simposio de Hidrogeología, Murcia	281-289
Casiot C, Bruneel O, Bonheur G, Personne JC, LeBlanc M & Elbaz-Poulichet F	2003 (in review)	Arsenic oxidation and bioaccumulation by the acidophilic protozoa <i>Euglena mutabilis</i> in acid mine drainage (Carnoulés, France)	The Science of the Total Environment	
Casiot C, LeBlanc M, Bruneel O, Personne JC, Koffi K & Elbaz-Poulichet F	2003 (in review)	Origin of As-rich waters ( $10^1$ - $10^2$ mM As) in a tailings impoundment (Carnoulés, France)	Applied Geochemistry	
Casiot C, Morin G, Bruneel O, Personné JC,	2003 (in press)	Bacterial immobilisation and oxidation of arsenic in acid mine drainage (Carnoulés creek,	Water Research	

LeBlanc M, Dusquesne C, Bonnefoy V & Elbaz-Poulichet F		France). Arsenic behaviour in the aqueous phase		
Cortina JL, Holtermann I, de Pablo J, Cama J & Ayora C	2003 (in press)	Passive in-situ remediation of polluted water with caustic magnesia	Environmental Science and Technology	
Doménech C, de Pablo J & Ayora C	2002	Oxidative dissolution of pyrite from the Aznalcóllar mine (SW Spain)	Chemical Geology	190, 337-351
Doménech C, de Pablo J & Ayora C	2002	Sludge weathering and mobility of contaminants in soil affected by the Aznalcóllar tailing dam spill	Chemical Geology	190, 353-368
Duquesne K, Casiot C, Morin G, Personne C, Elbaz- Poulichet F, LeBlanc M, Bruneel O & Bonnefoy V	2003 (in press)	Immobilisation of arsenite and ferric iron by <i>Acidothiobacillus ferrooxidans</i> in acid mine drainage	Applied and Environmental Microbiology	
Gibert O, de Pablo J, Cortina JL & Ayora C	2003 (in press)	Treatment of acid mine drainage by sulphate-reducing bacteria using permeable reactive barriers: a review from laboratory to full-scale experiments	Reviews in Environmental Science and Biotechnology	
Gibert O, de Pablo J, Cortina JL y Ayora C	2001	Evaluación de materia orgánica como material para su utilización en barreras permeables reactivas	En A. Medina y J. Carrera (Ed.): Las caras del aguas subterránea. IGME, Serie Hidrogeología y Aguas Subterráneas	1: 43-48
Koffi K, LeBlanc M, Jourde H, Casiot C, Pistre S, Gouze P & Elbaz- Poulichet F	2003	Reverse oxidation zoning at mine tailings stock generating arsenic-rich acid waters	Mine Water and the Environment	22, 7-14
Kroll, A., Amezaga, J.M., Younger, P.L., and Wolkersdorfer, C.	2002	Regulation of mine waters in the European Union: the contribution of scientific research to policy development.	Mine Water and the Environment	21, (4), pp 193-200.
Lagrega I, Lorenzo S, Cortina JL, de Pablo J y Ayora C	2001	Evaluación del óxido de magnesio como material reactivo en barreras geoquímicas permeables. Aplicación en el remedio in situ de aguas subterráneas contaminadas por el drenaje de aguas ácidas.	En A. Medina y J. Carrera (Ed.): Las caras del aguas subterránea. IGME, Serie Hidrogeología y Aguas Subterráneas	1: 49-56
LeBlanc M	2001	Un exemple de décontamination naturelle : le site minier de	Les Techniques de l'Industrie	11, pp94-101

		Carnoulès (Gard).	Minérale (Mining Industry Technical Review)	
LeBlanc M, Casiot C, Elbaz- Poulichet F & Personné C	2002 (in press)	Arsenic removal by oxidising bacteria in an heavily arsenic contaminated acid mine drainage system : Carnoulès (France).	Geological Society, London. Sp. pub. Mine water Hydrogeology and geochemistry	188, 267-275
Moreno N, Querol X, Ayora C, Fernandez-Pereira C y Janssen- Jurkovicova M.	2001	Utilisation of Zeolites Synthesized from Coal Fly Ash for the Purification of Acid Mine Waters	Environmental Science and Technology	35: 3526-3534
Morin G, Juillot F, Casiot C, LeBlanc M, Ildefonse P & Calas G	2003 (in press)	Bacterial formation of Tooeleite and mixed arsenic (V)/(II)-iron(III) gels in the Carnoulès AMD France. Acombined XANES, XRD and SEM study	Environmental Science and Technology	
Saaltink MW, Doménech C, Ayora C & Carrera J	2002	Modelling the oxidation of sulphides in an unsaturated soil	In Younger PL & Robins NS. Mine Water Hydrology and Geochemistry. Geol. Soc. London Spec. Pub.	198, 187-204
Spiessel SM, Sauter M, Viswanathan HS & Zheng C	2002	Simulation of dissolved uranium release from flooded underground mines under equilibrium conditions	In Kribek B & Zeman J (Eds). Uranium Deposits: from their genesis to their environmental aspects, Czech Geol. Survey, Prague	167-170
Spiessl SM, Prommer H, Sauter M & Zheng C	2002	Numerical simulation of uranium transport in flooded underground mines	In Merkel BJ, Planer-Friedrich B & Wolkersdorfer C (eds). Uranium in the Aquatic Environment, Springer Berlin	273-282
Spiessl SM, Sauter M, Zheng C & Liu G	2002	Simulation of contaminant transport in flooded underground mines using a coupled continuum-conduit transport model: Comparison of two numerical methods for advection in the pipe network.	ModelCARE 2002, 4th International Conference on Calibration and Reliability in Groundwater Modelling: A	46, 37-41

			few steps closer to reality, June 17-20 2002, Prague, Czech Republic. Acta Universitatis Carolinae-Geologica (eds. Kovar K & Hrkal Z)	
Viswanathan HS & Sauter M	2001	Contaminant migration from underground mines using a coupled continuum-pipe-flow model	Water-Rock Interaction (Cidu R (ed)) Proc 10 <sup>th</sup> Int. symposium WRI-10, Villasimius, Italy)	IAHS Publ. No.277
Viswanathan HS & Sauter M	2003 (in press)	Simulation of contaminant migration from underground mines using a coupled continuum-pipe-flow model	In Hoskin P. (Ed) Geology and Mineralogy of Radioactive Waste Repositories, Springer Verlag	
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Wolkersdorfer, C., and Younger, P.L.	2002	Passive Grubenwassereinigung als Alternative zu aktiven Systemen	Grundwasser	7, p 67-77
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