Groundwater Quality: Natural and Enhanced Restoration of Groundwater Pollution (Proceedings of the Groundwater Quality 2001 Conference held at Sheffield, UK. June 2001). IAHS Publ. no. 275, 2002.

Time-scale issues in the remediation of pervasively-contaminated groundwaters at abandoned mine sites

P. L. YOUNGER
Hydrogeochemical Engineering Research and Outreach (HERO), Department of Civil Engineering, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK
e-mail: p.l.younger@ncl.ac.uk

S. A. BANWART
Groundwater Protection and Restoration Research Group, Department of Civil and Structural Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK

Abstract Groundwater bodies in abandoned deep mine workings or perched within waste rock heaps or backfill are often pervasively contaminated with ecotoxic metals. Effective remediation of such groundwaters requires the interception and treatment (by passive or active means) of virtually the entire flow of groundwater. Design of remedial interventions has to be based on an adequate conceptualization of time-scale issues concerning the generation and dissipation of metal loadings and acidity. Combined laboratory, field and modelling studies of a number of mined systems are revealing the relative importance of geochemical attenuation and hydraulic flushing processes in determining the temporal evolution of groundwater quality at abandoned mine sites. Of particular importance in the short term is the flushing from the system of the products of the dissolution of hydroxy-sulphate salts, which are taken into solution during flooding of mines or waste rock repositories. In the longer term, the interplay between sources of acidity and alkalinity is seen to be the dominant factor. General lessons that can be drawn from these studies are well illustrated by the early evidence of substantial natural attenuation occurring at Lindsay Colliery, South Wales, which was flooded in 1998–99.

Key words acid mine drainage; acidity; alkalinity; attenuation; geochemistry; mining; pollution; remediation

INTRODUCTION

In contrast to many other groundwater pollution scenarios, in which one may encounter a plume of contaminated water within an otherwise "clean" aquifer, groundwater bodies in flooded mine workings and waste rock/tailings repositories are often pervasively contaminated. Sulphide oxidation processes (and consequent dissolution and desorption reactions) typically result in these groundwaters having highly elevated concentrations of SO_4 and various metals (Fe, Mn, Al, Zn, Cu etc.), which can cause ecological problems and degrade water resources (e.g. Banks *et al.*, 1997). Because these groundwater bodies are pervasively contaminated, effective remediation often demands the interception and treatment of virtually the entire flux through the anthropogenic aquifer system, prior to its natural discharge to the surface environment (Younger, 2000a). The most important hydrogeological/geochemical factor which influences remedial technology selection is the marked temporal changes in water quality which are usually observed in the years and decades following completion of mine flooding or cessation of waste rock/tailings disposal (e.g. Younger, 2000b). This paper examines the nature and causes of these changes and illustrates their operation with a recent case study.

ACIDITY RELEASE FROM MINED (ANTHROPOGENIC) AQUIFERS

Figure 1 categorizes the four main types of ground conditions associated with abandoned mine sites in terms of their propensity for imparting acidity to groundwaters in the long term. (Not shown is fully restored and remediated mined ground which is no longer generating acidic leachate in appreciable quantities.) As acidity generation is critically dependent on pyrite oxidation, and this ultimately requires proximity to atmospheric oxygen as the principal electron acceptor, then the more deeply buried a particular system is, the less likely will that system be to generate acidity in the long term.

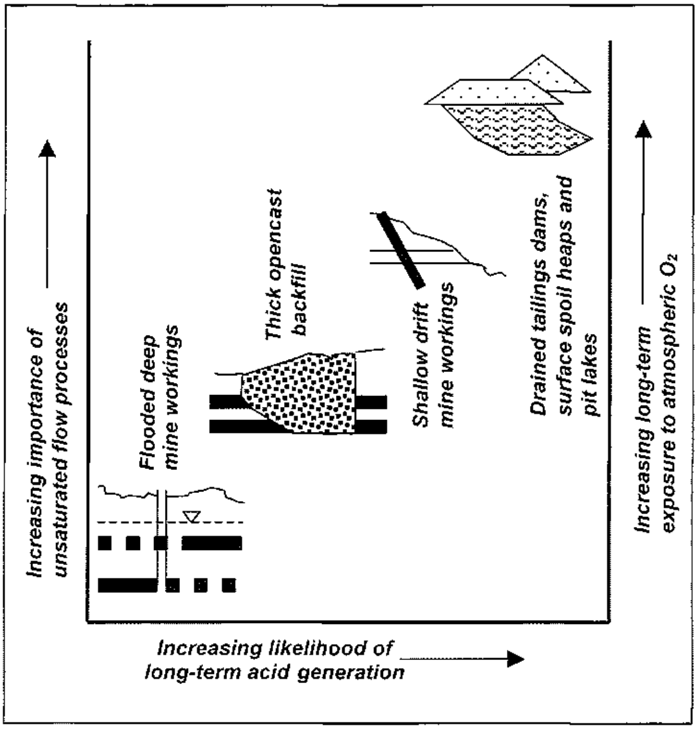

Fig. 1 Conceptual sketch emphasizing the links between ground conditions at abandoned mine sites and the likelihood of long-term acid generation.

From a management perspective, it is comforting that the largest systems (i.e. flooded deep mine workings) are least likely to continue generating acidity in the long term (even though they may develop large amounts of acidity upon first flooding, as explained in the following section). It is important to note that, while pyrite oxidation can only occur within and above the zone of water table fluctuation in flooded deep mines, the dissolution of buffering minerals (carbonates and silicates) can occur throughout the saturated zone as well. This means that the available alkalinity will often exceed the acidity generated, even where the rock mass as a whole has a molar ratio of pyrite to carbonates of around unity.

Shallow underground workings and surface deposits of tailings and waste rock usually remain in close contact with the atmosphere and will continue to release acidity until pyrite is exhausted. These are also the very systems in which unsaturated zone flow processes are most dominant, which is unfortunate given that these processes have proven to be particularly challenging to characterize and adequately model in the highly heterogeneous environment of most loose-tipped waste rock piles (e.g. Eriksson & Destouni, 1997).

TIME-SCALE ISSUES IN GROUNDWATER QUALITY EVOLUTION AT ABANDONED MINE SITES

The "first flush"

Recent studies of the temporal evolution of water quality following mine abandonment and flooding (e.g. Wood *et al.*, 1999; Younger, 2000b) have revealed that the concentrations of contaminants in groundwater flowing from the flooded workings commonly peak shortly after first emergence, and then decline markedly (usually exponentially) until some baseline quality is reached (Fig. 2).

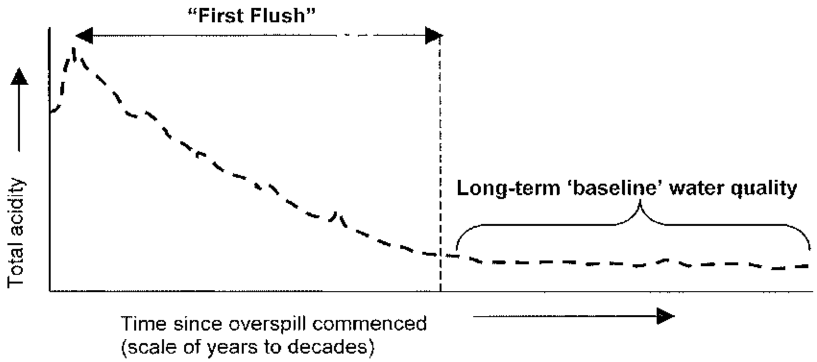

Fig. 2 Schematic diagram illustrating the improvement in the quality of groundwater flowing from abandoned mine workings (the first flush) which is generally observed in the period immediately after the mined system begins to overspill to an adjoining river or aquifer.

This pattern of behaviour has come to be termed the "first flush", and it is readily explicable as the outcome of two consecutive processes which occur after mine abandonment (Younger, 2000b):

(a) The rapid dissolution of hydroxy-sulphate minerals during flooding of the mine. These minerals form during the working of the mine, by pyrite oxidation in drier parts of the mine voids and the surrounding, fractured rock mass. When the mine floods, wholesale, congruent dissolution of these minerals occurs, leading to a peak in contaminant concentrations.

(b) The gradual flushing of the mine voids by fresh recharge, removing the products of hydroxy-sulphate mineral dissolution from the mine voids. Recent work has demonstrated that adaptations of standard advection–dispersion models adequately account for observed declines in iron concentrations.

The duration of the first flush has been studied by Wood *et al.* (1999), who studied all available data from Scotland and concluded that in the most extensive abandoned mine systems it can last as long as 40 years. In any particular case, the first flush duration will be a function of the volume of voids (= workings plus pores in enclosing strata) and the rate of recharge (e.g. Younger, 2000b).

Beyond the first flush

The classic first flush pattern shown in Fig. 2 would be anticipated where the amount of pyrite available for oxidation after flooding of the mine voids (i.e. that pyrite in and near the zone of water table fluctuation) is far exceeded by the availability of neutralizing minerals (especially calcite and dolomite, but also a number of silicate minerals) throughout the saturated zone. This is by far the most common scenario observed to date in the UK (e.g. Younger, 2001). An alternative scenario is conceivable (Fig. 3), in which the availability of neutralizing minerals is strictly limited, so that they are exhausted before pyrite. This is especially likely in waste rock piles with only a thin saturated zone, so that there is little scope for preferential dissolution of carbonates below the water table. In such circumstances, acidity production eventually begins to out-strip neutralization such that the water reverts to being acidic in the long-term (Fig. 3). A general hydrochemical framework for assessment of contaminant longevity

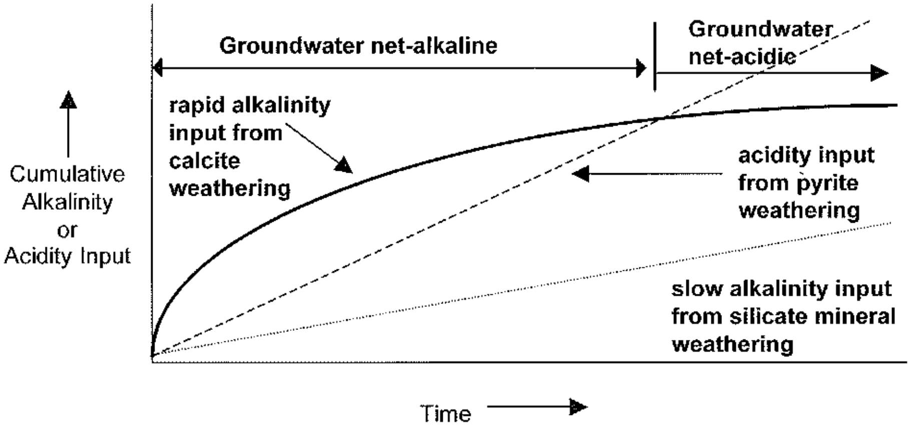

Fig. 3 Conceptual sketch of the circumstances in which the quality of groundwater in an abandoned mine system switches to become acidic in the long-term if calcite is depleted before pyrite (Banwart & Malmström, 2001).

beyond the first flush focuses on determining mineral weathering rates from solute fluxes at a site, relating these to mineral abundances and estimating the corresponding lifetime of the source minerals that generate acidity and alkalinity (Banwart & Malmström, 2001).

ILLUSTRATIVE CASE STUDY: LINDSAY COLLIERY, SOUTH WALES, UK

Mine workings and physical hydrology

Lindsay Colliery was the last underground coal mine to work the formerly prolific sequence of anthracitic coal seams of the Loughor Valley area in South Wales. The mining geology of this district has been studied for more than a century (e.g. Strahan *et al.*, 1907). However, the area is both structurally and sedimentologically complex, with numerous folds and thrusts, some of which are now known to have been active during deposition of the strata in what was essentially a foreland basin (Jones, 1991). This complexity has made correlation of seams even from one valley to the next very difficult. However, Lindsay (together with the associated, older workings of Crosshands and Cwmgwili Collieries) worked an internally well-defined block of strata between two faults, which effectively isolated these workings (both physically and hydraulically) from those of other collieries in the area.

Lindsay worked eight seams, and was active from 1960 to February 1996. Following a period of care-and-maintenance, the mine entrances were finally sealed in 1998. Prior to closure the mine was dewatered by pumping an average of about 19 l s^{-1} from a sump in the shallowest worked seam, which in turn received water from various subsidiary pumps within the workings. Most of the water (14 l s^{-1}) entered Lindsay from adjoining flooded workings of Crosshands Colliery (closed 1961), with minor amounts originating from shallow sources intercepted by the main Lindsay access drift (~4 l s^{-1}) and the remaining 1 l s^{-1} coming from existing flooded areas within the Lindsay workings. All of these water sources were still entering the workings when the last pumps were withdrawn, and were responsible for the subsequent flooding of some 2.25 km^2 of workings and overlying drained strata. Water was first observed overflowing from the Lindsay inclined drift portal in mid-December 1999. At first a trickle, the flow rate gradually increased to reach 17 l s^{-1} by 18 January 2000. Subsequent changes in flow rate are shown on Fig. 4.

Hydrochemical changes and natural attenuation

Figure 4 also shows the changes in total iron concentration in the Lindsay discharge since first emergence. Up to the end of January 2000, the water had less than 150 mg l^{-1} total Fe; subsequently it peaked at 236 mg l^{-1} in early April 2000. Much of the water that flowed from the mine before the end of January probably represents the uppermost portion of the water in the flooded mine system, comprising some 2×10^4 m^3 in the inclined access drift, and water in the shallowest workings. Given the flow rates observed in January 2000, the water present in the inclined drift at the commencement of overflow would have been drained within two to three weeks. Hence the observed

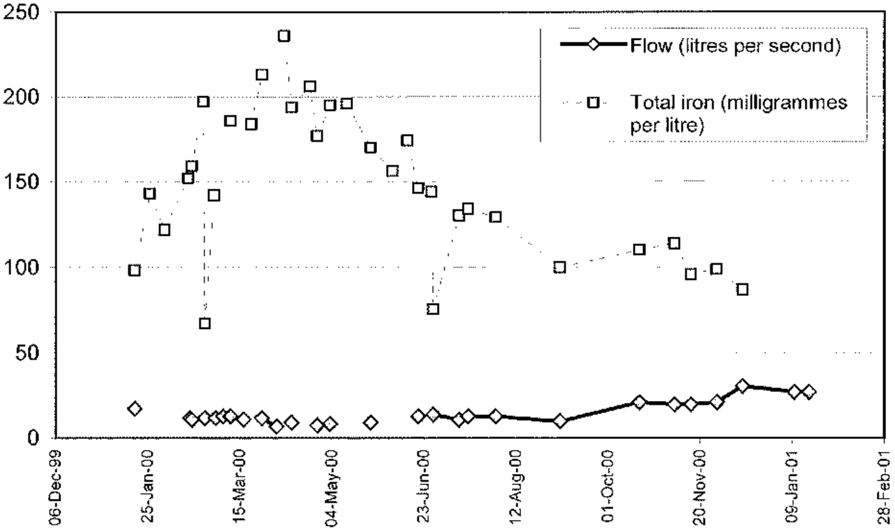

Fig. 4 Flow and total iron measurements for the Lindsay Colliery portal, December 1999 to January 2001.

rise in total iron during the period January–April represents gradual "sampling" of ever deeper parts of the flooded mine system by the overflow pathway.

The highest iron concentrations (>150 mg l^{-1}) were restricted to a period of about six months, during which the observed flow rate (10.4 l s^{-1}) is consistent with the drainage of some 1.6×10^5 m^3 of pore space. This is equivalent to about 50% of the estimated total volume of mined voids which became flooded after the final closure of Lindsay, suggesting that the peak in iron concentrations developed due to dissolution of iron-bearing hydroxy-sulphate salts in the shallowest workings (principally in the Big Seam), with the tailing in concentrations being attributable to flushing of these most recently-flooded workings by water entering Lindsay from Crosshands Colliery.

Geochemical modelling simulations are consistent with this conclusion. Formation of iron- and aluminium-hydroxy-sulphate minerals is expected during the weathering of pyrite in hydraulically unsaturated pore space within the walls confining the mined voids. The uncontaminated water associated with the pumped discharge prior to rebound is grossly undersaturated with respect to such phases. Simulated dissolution of equimolar amounts of the iron phases melanterite and potassium jarosite while maintaining chemical equilibria with calcium-carbonate and -sulphate phases, iron oxyhydroxide and ion exchange surfaces gives rise to a calculated ionic composition, pH and alkalinity that is similar to the Lindsay discharge. Dissolution of aluminium-bearing secondary phases cannot explain the observed discharge chemistry, however. Simulations demonstrate that solubility equilibria with such minerals are achieved at sulphate concentrations that are far too low compared to those observed for the discharge. The current discharge remains undersaturated with respect to calcite. Due to the rapid dissolution and precipitation kinetics of calcite, this suggests that the mineral is either depleted within the discharge flow path or that dilution occurs along the flow path subsequent to equilibration with the mineral.

Acknowledgements We gratefully acknowledge research funding from the NERC Environmental Diagnostics Programme (Grant no. GST/02/2060), and two EU Fifth Framework projects, PIRAMID (EVK1-CT-1999-00021) and ERMITE (EVK1-CT-2000-00078). The UK Coal Authority kindly provided the data used in the Lindsay case study. The opinions expressed in this paper cannot be construed as representing the policy of any of the supporting organizations.

REFERENCES

Banks, D., Younger, P. L., Arnesen, R.-T., Iversen, E. R. & Banks, S. D. (1997) Mine-water chemistry: the good, the bad and the ugly. *Environ. Geol.* **32**, 157–174.

Banwart, S. & Malmström, M. (2001) Hydrochemical modelling for preliminary assessment of minewater pollution. *J. Geochemical Exploration* **74**, 73–97.

Eriksson, N. & Destouni, G. (1997) Combined effects of dissolution kinetics, secondary mineral precipitation, and preferential flow on copper leaching from mining waste rock. *Wat. Resour. Res.* **33**, 471–483.

Jones, J. A. (1991) A mountain front model for the Variscan deformation of the South Wales coalfield. *J. Geol. Soc.* **148**, 881–891.

Strahan, A., Cantrill, T. C., Dixon, E. E. L. & Thomas, H. H. (1907) *The Geology of the South Wales Coalfield Part VII. The Country around Ammanford.* Memoirs of the Geological Survey of Great Britain, 230. HMSO, London, UK.

Wood, S. C., Younger, P. L. & Robins, N. S. (1999) Long-term changes in the quality of polluted minewater discharges from abandoned underground coal workings in Scotland. *Quart. J. Engng Geol.* **32**, 69–79.

Younger, P. L. (2000a) Holistic remedial strategies for short- and long-term water pollution from abandoned mines. *Trans. Inst. Mining and Metallurgy (Section A: Mining Technology)* **109**, A210–A218.

Younger, P. L. (2000b) Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: a first approximation. *J. Contam. Hydrol.* **44**, 47–69.

Younger, P. L. (2001) Mine water pollution in Scotland: nature, extent and preventative strategies. *Sci. Total Environ.* **265**, 309–326.