Hydrogeological and geochemical consequences of the abandonment of Frazer's Grove carbonate hosted Pb/Zn fluorspar mine, north Pennines, UK

K. L. JOHNSON & P. L. YOUNGER

Hydrogeochemical Engineering Research & Outreach (HERO), Department of Civil Engineering, University of Newcastle, NE1 7RU UK (e-mail: k.l.johnson@ncl.ac.uk)

Abstract: The problems associated with predicting where mine water will emerge and what the quality will be in a post-closure situation are recognised world-wide. The closure of Frazer's Grove, a fluorspar mine in the North Pennines in the UK has given the opportunity to study in detail the relationship between rising groundwater and the strata/mineworkings through which it is rising. Detailed sampling and surveys both above and underground were carried out before, during and after rebound. During the rebound phase the mine water was stratified. Since the mine water emerged in August 1999, stratification has broken up and re-established itself twice to date. The possible causes of the break-up of stratification are examined with the aid of hydrogeochemical data and geophysical techniques. The main contaminants present in the mine water are zinc, manganese, iron and sulphate. A general exponential decrease in dissolved metal concentration in the mine water is seen with time. The hydrogeochemical data also establishes the origin of the contamination in the mine water discharge with zinc and manganese originating from Frazer's Grove mine itself and iron from several sources. The Frazer's Grove mine investigation provides insight into water quality and its likely development with time in abandoned mines.

Mine water discharges from abandoned workings cause a great deal of problems world-wide and their environmental impacts are well documented (for example, Hamilton *et al.* 1999). The problems associated with the prediction of both discharge quality and mine water emergence are also widely appreciated. Frazer's Grove has provided an excellent opportunity to study an abandoned mine both before and after abandonment. Frazer's Grove mine is of international interest as there are many similar ore bodies which are currently being mined such as the Olkusz region in Poland (Adamczyk *et al.* 2000). The implications of neutralisation of acidic mine drainage by limestone country rock are of particular relevance to other geologically similar workings. Observations on the temporal and spatial geochemical nature of mine water within the mine workings have allowed a greater understanding of the process of stratification.

Frazer's Grove mine is situated in the North Pennines in County Durham, UK (see Fig. 1). It consists of four interconnected mines: Frazer's Hush, Rake Level/Firestone Incline workings, Grove Rake and Greencleugh, as shown in Fig. 2. The mine has been worked since the 9th century for lead, zinc, barium and fluoride (in the form of fluorite, locally termed "fluorspar"). More recently only fluorspar has been worked in the deeper sections of Frazer's Hush and the shallower workings of the Rake Level/Firestone Incline mine. However, when fluorspar prices plummetted in the nineties, mining operations were severely reduced. Mining of the deep workings was stopped at the end of 1998. The dewatering pumps for the deeper sections (which are situated in Grove Rake No.2 Shaft) were switched off and removed on March 5th 1999, at which point the groundwater started to rise. Mining of the shallower workings in the Rake Level/Firestone Incline workings continued until July 1999 when all mining operations ceased and this, the last mine in the North Pennines was closed.

During mining, the average pumped discharge from both the deeper and shallower workings of Frazer's Grove mine was 1895 m^3/d (Younger 2000*a*). The majority of this water came from the Great Limestone (an extensive minor aquifer) and was strongly net-alkaline, with circum-neutral pH. This pumped discharge was monitored from January to April 1998 and the only contaminant present at problematic concentrations was zinc (average concentration ~12.3 mg/l) (Younger

From: YOUNGER, P.L. & ROBINS, N.S. (eds) 2002. *Mine Water Hydrogeology and Geochemistry.* Geological Society, London, Special Publications, **198**, 347–363. 0305-8719/02/$15.00

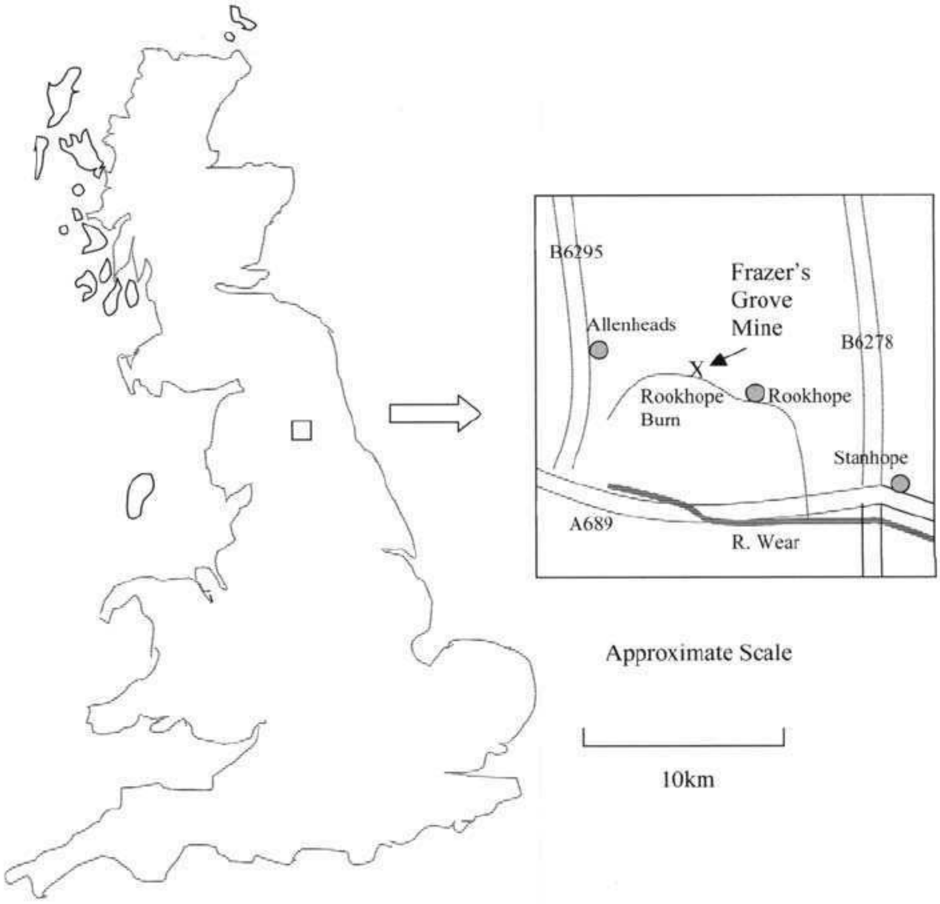

Fig. 1. Location map of Frazer's Grove Mine.

2000*a*). Since discharges from recently abandoned mines are usually of worse quality than pumped discharges from working mines, a sampling routine was devised in conjunction with the Environment Agency (EA) to monitor any environmental implications of the closure of Frazer's Grove Mine (Johnson & Younger 2000). The monitoring programme ran from April 1999 to February 2001 when it was interrupted by the outbreak of foot and mouth disease in the local area.

Geological setting

The Carboniferous rocks of the North Pennines are cut by numerous mineral veins. The veins are associated with the Caledonian Weardale granite. The granite batholith is not thought to have been the principal source of heat for mineralisation but it may have directed hot mineralising fluids through the Carboniferous sediments (Dunham *et al.* 1965). Many veins are little over 1 m wide but in places widths of over 10 m have been recorded; veins of up to 3 m wide can be seen in the Firestone Incline at Frazer's Grove mine today. There is a marked zonation of the constituent minerals within the orefield, especially between the non-metalliferous or gangue minerals. Deposits in the central zone carry abundant fluorite (CaF_2), with quartz, chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS) also present. Surrounding the fluorite zone is a wider zone of deposits in which barium minerals including baryte ($BaSO_4$) and witherite ($BaCO_3$) are the characteristic gangue minerals. The presence of galena and other sulphide minerals is less common in this zone. The mineral zonation reflects progressively lower temperatures of crystallisation from mineralising fluids as they flowed outwards from central 'emanative centres' above high spots (cupolas) on the underlying Weardale Granite (Dunham 1990).

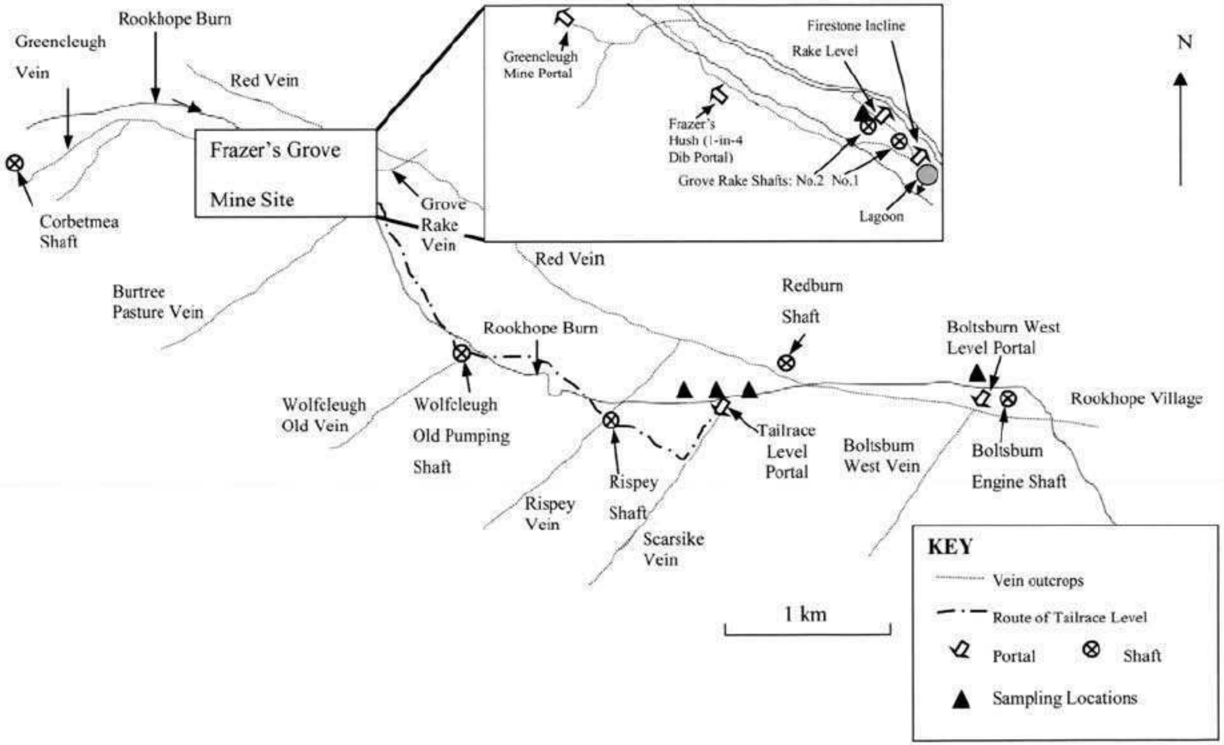

Fig. 2. Sketch map of Frazer's Grove Mine showing the sampling locations.

Frazer's Grove Mine is located above this emanative centre within the fluorite zone. A simplified cross-section of the mine and representative geological log for the mine are presented as Fig. 3 and Table 1 respectively.

Monitoring locations

Water samples have been taken on a monthly basis since April 1999 to February 2001 from both above ground and underground. Both the Boltsburn (NY 9365 4283) and Tailrace Levels (NY 9162 4271) were sampled at the same time as the depth sampling in the No.2 Shaft (NY 8949 4410). The No.2 Shaft was sampled using a SEBA 1L depth sampler. It was assumed that the shaft water at depth is at equilibrium with the minerals in the corresponding strata. Samples were taken every 10 m between the water surface (currently stable at ~373 m aOD in the No.2 Shaft) and a depth of 315 m aOD: it was not possible to sample below 315 m aOD due to a platform across the shaft.

The Boltsburn Level is situated on outcropping Great Limestone and its discharge is typical of Great Limestone groundwaters (Ca ~ 100 mg/l, HCO_3 ~ 180 mg/l, conductivity ~500 μS/cm) (Dunham 1990). However, it does drain some old mineworkings and although it contains < 0.5 mg/l of both manganese and zinc it has variable iron concentrations (1–10 mg/l). The Level is not directly connected to Frazer's Grove mine and was monitored in order to assess any changes in flow or chemistry in the Great Limestone aquifer. The Tailrace Level drains old mineworkings but also carries a significant component of surface run-off which enters the level via crownholes. The water quality in the Tailrace Level was also fairly constant (Ca ~60 mg/l, HCO_3 ~130 mg/l, conductivity ~400 μS/cm) until the shaft water overflowed into it on the 25th August 1999.

The Rookhope Burn was also sampled approximately 200 m both up and downstream of the Tailrace discharge. All sampling locations are shown on Fig. 2.

Methodology

pH, temperature, Eh and conductivity were measured on site using a calibrated Camlab MY/6P meter and alkalinity was measured using a Hach digital titrator. Two 200 ml sample bottles (one being acidified with 2 drops of concentrated nitric acid) were filled and returned to the Environmental Engineering Laboratory at Newcastle University for anion and cation analysis. Dilutions were frequently necessary as sulphate was present at high concentrations. However, the dilution resulted in less accurate measurement of anions which are present at low concentrations in the mine water (such as chloride) as any percentage errors in analysis are increased dramatically on multiplication by the dilution factor. For this reason, the chloride results presented in Table 2 should be treated with caution.

The hydrochemical results from Frazer's Grove mine were modelled using WATEQ4F (Ball & Nordstrom 1991). This modelling was carried out to calculate the saturation indices of relevant minerals rather than determine the hydrogeochemical nature of the mine.

Robertson's geophysical sondes were used for geophysical logging in the No.2 Shaft in June 2000. Two sondes were used, one of which measured temperature and conductivity and the other measured the flow velocity using an impeller. The latter also measured natural gamma but as the shaft was wide the natural gamma signal was too weak for interpretation. A Portalog2 unit was used above ground to interpret the data received.

Rising groundwater was monitored both manually and with data-loggers. Manual measurements were taken in the No.2 Shaft every week or fortnight. Data-loggers were installed in the No.2 Shaft and in Frazer's Hush from March and February 1999 respectively. As the Hush is a 1-in-4 dib (inclined level) it was not possible to measure the rise in water level using a conventional pressure transducer. However, access to the Hush was also limited as the entrance to the workings was sealed in July 1999 for safety reasons. The Environment Agency, however, had designed a mechanism which allowed the rise of water in the Hush to be monitored from the surface. This consisted of a series of switches which were placed every 10 m along the length of the Hush. The switches were triggered on contact with the rising water and this event was recorded on a conventional data logger situated above ground. The location of the switches was translated into metres above Ordnance Datum. This allowed a comparison between groundwater rebound in the No.2 Shaft and the Hush to be made, thereby confirming that the water was rising evenly throughout the mine workings.

Lithological samples were taken in December 1998 which was the last opportunity to gain access to the deeper workings. Samples of acid generating minerals were taken for X-ray Diffraction (XRD) analysis. A small amount of the dried and ground sample (0.5 g) was equilibrated with 20 ml of de-ionised water and agitated for 30 minutes and repeated three

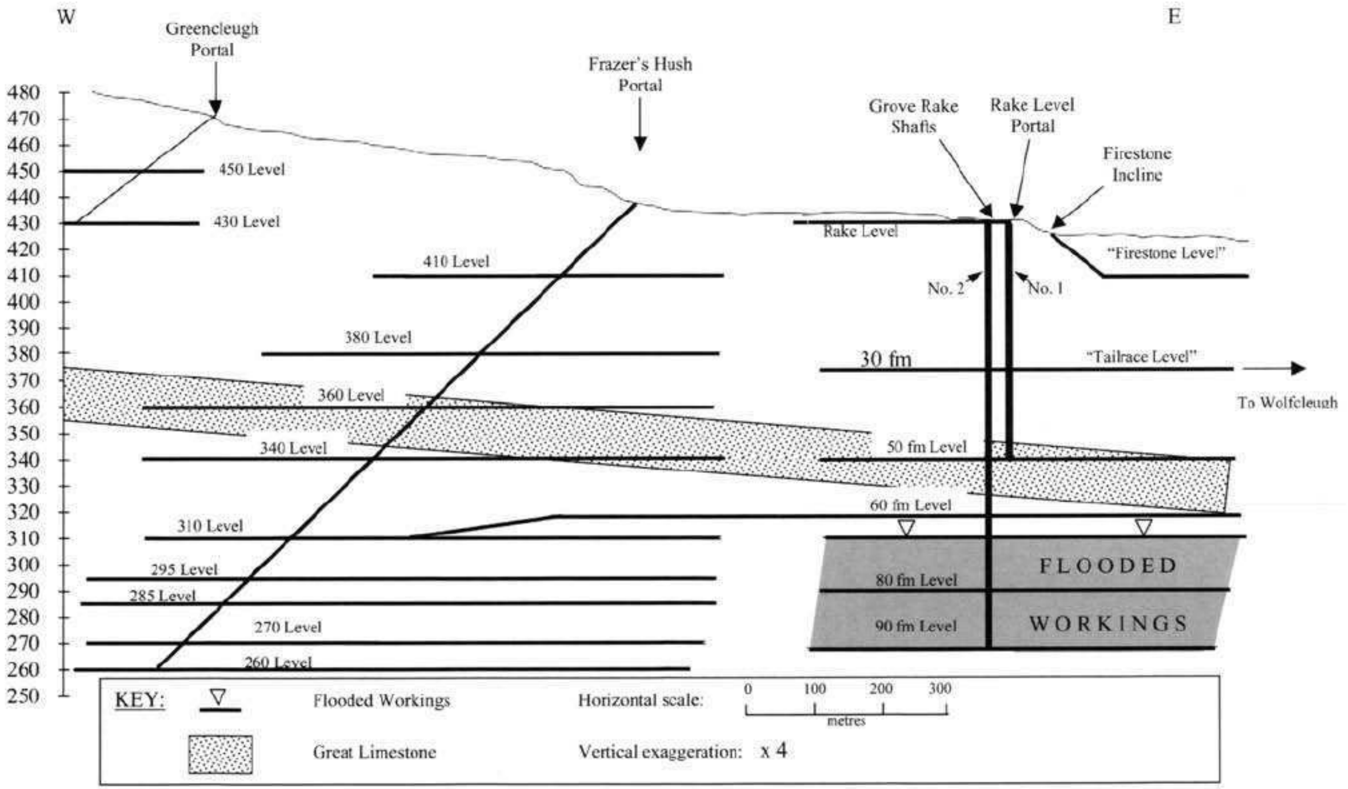

Fig. 3. Sketch diagram of cross-section of Frazer's Grove Mine.

Table 1. *Simplified Geological Succession for the Frazer's Grove Mine Site*

Unit Name (key units in bold typeface)	Approx. elevn. of (m aOD) at Grove Rake Shafts*	Lithology†	Thickness (m)	Hydrogeological Classification
Low Slate Sill	434.6	Sst(silty)	11.3	Aquitard
Knuckton Shell Beds	423.3	Slt/Mdst	19.8	Aquitard
Crag Limestone	403.5	Lst	0.15	Aquitard
Plate beds	403.4	Mdst/Sst	1.4	Aquitard
Firestone Sill	402	Sst	8.2	Minor aquifer
Plate beds	397.3	Mdst	4.7	Aquitard
White Sill	391.3	Sst	6	Minor aquifer
Plate beds	381.9	Mdst	9.4	Aquitard
Girdle Beds	377.5	Sst/Mdst	4.4	Aquitard
Pattinson's Sill	373.2	Sst	4.3	Minor aquifer
Plate beds	367.9	Mdst	5.3	Aquitard
Little Limestone	364.5	Lst	3.4	Minor aquifer
Sandstone beds	359.9	Sst	4.6	Minor aquifer
Plate beds	357.2	Mdst	2.7	Aquitard
High Coal Sill	355.6	Sst	1.6	Minor aquifer
Coal	355.45	Coal	0.15	Aquitard
Plate beds	350.05	Mdst	5.4	Aquitard
Coal	350	Coal	0.06	Aquitard
Low Coal Sill	349	Sst	1	Aquitard
Plate beds	346.2	Mdst	3.8	Aquitard
Great Limestone	325.8	Lst	20.4	Major aquifer
Tuft	323.7	Sst/Slt	2.1	Minor aquifer
Plate beds	322	Mdst (py)	3.5	Aquitard
Iron Post Limestone	320.3	Lst/Mdst	1.7	Aquitard
Quarry Hazle	308.9	Sst	11.4	Minor aquifer
Plate beds	297.3	Mdst	11.6	Aquitard
Four FathomsLimestone	291.7	Lst	5.6	Minor aquifer
Plate parting	291.1	Mdst	0.6	Aquitard
Nattrass Gill Hazle	278.8	Sst	12.3	Minor aquifer
Grey beds	265.6	Slt/Sst	13.2	Aquitard
Three Yard Limestone	263	Lst	2.6	Minor aquifer
Six Fathom Hazle	254	Sst	9.0	Minor aquifer
Plate beds	245.9	Mdst	8.1	Aquitard
Five Yard Limestone	243.3	Lst	2.6	Minor aquifer
Grey beds	223.8	Slt/Sst	19.5	Aquitard
Scar Limestone	213	Lst/Mdst	10.5	Minor aquifer

* Note: OD elevations in Frazer's Hush workings are higher, because of the regional dip of ~ 1.5° ENE (ie about 0.025 m drop per m travelled ENE) eg the Great Limestone Base at Frazer's Hush (600 m W of Grove Rake shafts) should be $600 \times 0.025 - 15$ m higher than at Grove Rake shafts. This is indeed the case with the Great Limestone base being seen at the 340 Level in Frazer's Hush.

† Sst = sandstone; Slt = siltstone; Mdst = mudstone; Lst = limestone; (py) = pyritic

times so that zinc, manganese, iron and sulphate concentrations could be measured.

V-notch weirs were installed at the Tailrace Level and the Boltsburn Level as part of the monitoring programme and data-loggers were installed in order to record flow on a daily basis whenever possible. Unfortunately, flow measurement was not possible at the Tailrace Level after the mine water emerged on 25 August 1999 due to construction works for a mine water treatment system.

Frazer's Grove mine

Previous work has included an extensive sampling routine both above ground in the Rookhope Burn and underground within the mine (Younger 2000*a*). Underground inspections of the mine geology were carried out during 1998. The most significant features noted were the 20 m thickness of Great Limestone and the presence of yellow/grey highly weathered shales which contained acid generating minerals just

Table 2. *Typical key water quality data from Spring 1999 to Spring 2001 from Frazer's Grove Mine and surrounding area*

Name	Height (m aOD)	Date	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Mn (mg/l)	Zn (mg/l)	Cl (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	pH	Cond (μS/cm)	Eh	Temp (°C)
No2 Shaft	337	22/4//99	35.8	33.7	386.8	100.5	12.0	31.7	35.1	114.7	1328.5	146	6.22	2376	117	9.1
No2 Shaft	330	22/4//99	35.7	25.2	404.5	101.6	11.7	32.7	34.1	90.2	1403.0	60	6.03	2380	112	8.9
No2 Shaft	320	22/4//99	38.0	20.8	446.7	122.4	33.0	65.4	61.8	37.5	1795.5	0	4.35	2861	250	10
No2 Shaft	315	22/4//99	34.2	18.6	464.8	119.3	30.0	66.1	63.1	173.4	1785.9	0	3.82	2874	344	8.9
Tailrace Level		22/4//99	11.8	5.7	52.3	9.8	4.1	0.1	0.1	17.5	34.1	180	6.00	335	146	8.2
Boltsburn Level		22/4//99	14.2	6.2	72.0	12.9	0.1	0.2	0.1	18.5	62.6	178	6.79	492	50	10.2
No2 Shaft	360	1/9/99	30.5	23.6	673.0	194.0	24.6	114.4	88.0	212.0	1997.0	58	5.09	3033	89	11.7
No2 Shaft	350	1/9/99	27.7	20.4	662.0	198.0	24.8	120.8	93.0	169.0	1662.0		5.30	2850	73	11.4
No2 Shaft	340	1/9/99	25.8	19.3	623.0	185.0	27.9	106.8	87.0	0.0	1844.0	56	5.58	1981	45	10.8
No2 Shaft	330	1/9/99	22.1	17.6	567.0	182.0	25.6	109.3	95.0	99.0	1808.0	32	5.36	3160	74	11.5
No2 Shaft	315	1/9/99	20.7	14.2	623.0	215.0	67.9	138.1	111.0	138.0	2178.0	26	5.05	3188	80	11.4
Tailrace Level		1/9/99	16.4	11.0	303.0	82.0	7.1	44.0	35.6	258.0	907.0	92	5.90	1805	50	10.3
Burn d/s TRL		1/9/99	11.4	6.8	176.0	22.0	3.4	18.2	20.0	305.0	518.0	60	6.32	1106	n/a	14.4
Boltsburn Level		1/9/99	11.5	6.3	123.0	15.6	1.2	0.3	0.0	29.0	82.0	243	6.62	604	n/a	11.2
No2 Shaft	370	26/2/00	10.9	6.6	66.8	15.2	0.0	3.0	5.6	24.0	191.0	30	6.36	488	n/a	8.4
No2 Shaft	360	26/2/00	10.7	9.2	88.1	23.2	0.0	6.3	4.1	24.0	342.0	80	6.67	659	n/a	7.6
No2 Shaft	350	26/2/00	24.0	25.0	451.0	94.1	14.9	61.1	22.2	28.0	1011.8	180	6.17	2364	n/a	8.3
No2 Shaft	340	26/2/00	28.0	30.0	565.0	115.0	18.3	75.6	26.6	24.0	1514.5	186	6.12	2486	n/a	9.1
No2 Shaft	320	26/2/00	26.4	27.3	540.5	113.7	19.3	75.9	27.7	24.0	2501.0	180	6.06	2610	n/a	9.0
Tailrace Level		26/2/00	14.7	12.1	283.9	67.9	3.9	36.5	16.2	24.0	842.4	106	6.52	1630	n/a	8.6
Burn u/s TRL		26/2/00	6.3	1.1	8.1	3.0	0.5	0.2	0.2	13.0	9.9	18	6.70	91	n/a	4.5
Burn d/s TRL		26/2/00	7.5	3.0	48.0	11.6	1.2	6.0	2.3	34.6	132.0	30	6.85	406	n/a	5.4
Boltsburn Level		26/2/00	11.2	6.2	77.0	15.3	0.4	0.8	0.2	27.2	76.4	180	7.57	548	n/a	7.5
No2 Shaft	365	24/1/01	9.1	6.3	68.0	10.4	0.1	1.5	2.9	97.7	185.1	n/a	6.37	483	152	6.4
No2 Shaft	350	24/1/01	9.1	6.3	70.2	10.3	0.1	1.5	2.9	130.0	186.9	n/a	6.51	513	155	7.8
No2 Shaft	340	24/1/01	9.1	6.4	64.6	10.3	0.1	1.5	2.8	98.8	210.9	n/a	6.62	516	164	7.8
No2 Shaft	330	24/1/01	12.0	16.9	238.0	41.2	21.0	27.3	7.7	218.6	818.0	n/a	6.35	1317	36	8.0

Table 2 – *continued*

Name	Height (maOD)	Date	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Mn (mg/l)	Zn (mg/l)	Cl (mg/l)	SO_4 (mg/l)	HCO_3 (mg/l)	pH	Cond (μS/cm)	Eh	Temp (°C)
Tailrace Level		24/1/01	10.1	9.2	131.8	17.9	4.7	11.7	3.6	101.0	328.4	118	6.69	917	16	7.4
Burn u/s TRL		24/1/01	5.0	1.6	6.1	1.8	0.6	0.5	0.2	23.7	17.9	16	7.90	89	13	3.7
Burn d/s TRL		24/1/01	4.8	1.7	7.3	2.1	0.6	0.7	0.2	23.6	22.6	14	7.18	103	18	2.6
Boltsburn Level		24/1/01	11.3	4.9	63.0	9.4	0.8	0.8	0.2	88.1	114.0	162	6.79	518	83	7.5

below the limestone (see Fig. 3 & Table 1). The Great Limestone is a prolific aquifer throughout the North Pennines and plays an important part in the hydrogeology of the mine.

The underground surveys suggested that around two thirds of the Frazer's Grove water-make comes from the Great Limestone aquifer with the remaining one third from the Firestone Sill and surface inflows (Younger 2000*a*). It was predicted that after abandonment the water table would rise above the aquifer and this source of head-dependent water would stop. A final post-rebound water-make of only ~680 m^3/d was expected. It was thought that most of the rising groundwater would dissipate into the Great Limestone and that mixing between mine and limestone water would result in satisfactory discharge water quality (according to EA regulations). However, it was also pointed out (in an unpublished and confidential report to the EA in October 1998) that if the limestone could not take up this water there would be a discharge at the Tailrace Level which is the lowest surface discharge point at 364 m aOD for the water. This discharge would end up in the Rookhope Burn. The Burn contains few fish (with the exception of some hardy brown trout) probably due to the mining legacy. The pumped discharge from the working mine contained significant dissolved zinc (up to 40 mg/l) which would have had a major deleterious effect on life in the Burn.

The highest zinc concentrations encountered in the surveys was 40 mg/l in water draining through a disused hopper deep within the Frazer's Hush workings at 285 m aOD (Younger 2000*a*). However, the highest zinc concentrations seen in the pumped discharge occurred in the spring of 1996 when the No.2 Shaft pumps temporarily failed. The water rose to 328 m aOD flooding the pyritic shales just below the Great Limestone. The water quality deteriorated rapidly as acid generating minerals in the shales dissolved resulting in a pH of 3.6 and most notably zinc concentrations of 27 mg/l (Younger 2000*a*).

Results and discussion

Lithological samples

Ground samples of the acid generating minerals found below the Great Limestone equilibrated with de-ionised water gave a resulting solution with a pH of 2.7 and concentrations of manganese ~1.9 mg/l, iron ~1.7 mg/l, zinc ~1.0 mg/l and sulphate ~100 mg/l.

Three X-Ray Diffraction (XRD) analyses of the acid generating minerals gave consistent results but identification of all the minerals present proved difficult. The XRD results are not presented here but it is clear from the presence of peaks in the 3.4 Å and 10 Å area that both quartz and illite were present. However the dissolution of quartz or illite would not give the metal concentrations or the pH which were observed in laboratory experiments. The unnassigned peaks in the XRD analyses do suggest that another mineral is present but there are insufficient peaks present for an identification to be made. One possibility considered was the mineral franklinite which has the chemical formula $Zn_{0.6}Mn_{0.8}Fe_{1.6-}O_4$. However, although franklinite is associated with the weathering of zinc-rich orebodies it is usually associated with limestone and not with shales/clays. It is very common for other iron and manganese oxides to be present in association with clay minerals (Reddy & Perkins 1976). Manganese and iron oxides are recognised as scavengers of cations and any dissolved zinc arising from sphalerite dissolution within the mine (Younger 2000*a*) is likely to have been adsorbed onto their surface (Jenne 1967). This could explain the metal concentrations seen in the laboratory experiments but would not explain the high sulphate concentrations and low pH which was observed. Sulphate is present in the mine from the oxidation of sphalerite (Younger 2000*a*) and could be sorbed onto the surface of iron-manganese oxides (Geelhoed *et al.* 1997) which would explain the observed acidity. There is at present, insufficient data to identify this mineral and with very little in the literature about the nature of these acid generating minerals, there is a real need for more research into this area.

Hydrogeology

Groundwater rose at varying rates depending on the available void space within the mine; the average rate of rise between March 1999 and August 1999 was between 25 and 30 cm/day (Fig. 4). The groundwater stopped rising on the 25th August 1999 at ~373 m aOD which is 1 m above where the Tailrace Level enters the No.2 Shaft (see Fig. 3). An increased discharge was noted at Tailrace Level on the same day and water quality in the Level deteriorated.

It was anticipated that the Great Limestone would accommodate the majority of the rebounding mine water. However this did not happen and in fact the majority of water discharged to the surface via the Tailrace Level. With hindsight a possible explanation has been formulated which is illustrated by Figs 5 and 6. The Great Limestone is a confined aquifer and so the peizometric head is above the top of the aquifer. It is the weight of the overburden above the aquifer which drives the water through the fractures of the Great Limestone. Before mining severely altered the nature of the Great Limestone aquifer in the Frazer's Grove area, the aquifer would easily have accomodated an extra ~680 m^3/d. However the Great Limestone has been severely modified by the workings at

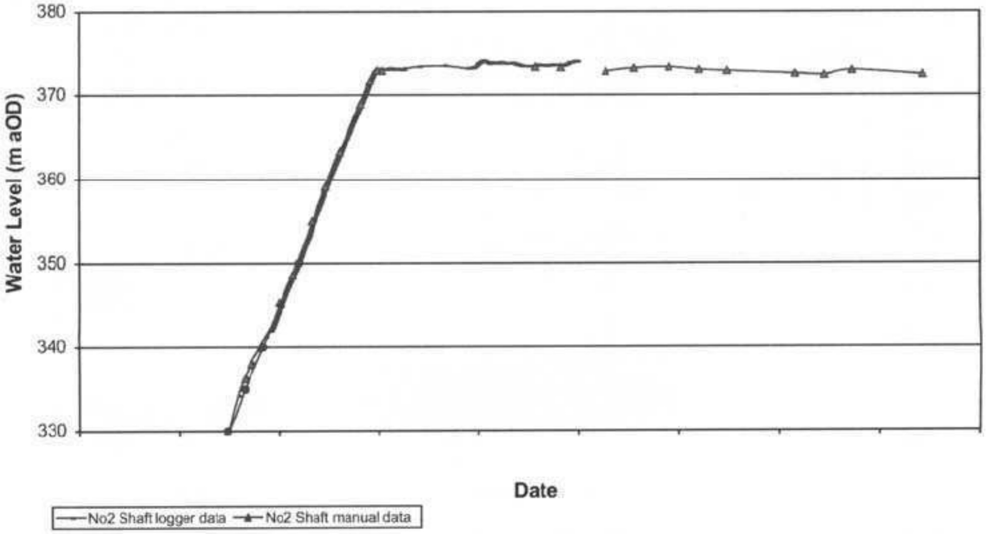

Fig. 4. Logger and manual data for the rising water table at Frazer's Grove mine from Spring 1999–Spring 2001.

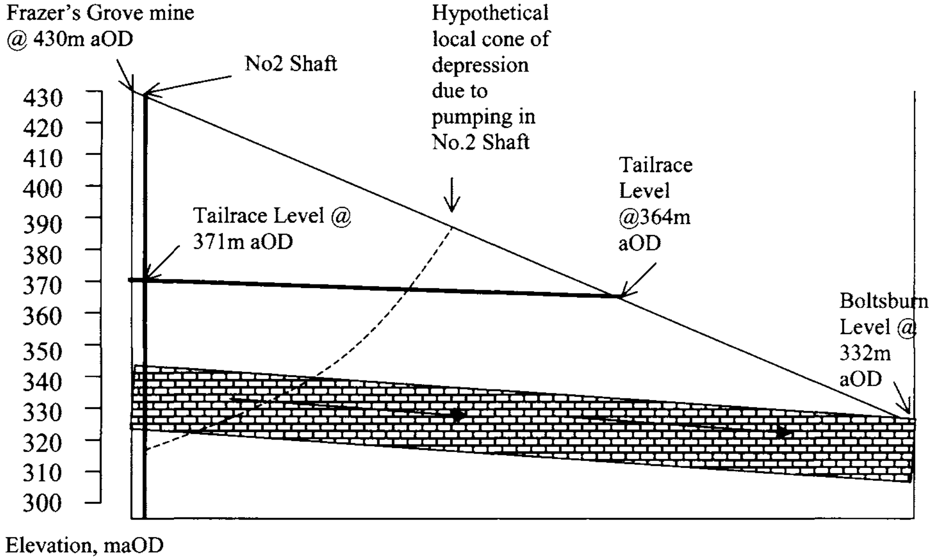

Fig. 5. Sketch diagram of hydrogeology of Great Limestone during mining.

Frazer's Grove mine. It is no longer a confined aquifer in the vicinity of Frazer's Grove mine as the overburden which creates the necessary environment for confined conditions has been breached. During mining the water table is artificially lowered and so there is no chance of a surface discharge (see Fig. 5). When the groundwater rebounded, the mine water rose above the aquifer and flowed in the channelised system of mine workings towards the Tailrace Level portal as there was insufficient pressure to drive the water through the aquifer (see Fig. 6).

Geophysics

The temperature and conductivity logs from June 2000 correlate with the stratigraphy in the No.2 Shaft as shown in Fig. 7. The data confirm that

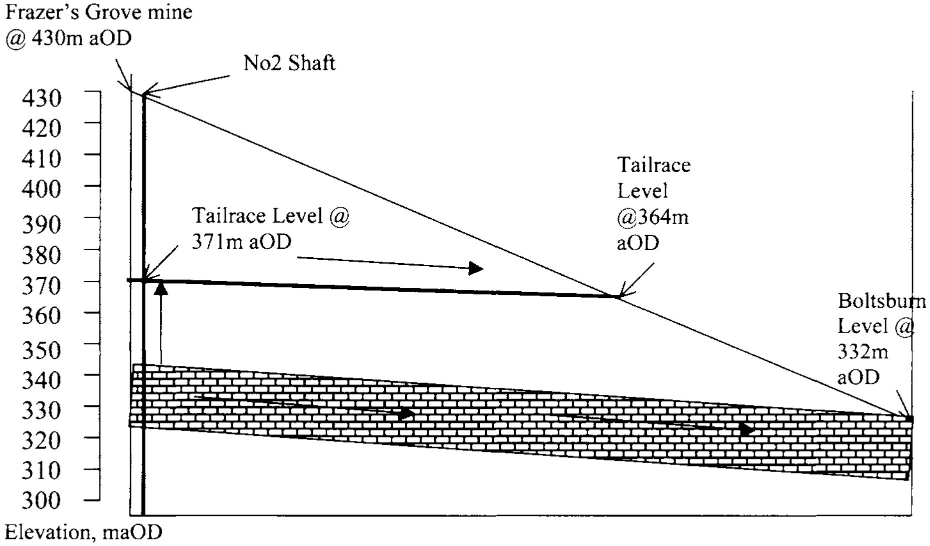

Fig. 6. Sketch diagram of hydrogeology of Great Limestone after mining.

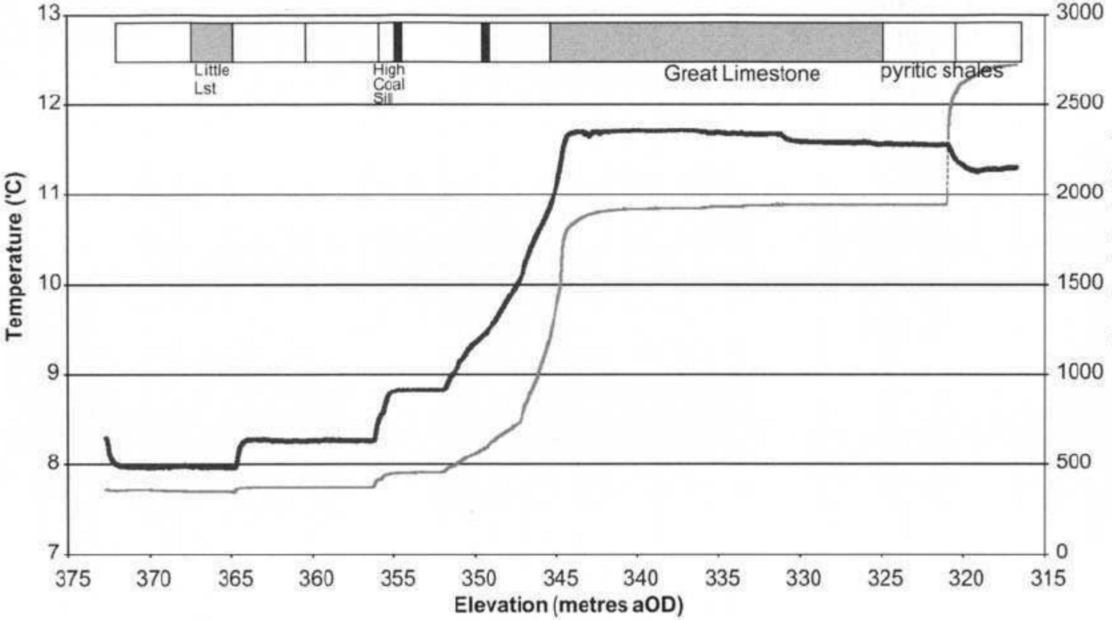

Fig. 7. Conductivity and temperature log of No.2 Shaft at Frazer's Grove Mine.

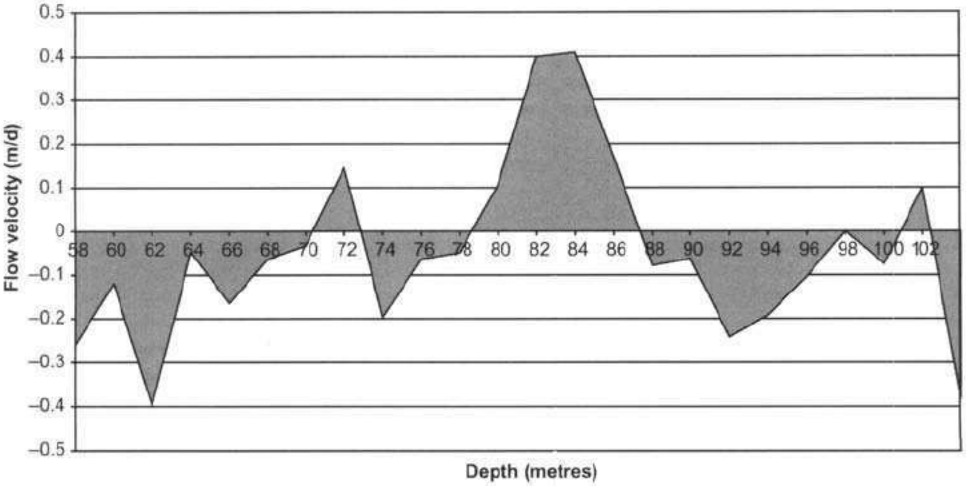

Fig. 8. Velocity flow log of water column in the No.2 Shaft at Frazer's Grove Mine.

the worst quality water (with the highest conductivity) is encountered where the pyritic shales are present at 350 m aOD. This poor Shaft water quality then persists throughout the Great Limestone formation.

The velocity flow log (Fig. 8) shows that water was mainly moving down the shaft as would be expected but that there was a significant component moving up towards 350 m aOD. This suggests that a proportion of the mine water is flowing at 350 m aOD which is the top of the Great Limestone where most fractures occur.

Hydrochemistry

A standard geochemical modelling program, WATEQ4F (Ball & Nordstrom 1991) has been used to model the water chemistry in the shaft. Results showed that goethite was supersaturated and that gypsum was close to saturation. The goethite saturation explains the orange ochreous precipitates in the samples taken and why, of the three metals measured, iron concentrations are by far the lowest.

Typical key hydrogeochemical data from both before and after mine water emergence are given in Table 2. The data are also presented graphically in Figs 9–12. Metal and sulphate concentrations increased in the No.2 Shaft as the water rose through the highly weathered acidic shales and then improved following contact with the Great Limestone. The water column within the shaft was stratified as it rose until 25 August when it overflowed into the Tailrace adit. The energy of the process caused complete mixing resulting in very homogenous shaft water geochemistry. Peak toxic metal concentrations seen within the shaft occurred on 25 August 1999 with iron, manganese and zinc concentrations as high as 50 mg/l, 130 mg/l and 120 mg/l respectively. It remained mixed until the end of 1999 when it once again became stratified. The current situation where the Tailrace water is more contaminated than the water at the top of the shaft can be explained if the Tailrace adit is blocked at the No.2 Shaft. Historically, water was pumped from lower workings into the adit and allowed to drain through it; however, the Tailrace adit was never a successful gravity drainage feature as it tended to silt up. If this adit entrance is blocked at the No.2 Shaft the water has found an alternative route.

The next route is along the 40 fathom level (340 m aOD) and up the No.1 shaft to the Tailrace Level (see Fig. 3). The water above the 340 m aOD level is then free to stratify on top of the turbulent and mixed water column beneath. A similar pattern of stratified mine water on top of a mixed column has also been observed at Wheal Jane in Cornwall (Adams & Younger, this volume). Hydrochemical evidence supports this theory as the correlation between metal concentration in the shaft and the Tailrace Level is best at the depth 340 m aOD as is shown in the matrix plot below (Fig. 13). The correlation is equally strong for zinc but not for iron suggesting that the relationship for iron is more complicated. As goethite is supersaturated in the shaft water there may, therefore, be more geochemical sinks for iron than for either manganese or zinc. There may also be iron oxides and oxyhydroxide deposits present within the Tailrace Level which could affect the geochemistry of the emerging discharge.

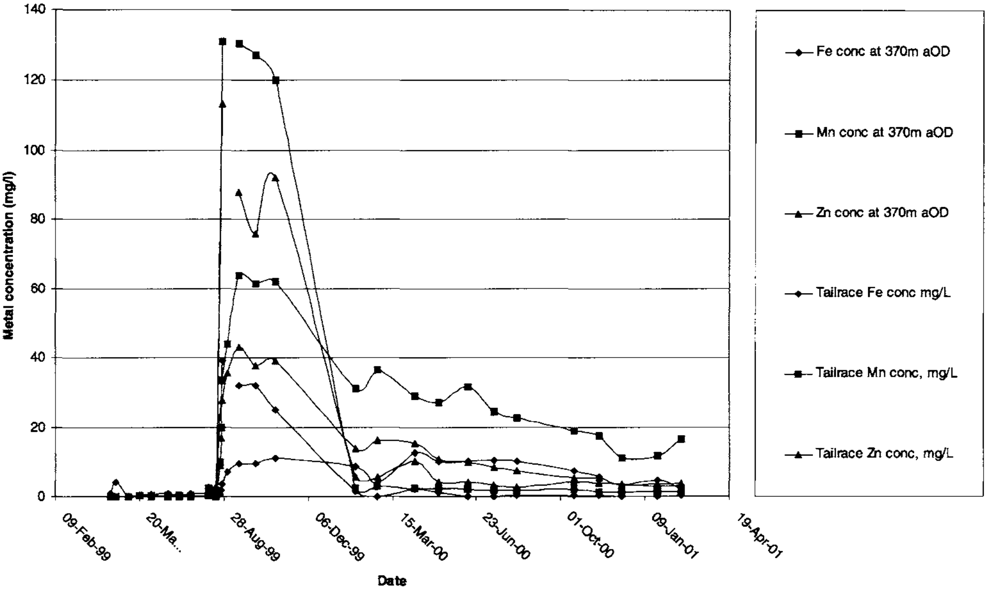

Fig. 9. Metal concentration at 370 m aOD in the No.2 Shaft at Frazer's Grove Mine compared with metal concentration in the Tailrace Level.

Three interesting points arise from the hydrogeochemical data presented in Figs 9–12. They are represented on Fig. 10 by arrows marking out points A, B and C:

(a) Firstly, the data show that between 22nd June and the 7th July 1999 there was an unexpected increase in metal concentration at depth 350 m aOD as highlighted in Fig. 10 by 'A'. The increase in metal concentration can also be seen at later dates throughout the water column at the depths 340 m and 330 m aOD but it occurs first and is most distinct at 350 m aOD suggesting that the source of the increase

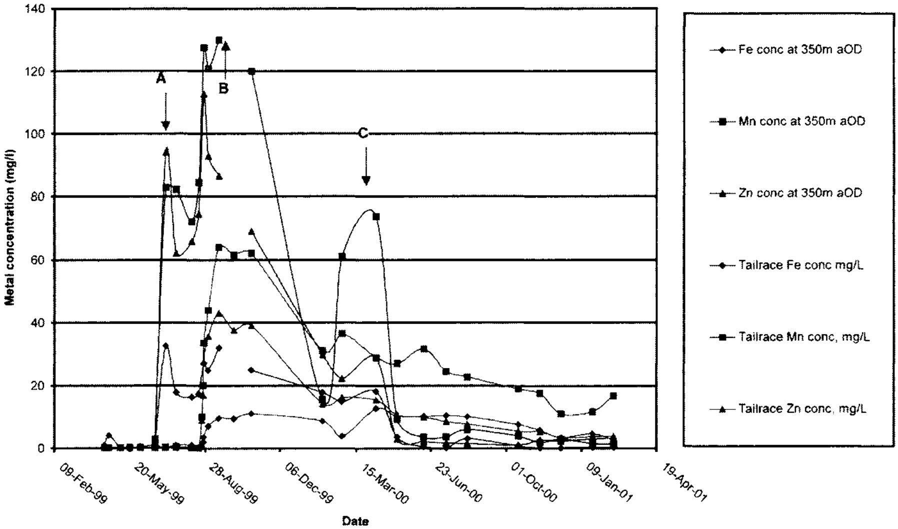

Fig. 10. Metal concentration at 350 m aOD in the No.2 Shaft at Frazer's Grove Mine compared with metal concentration in the Tailrace Level.

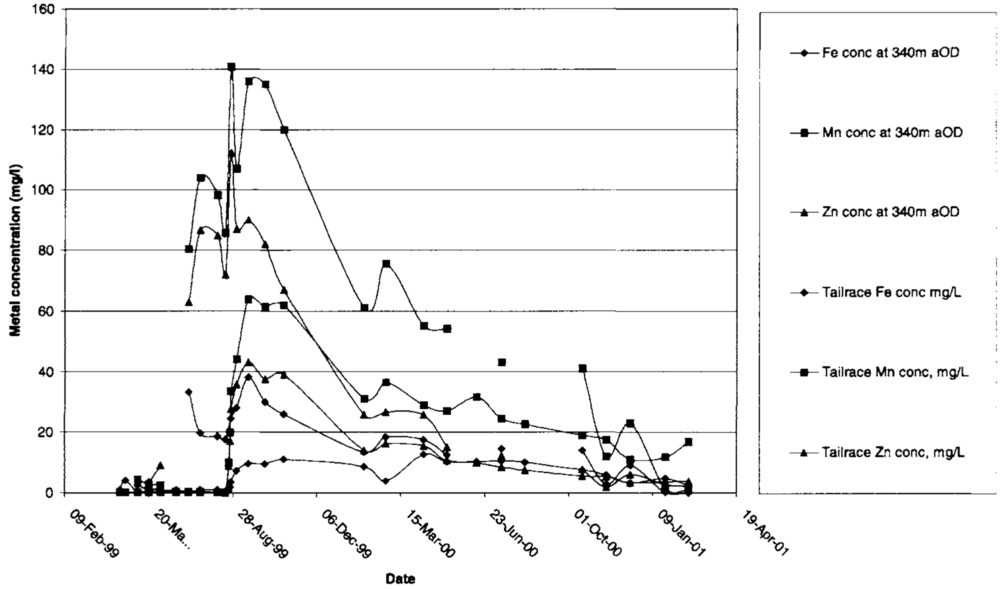

Fig. 11. Metal concentration at 340 m aOD in the No.2 Shaft at Frazer's Grove Mine compared with metal concentration in the Tailrace Level.

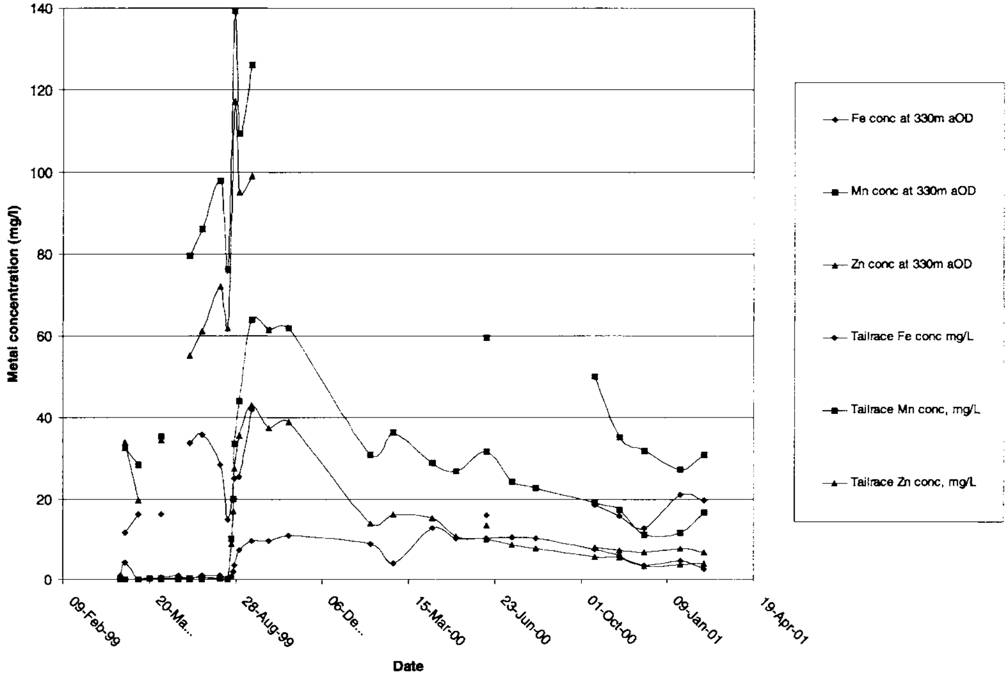

Fig. 12. Metal concentration at 330 m aOD in the No.2 Shaft at Frazer's Grove Mine compared with metal concentration in the Tailrace Level.

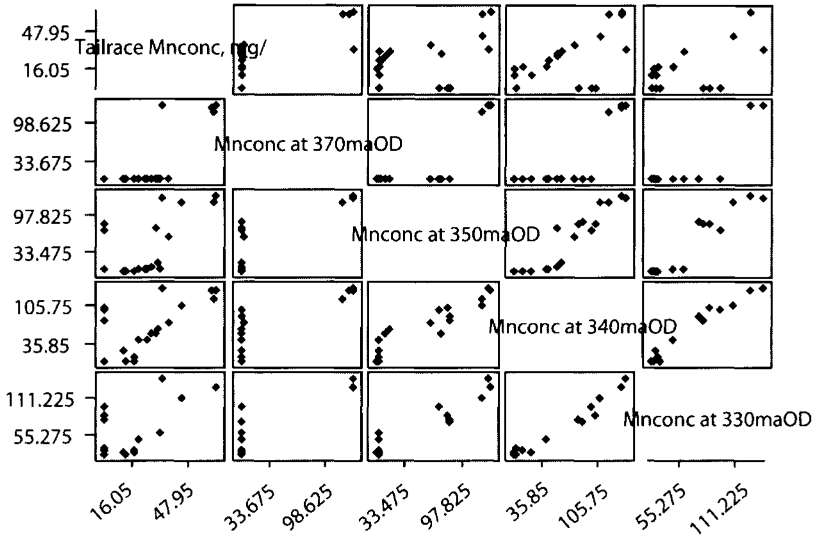

Fig. 13. Matrix plot of Mn concentrations at various depths in No.2 Shaft and the Tailrace Level.

came from this level. The water level during this period was between 355 m aOD and 359 m aOD and Table 1 shows that the strata present around this depth are 'Plate beds' and coal and sandstone beds beneath the Little Limestone. It was not possible to take samples from these beds during underground surveys. A literature survey has also revealed little information on their petrological nature. These beds are likely to contain acid generating minerals as they are probably of a similar nature to the marine cyclothems which are present beneath the Great Limestone. If this is the case then pyritic material present in these beds could offer an explanation for the dramatic decrease in shaft water quality between 22 June and the 7 July 1999.

(b) Secondly, water quality in the shaft deteriorates on 25 August when the water overflows into the Tailrace Level. Water quality in the Tailrace Level shows a peak value in metal concentrations (~40 mg/l Zn, 62 mg/l Mn, 10 mg/l Fe, conductivity ~1700 μS/cm) on 15 of September and water quality has slowly improved since with concentrations in February 2001 at ~4 mg/l Zn, 15 mg/l Mn, 3 mg/l Fe and conductivity ~1060 μS/cm.

(c) Thirdly, at point C (between 31 January 2000 and 11 April 2000) metal concentration increases dramatically within the shaft between 330–350 m aOD with the clearest increase at the 350 m aOD level suggesting that a further change in the shaft stratification has occurred.

The water quality of the mine water discharge was expected to improve as flushing of flooded workings occurs. Younger (2000*b*) found that it was possible to relate the total length of this initial period of flushing (initial worst water quality) empirically to the rebound time:

$$t_f = 4t_r$$

where:

t_f is the total length of the first flush period
t_r is the 'rebound period' (ie the time taken for the mine to fill to overflowing)

In this case, the 'rebound period' was approximately five months and therefore the total length of first flush period was estimated to be 20 months. During this time, zinc and manganese concentrations decreased exponentially until they reached a relatively stable value of approximately 4 mg/l zinc in Spring 2001 (Johnson & Younger 2000). Since initial zinc concentrations in the Tailrace effluent were about 40 mg/l, this figure if ~1/10th of the first-flush value (Younger 2000*b*).

The high zinc concentrations in the rebounding mine water may seem surprising given that the highest zinc concentration recorded during the underground surveys was only ~40 mg/l (Younger 2000*a*). However, these values were recorded before the groundwater rebounded and dissolved the acid generating minerals present within the mine. Water levels rebounded to 328 m aOD when the pumps failed in 1996 and in this case zinc concentrations reached only 27 mg/ l. However, on 25 August 2000 when complete groundwater rebound had occurred, the water level reached 373 m aOD and, therefore, (hydrochemical evidence suggests) passed through not just one but two separate lots of acid generating minerals. With the break-up of stratification at the end of August 1999, zinc concentrations peaked at 120 mg/l. Such high zinc concentrations have never been seen in a North Pennines' mine before. It is presumed that the high zinc concentrations have been caused by dissolution of acid generating minerals in the shales and mudstones both above and below the Great Limestone.

Conclusions

Frazer's Grove has provided an excellent opportunity to study an abandoned limestone-hosted metal mine both before and after abandonment. It has generally been assumed that the environmental impact from limestone-hosted metal mines would be minimal due to the neutralising effect of the limestone. However, although the post-abandonment discharge from Frazer's Grove mine is circum-neutral it had a very high dissolved metal content. The source of the dissolved metals was the acid generating minerals in the shales and mudstones present both above and below the Great Limestone within the mine. The weathered shales may contain a new mineral which has yet to be named and more research must be carried out into the nature of these acid generating minerals. As pyritic shales are often found in association with limestone since both are of marine origin, Frazer's Grove post abandonment hydrochemistry may be representative of other limestone-hosted mines.

Water quality has improved exponentially with time giving more credence to the empirical formula presented by Younger (2000*b*). This is a powerful tool for the prediction of water quality in a post-abandonment situation for a given mine. It was presumed at Frazer's Grove that mine water quality would be superior by further contact with the limestone strata if the rebounding mine water had travelled through the aquifer to its surface discharge point. However, an important observation arising from Frazer's Grove mine is that mining severely alters the hydrogeology of area. When mine workings have intercepted a confined aquifer, rebounding water is likely to take the easiest route to the surface along the mine workings rather than via the aquifer. This has serious implications for the prediction of both water quality and on where rebounding mine water will emerge.

Observations on the temporal and spatial geochemical nature of mine water within the mine workings have allowed a greater understanding of the process of stratification and of the development of water quality with time in abandoned mines. It is often assumed that water quality at the highest point within the mine for example at the top of a shaft will be representative of the emerging discharge water quality. However, Frazer's Grove mine has confirmed that this is not always the case as water in the mine can be stratified. Surface discharge water quality should be assumed to be closer in nature to the worst quality water in the mine rather than the best. This allows for the development of the most appropriate treatment technology for the resultant discharge and for any changes in its chemical nature. It is interesting to note that the pattern of break up of stratification and restratification at Frazer's during rebound could not have been predicted and that the hydrogeology of the mine is a dynamic process which evolves with time. However, it has highlighted the importance of careful monitoring and sampling which allowed us to ascertain the probable cause of restratification. Such an event may reoccur if the current exit point for the mine water also becomes blocked leading to a further possible change in discharge quality.

We would like to acknowledge the Engineering and Physical Sciences Research Council for funding this work at the University of Newcastle upon Tyne (Award Reference No.98316317). We would also like to thank Paul Allison who owns Frazer's Grove Mine for his continued patience and assistance. Thanks goes also to Dr Adam Jarvis who allowed us to use some of his diagrams (Figs 2 and 3).

References

ADAMCZYK, Z., MOTYKA, J. & WITOWSKI, A.J. 2000. Impact of Zn-Pb ore mining on groundwater quality in the Olkusz region. *Mine Water and the Environment, 7th International Mine Water Association Congress, Ustron, Poland, September 2000.*

ADAMS, R. & YOUNGER, P.L. 2002. A physically based model of rebound in South Crofty tin mine, Cornwall. *This volume.*

BALL, J.W. & NORDSTROM, D.K. 1991. User's Manual for WATEQ4F, with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters. *US Geological Survey Open-file Report*, 91-183.

DUNHAM, K.C., DUNHAM, A.C., HODGE, B.L. & JOHNSON, G.A.L. 1965. Granite beneath the Viséan sediments with mineralisation at Rookhope, Northern Pennines. *Quarterly Journal of the Geological Society, London*, **121**, 383–417.

DUNHAM, K.C. 1990. *Geology of the North Pennine Orefield, Volume One – Tyne to Stainmore*, HMSO, London, 118–150.

GEELHOED, J.S., VAN RIEMSDIJK, W.H. & FINDENEGG, G.R. 1997. Effects of sulphate and pH on the plant-availability of phosphate adsorbed on goethite. *Plant and Soil*, **197**, 241–249.

HAMILTON, Q.U.I., LAMB, H.M., HALLETT, C. & PROCTOR, J.A. 1999. Passive treatment systems for the remediation of acid mine drainage at Wheal Jane, Cornwall. *J.C.I.W.E.M*, **13**, 93–103.

JENNE, E. A. 1967. Controls on Mn, Fe, Co, Ni, Cu and Zn concetrations in soils and water: the significant role of hydrous Mn and Fe oxides in *Trace Inorganics in Water*, Advanced Chemistry Series 73, 1968.

JOHNSON, K.L. & YOUNGER, P.L. 2000. Abandonment of Frazer's Grove Fluorspar Mine, North Pennines, UK: Prediction and observation of water level and chemistry changes after closure. In: *Mine Water and the Environment: 7th International Mine Water Association Congress, Ustron, Poland, 11–15 September 2000.*

REDDY, M.R. & PERKINS, H.F. 1976. Fixation of manganese by clay minerals. *Soil Science*, **121**, 21–24.

YOUNGER, P.L. 2000*a*. Nature and practical implications of heterogeneities in the geochemistry of zinc-rich, alkaline mine waters in an underground F-Pb mine in the UK. *Applied Geochemistry*, **15**, 1383–1397.

YOUNGER, P.L. 2000*b*. Predicting temporal changes in total iron concentrations in groundwaters flowing from abandoned deep mines: a first approximation. *Journal of Contaminant Hydrology*, **44**, 47–69.