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Verification of the “first flush” phenomenon in mine water from coal mines in the Upper Silesian Coal Basin, Poland

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Abstract

Case studies of Grodziec and Siersza mines in the Upper Silesian Coal Basin confirm that mine water accumulating in and overflowing from abandoned coal mines is subject to a “first flush” phenomenon. The accumulated products of sulphide oxidation are dissolved in the rising mine water and flushed out at concentrations several times those observed during mine operation. Following the first overflow, sulphate concentration and hydrogen ion activity decay exponentially. In the case of workings in Siersza, decay constants of -0.003 to -0.005 day^{-1} are observed, corresponding to flushing times of 480 to 820 days, some 10–20 times the period required for the workings to flood. Quantities of leachable sulphur in the abandoned workings of 0.02–0.03% are adequate to explain the observed concentrations of sulphate in the first flush, and this figure is tentatively supported by laboratory analyses.

Keywords: Upper Silesia; Poland; Siersza; Grodziec; Coal; Sandstone; Sulphate; pH

1. Introduction

The geological environment is generally reducing and basic, while the atmospheric environment is acidic and oxidising. The zone of groundwater circulation is the natural reaction front between these two environments and is characterised by acid–base (e.g. carbonate and

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silicate hydrolysis) and redox reactions. Reaction rates are limited by the rate at which groundwater circulation renews the supply of acidic species (e.g. dissolved carbon dioxide) and electron acceptors (e.g. dissolved oxygen, nitrate). When mining occurs, we accelerate the rate of groundwater circulation and also introduce the atmospheric environment deep into the geosphere. Mineral reaction rates may thus be dramatically accelerated. Mining environments are often characterised by the oxidation of sulphides, such as pyrite or marcasite (FeS_2), which are ubiquitous in many coal and metal ore deposits. The pyrite oxidation reaction is often written as:

$$2FeS_2 + 2H_2O + 7O_2 = 2Fe^{2+} + 4SO_4^{2-} + 4H^+, \tag{1}$$

implying the release of dissolved iron, sulphate and acid (protons or hydrogen ions). This solution may be immediately released to mine drainage water that is pumped from an operating mine, or it may be retained in pore spaces in the rocks of the mine. Additional pyrite oxidation products (POP), such as secondary sulphate minerals (Younger, 2000; Banks, 2004) may be formed: for example, gypsum ($CaSO_4{\cdot}2H_2O$), melanterite ($Fe^{II}SO_4{\cdot}7H_2O$) or jarosite ($HFe^{III}(SO_4)_2(OH)_6$):

$$2FeS_2 + 10H_2O + 7O_2 + 4CaCO_3 = 2Fe^{2+} + 4HCO_3^- + 4CaSO_4{\cdot}2H_2O \tag{2}$$

$$2FeS_2 + 7O_2 + 16H_2O = 2FeSO_4{\cdot}7H_2O + 2SO_4^{2-} + 4H^+ \tag{3}$$

$$12FeS_2 + 30H_2O + 45O_2 = 4HFe_3^{III}(SO_4)_2(OH)_6 + 32H^+ + 16SO_4^{2-} \tag{4}$$

Other examples of secondary sulphate minerals which may occur in mining environments include the following:

- Coquimbite: $Fe^{III}{}_2(SO_4)_3{\cdot}9H_2O$
- Copiapite: $Fe^{II}Fe^{III}{}_4(SO_4)_6(OH)_2{\cdot}20H_2O$
- Römerite: $Fe^{II}Fe^{III}{}_2(SO_4)_4{\cdot}14H_2O$
- Alunite: $KAl_3(SO_4)_2{\cdot}(OH)_6$
- Jurbanite: $AlSO_4OH{\cdot}5H_2O$
- Other members of the jarosite or alunite families; e.g. Na–jarosite: $NaFe_3(SO_4)_2{\cdot}(OH)_6$

When a mine is abandoned, dewatering often ceases and water levels rise in the mine. Stratification may develop in the water column (Nuttall and Younger, 2004) and the rising mine water will usually dissolve the acidic pore water and/or residual secondary sulphate minerals (so-called "vestigial acidity") from the rocks in the vicinity of the mine workings; e.g. for jarosite:

$$\begin{aligned} HFe_3^{III}(SO_4)_2.(OH)_6 + 3H_2O &= 3Fe^{3+} + 2SO_4^{2-} + 5OH^- + 4H_2O \\ &= 3Fe(OH)_3 + 4H^+ + 2SO_4^{2-}. \end{aligned} \tag{5}$$

Thus, the water which initially fills and discharges from an abandoned mine may be substantially more environmentally aggressive (acidic, sulphate and metal-rich) than that which was pumped from the mine during operation. This phenomenon was documented as early as the mid 20th Century at Mainsforth Colliery, County Durham, UK, by Cairney and Frost (1975), while Younger (1997) has subsequently termed it the mine water "first flush" phenomenon. Furthermore, Frost (1979) argued that iron concentrations (C_{Fe} in mg/L) in water discharged from the flooded mine decayed with time (t in days), following "first flush", in an exponential manner described by:

$$\log(C_{\mathrm{Fe}}) = 1.684 + 0.102\log Q^* - 0.000858t \tag{6}$$

which corresponds to:

$$C_{\mathrm{Fe}} = 15.15 \times Q^{0.102} \times \exp(-0.00198t) \tag{7}$$

Where Q^* and Q are the discharge rates in $\mathrm{m^3/s}$ and $\mathrm{m^3/day}$ respectively. This equation implies a half life of 350 days for the iron concentration. Younger and colleagues also noted that the concentrations of solutes related to sulphide oxidation decrease over time, in a quasi-exponential fashion, as the mine workings are flushed clean of residual pore water and the secondary products of pyrite oxidation. Strictly speaking, Younger (2000) favoured the application of a more complex dispersive transport equation but found that, in practice, parameterisation was too problematic. Eventually, after a time t_{f} (the "flushing time"), the concentrations of solutes approximately stabilise at some "background concentration" (C_{b}). Indeed, Younger (2000) and Younger et al. (2002) were bold enough to suggest that:

- in coal mines, the iron (and, presumably, sulphate) contents of the first flush can be related to coal seam sulphur content;
- the half-life of the first flush is approximately equal to t_{r}, the time required for the mined void to flood following cessation of pumping; and
- the time for the first flush to be completed is given by

$$t_{\mathrm{f}} = (3.95 \pm 1.2).t_{\mathrm{r}}. \tag{8}$$

This paper will examine the data from two recently abandoned coal mines in the Upper Silesian Coal Basin (USCB) of Poland to ascertain whether the above observations from investigations of British mines are more universally applicable. The objective of these studies is to validate existing conceptual models of the post-closure hydrochemical behaviour of abandoned flooded mines and, in particular, to enhance our understanding of the physical processes underlying simple exponential decay models and the potential variability in the parameterisation thereof.

2. Geological context

The Siersza and the Grodziec mines are located on the north-eastern and northern flanks of the Upper Silesian Coal Basin (USCB) of southern Poland (Fig. 1). The USCB is a synformal basin structure of approximate extent 90 km from north to south and 120 km from east to west. The coal mines of the basin have provided the raw materials for Poland's main heavy industrial region (iron and steel industries, chemical industry), centered around the metropolitan areas of Katowice, Sosnowiec and Gliwice.

The coal-bearing sequence of the USCB can reach 8000 to 8500 m in thickness (Gmur and Kwiecińska, 2002; Nowak, 2004). The sediments therein are regarded as having been laid down as a molasse-type deposit in a Variscan foredeep basin, with the continental sediment source in the north-east. Four main lithostratigraphic Series can be recognised within it (Table 1). The sequence essentially progresses downwards from the terrestrial, coarse-grained, freshwater Krakow

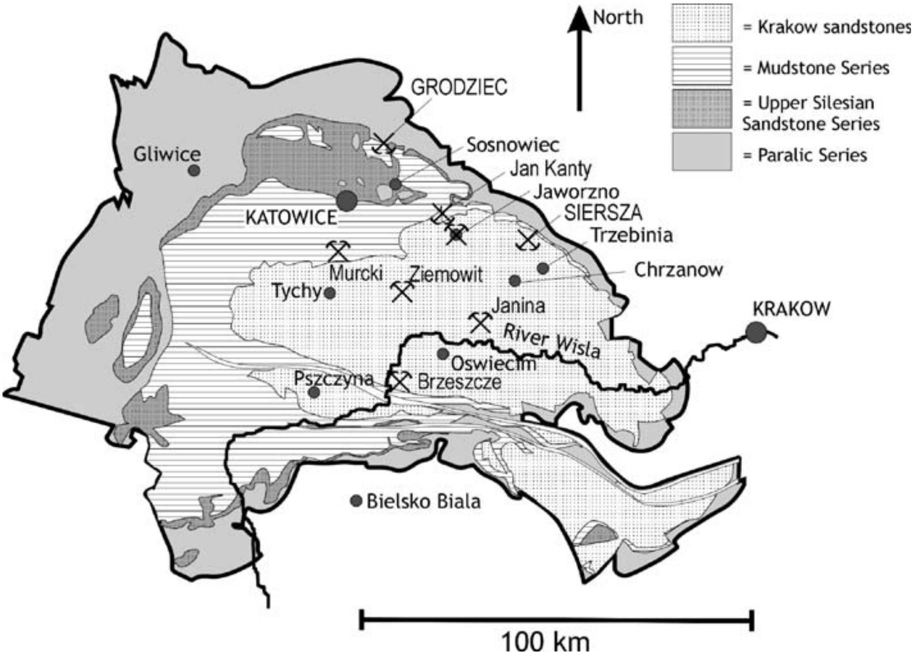


Fig. 1. Geological map of the top surface of the coal-bearing Carboniferous of the Upper Silesian Coal Basin. Note that this is not a conventional geological map of a land surface: it is a map at the level of the unconformity between Carboniferous and post-Carboniferous strata. The Carboniferous strata are themselves covered by various deposits, Permian to Quaternary age. Redrawn and simplified after Buła and Kotas (1994).

Sandstones (and conglomerates), to the more distal, deltaic to shallow marine shale sequence of the Paralic. The Kulm Measures (not shown in Table 1) are essentially the non-coal-bearing, siliciclastic marine sedimentary facies (flysch) of the Namurian Series.

The USCB is overlain unconformably by a variety of later deposits (Kotas, 1994). In the south of the basin, these are dominantly Miocene argillaceous sediments deposited in a fore-basin of the

Table 1
Stratigraphic sequence within the coal-bearing portion of the Carboniferous of the Upper Silesian Coal Basin (after Buła and Kotas, 1994)

Series	Age	Unit
Krakow Sandstone Series	Stephanian	Kwaczała Arkose
	Westphalian D	Libiąż Beds
	Westphalian C, D	Łaziska Beds
Mudstone Series	Westphalian A, B	Orzesze Beds
	Westphalian A, B	Załęże Beds
Upper Silesian	Namurian C	Ruda Beds
Sandstone Series	Namurian B	Anticlinal (Siodłowe) Beds
	Namurian A	Jejkowice Beds
Paralic Series (Upper)	Namurian A	Poruba (Porębskie) and Jaklowieckie Beds (western USCB) Grodziec Beds (central and eastern parts of USCB)
Paralic Series (Lower)	Namurian A	Gruszow and Pietrzkowice Beds (western USCB). Flora and Sarnów Beds (central and eastern parts of USCB)

Carpathian Mountains (which lie to the south). In the north of the USCB, the Carboniferous coal-bearing strata are overlain by Permian, Triassic or Quaternary strata, typically of hydraulically conductive character (sandstones, conglomerates, limestones, dolomites and sands). It is widely accepted that the bulk of groundwater recharge to the USCB occurs through the permeable cover of the northern half of the USCB, rather than the Miocene-covered southern half.

3. Sulphur in the Upper Silesian Coal Basin

Several researchers (e.g. Spears et al., 1999) have noted that the sulphur content of coals is broadly related to the degree of marine influence at the time of deposition and the stratigraphic proximity to marine marker horizons. Furthermore, there is a reported tendency for the importance of pyrite to be greater (compared to organic sulphur) in marine coals. This hypothesis is not confirmed by the coal-bearing sequence of the USCB (Table 2). Indeed, the most sulphur-rich coals are found in the continental Krakow Sandstone beds of the eastern USCB, while the better quality coals are found in the stratigraphically lower deposits of the northern USCB. Note, however, that the sulphur content of the host rock appears to be lowest in the continental sandstones and to increase downwards. The average content of the $n=201$ coal seams examined by Chmura and Nowak (1990) was 1.0% sulphur. On average within the USCB, 69% of the sulphur content of coal was pyritic (range 49–88% for the various beds of Table 2) and 31% organic (range 12–51%). The coals' average content of pyritic sulphur ranged between 0.33% and 1.83% for the various beds of Table 2, while the average organic sulphur content varied from 0.22% to 0.48%.

Furthermore, for any given stratigraphic formation in Table 2, the coals' sulphur content decreases with depth below ground surface. Thus, the highest sulphur contents are found in mines where coals in the Krakow Sandstones are exploited at shallow depths, such as Siersza mine. There is no evidence to suggest that the high sulphur content of the coals of the Krakow Sandstones is organic, rather than pyritic; on the contrary, Chmura and Nowak (1990) found the highest pyrite contents in the sulphur-rich coals of the Sandstones. Field examination of weathered Krakow Sandstone coal seams *in situ* (seams 118 and 119, Janina Mine 27/9/05) confirms the observed existence of secondary pale yellow-orange mineral in exposed coal faces and cleat, together with bright orange-red drops of leachate forming on these surfaces. Subsequent X-ray diffraction (XRD) analysis confirmed the secondary mineralisation to be dominated by Na–jarosite and gypsum (Banks, 2006b).

Table 2
Sulphur contents of coals and host rocks within the coal-bearing formations of the Upper Silesian Coal Basin

Formation	Coal seam numbers	Mean S content of coal (%)	Range of S content of coal (%)	Mean S content of host rock (%)
Libiąż Beds	100	2.47	0.50 to 7.15	0.18
Łaziska Beds	200	2.29	0.55 to 7.01	0.25
Orzesze Beds	300	1.11	0.27 to 4.72	0.45
Ruda Beds	400	0.89	0.29 to 3.30	0.55
Anticlinal (Siodłowe) Beds	500	0.75	0.19 to 4.43	
Poruba (Porębskie) Beds	600	1.19	0.44 to 5.34	
Jaklowieckie Beds	700	0.96	0.44 to 5.34	
Gruszow Beds	800	1.50	0.45 to 3.32	

Data from Chmura and Nowak (1990).

4. Case study 1: The Grodziec mine

4.1. Location

Grodziec Mine is located around 20–25 km NNE of the city of Katowice. The ground surface at Grodziec is c. 297 m above sea level (m asl) and the mine base is at −540 m asl, giving a maximum depth of 837 m. The main mined seams are in the sequence 600–800 (i.e. Poruba to Gruszow Beds, Table 2), within the marine-influenced, dominantly argillaceous Paralic Series of alternating sandstones, mudstones and coals. The top of the Carboniferous is at a depth of around 100 m. The overburden comprises Triassic limestones and marls (Muschelkalk and Roethian) of up to 180 m thickness, and Quaternary (glaciofluvial and fluvial sands and gravels) of maximum thickness 40 m.

A map by Kaziuk (1994) reports a sulphur content in the coals extracted from Grodziec mine of 1.1%, while Chmura and Nowak (1990) confirm a similar figure.

4.2. Operational mine water quantity and quality

During operation, the main drainage and pumping levels of Grodziec Mine were located in Shaft II at nominal depths of 300 m (“Level 300”) and 500 m (Fig. 2). In the period 1991–2000, the average water make from Level 300 was 49.8 L/s and from Level 500 36.3 L/s, giving a total mine water make of 86.2 L/s (Frolik et al., 2005). Extensive water quality data have not been

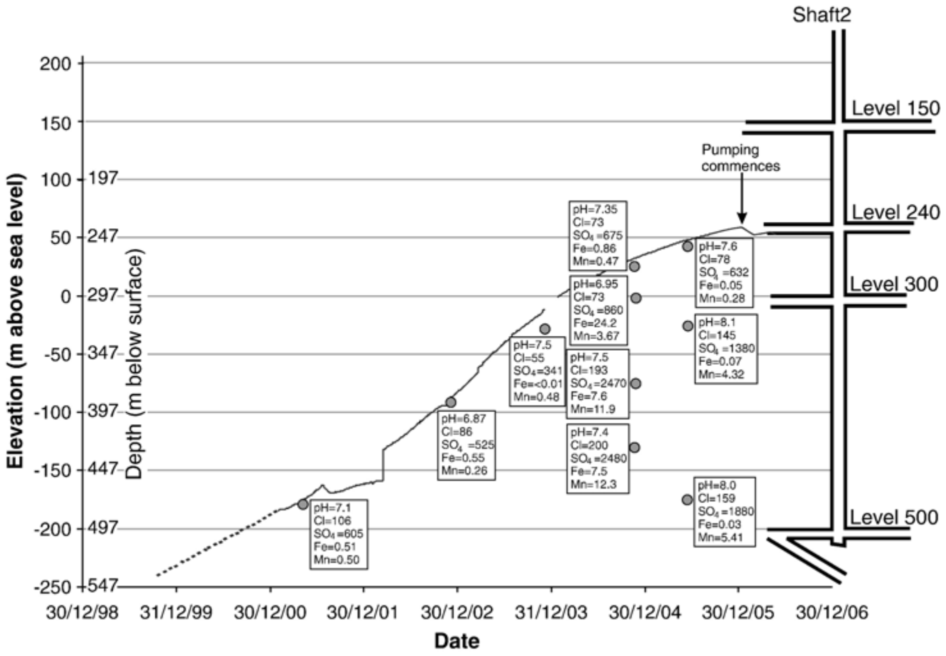


Fig. 2. A hydrograph of the rising mine water level in Shaft II of Grodziec Mine. Locations and times of samples collected (with a summary of pertinent hydrochemical characteristics) are shown. To the right, a conceptual sketch of the Shaft layout is indicated.

available for the operational phase of the mine, but such data as are to hand (Frolik et al., 2005) can be summarised as follows:

- Water pumped from Level 300; average concentrations 1993–1999: chloride 66 mg/L, sulphate 475 mg/L, pH 7.9, calcium 194 mg/L and magnesium 53 mg/L.
- Water pumped from Level 500; concentrations in 1998: sulphate 474 mg/L, chloride 1647 mg/L. There are saline inflows to deep workings draining to Level 500 of Na–Cl–SO_4 water (maximum mineralisation 47–65 g/L).

The Grodziec mine was abandoned and pumped drainage ceased in October 1999. From this date, water started rising in Grodziec mine.

4.3. Methods

During the period of mine water recovery following the abandonment of Grodziec mine, water level was measured in Shaft II on a daily basis by the Central Mine Dewatering Department (CZOK) of a mine restructuring company, using an electronic data logger. Furthermore, at yearly intervals, water samples were taken from just below the rising mine water surface using a simple bailer. In years 2004 and 2005, additional water samples were collected at specific depths within the shaft using a ball-valve operated depth sampler.

The water samples from the depth profiles were not field-filtered or preserved on site. Rather, a single clean flask of sample water was returned immediately to the laboratory of the Central Mining Institute in Katowice, where the sample was filtered on arrival and analysed on the day of sampling. Analysis was accomplished by ICP-OES techniques for cations and metals, silver nitrate titration for chloride, gravimetric analysis for sulphate and spectrophotometric techniques for nitrogen species. The laboratory of the Central Mining Institute is quality assured according to Polish Centre of Accreditation PCA-AB145. The lack of field filtration or preservation techniques renders the analytical results for some elements (e.g. iron) difficult to interpret. The values presented here should probably be regarded as a minimum estimate of the dissolved iron content of the water.

4.4. Results: post-abandonment mine water quality

The water level hydrograph for Shaft II is shown in Fig. 2. Water was permitted to rise to a level of 57 m asl, at which point pumping recommenced to prevent mine water overflowing along the Level 240 workings to adjacent mines. This point was reached at the end of December 2005. Thereafter, an average pumping rate of 44 L/s was recorded during the period January–April 2006 in order to maintain this level.

In 2001, 2002 and 2003, one annual bailer sample was taken from just below the surface of the rising mine water body. The main chemical characteristics of these samples are plotted on Fig. 2, while the full analysis for 2003 is reproduced in Table 3. In 2004 and 2005, depth sampling was carried out, with samples being recovered from various depths down to 470 m. The analytical results are provided in Table 3, and the main features plotted in Figs. 2 and 3. Table 3 also includes one sample from June 2006, collected from the pumped water flux, after pumping had recommenced to stabilise water levels. This sample was correctly field filtered at 0.45 μm and analysed at the laboratory of the Central Mining Institute (GIG).

During the filling of the mine, the sulphate concentrations were in the range 340 to 680 mg/L immediately below the water surface. These are not substantially in excess of concentrations

Table 3
Hydrochemical characteristics of water samples from 2003 to 2006 from Shaft II, Grodziec mine

Year		2003	2004	2004	2004	2004	2005	2005	2005	2006
Sample depth	m bgl	325	270	300	370	430	252	320	470	Pumped
Temp.	°C	–	11	12	13	14	–	–	–	–
EC	μS/cm	1570	1830	2180	5530	5750	1800	3690	4470	3740
TDS	mg/L	1135	1607	1941	5107	5172	1600	3200	4050	3410
Susp. solids	mg/L	<10	<10	62	25	27	<10	22.1	29.2	–
pH		7.50	7.35	6.95	7.50	7.40	7.55	8.10	8.00	6.90
t-alkalinity	meq/L	9.20	7.85	8.80	18.60	19.30	8.00	13.70	14.70	14.4
Ca	mg/L	160.1	252.9	254.5	262.5	252.5	238.5	197.8	230.5	200.4
Mg	mg/L	66.8	96.8	113.5	178.6	177.4	91.25	125.1	151.9	136.1
Na	mg/L	100.0	86.9	149.2	1087	1127	91.5	616.1	795.5	646.0
K	mg/L	11.14	20.72	15.44	41.84	42.23	10.56	27.37	34.02	23.85
Fe	mg/L	<0.01	0.86	14.2	7.6	7.5	0.045	0.073	0.025	13.5
Mn	mg/L	0.48	0.47	3.67	11.9	12.3	0.28	4.32	5.41	3.8
Al	mg/L	–	–	–	–	–	–	–	–	0.06
NH_4^+	mg/L	<0.05	<0.05	0.84	2.46	2.61	<0.05	1.41	1.08	2.21
Cl^-	mg/L	55.0	73.1	73.5	192.6	200.2	78.24	144.5	158.6	85.6
SO_4^{2-}	mg/L	341	675	860	2470	2480	632	1380	1880	1640
Alkalinity	meq/L	9.2	7.85	8.8	18.6	19.3	8.0	13.7	14.7	14.4
NO_3^-	mg/L	<2	1.25	0.42	0.90	0.49	1.83	1.65	0.88	<0.5
Zn	mg/L	0.15	1.44	0.32	0.55	0.48	1.05	0.21	0.53	0.10
Ni	μg/L	<10	17	37	56	56	19	45	39	21
Cd	μg/L	<2	3.7	<2	2.8	<2	2.7	<2	2	<2
Pb	μg/L	<20	240	170	180	140	<10	<10	<10	<10
Cu	μg/L	12	280	86	110	76	92	68	51	<10
Cr	μg/L	<10	<10	<10	<10	<10	<10	<10	<10	<10
IBE	%	0.8	2.0	1.4	1.0	1.0	0.6	1.5	1.2	0.3

EC = electrical conductivity; TDS = total dissolved solids; IBE = ion balance error. Data from Frolik et al. (2005). The last sample was taken from the pumped shaft on 12/6/06 and analysis of metals was performed on an aliquot of sample field-filtered at 0.45 μm.

determined during operational conditions from Level 300 and are most likely due to continued direct run-in of water from that level (and, possibly, from higher levels or leakage from the overlying Triassic/Quaternary aquifers).

During mine filling, sulphate concentrations increased rapidly with depth to concentrations in excess of 2400 mg/L, confirming the existence of Younger et al.'s "first flush" phenomenon. The concentrations measured during mine water recovery are around 4–5 times higher than operational concentrations. Furthermore, iron and manganese concentrations reach very high concentrations in excess of 10 mg/L (in 2004 samples). Note the rather low iron concentrations detected in 2005. The reasons for this are outlined above, and illustrate the difficulty of obtaining reproducible iron concentrations unless great care is taken with field and laboratory filtration and preservation.

Stratification developed in the mine water column in the shaft. In the 2004 (Fig. 3) samples, a significant transition is noted between 300 and 370 m, characterised by the following features:

(i) Concentrations of Fe, SO_4^{2-}, Mn rise significantly, to levels exceeding those observed during operational mine dewatering. This first transition is believed to represent the boundary between overlying, relatively dilute recharge water and run-in from unflooded

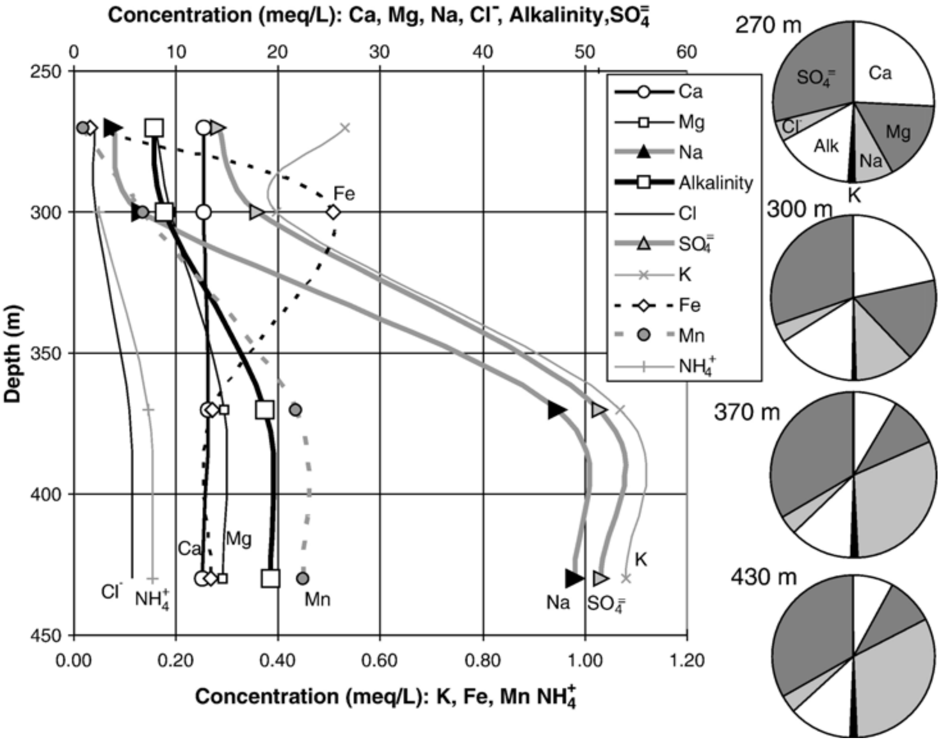


Fig. 3. Hydrochemical profiles of Shaft II, Grodziec for samples taken in 2004. Note that concentrations are plotted as meq/L. The pie diagrams indicate the major ion composition of the water as the meq/L proportions of the total ionic content.

shallow workings, and more concentrated "first flush" water containing the dissolved secondary products of pyrite weathering.

(ii) The water type changes from a dominantly Ca–SO_4 water to an Na–SO_4 water type. The upper water type is believed to reflect the interaction between sulphide weathering products and a natural calcium-bicarbonate groundwater at shallow levels (derived by calcite dissolution). At deeper levels, the natural groundwater in many coal-bearing sequences (e.g. Banks, 1997; Frengstad and Banks, 2000) is an alkaline sodium-(bi)carbonate type (due to plagioclase hydrolysis coupled with saturation and precipitation of calcite). The interaction of sulphide weathering products with an alkaline sodium (bi)carbonate water will result in the observed sodium sulphate water type.

$$4Na^+ + 2CO_3^= + Fe^{2+} + 2SO_4^{2-} + 2H^+ = 4Na^+ + 2HCO_3^- + Fe^{2+} + 2SO_4^{2-} \tag{9}$$

Furthermore, XRD analysis from the nearby Janina mine (Banks, 2006b) indicated that the main detectable secondary sulphate mineral was sodium jarosite, whose dissolution during first-flush would be expected to result in a sodium sulphate water type.

(iii) There is a significant increase in chloride, ammonium and alkalinity at depth. This is suspected to represent a deep inflow of chloride-containing, reducing alkaline Na–HCO_3 water from the deepest level of the mine (chloride brines were observed during operation in the deepest levels).

The first flush iron concentrations of up to c. 10 mg/L total iron are broadly in accordance with those predicted by Younger (2000) for coal workings with c. 1% sulphur.

5. The Siersza mine

5.1. Location

The Siersza mine lies near the town of Trzebinia, to the north of Chrzanow and to the east of Jaworzno (Fig. 1). It has been exploited since 1808 via various workings and shafts. These were independent at first but the 1947 drift between the Artur and Zbyszek Mines created a large interconnected “Siersza Mine” complex (Rogoż et al., 1999). The nominal ground surface at Artur shafts is +350 m asl, with the mine’s lowest point at 545 m depth at the base of Artur 1 shaft (−195 m asl).

The Carboniferous strata of the mine (Krakow Sandstones) subcrop below Quaternary drift deposits (some tills, mainly glaciofluvial and fluvial sands and gravels) at the northern end of the mining area. Towards the south and east, a relatively thin overburden of Triassic and Permian limestones, dolomites, marls, sandstones and conglomerates intervenes.

The exploited coal deposits of Siersza are dominantly within the Krakow Sandstone Series (seams 118–301), and the upper part of the Orzesze beds of the Mudstone Series (seams 301–304). The Krakow Sandstones typically comprise medium-to-coarse grained molasse type sandstone and fine conglomerate units, laid down in sandy braided river conditions in the Variscan foredeep basin. The clasts are often poorly sorted and sub-angular. The sandstones are weakly to moderately cemented and the cementation is believed to be largely argillaceous. The coals within the sandstone are often located within finer grained mudstone units extending up to 3 m from the coal seam, themselves sandwiched between the thick sandstone successions. These finer sedimentary units may represent infills of inactive channels. The coals themselves are typically banded and banded bright coals of very low coalification rank, deposited in wet forest swamp (peat bog) conditions (Gmur and Kwiecińska, 2002).

Seam 301 represents the nominal transition from the Krakow Sandstones to the underlying Mudstone Series. As the name suggests, the proportion of mudstone relative to sandstone is significantly higher in the latter Series.

The typical reported mean sulphur contents of Krakow Sandstone coals range from 1.99% S (Gmur and Kwiecińska, 2002) to 2.47% (Chmura and Nowak, 1990; Table 2). The sulphur content of coals exploited by Siersza mine are reportedly some of the highest in the USCB, with Chmura and Nowak (1990) reporting a mean for the mine of around 2.5% and the map of Kaziuk (1994) reporting 3.46%. More detailed studies of individual seams reveal wide ranges with means of 2.65%S and 2.47%S in seams 207 and 209/210, respectively, at Siersza (Gmur and Kwiecińska, 2002).

Siersza mine was abandoned in early 2001 and is currently filling with mine water. Readings at a single observation borehole (well P1; Banks, 2006a) suggest that water levels had risen to around +163 m asl by March 2006 (around 177 m below surface).

5.2. Operational mine water quantity and quality

Within the mine area, but outside the zone of active working and consequent dewatering, groundwater is abstracted for public supply from a network of boreholes around an aborted mine shaft (aborted due to problems with excessive groundwater inflows and running sand during sinking). This provides an indication of natural background groundwater quality within the Krakow Sandstones (Table 4).

The mine complex was drained by a network of adits at three main levels.

- Level IV: 190 m depth or +160 m asl;
- Level V: 256 m depth or c. +94 m asl;
- Level VI: 350 m depth or c. 0 m asl.

The water from each pumping station was discharged via the main drift (the Magistrala Węglowa) to surface settlement ponds. The typical water quantity and quality pumped from each station before closure are presented in Table 5. Pre-closure sulphate concentrations ranged from 226 to 442 mg/L in the main pumping stations, with pH in the range 6.5 to 7.8. At the base of Shaft 1, there were indications of elevated chloride concentrations, suggesting the existence of a more saline groundwater body at depth.

5.3. Methods

In this study, particular attention was paid to two areas of workings where pumping ceased and which were allowed to flood, prior to the closure of the main mine. These were areas of workings in seams 214 and 301 at Level VI in the mine. The characteristics of these zones are summarised in Table 6. Before flooding, the void space associated with these workings was estimated from geometry and assumptions about goaf compaction.

Following flooding, samples were taken on a weekly basis of the water overflowing from the workings. The samples were neither field filtered nor preserved. They were returned to the surface immediately and analysed in the laboratory of the Siersza Mine for sulphate, chloride and pH, using gravimetric, Ag-titration and pH electrode techniques, respectively.

5.4. Results: post-abandonment mine water quality

The workings were allowed to flood from the end of 1997. After 39–42 days, the workings overflowed, allowing the apparent floodable void space to be recalculated from the water make and the time delay (Table 6).

Table 4
Range in hydrochemical quality of groundwater abstracted from the Lech wellfield, in the Krakow Sandstone/Quaternary aquifer unit immediately north of Siersza mine

Parameter	Range of concentrations 1993–1998
pH	7.5 to 7.9
Cl^-	7.0 to 7.5 mg/L
SO_4^{2-}	60 to 150 mg/L
Fe	20–90 μg/L
Mn	<10 to 10 μg/L
NO_3^-	2.0 to 2.7 mg/L
Ammoniacal N	<0.01 to 0.01 mg/L

Data from Korczak et al. (1999).

Table 5
Average mine water quantities (1996–1998) pumped by each of the main pumping stations (PS) at Artur Shaft, and the total water make discharged to surface by way of the Magistrala Węglowa Drift

		Main level IV PS, Artur	Main level V PS, Artur	Main level VI PS, Artur	Base of Artur shaft 1, Level VII	Total combined discharge to surface
Average natural water make (1996–1998)	L/s	40.1	199.8	217.1	Minimal	456.9
Date		12/02/98	29/12/98	29/12/98	12/08/98	29/12/98
pH		7.81	6.50	7.04	7.00	6.87
TDS	mg/L	850	650	1020	430	830
Colour	mgPt/L	13	15	6	22	3
Ca	mg/L	101	70	104	39	95
Mg	mg/L	45	66	105	16	60
Na	mg/L	11.8	5.7	12.7	59.5	12.5
NH_4^+	mg/L	–	–	0.2	–	–
Mn	mg/L	0.1	0.1	0.3	0.1	0.2
Cl^-	mg/L	16.7	13.0	16.6	88.2	15.6
SO_4^{2-}	mg/L	240	226	442	85	256
Alkalinity	meq/L	4.29	4.20	5.00	3.80	4.39
NO_3^-	mg/L	0.1	nd	0.1	0.1	0.1
IBE	%	−2.6	−0.5	−0.9	−15.9	0.3

Also shown is typical mine water quality at each pumping station during late 1998 (data from Rogoż et al., 1999). TDS = total dissolved solids; IBE = ion balance error.

Figs. 4 and 5 illustrate the evolution of mine water quality flowing from the workings with time (t) after the commencement of overflow. In both cases, it will be noted that chloride shows no significant evolutionary trend with time. The chloride concentrations are believed to be representative of pre-industrial chloride in rainfall recharge and are not related to any "first flush" phenomenon.

The initial sulphate concentrations of around 2150 mg/L in Seam 214 and 1430 mg/L in Seam 301 are significantly higher than the pre-flooding concentrations. The initial pH values of 6.2–6.3 and 6.4 respectively, are lower than the pre-flooding values. Again, the first flush phenomenon is confirmed. Rising mine water is washing out residual pore waters and dissolving secondary sulphate minerals that are the vestiges of pyrite oxidation during the mine's operation history.

As predicted by Younger (2000), sulphate concentrations in both sets of workings decay quasi-exponentially. pH shows a quasi-linear rise, which is also indicative of the exponential decay of

Table 6
Characteristics of the two flooded areas of workings in Seams 214 and 301 in Siersza mine, Level VI (after Frolik et al., 2005)

	Level VI, Seam 214	Level VI, Seam 301
Estimated void space associated with workings (m^3)	35,000	393,000
Q = Water make from workings (m^3/day)	1152	3600
SO_4^{2-} concentration on 11/12/97 prior to flooding (mg/L)	382	86.4
Cl^- concentration on 11/12/97 prior to flooding (mg/L)	9.95	7.09
pH on 11/12/97 prior to flooding	6.43	6.87
t_r = Time taken for workings to flood (days)	42	39
Recalculated flooded void space = $Q.t_r$ (m^3)	48,384	140,400

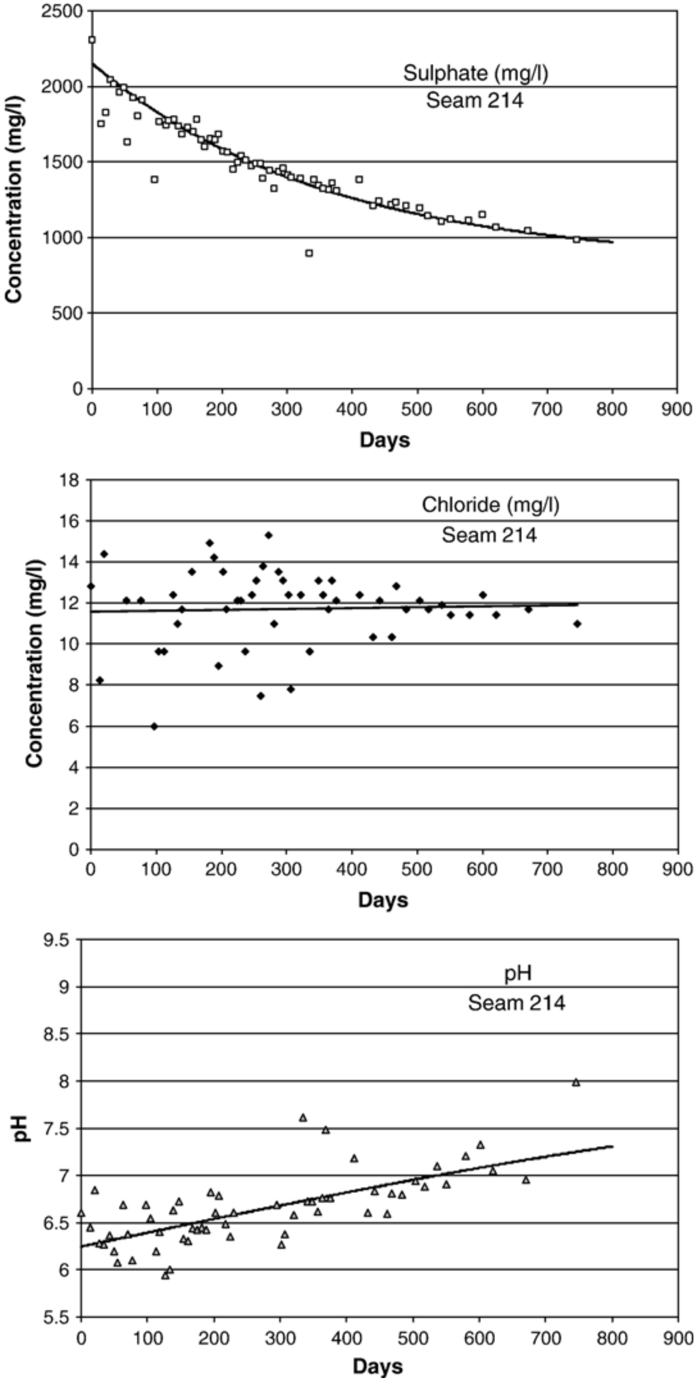


Fig. 4. The evolution of the hydrochemistry of mine water flowing from abandoned workings in Seam 214 in Level VI of Siersza mine. Note that, for chloride, little apparent trend is noted (a linear best fit is shown). For sulphate, an exponential decay line is plotted, of the form $C = C_V \cdot \exp(mt) + C_b$, where values of the various parameters are shown in Table 7. For pH, the trend plotted corresponds to the similar exponential decay of hydrogen ion activity (Table 7).

hydrogen ion activity in solution. In each case, exponential decay curves can be fitted to the data, with the form:

$$C = C_V \exp(mt) + C_b \tag{10}$$

$$C_b = C_n + C_j \tag{11}$$

$$C_V = C_0 - C_b \tag{12}$$

where C=the concentration of sulphate (mg/L) or the activity of hydrogen ions (mmol/L) at time t after overflow commences; C_0=the initial concentration of solute at time t=0; C_b=the background concentration of solute, which the curve approaches, as $t \rightarrow \infty$; C_n=the natural concentration of the solute in groundwater; C_j=the "juvenile" concentration of solute released due to continued oxidation of sulphide in the flooded workings; and C_V=the initial "vestigial" concentration of solute, due to flushing phenomenon, at t=0.

Table 7 shows the values of the various constants derived from Figs. 4 and 5. It is noteworthy that the background sulphate concentrations towards which the curves appear to be trending are *higher* than the pre-flooding sulphate concentrations. There is no clear explanation for this, apart from the obvious uncertainty in fitting curves to a scattered data set where exponential decay is not yet complete, and possible uncertainty regarding the representativity of the pre-flooding samples (Table 6).

From the decay curves, it is possible to estimate the likely time for 90% decay (t_{90}) towards background concentration (i.e. $C = C_b + C_V/10$) from:

$$t_{90} = \frac{\ln(0.1)}{m} \tag{13}$$

From Table 7 we see that the time for 90% completion of the first flush ranges from 480 to 822 days, around 10 to 20 times t_r (the period that the workings took to flood). This suggests that Younger's (2000) assertion that the period for flushing (t_f) is around 4 times the period for the workings to flood (t_r) is not universally applicable. In the Siersza workings, the decay is less than 40% complete after a period $4.t_r$.

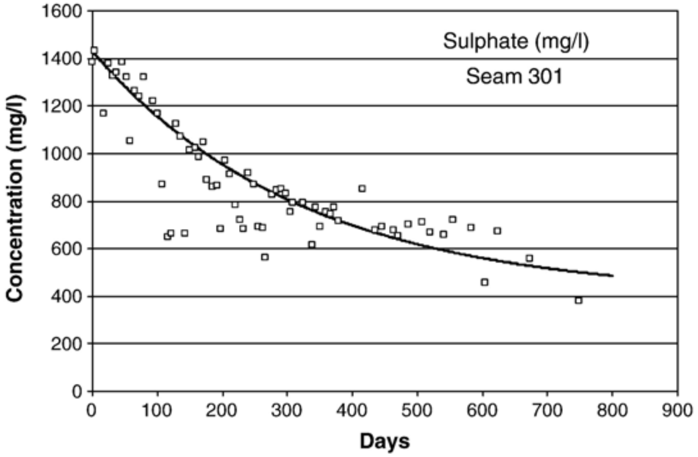
Finally, we can use the decay curves to estimate the total quantity (M_{SO_4}) of "vestigial" sulphate flushed from the workings during the first flush.

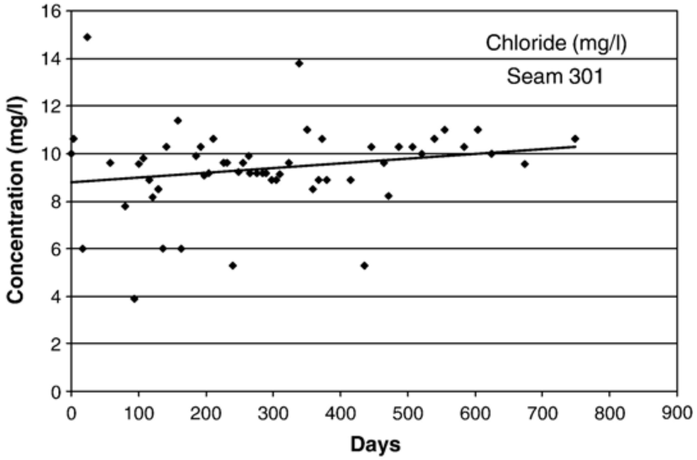
$$M_{SO_4} = Q\left(\int_0^{t_{90}} (C_V.\exp(mt) + C_b)\mathrm{d}t - t_{90}.C_b\right) \tag{14}$$

where the integration is between t=0 and t=t_{90}. This gives

$$M_{SO_4} = \frac{Q.C_V.(\exp(mt_{90}) - 1)}{m} \tag{15}$$

From this, we can calculate the mass of vestigial sulphur leached from the workings. If we then assume a porosity (22%) for the goaf and rock within the worked area, and a bulk density for this material (2.3 t/m^3), we can estimate the quantity of vestigial (readily leachable sulphur) per unit mass of goaf. The results for the Siersza workings are shown in Table 7. They are surprisingly small quantities, but are consistent at around 0.02 to 0.03%. Fortunately, there are independent means of checking this figure. Fortunately, literature and laboratory results are available for analyses of waste rock produced in other coal mines in the Krakow Sandstones and Mudstone Series. The results (Table 8) yield values of sulphur content in the waste rock of some 0.15–


Sulphate (mg/l)
Seam 301
Concentration (mg/l)
0
200
400
600
800
1000
1200
1400
1600
Days
0
100
200
300
400
500
600
700
800
900


Chloride (mg/l)
Seam 301
Concentration (mg/l)
0
2
4
6
8
10
12
14
16
Days
0
100
200
300
400
500
600
700
800
900

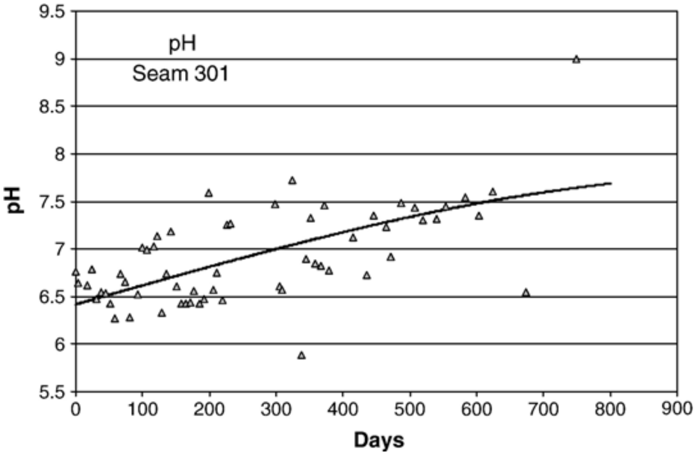

pH
Seam 301
pH
5.5
6
6.5
7
7.5
8
8.5
9
9.5
Days
0
100
200
300
400
500
600
700
800
900

Table 7
Parameters describing exponential decay curves fitted to data in Figs. 4 and 5 and calculated parameters derived from the decay curves

	Seam 214	Seam 301
Sulphate decay		
C_V (mg/L)	1320	1030
m (day^{-1})	−0.0028	−0.0031
C_b (mg/L)	830	400
Time for 90% decay (days) based on sulphate	822	743
pH (hydrogen ion activity) decay		
C_V (mmol/L)	0.00055	0.00037
m (d^{-1})	−0.0035	−0.0048
C_b (mmol/L)	1.58E−05 (pH 7.8)	1.26E−05 (pH 7.9)
Time for 90% decay (days) based on hydrogen activity	658	480
M_{SO_4}=mass (t) of sulphate flushed during t_{90}	489	1077
M_S=mass (t) of sulphur flushed during t_{90}	163	359
Mass of goaf/rock flushed (t) (assume n=22% and density=2.3 t/m^3)	506,000	1,470,000
Sulphur leached per unit mass of rock/goaf (% m/m)	0.03	0.02

0.32%, comparable to the values cited for Krakow Sandstones in Table 2. Moreover, leaching tests indicate a wide range of leachable sulphur contents, but with values of 0.01 to 0.04% being typical, wholly consistent with the "guestimates" of Table 7.

6. Discussion

6.1. The mixing tank model for exponential decay

Intriguingly, although most authors agree that flushing of contaminants from a mine system is an exponential process, it would appear that little thought has been given to the physical processes behind this exponential decay. The simplest explanation is that favoured by Younger (2000), the flushing of a reservoir of water-filled void space. If the volume of the mine void is V, containing a water with an initial solute concentration C_o and if it is being flushed by pure water at rate Q, assuming perfect mixing throughout the reservoir, then the concentration (C) at time t is given by:

$$\ln(C/C_0) = -Qt/V \text{ or } C = C_0.\exp(-Qt/V) \tag{16}$$

In this simple "mixing tank" model the time to achieve a 90% reduction in the first-flush concentration is given by $2.3V/Q$. If the water throughflow in the mine is constant, then V/Q is also the time the mine would have taken to flood, following abandonment. In other words, the time for recovery from first flush (t_f) is related to the time (t_r) required for the mine to initially flood: $t_f \approx t_{90}=2.3.t_r$. If (as is often the case: Banks, 2001) the mine inflow rate is head-dependent and inflow rate decreases during flooding, then t_f may be somewhat greater than $2.3.t_r$. In fact, we can begin to appreciate the physical basis for Younger's (2000) assertion that t_f=$(3.95\pm1.2)t_r$. We can suggest that, in mines where inflow of water is not head-dependent, the

Fig. 5. The evolution of the hydrochemistry of mine water flowing from abandoned workings in Seam 301 in Level VI of Siersza mine. Note that, for chloride, little apparent trend is noted (a linear best fit is shown). For sulphate, an exponential decay line is plotted, of the form $C=C_V.\exp(mt)+C_b$, where values of the various parameters are shown in Table 7. For pH, the trend plotted corresponds to the similar exponential decay of hydrogen ion activity (Table 7).

Table 8
Analyses of mining wastes from mines where exploitation was predominantly in the Krakow Sandstones or Mudstone Series coal seams

Mine		Brzeszcze[1]	Brzeszcze[2]	Ziemowit[3]	Ziemowit[2]	Murcki[3]	Siersza[2]	Janina[2]	Jaworzno[2]	Jan Kanty[2]
Whole rock XRF analysis (Element cited as oxide, except S)										
SiO_2	(% m/m)	51.83		72.00		36.19				
Al_2O_3	(% m/m)	18.87		11.33		16.90				
Fe_2O_3	(% m/m)	7.67		4.04		5.86				
CaO	(% m/m)	0.67		0.32		1.04				
MgO	(% m/m)	1.77		1.33		1.61				
Na_2O	(% m/m)	0.89		0.59		0.23				
K_2O	(% m/m)	2.91		3.48		2.25				
Loss on ignition	(% m/m)	13.48		5.16		33.84				
S	(% m/m)	0.15		0.21		0.32				
Leachable ions (1:10 dry rock to water mass ratio)										
SO_4^{2-}	mg/kg	354	1180	556	361	<100	1240	203	3700	3480
Cl^-	mg/kg	763.7	68	4256	1380	<35	83	1440	86	64
Na	mg/kg	4843.1	45	2304	1450	334.2	86	1730	84	72
K	mg/kg	167.3	43	138	109	36.3	39	118	77	41
Fe	mg/kg		0.6		12.5		3.4	2	1.5	0.55
Mn	mg/kg	0.19	1.9	0.48	1.8	1.62	nd	0	18.9	23
Leachable S	%	0.012	0.039	0.019	0.012	<0.003	0.041	0.007	0.123	0.116

The first section shows whole rock (and sulphur) composition by X-ray fluorescence (XRF), the latter section shows leachable ions and elements by leaching waste rock in distilled water at a ratio of c. 1:10 mass ratio. Note that some samples have very high leachable contents of chloride, suggesting residual brine pore waters. It is possible that some of the leachable sulphur in these samples may also be from the same source and not the product of pyrite oxidation. Sources: [1]Kompania Węglowa SA (2005); [2]Ratomski and Zapał (2005), here leachable contents are estimated by multiplying leachate concentrations by a factor of 10; [3]GIG (2002).

value of the constant of proportionality is low ($t_f=2.3.t_r$). In mines where inflow is strongly head dependent, the post-flooding equilibrium throughflow will be much lower than the inflow rate during flooding and $t_f>3.95t_r$. This provides one potential explanation for the observed duration of flushing at Siersza.

6.2. Influence of different flushing regimes in a single mine

Even if we accept the “mixing tank” model outlined in Section 6.1, it may be that a single mine cannot always be regarded as a single void space being flushed at a constant rate. For example, the upper portion of a mine may be flushed rapidly by a large throughflow of water. The lower part of a mine, characterised by lower permeability, fewer inflows and dense, highly concentrated mine water (note the stratification of mine water present at Grodziec, for example) may be flushed at a different, slower rate (Fig. 6). In reality, therefore, it may be that an apparently exponential solute decay curve in a mine water system is composed of several superimposed exponential decay curves corresponding, for example, to the rapid flushing of the upper part of the mine, to the slower flushing of other isolated or deeper parts of the mine or even to the slow release of solutes from pore space in the mine wall (see Section 6.4). A long “tail” to an apparently exponential decay curve would be a clue to the presence of these slower mechanisms.

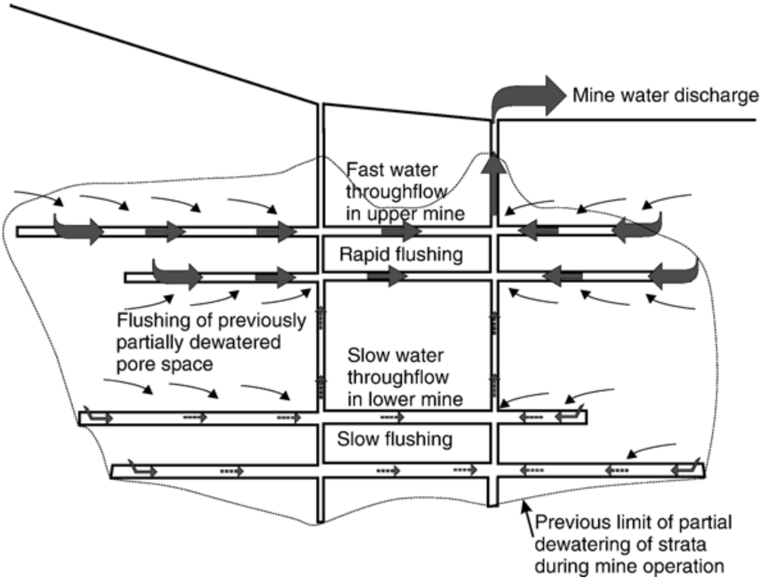


Fig. 6. A conceptual and schematic cross-section through an underground mine, showing some of the hydrological processes that that might affect the rate of flushing of contaminants following flooding.

6.3. Influence of dewatered host rock

The mixing model outlined in Section 6.1 assumes that the mine has a discrete void volume V. In mines, such as Siersza, which are located in highly porous sandstones, it is likely that considerable volumes of pore space in the sandstone were *partially* desaturated during mining (Banks, 2006a) and these *may* contain pyrite oxidation products. The volume of mine void and pore space that must be flushed of POP is greater than the volume which must be re-saturated following abandonment, as the water content of the “dewatered” pore space will not have been zero, but finite. In other words, the flooding time underestimates the total volume that must be flushed and $t_f > (3.95 \pm 1.2) t_r$. This is believed to represent a likely explanation for the long flushing times at Siersza.

6.4. Migration of solute from pore space as a rate-constraining factor

Other mechanisms have been proposed for post-abandonment exponential mine flushing. Frost (1979) envisages pores in an oxidised zone of rock in the wall of the mine workings being the main solute reservoir in the mine, being filled with a solution derived from the readily soluble pyrite oxidation products (POP). He envisages the slow diffusion/migration of the POP solution from pore spaces into the main flux of relatively dilute minewater in the mined voids as being the controlling factor for the evolution of mine water solute concentrations. He demonstrates that, if the concentration of solute in the pore space (C_s) is far greater than the concentration of solute in the mine water (C), then:

$$C = C_0.\exp(-pk_cAt) \tag{17}$$

where k_c is a mass transfer coefficient from pore spaces in the mine walls, across a surface film and into the main flow of mine water in void space, A is the area of mine wall over which this process occurs and p is a proportionality coefficient.

6.5. *Mineral dissolution rates as a rate-constraining factor*

Finally, we could envisage a process whereby exponential decay of mine water contaminant concentrations is controlled by the rate of dissolution of a solid secondary mineral phase present in the mine. If the initial mass of the solid phase in the mine is M_0, if it progressively dissolves into pure water flowing past at a rate Q (that is large enough for the concentration of dissolved solute in the mine water to be low relative to the equilibrium concentration of the mineral's dissolution products), and if the rate of dissolution is k_{diss} in s^{-1}, the solute concentration (C) at time (t) is given by:

$$C = C_0.\exp(-k_{\text{diss}}t) \text{ where } C_0 = k_{\text{diss}}M_0/Q \tag{18}$$

The XRD results from Janina mine (Banks, 2006b) indicate Na–jarosite and gypsum to be the predominant POP minerals. If mineral dissolution rate is a determining factor for overall solute concentration decay and if gypsum dissolves more slowly than Na–jarosite, one might expect to see a slower solute decay rate for sulphate than for iron and acidity. Table 7 offers very tentative support for this hypothesis, although the differences between the flushing times for sulphate and acid (pH) are not so large that they fall outside the likely limits of experimental uncertainty.

7. Conclusions

Two case studies of mine water conditions in abandoned coal mines in the Upper Silesian Coal Basin have confirmed the observation of the “first flush” phenomenon of Younger (1997, 2000). In Grodziec Mine, rising mine water exhibited stratification of water quality, with Ca–SO_4 water of modest sulphate concentration overlying Na–SO_4 water with sulphate concentrations 4–5 times greater than operational concentrations. Maximum total iron concentration of over 10 mg/L was found in the rising mine water, consistent with Younger's (2000) predicted values for coal seams of around 1% sulphur content.

In Siersza Mine, the flooding and overflowing of two limited sets of workings was observed in terms of hydrochemical evolution. Apparent exponential decay of sulphate concentrations and hydrogen ion activities was observed, of the form:

$$C = C_V\exp(mt) + C_b \tag{19}$$

The decay constant m was typically in the range -0.003 to -0.005 day^{-1}, corresponding to 90% decay times of 480 to 820 days. In this case, then, t_f is around 10 to 20 times t_r, rather than the factor of 3.95 ± 1.2 suggested by Younger (2000). These findings do not invalidate Younger's (2000) hypothesis; they merely suggest that other factors may be at work in certain circumstances, e.g.:

- In mines with porous host rocks (such as Siersza), the volume requiring flushing may exceed the volume being flooded/resaturated after abandonment.
- The presence of pyrite oxidation products in pore spaces in goaf and host rock at Siersza, may mean that the rate of exponential decay is not constrained by a simple “mixing tank”

consideration, but by the rate of diffusion of solutes from pore spaces and across a boundary film into the main minewater stream.

- The possibility that the dissolution rate of certain secondary minerals (e.g. gypsum) could be a rate constraining factor.

The discrepancy may also be related to the fact that Younger (2000) considered whole mine systems, whereas this study merely considers individual sets of workings within a single mine complex.

Mass balance calculations suggest that a leachable sulphur content of 0.02–0.03% in the abandoned workings is adequate to account for the observed sulphur concentrations in Siersza during “first flush”. This figure is supported by empirical analysis of leachable sulphate in waste rock from mines in the region.

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