

Influence of mine hydrogeology on mine water discharge chemistry

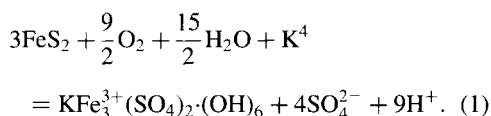
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Abstract: Using data for 81 coal mine discharges in the UK, the influence of discharge hydrogeology on discharge chemistry is assessed and typical chemical parameters derived for five discharge types. A combination of modified and new classification schemes is used to differentiate between the various discharge sources. Drainage from spoil tips generally has a pH below 5 and net-alkalinity values as low as $-2500 \text{ mg l}^{-1} \text{ CaCO}_3$. Drainage from flooded workings and pumped discharges are net-alkaline, while drainage from flooded and free draining workings are either moderately net-alkaline or net-acidic. Iron is the major contaminant of concern, although many mine waters contain less than 30 mg l^{-1} and Fe/SO_4 ratios are less than unity. The classification schemes developed can be used to assess mine water treatment requirements and processes operating in passive treatment systems.

The process of mining can lead to the exposure of potentially reactive mineralogy to the atmosphere. During underground coal mining below the water table, the creation of void space in the coal seam and the intervening strata allows the ingress of atmospheric oxygen to otherwise saturated areas. As a result, aerobic sulphide oxidation can occur. In such circumstances, sulphide oxidation results in the formation of secondary salts on the surface of exposed void areas such as the floor, wall and roof rocks. These secondary salts can contain ferric Fe and SO_4 , as shown by the formation of potassium jarosite:



Other potential secondary salts include copiapite, melanterite, jarosite and shwertmannite (Bowell *et al.* 2000).

Following the cessation of pumping, the secondary salts are 'flushed' into solution as the water table recovers due to their high solubility. As a result, the concentration of total $\text{Fe}_{\text{Unfiltered}}$ and SO_4 can significantly increase. This process has recently been cited as an explanation for the trend in water chemistry observed at the former Lindsay Colliery, South Wales (Younger & Banwart 2002). Prior to February 2000, the discharge from the abandoned colliery contained less than 150 mg l^{-1} total $\text{Fe}_{\text{Unfiltered}}$. However, by April of the same year, the Fe content peaked at

236 mg l^{-1} . Subsequently, the Fe content decreased and by the end of 2000 the discharge contained less than 100 mg l^{-1} .

Following water table equilibration, the processes of sulphide oxidation and secondary salt formation can only potentially continue within and above the zone of seasonal water table fluctuation, as aerobic sulphide oxidation within the now flooded workings is not possible due to limited oxygen diffusion (Perry 2001). Beyond the initial flush event, the long-term chemistry of the discharge is governed by the recharge water chemistry, the relative abundance of acid-generating and buffering mineral assemblages in the mine, and their relative reactivity (Younger & Banwart 2002).

As underground workings above the water table are free draining, they never become completely flooded and oxygen ingress can still occur following mining. Therefore, sulphide oxidation can potentially continue generating acidity. Depending on the availability and morphological nature of the sulphides, this can lead to a long-term source of secondary salts. Also, as there is no groundwater 'flush', any secondary salts produced can accumulate, potentially providing a long-term source of secondary constituents to any interflow passing through the workings.

In addition to the effect on the groundwater regime during and post-mining, material classified as 'waste' is generated. In coal mining areas, this is often present at surface as loose tipped spoil tips or waste rock piles. Like the flooded

and free draining settings, spoil tips also have their own unique hydrogeological properties that can potentially affect the chemistry of any associated drainage. Depending upon the environment, mine spoil can exhibit characteristics of both porous medium and double-porosity aquifers (PDEP 1998). For example, relatively continuous water tables and multiple water tables have been observed in spoil tips and, as a result, the water contact time can vary considerably. Coupled with the exposure of greater mineral surface area within a spoil tip, the processes of sulphide oxidation and secondary salt formation can therefore be more prevalent in spoil tips than in underground workings.

A summary of the different properties of each mine setting described are conceptually illustrated in Fig. 1, along with the main processes occurring that can affect the chemistry of associated discharges. Although discharge sources can, in some cases, be readily identified from mine plans and the history of the discharge, an understanding of the processes that affect discharge chemistry can prove a useful tool where such information is lacking or inconclusive. From a management perspective, the identification of the discharge source is vital for successful treatment, as this can influence long-term treatment requirements (Younger &

Banwart 2002). As the discharge chemistry must be known for treatment purposes, it is, therefore, cost-effective to also use this to help characterize the discharge source.

Using chemical data for 81 coal mine discharges from the UK, typical chemical properties for each discharge type are derived and the reason for the differences explained. The discharges assessed are located in the South Wales, Scottish and County Durham coalfields, as summarized in Table 1. The time since first emergence of each discharge used in the assessment ranges from less than 5 years to over 100 years. Based on the author's knowledge, published information and contact with other workers, five different types of discharge source have been identified. These are flooded workings, flooded and free draining workings, pumped discharges, free draining workings, spoil heap drainage and discharges from an unknown source. Many of the discharges have not received detailed historical monitoring, so the amount of chemical data available is often limited. Therefore, a limited chemical dataset has been purposely selected to demonstrate how such data can still be used to characterize discharges. As summarized in Table 2, the chemical parameters used are Ca, Mg, Na, K, Cl, SO_4 , HCO_3 , acidity, pH, redox potential and Fe.

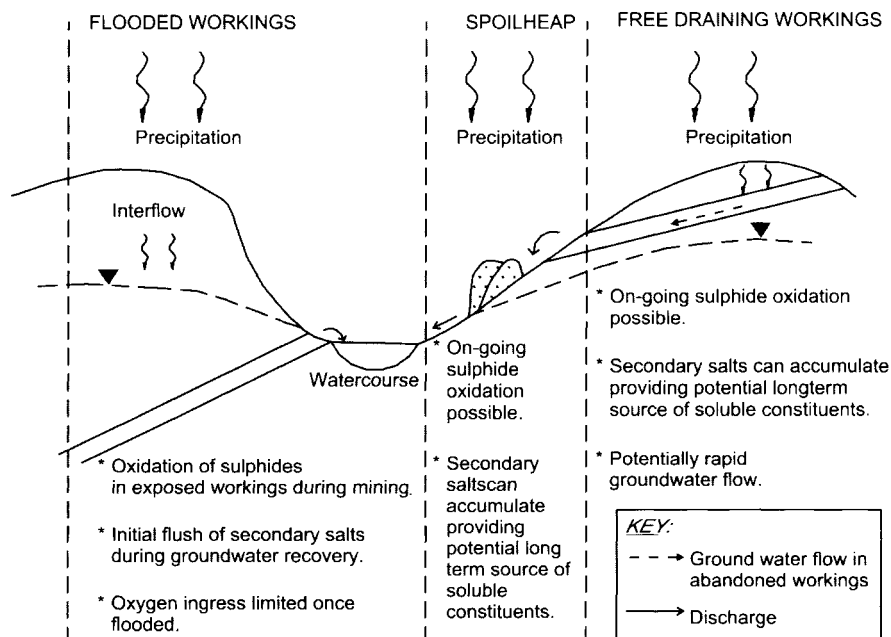


Fig. 1. Summary of processes occurring in flooded workings, spoil tips and free draining workings that can affect discharge chemistry.

Table 1. Mine water discharge name, source and time since first emergence (age)

Discharge point	Drainage source	Age (years)	Discharge point	Drainage source	Age (years)
SOUTH WALES			Douglas	Flooded	c. 40
Craig Yr Aber	Free draining	40	Pool Farm	Flooded and free draining	c. 40
Cedfw	Flooded	?	Blairnbathie	Unknown	c. 35
Cwmgors	Unknown	?	W. Colquhally	Unknown	c. 35
Mountain Gate	Unknown	?	Cardenden	Unknown	34
Lash	Unknown	?	Parson's Mill	Unknown	34
Tan-y-garn	Flooded	10	New Carden	Unknown	33
Llechart	Flooded	20	Kinglassie	Unknown	34
Garwed	Unknown	?	Balgonie Bing	Spoil heap	c. 50
Ynysarwed	Flooded	7	Randolph Bing	Spoil heap	c. 30
Nant y Fedw	Flooded	?	Frances Colliery	Pumped	
Goytre	Unknown	?	Michael Colliery	Pumped	
Corrwg	Flooded and free draining	c. 40	Dalquharran Mine	Flooded and free draining	22
Gwynfi	Flooded and free draining	?	Roughcastle	Flooded	5
Gwenffrwd	Flooded and free draining	c. 30	COUNTRY DURHAM		
Whitworth No.1	Flooded and free draining	c. 30	Broken Banks	Flooded	45
Whitworth A	Flooded and free draining	c. 30	Quaking Houses	Spoil heap	c. 25
Whitworth B	Flooded and free draining	c. 30	Stoney Heap	Flooded	20
Garth Tonmawr	Flooded and free draining	c. 30	Tindale Colliery	Flooded	33
Dunvant Square	Flooded	?	Kibblesworth	Pumped	
Dunvant Clyne Trib	Flooded	65	Lumley 6th Pit	Pumped	
Lindsay	Flooded	2	Chester Moor	Pumped	
Rhymney	Flooded and free draining	10	Kimbleworth	Pumped	
Maerdy	Unknown	?	Nicholson's Pit	Pumped	
Ynyswen	Unknown	?	Sherburn hill	Pumped	
Six Bells	Flooded and free draining	c. 50	Ushaw Moor	Pumped	
Taff Merthyr	Flooded	6	Page Bank	Pumped	
Abersychan	Unknown	26	Vinovium	Pumped	
Penrhiwfer	Spoil heap	?	Helmington Row	Flooded	21
Ynysybwll	Unknown	?	Burnopfield	Flooded	> 10
Blackwood	Partially flooded workings and seeps	8	Milkwell Burn	Flooded	> 10
N. Celynen	Flooded	10	Pont Waterlevel	Flooded	> 10
Tram Road	Flooded	10	West Kyo	Flooded	> 10
Trosnant Brook	Unknown	?	Data for the Welsh discharges come from the Environment Agency Wales mine waters database. The County Durham and Scotland data are taken from Younger (1995a, 1998, 2001) and Wood <i>et al.</i> (1999).		
SCOTLAND			Mine water characterization		
Lathallan Mill	Flooded	100	<i>Piper plot</i>		
Star Road	Flooded	106	Comparison of the major ion chemistry of all the discharges in Table 2 using a Piper diagram indicates that cation proportions (Na, K, Ca and Mg) are broadly similar between the different discharge types, with the exception of most pumped discharges and a small number of other types of discharge (Fig. 2). As a proportion of total cations (expressed as meql ⁻¹), most discharges contain less than 20% Na, and between 40 and 60% Ca and Mg. In comparison, anion		
Elginhaugh	Flooded	35			
Blackwood	Flooded	117			
Cairnhill	Flooded	20			
Pennyvenie No 3	Flooded	18			
Brora No 1	Flooded	c. 40			
Macrihanish	Flooded	c. 50			
Baads Bing	Spoil heap	c. 40			
Minto No 2	Flooded	34			
Kames No 1	Flooded	28			
Fordell Day Level	Unknown	c. 40			
Cuthill No 1	Free draining	c. 40			

Table 2. Mine water discharge data for Wales, Scotland and Country Durham*

Units	pH	Redox Potential (mV)	Acidity (mg l ⁻¹) CaCO ₃	Alkalinity (mg l ⁻¹) CaCO ₃	Cl (mg l ⁻¹)	SO ₄ (mg l ⁻¹)	Na (mg l ⁻¹)	K (mg l ⁻¹)	Mg (mg l ⁻¹)	Ca (mg l ⁻¹)	Total Fe	
											Filtered (mg l ⁻¹)	Unfiltered (mg l ⁻¹)
Wales												
Craig Yr Aber	6.87	177	37.40	122.18	21.53	573.37	57.47	11.72	64.09	124.95	20.33	22.13
Cedfw (3)	6.74	171	24.00	101.75	nm	15.10	nm	nm	7.66	31.43	19.92	17.46
Cedfw (2)	7.03	215	15.20	115.25	nm	3.63	nm	nm	10.48	27.40	8.85	8.39
Cedfw	6.33	196	42.25	55.75	nm	73.78	nm	nm	13.75	21.60	17.10	17.29
Cwmgors	7.48	186	15.35	418.00	nm	266.67	nm	nm	29.60	41.53	6.36	6.67
Mountain Gate	6.94	269	39.15	376.33	14.70	131.33	22.57	29.70	56.10	75.43	3.29	3.75
Lash (Brooklands)	7.35	270	21.49	361.67	21.83	245.67	17.53	28.53	74.33	96.80	1.61	2.70
Lash (Derwen)	6.90	292	38.25	212.67	16.60	192.67	12.83	8.96	49.87	73.90	8.86	22.57
Tan Y Garn (Mountain Colliery)	6.32	256	18.16	34.45	nm	679.17	nm	nm	71.47	151.83	20.08	20.60
Tany Garn (Cathan)	6.13	145	103.22	35.15	12.70	346.73	11.76	6.07	36.93	53.65	61.66	68.03
Llechart (2)	5.99	388	18.31	15.26	9.75	66.85	7.63	1.58	11.52	11.96	1.04	1.55
Llechart	6.72	nm	7.69	31.12	9.98	142.48	nm	nm	21.53	32.19	3.15	3.70
Garwed (Lower)	3.52	473	55.21	nm	nm	193.61	nm	nm	19.37	25.06	5.57	5.62
Garwed (Upper)	3.05	490	205.00	nm	12.70	683.43	12.43	8.44	63.01	80.50	48.83	49.99
Ynysarwed	5.55	74	396.83	45.81	15.86	2364.97	143.21	26.39	184.64	299.33	237.33	256.38
Nant Y Fedw (Gelli Farm)	7.44	360	4.64	80.33	8.70	28.57	5.92	2.18	11.96	22.43	1.56	1.75
Nant Y Fedw (lower)	7.23	335	12.86	74.33	9.00	68.63	3.36	3.36	17.10	27.70	2.77	3.36
Nant y Fedw (Middle)	7.26	377	23.00	99.50	nm	207.50	nm	nm	34.90	59.50	25.20	25.40
Goytre	7.30	353	15.59	92.00	21.25	94.80	19.67	4.21	18.50	35.00	5.13	8.92
Corrwg (Lower)	6.82	174	26.23	80.90	nm	277.80	nm	nm	40.84	66.16	18.06	18.75
Corrwg (Upper)	6.48	262	35.65	52.00	nm	165.71	nm	nm	23.94	37.89	8.43	9.63
Corrwg Fechan	6.96	239	28.44	121.78	nm	149.56	nm	nm	32.20	52.39	12.87	13.56
Gwynfi	6.61	286	13.21	38.62	9.78	102.95	6.51	4.33	16.43	27.41	5.06	5.57
Gwenffrwd	5.22	319	17.10	10.45	12.00	82.78	3.21	0.00	9.63	17.33	3.66	4.09
Whitworth No. 1	6.33	155	38.65	41.02	10.93	343.47	12.24	13.05	39.59	71.67	22.84	24.62
Whitworth B	5.90	222	134.76	9.73	17.96	97.14	5.62	2.94	13.04	19.86	5.51	5.48
Whitworth A	5.94	164	344.75	23.66	12.75	334.86	11.90	9.44	34.38	56.95	57.87	59.53
Garth Tonmawr	5.59	231	286.46	14.09	12.11	271.91	7.64	8.56	31.33	47.19	27.10	28.49
Nantffyfflon	6.94	337	22.50	103.00	14.16	100.00	nm	nm	21.30	38.00	6.50	6.50
Dunvant Square	7.72	212	3.21	128.20	nm	75.58	nm	nm	17.02	52.10	2.03	2.62
Dunvant Clyne Trib	7.53	nm	5.68	149.33	nm	51.27	nm	nm	18.23	52.73	1.51	2.14
Rhymney	7.04	225	16.21	225.28	16.31	449.08	21.95	12.28	69.66	141.81	5.27	7.08

Maerdy	6.84	287	18.33	64.00	6.13	22.13	4.45	1.96	10.44	16.23	4.15	8.00
Ynyswen	7.64	167	1.93	100.33	9.53	15.77	9.09	5.75	12.53	18.30	1.08	1.27
Six Bells	7.60	63	35.35	877.25	33.48	1391.25	464.00	90.93	171.75	193.75	28.58	35.30
Taff Merthyr	7.93	104	11.61	247.33	12.57	471.00	15.63	15.97	67.63	165.00	14.26	20.33
Abersychan	7.55	180	12.53	230.00	12.33	250.67	15.67	24.06	50.20	100.07	2.69	3.24
Penrhiwfor	6.21	250	3.27	8.30	13.43	11.77	6.58	0.91	2.33	5.46	1.37	1.72
Ynysybwll	6.79	359	2.04	23.00	12.97	24.37	5.96	1.14	6.49	8.58	0.21	0.38
Blackwoodsunningdale	6.71	302	24.55	149.33	22.23	594.67	17.90	8.76	90.93	149.33	3.85	4.08
North Celynen	7.07	124	21.91	276.33	17.74	427.67	26.47	9.29	71.27	161.00	10.53	11.77
Tram Road	6.98	236	14.58	222.00	22.51	494.00	26.93	11.70	72.40	153.00	5.77	6.56
Trosnant Brook	7.76	282	5.25	132.76	12.43	80.43	9.17	4.55	21.63	50.17	0.64	1.10
Scotland												
Lathallan Mill	6.10	17	20.80	182	35	214	16	6	41	87	nm	11
Star Road	6.50	— 57	10.00	173	34	53	13	12	21	61	nm	4
Elginhaugh	5.70	6	192.00	207	22	1100	16	23	188	256	nm	93
Blackwood	7.20	— 40	3.00	265	30	37	17	12	27	76	nm	1
Cairnhill	7.60	— 76	27.00	80	23	1346	28	72	88	385	nm	7
Pennyvenie No 3	6.90	— 7	2.00	854	21	142	302	24	42	58	nm	0
Brora No 1	3.60	nm	90.71	0	123	340	72	20	18	125	nm	8
Macrihanish	6.10	nm	153.51	285	57	51	26	8	20	46	nm	60
Randolph Bing	3.70	nm	1565.75	0	103	2475	26	6	115	229	nm	43
Michael colliery	6.90	nm	67.34	410	2662	1713	1304	78	318	312	nm	34
Frances Colliery	6.90	nm	29.55	162	5880	1240	4290	60	320	160	nm	12
Baads Bing East	2.80	nm	2420.00	0	16	3077	19	7	32	407	nm	550
Baads Bing West	3.50	nm	190.00	0	10	304	10	3	36	84	nm	6
Minto No 2	6.80	nm	32.00	670	nm	1550	nm	nm	nm	nm	nm	13
Kames No 1	5.80	nm	28.83	232	9	247	9	8	60	130	nm	14
Fordell Day Level	6.40	nm	29.00	270	nm	1200	nm	nm	nm	nm	nm	16
Cuthill No 1	5.50	nm	68.35	247	40	932	75	15	97	345	nm	37
Douglas	6.00	nm	75.00	190	15	595	11	12	73	180	nm	40
Pool Farm	5.60	nm	18.00	98	26	240	7	4	27	66	nm	8
County Durham												
Helmington Row	4.80	264	214.47	0	65	810	22	7	93	185	nm	79.80
Burnopfield	6.50	— 40	14.44	146	73	301	39	9	55	97	nm	5.20
Milkwell Burn	6.70	— 45	14.54	216	29	35	15	2	14	97	nm	5.40
Pont Waterlevel	6.30	— 15	20.76	319	49	724	37	16	123	174	nm	1.80
West Kyo	6.60	— 45	25.08	187	27	104	40	3	26	46	nm	9.30
Kibblesworth	7.02	nm	2.36	755	909	395	782	27	52	162	nm	0.88
Lumley 6th Pit	6.88	nm	11.28	895	462	420	577	27	61	149	nm	4.21
Chester Moor	7.58	nm	2.28	1050	132	672	683	20	35	79	nm	0.85

Table 2 – (continued).

Units	pH	Redox Potential (mV)	Acidity (mg l ⁻¹) CaCO ₃	Alkalinity (mg l ⁻¹) CaCO ₃	Cl (mg l ⁻¹)	SO ₄ (mg l ⁻¹)	Na (mg l ⁻¹)	K (mg l ⁻¹)	Mg (mg l ⁻¹)	Ca (mg l ⁻¹)	Total Fe	
											Filtered (mg l ⁻¹)	Unfiltered (mg l ⁻¹)
Kimbleworth	7.22	nm	4.50	835	138	358	446	16	34	90	nm	1.68
Nicholson's Pit	6.96	nm	16.15	735	112	1052	530	26	71	173	nm	6.03
Sherburn hill	6.71	nm	20.63	550	96	967	238	23	107	221	nm	7.70
Ushaw Moor	6.69	nm	1.49	700	51	232	178	23	67	108	nm	0.56
Page Bank	6.71	nm	2.29	654	113	601	350	30	73	142	nm	0.85
Vinovium	6.81	nm	1.35	625	79	510	216	23	85	149	nm	0.51
Broken Banks	6.50	39	4.89	364	60	137	27	11	61	101	nm	1.80
Crook	4.80	264	214.48	0	65	810	22	7	93	185	nm	79.80
Quaking Houses	4.10	327	49.90	0	1012	1358	464	57	103	255	nm	18.00
Stoney Heap	6.30	36	70.51	188	102	325	28	7	50	84	nm	26.30
Tindale Colliery (Brus-selton)	6.40	– 50	4.89	357	75	890	80	13	107	262	nm	1.80

* Data for the Welsh discharges come from the Environment Agency Wales mine waters database. The County Durham and Scotland data is taken from Younger (1995a, 1998, 2001) and Wood *et al.* (1999). The data for the Welsh discharges is based on average values since monitoring was initiated, while the County Durham and Scottish discharge data are based on data for a specific date and are not averaged.

nm, not measured; nd, not detected.

proportions show greater variation with HCO_3 and SO_4 , the dominant end-members, and only a small number of discharges contain greater than 20% Cl.

The pumped discharges contain a greater Na, K and Cl component, as they have been shown to either contain a sea-water component or to have interacted with deep basin brines and undergone extensive ion exchange (Younger 1995a, 1998). However, a similar explanation is not applicable for the other discharge types that plot in a similar position to the pumped discharges. The discharge classified as arising from flooded and free drainage workings is the discharge at Six Bells, South Wales, and it may be that this water has interacted with evolved Devonian formation water in the mine. The higher proportion of Na, K and Cl in two spoil tip discharges may reflect rapid water flow in these settings and also a lack of carbonate buffering.

Owing to the evolved nature of most of the pumped mine waters, they plot in a distinct position of the Piper-plot and are generally characterized by either a $\text{Na}-\text{HCO}_3$ or $\text{Na}-\text{SO}_4$ hydrochemical signature. Unfortunately, the other discharge types are not so readily distinguished as there is overlap between their hydrochemical signatures. For instance, discharges from flooded workings have a $\text{Ca}-\text{Mg}-\text{SO}_4$ and a $\text{Ca}-\text{Mg}-\text{HCO}_3$ hydrochemical signature. Similarly, discharges from flooded and free draining workings also generally have a $\text{Ca}-\text{Mg}-\text{SO}_4$ signature. As a result, the Piper diagram cannot be used alone to distinguish between different discharge types, although the characterization of major ions is useful. The reason the Piper plot is insufficient in classifying mine waters can be seen by comparing the plotting positions of the majority of the spoil tip discharges and the discharges from flooded and free draining workings.

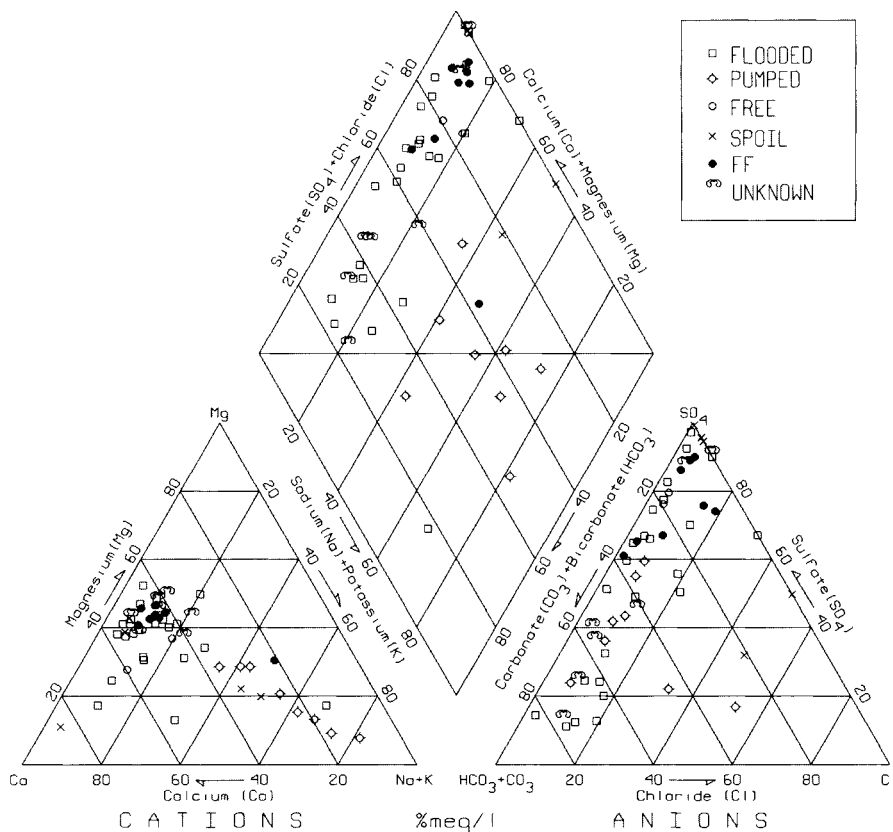


Fig. 2. Piper diagram summarizing major ion chemistry of different discharge types. Flooded refers to discharges from flooded workings; FF refers to drainage from flooded and free draining workings; Spoil refers to discharges from spoil tips; Pumped refers to discharges that are pumped; Free draining refers to discharges from free draining workings; Unknown refers to discharges for which a source is not known.

Many of the spoil tip discharges do not contain alkalinity. However, their hydrochemical signature, according to the Piper plot, is the same as the flooded and free draining discharges, and so the distinct chemical difference is lost.

Net-alkalinity versus $Cl/Cl + SO_4$

Such limitations of the Piper plot have been noted previously by Younger (1995a), who subsequently proposed a different method of classifying mine water discharges (Fig. 3). In this plot, an earlier classification system proposed by Hedin *et al.* (1994) is modified slightly and plotted against the ratio of Cl to the sum of Cl and SO_4 expressed in $meq\ l^{-1}$.

With such a diagram, net-acidic, high- SO_4 waters plot to the lower left, waters affected by bacterial sulphate reduction (BSR) to the upper right and waters affected by carbonate dissolution to the upper left. Younger (1995a) concluded that such a diagram would enable the hydrological source of a discharge to be identified as these basic geochemical processes controlling mine water chemistry are presented.

As expected, the spoil tip discharges are located in the bottom left-hand corner. However, a number of other discharges also plot in a similar position. Therefore, as with the Piper plot, this figure does not enable the differentiation of the discharge sources.

Proposal for a modified classification scheme

In the scheme proposed by Hedin *et al.* (1994), mine waters were classified as being either net-alkaline or net-acidic based on the difference between alkalinity and combined proton and mineral acidity content. Younger (1995a) modified the classification scheme and plotted the alkalinity as a percentage of total alkalinity and acidity. As a result, mine waters with zero alkalinity but different acidity (proton and mineral) content are not differentiated and all plot with a zero y-axis value on Fig. 3. Therefore, a modified classification scheme is proposed that uses the absolute net-alkalinity values (Fig. 4).

In this diagram, differences between the mine water discharge sources are more readily identifiable as the absolute alkalinity and acidity values are illustrated. Based on this diagram, typical ranges in net-alkalinity for each discharge type can be identified. These are summarized in Table 3, along with the Piper classifications from Fig. 2 and also a summary of the range in pH values for each discharge type from Table 2.

Spoil tips are the most net-acidic waters encountered, with values almost as low as $-2500\ mg\ l^{-1}\ CaCO_3$. This is because sulphide oxidation and secondary salt formation and mobilization are the dominant processes occurring due to the exposure of greatest mineral surface area and potentially rapid water throughflow.

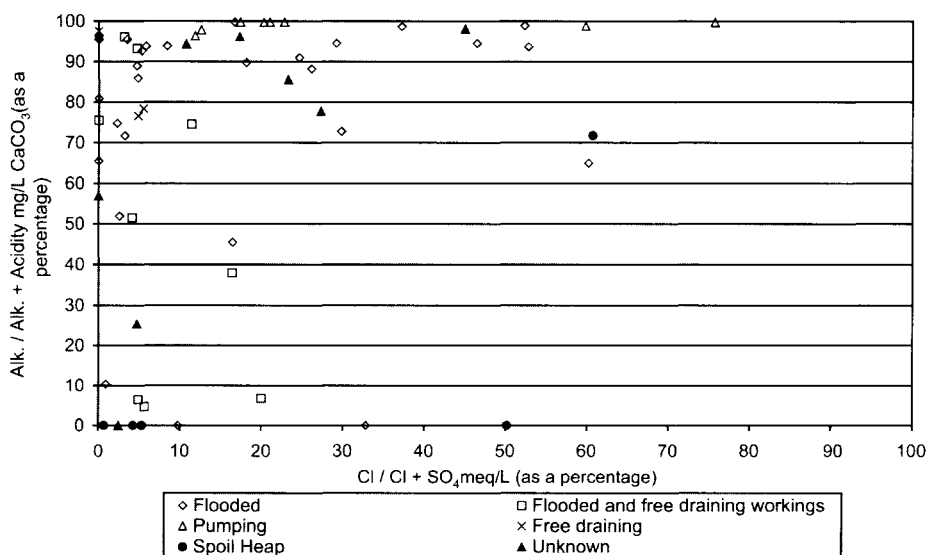


Fig. 3. Classification scheme used to originally assess Scottish mine waters according to Younger (1995a).

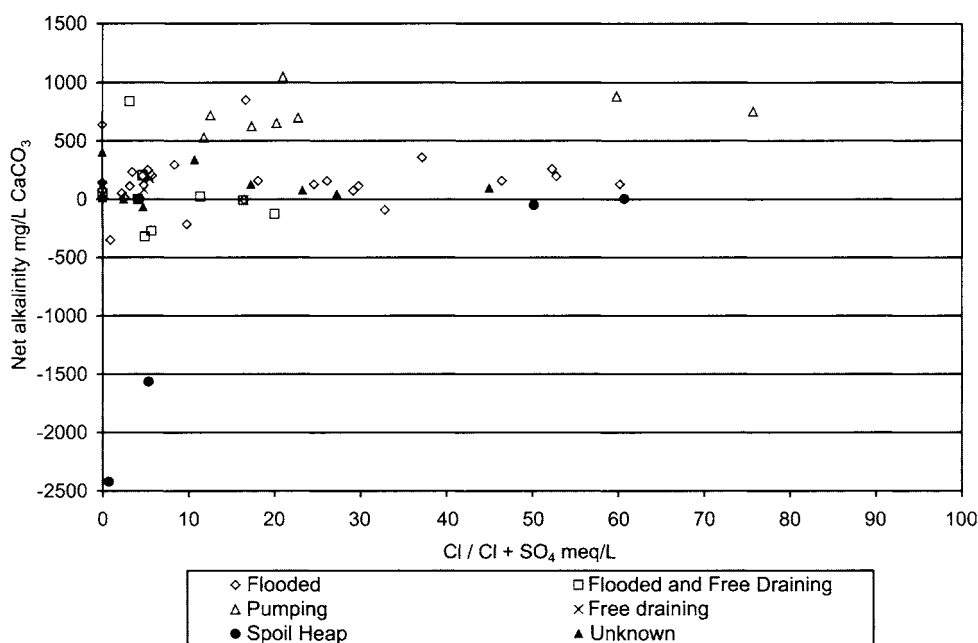


Fig. 4. Modified mine water classification scheme.

Drainage from flooded workings and flooded and free draining workings are more net-alkaline than spoil tip drainage, with flooded workings the most net-alkaline. In both settings, sulphide oxidation will be less prevalent compared to a spoil tip exposed to the atmosphere, and buffering reactions will play a more significant role in controlling water chemistry. Flooded workings generally give rise to more net-alkaline discharges compared to flooded and free draining workings as aerobic sulphide oxidation is not possible within the flooded workings, whereas the dissolution of buffering mineral assemblages, such as carbonates, can continue (Younger & Banwart 2002).

Iron chemistry

Owing to the oxidation of iron sulphides, such as pyrite, the major contaminant of concern in UK

coal mine drainage is Fe (Table 2). The proposed classification scheme can be used to assist in identifying between discharges on the basis of net-alkalinity, but it does not include an assessment of potential differences in Fe content between the various types of discharge. Interestingly, regardless of the discharge source, many of the discharges do not contain more than approximately 30 mg l^{-1} total $\text{Fe}_{\text{Unfiltered}}$, as illustrated in Fig. 5. This has been noted to be particularly the case for discharges from flooded shafts that have been flowing for approximately 40 years (Wood *et al.* 1999). On this basis, a classification scheme including Fe may not be beneficial in the long term. However, there are discharges that do contain in excess of 30 mg l^{-1} , even though they have been flowing for more than 40 years (Tables 1 and 2). Consequently, a brief attempt has been made to develop a scheme to better define these waters.

Table 3. Summary of typical chemical properties for each type of discharge

Discharge source	pH	Net-alkalinity $\text{mg l}^{-1} \text{CaCO}_3$	Piper classification
Flooded workings	<5–8	0 to +500	Ca–Mg– SO_4/HCO_3
Spoil tip	<5	–2500 to 0	Ca–Mg– SO_4
Free draining workings	5–7	+80 to +180	Ca–Mg– SO_4
Flooded and free draining workings	>5 < 8	–350 to +200	Ca–Mg– SO_4
Pumped	6.5–7.5	+500 to +1000	Na– HCO_3/SO_4

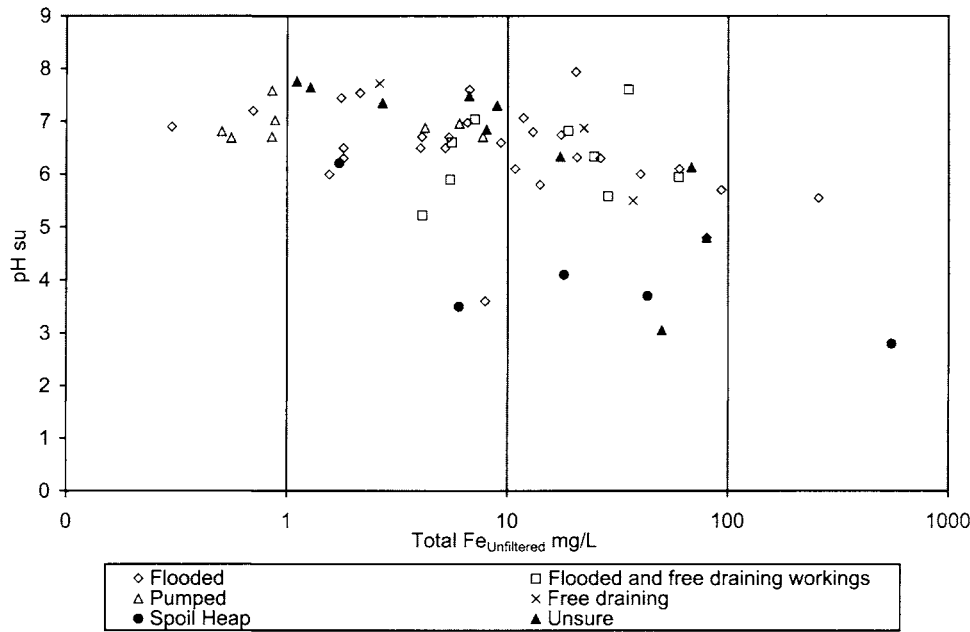


Fig. 5. Variation of total $\text{Fe}_{\text{Unfiltered}}$ with pH.

In many circumstances, historical information about Fe speciation is not available and only total $\text{Fe}_{\text{Unfiltered}}$ will have been measured. Although it is useful to have total $\text{Fe}_{\text{Filtered}}$ concentrations, Fig. 6 indicates that the majority of UK mine

waters have total $\text{Fe}_{\text{Filtered}}$ values that account for over 80% of total $\text{Fe}_{\text{Unfiltered}}$. Therefore, total $\text{Fe}_{\text{Unfiltered}}$ values have been used.

The classification scheme of Younger (1995a) indicated the benefit of using elemental

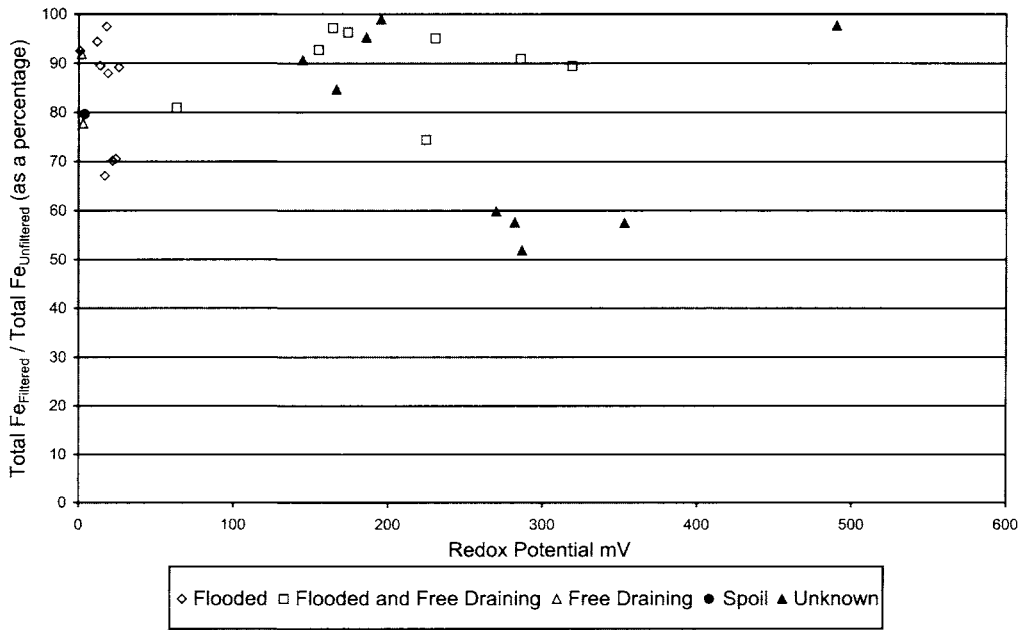


Fig. 6. Redox potential vs total $\text{Fe}_{\text{Filtered}}$ as a percentage of total $\text{Fe}_{\text{Unfiltered}}$.

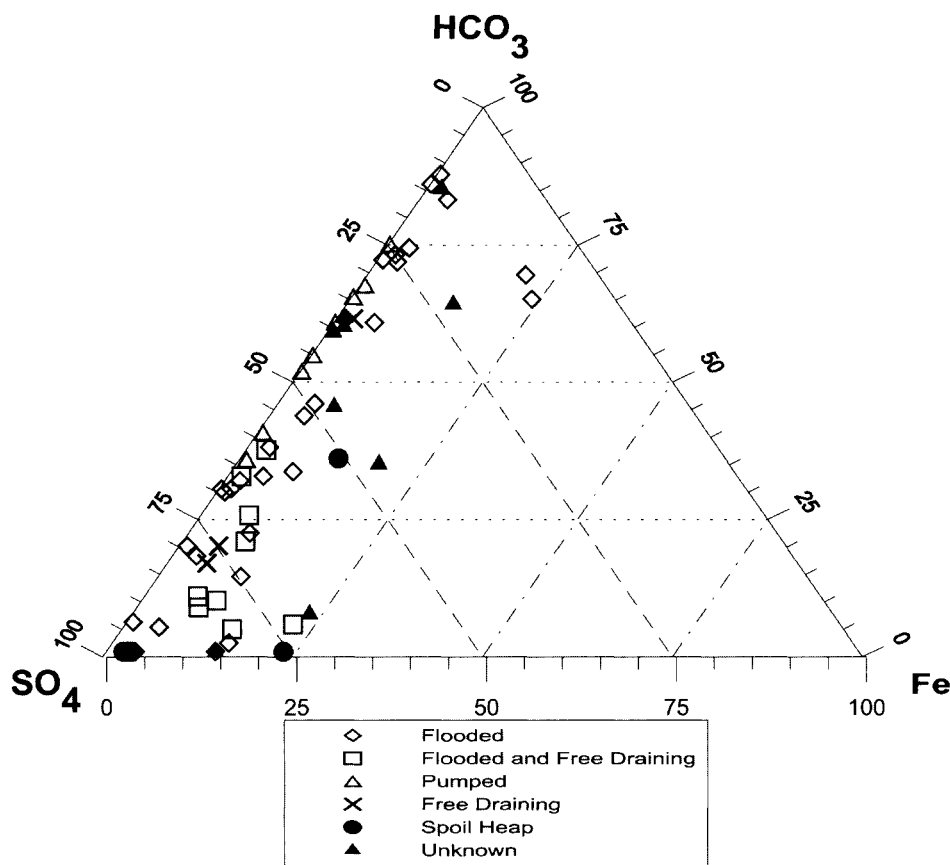


Fig. 7. Ternary diagram comprising Fe, SO_4 and HCO_3 . All values expressed as meq l^{-1} .

ratios to differentiate between basic geochemical processes. Therefore, if Fe is to be incorporated into a classification scheme it was considered best that it was represented as part of the overall chemistry and that absolute values were not used. In addition to the use of ratios, this can be achieved by using a ternary diagram (Fig. 7). On this diagram, three important mine water variables are presented as meq l^{-1} . As noted from the Piper plot (Fig. 2), and reflected in the net-alkalinity values in Fig. 4 and Table 3, there is a degree of overlap between the different discharge types in terms of the proportions of HCO_3 and SO_4 . Also, the inclusion of Fe does not assist in source characterization using this method. This is because the majority of discharges have total $\text{Fe}_{\text{Unfiltered}}$ less than 30 mg l^{-1} , and the ratio of Fe/SO_4 (in terms of meq l^{-1}) is less than unity, as Fe is susceptible to oxidation and precipitation to a greater extent than SO_4 . Also, during complete aerobic

oxidation of pyrite (FeS_2), for every 1 mol of Fe released, 2 mol of sulphate are released.

Although Fig. 7 is limited in assisting discharge source characterization, it can certainly be used to assess mine water treatment requirements and processes operating in passive treatment systems, such as wetlands. For instance, spoil tip drainage is typified as strongly net-acid with elevated SO_4 and Fe and low pH (Table 2). Therefore, successful treatment requires the lowering of acidity (increase of alkalinity) and the removal of Fe and SO_4 . Such improvements in water quality can be achieved using a passive system such as the Successive Alkalinity Producing System (SAPS), which comprises aerobic and anaerobic Fe and SO_4 removal and carbonate dissolution (Younger 1995b; Rees *et al.* 2001). As these reactions influence the three components illustrated in Fig. 7, changes in water quality occurring during the different treatment stages could potentially be readily traced.

Summary

Hydrogeological conditions of a mine discharge play a significant role in controlling discharge chemistry. Within the coalfields studied, five types of mine settings have been identified and differentiated on the basis of a number of lines of chemical evidence. The observations made should assist future workers aiming to characterize the source of a coal mine discharge. In order to assist with source characterization a number of modified and new classification schemes have been proposed. These schemes can also be used for assessing treatment requirements and processes operating within passive treatment systems.

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