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Acid-generating salts and their relationship to the chemistry of groundwater and storm runoff at an abandoned mine site in southwestern Indiana, U.S.A.

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ABSTRACT

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Cation distributions in twenty samples of acid-generating salts were compared to those in groundwater and storm runoff from a coal-refuse deposit in an effort to identify source-product relationships. Two mineral suites, one primarily composed of melanterite, rozenite and szomolnokite, and the other composed almost entirely of copiapite, were found to be most abundant at the study site. Comparisons of cation distributions in salts with those in water samples lead to an hypothesis that a copiapite-rich suite precipitated from vadose-zone groundwater that was brought to the surface by evaporative forcing. The copiapite-rich suite, which contained larger concentrations of aluminum, calcium and zinc than the melanterite–rozenite–szomolnokite mineral suite, was the primary source of solutes in captured storm runoff. An analysis of samples collected during a summer thunderstorm indicated that the chemistry of surface runoff varied little with time or with distance downstream. The cation distributions in samples of groundwater indicated that iron-rich pore waters observed near the surface in late autumn may have influenced water chemistry in the deeper portions of the unsaturated zone during the 1989 recharge season. The results of this study show that the solutes produced by the two observed salt suites can be distinguished by their mole percent iron and that the source–product relationships can explain observed variability in mine drainage chemistry at the study site.

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INTRODUCTION

Hydrated iron sulfate minerals have been shown to occur as primary oxidation products on the surface of pyrite and marcasite (Huggins et al., 1983) and as secondary minerals that precipitate from evaporating mine drainage (Jambor and Traill; 1963; Nordstrom et al., 1979). They also form as dehydration products of other hydrated iron sulfate minerals (Ehlers and Stiles, 1965; Zodrow and McCandlish, 1978a). Because of their high solubilities (4860 g L^{-1} $FeSO_4 \cdot 7H_2O$; Weast, 1973), and rapid kinetics of formation ($<$ 1 h; Ehlers and Stiles, 1965), hydrated iron sulfate minerals provide a relatively instant source of contamination for surface runoff from pyritic coal refuse deposits.

In a companion paper describing water chemistry and acid drainage from a pyritic coal-refuse deposit at the Friar Tuck abandoned mine complex in southwestern Indiana (Olyphant et al., 1991), we showed that a substantial portion of the total acidic outflow occurred as surface runoff during rainstorms. Hydrated iron sulfate minerals, which were ubiquitous on the surface of the refuse, were hypothesized to be the source of acidity in storm runoff. However, the presumed relationships that exist between salt and solute chemistry have not been clearly demonstrated.

The objectives of this paper are: (1) to present data concerning the mineralogy and chemical composition of acid-generating salts; and (2) to provide a quantitative basis for inferring source–product relationships between the salts and the observed ground- and surface-water chemistry at the study site.

FIELD SITE AND COLLECTION OF WATER SAMPLES

In the summer of 1988, a small (500 m^2), gullied watershed was instrumented for detailed studies of soil moisture, groundwater chemistry and storm runoff (Fig. 1). The instrumented watershed was located on a large lobate deposit of pyritic coal refuse, having a maximum thickness of $\sim$6 m. The refuse is underlain by $\sim$5 m of relatively impermeable glacial drift (Fig. 2). Surface drainage only occurred during rainstorms, and the runoff was almost exclusively Hortonian overland flow. A detailed description of the instrumented watershed is provided in our companion paper (Olyphant et al., 1991).

Data concerning water chemistry are based on samples collected during a period of monitoring that commenced in August 1988 and ended in June 1990. The samples of saturated- and unsaturated-zone groundwater were collected at 2- to 4-week intervals from the twelve locations identified in Fig. 2, and the samples of storm runoff were captured at the watershed outlet. Inorganic anion and cation concentrations were determined by personnel of the Geo-

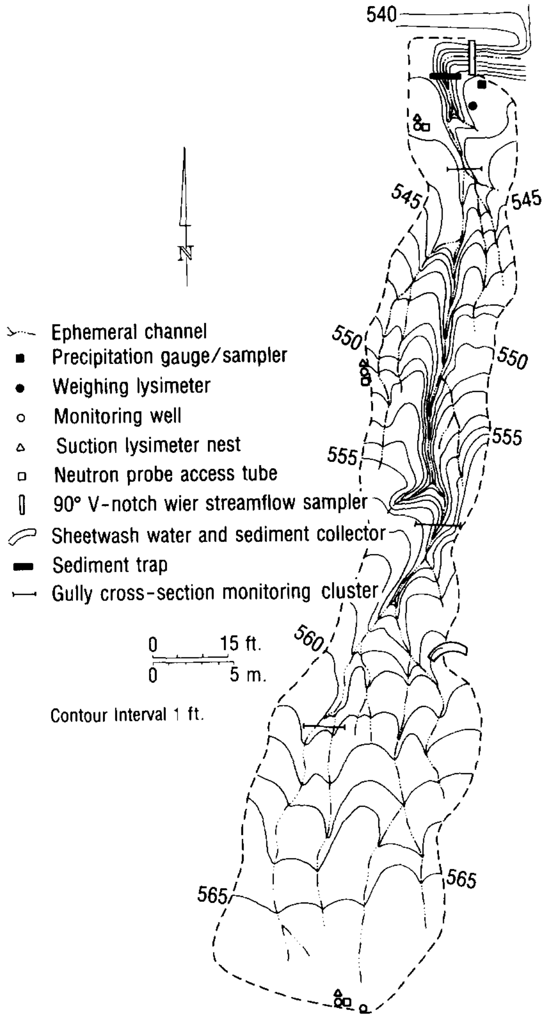

Fig. 1. Instrumented watershed at the Friar Tuck site for studying aspects of storm runoff and groundwater chemistry. Samples of storm runoff were collected immediately upstream of the V-notch weir and at the sheetwash collector. Subsurface waters discussed in this paper were collected using pressure vacuum soil water samplers (suction lysimeters).

chemistry Section, Indiana Geological Survey, using liquid chromatography and inductively-coupled plasma spectroscopy.

OCCURRENCE OF IRON SULFATE SALTS

Two kinds of acid-generating salt were observed at the instrumented watershed: (1) irregularly-shaped (perhaps botryoidal) agglomerates of yellow minerals, and (2) white or pale-green filamentous needles. The yellow salts

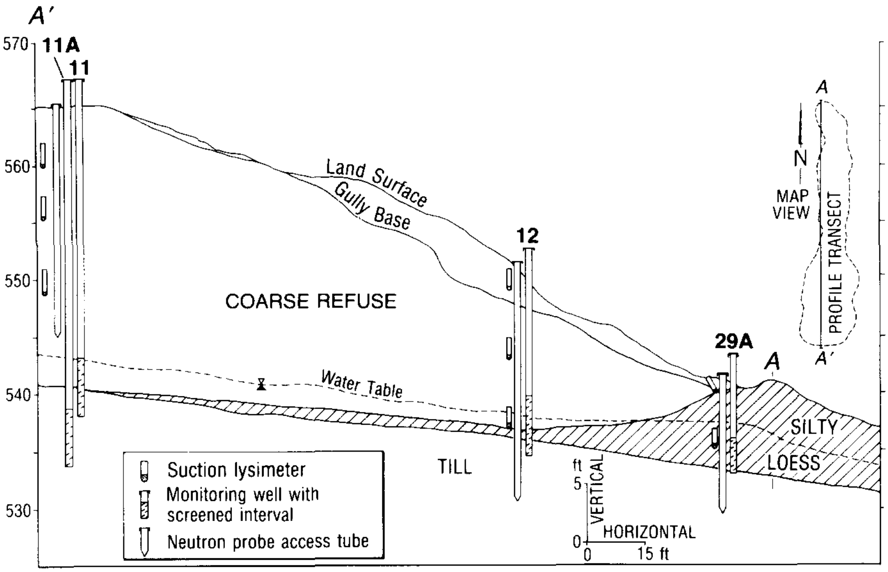

Fig. 2. Geological section across the instrumented watershed showing subsurface monitoring installations, stratigraphy and average water table.

typically occurred as disseminated zones of mineral accumulation on the surface of gully walls and in capillary pathways of the shallow (< 1 m) unsaturated zone. The white and pale-green minerals were most commonly observed on the undissected interfluves and were particularly noticeable on pyrite fragments that littered the watershed surface. The salts were scarce during winter and early spring when evaporation rates were low and most rain or melting snow infiltrated the refuse surface. During summer and early autumn, the minerals occurred abundantly, except during and immediately following rainstorms. The white to pale-green salts normally reappeared within 24 h after a rainstorm ended, while the yellow salts normally required 3–5 days to reform.

LABORATORY ANALYSIS OF THE IRON SULFATE SALTS

In August 1989, ten samples of each salt type were collected from the surface of the refuse. Extreme care was taken to collect only the mineral agglomerate and to preserve the agglomerates immediate metastable environment by sealing them in air-tight containers. Three types of analyses were performed on each salt sample: (1) X-ray diffractometry (XRD) to determine the minerals present in each agglomerate; (2) elemental analysis of dissolved salt solutions to assess complete cation compositions; and (3) mass-balance calculations based on the dissolved salt chemistry to estimate quantified mineralogy. The XRD data and mass-balance results are summarized in Table

TABLE 1

Summary of XRD analyses for hydrated iron sulfate minerals at the Friar Tuck site and computer calculated mineral abundances

Sample No.	X-ray diffraction data normalized primary peak intensities*1				Computer calculations estimated mineral assemblages (mole%)*2			
I_{max}(*3)	Cop (9.6)	Mel (18.1)	Roz (19.8)	Szom (25.3)	Cop (9.6)	Mel (18.1)	Roz (19.8)	Szom (25.3)
Melanterite–rozenite–szomolnokite suite:								
1		28	31	41		44	37	19
2			47	53			43	57
3		75	25			59	41	
4			100				100	
5		51	49			59	41	
6		74	26			93	7	
7		73	27			100		
8		92	8			75	25	
9			79	21				100
10		20	44	36		69	31	
Copiapite-rich suite:								
11	82		18		69		31	
12	50		50		100			
13	44		56		100			
14	61		39		100			
15	43		19	38	86		14	
16	72		28		100			
17	100				100			
18	100				100			
19	49	51			100			
20	100				100			

Mineral names: Cop = copiapite; Mel = melanterite; Roz = rozenite; Szom = szomolnokite.

*1 Tabulated values represent the normalized intensity of the strongest peak.

*2 mole% = (moles of individual mineral)/(total mineral moles in suite) × 100%.

*3 Value in parentheses is peak of strongest reflection for the indicated mineral (Chen, 1977).

1. The cation concentrations of the dissolved salts are presented in Table 2 along with a statistical comparison of the differences in the observed concentrations of the two mineral suites.

X-ray mineralogy

Each salt sample was examined using XRD. Powder slides were analyzed using a Philips® Electronics Instruments XRG-*2500* X-ray diffractometer equipped with a Cu-K_α radiation source and a nickel filter. An attempt was made to prepare slurry slides using acetone (as in Ehlers and Stiles, 1965), but

TABLE 2

Elemental concentrations (moles element/total cation moles) in solutions of dissolved salts and a statistical summary of the elemental analyses

Sample No.	Ca	Mg	K	Na	Fe	Mn	Zn	Ni	Cu	Al	Si	Total
Melaterite–rozenite–szomonokite suite:												
1	0.00	0.00	1.21	0.00	93.38	0.14	0.00	0.00	0.00	5.26	0.00	100
2	0.00	0.00	0.76	0.00	98.14	0.00	0.00	0.00	0.00	1.10	0.00	100
3	0.00	5.92	0.80	0.00	78.28	0.23	0.76	0.11	0.00	13.91	0.00	100
4	0.00	3.12	0.83	0.00	93.06	0.00	0.00	0.18	0.00	2.81	0.00	100
5	0.00	1.52	0.71	0.00	94.18	0.00	0.00	0.16	0.00	3.43	0.00	100
6	0.00	0.00	1.07	0.00	98.17	0.00	0.00	0.24	0.00	0.52	0.00	100
7	1.12	1.85	0.00	0.00	95.36	0.00	0.00	0.00	0.00	1.67	0.00	100
8	2.50	1.65	0.51	0.00	92.76	0.18	0.00	0.17	0.00	1.86	0.36	100
9	1.07	2.12	0.44	0.00	90.98	0.16	0.00	0.15	0.00	4.78	0.31	100
10	6.49	4.70	0.49	0.28	71.60	0.23	0.58	0.11	0.00	15.29	0.23	100
Copiapite-rich suite:												
11	4.10	1.55	0.88	0.00	79.69	0.12	0.1	0.06	0.05	13.20	0.24	100
12	4.19	0.00	0.98	0.00	86.96	0.00	0.12	0.13	0.00	7.63	0.00	100
13	5.69	1.43	0.76	0.00	82.87	0.09	0.08	0.08	0.00	9.00	0.00	100
14	3.73	2.05	0.42	0.00	82.54	0.15	0.51	0.14	0.00	10.16	0.30	100
15	1.33	5.02	0.39	0.00	72.92	0.42	0.58	0.13	0.00	18.94	0.27	100
16	1.76	3.18	0.40	0.17	89.84	0.17	0.41	0.05	0.00	4.24	0.21	101
17	5.87	2.05	0.58	0.39	82.25	0.12	0.13	0.08	0.00	9.02	0.16	100
18	0.30	1.93	0.39	0.00	79.74	0.13	0.04	0.07	0.00	17.40	0.14	100
19	0.05	2.10	0.44	0.00	80.76	0.15	0.17	0.12	0.06	16.30	0.63	101
20	0.70	3.07	0.36	0.00	71.70	0.19	0.51	0.13	0.04	23.46	0.28	100
Mel–Roz–Szom suite median	0.00	1.75	0.74	0.00	93.22	0.07	0.00	0.13	–	3.12	0.00	
Copiapite-rich suite median	2.75	2.05	0.43	0.00	81.50	0.14	0.15	0.10	–	11.68	0.23	
Significance level*	0.03	0.65	0.19	0.58	0.02	0.49	0.02	0.47	–	0.01	0.12	

Mineral names: Mel = melanterite; Roz = rozenite; Szom = szomolnokite. – = statistical analyses not possible because Cu concentrations in the melanterite–rozenite–szomolnokite suite were less than detection limit.

*Significance levels were calculated using the Mann–Whitney test for difference in two populations. Populations were considered unique if the significace level was <0.05.

peak resolution was poor. Pulverizing salt samples was minimized to avoid changing the mineral's dehydration state. Powder slides produced clear patterns, but occasionally peaks of minor intensity were found that did not correspond to recognized or likely phases (as in Jambor and Traill, 1963; Weise et al., 1987; Zodrow et al., 1978).

Typical powder slide X-ray diffractograms are presented in Fig. 3. An analysis of the X-ray diffractograms indicated that the salts consist of the

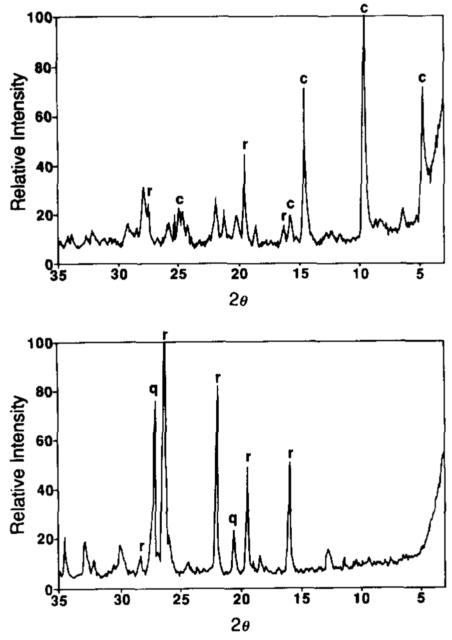

Fig. 3. Typical X-ray diffractograms for a copiapite-rich and rozenite-rich mineral suite observed at the instrumented watershed. Diffractogram peaks are identified for the minerals copiapite (*c*), rozenite (*r*) and a quartz powder filler (*q*) used in slide preparation. (Source of 2Θ data: Chen, 1977.)

minerals copiapite ($Fe^{2+}(Fe^{3+})_4(SO_4)_6(OH)_2 \cdot 20H_2O$), melanterite ($FeSO_4 \cdot 7H_2O$), rozenite ($FeSO_4 \cdot 4H_2O$) and szomolnokite ($FeSO_4 \cdot 4H_2O$), and each salt type has distinctly different mineral abundances. The yellow salt is a copiapite-rich suite that consists of copiapite in all ten samples, rozenite in six of the samples, and szomolnokite and melanterite in one sample (Table 1). The white to pale-green salt contains rozenite in all ten samples, melanterite in seven samples, and szomolnokite in four samples. These observations are consistent with those of other researchers who have conducted XRD analyses of hydrated iron sulfate minerals (e.g., Ehlers and Stiles, 1965; Nordstrom, 1977; Zodrow and McCandlish, 1978; Nordstrom et al., 1979; Weise et al., 1987).

Dissolution chemistry

The chemical composition of each salt sample was determined by dissolving 0.5 g of mineral agglomerate in 0.1 L of deionized water and agitating the mixture on a magnetic stir plate for 2 min. The pH, Eh, specific conductance and temperature of each solution was measured and samples were filtered through a 0.1-μm membrane. Filtration residue, representing the insoluble (non-salt), portion of the sample, was subtracted from the total mass of dissolved salt in order to obtain the actual mass of dissolved salt. The filtrate was split, preserved, and submitted for major- and minor-ion analyses.

Results of the dissolution experiments showed that most samples of the melanterite–rozenite–szomolnokite suite and the copiapite-rich suite contained measurable concentrations of aluminum, calcium, iron, magnesium, manganese, nickel, potassium, silicon and zinc (Table 2). Barium, cadmium, copper, sodium and strontium occurred infrequently and in much lower concentrations. Preliminary statistical analyses (using the Mann–Whitney non-parametric test for differences in two samples) indicated that concentrations of aluminum, calcium and zinc were significantly greater (95% confidence level) in the copiapite-rich suite than in the melanterite–rozenite–szomolnokite suite, but iron occurred in significantly greater concentrations in the melanterite–rozenite–szomolnokite suite. Mean elemental distributions in the dissolved salt samples were as follows:

$$\mathrm{Al}_{3.12}\mathrm{Ca}_{0.0}\mathrm{Fe}_{93.22}\mathrm{Mg}_{1.75}\mathrm{Mn}_{0.07}\mathrm{Na}_{0.0}\mathrm{Ni}_{0.13}\mathrm{Si}_{0.0}\mathrm{Zn}_{0.0}(\mathrm{SO}_4)_X \cdot (1\text{–}7)(\mathrm{H}_2\mathrm{O}) \qquad (1)$$

for the melanterite–rozenite–szomolnokite suite, and

$$\mathrm{Al}_{11.68}\mathrm{Ca}_{2.75}\mathrm{Fe}_{81.50}\mathrm{Mg}_{2.05}\mathrm{Mn}_{0.14}\mathrm{Na}_{0.0}\mathrm{Ni}_{0.10}\mathrm{Si}_{0.23}\mathrm{Zn}_{0.15}(\mathrm{SO}_4)_X(\mathrm{OH})_2 \cdot 20(\mathrm{H}_2\mathrm{O}) \qquad (2)$$

for the copiapite-rich suite. In these formulations the cations are subscripted with the median percent of total cation moles (Table 2) and X is a charge-balance factor. Notice that aluminum, calcium, iron and magnesium constitute >98% of the total cation moles and sulfate constitutes 97–100% of the total ligands in solution.

Dissimilar cation distributions in the copiapite and melanterite–rozenite–szomolnokite suites were anticipated; while copiapite theoretically includes 80% trivalent iron and 20% divalent iron, melanterite, rozenite and szomolnokite ideally contain only the divalent form. The dissolution experiments in fact indicated larger concentrations of trivalent cations (like aluminum) substituting for iron in the copiapite-rich salts than the melanterite–rozenite–szomolnokite suite (Table 2). With the exception of iron, all mono-, di- and trivalent cations occurred in greater concentrations in the copiapite-rich suite. Titrations to determine the oxidation state of iron in the salts were not performed, but Eh measurements in the dissolved salt solutions suggested a higher redox state in the copiapite-rich salts that may be attributed to higher concentrations of trivalent iron.

Mass-balance calculations

It is difficult to quantify mineralogy using XRD because of factors related to crystallinity, crystal size, chemical substitution and preferred mineral orientation which can bias the determinations (Bayliss, 1986). As an alternative, we utilized the aqueous chemistry produced by the salt dissolution experiments as input to a computer algorithm for mass-balance calculations. The algorithm approximated the number of moles of copiapite, melanterite, rozenite and szomolnokite in each salt sample based upon the following four equations:

$$[w(G_c)+x(G_m)+y(G_r)+z(G_s)]1000 = m_T \tag{3}$$

$$[w(5)(0.8150)(G_{Fe})+x(0.9322)(G_{Fe})+y(0.9322)(G_{Fe})z(0.9322)(G_{Fe})]1000 = M_{Fe}V \tag{4}$$

$$[w(6)(G_{SO_4})+x(G_{SO_4})+y(G_{SO_4})+z(G_{SO_4})]1000 = M_{SO_4}V \tag{5}$$

$$[w(20)(G_{H_2O})+x(7)(G_{H_2O})+y(4)(G_{H_2O})+z(G_{H_2O})]1000 = m_T-(M_{cations}+M_{SO_4})V-(w(2)G_{OH})1000 \tag{6}$$

In these equations the variables w, x, y and z represent the number of moles of copiapite, melanterite, rozenite and szomolnokite, respectively, that are present in the dissolved salt sample; G represents the gram formula weight of the subscripted mineral or specie (g mol^{-1}); and M is the laboratory measured concentration of the subscripted specie (mg L^{-1}). The subscripts Fe, SO_4, H_2O and OH refer to species Fe^{2+} or Fe^{3+}, $SO_4{}^{2-}$, H_2O^0 (liquid) and OH^-, respectively. The subscript "cations" refers to the total of all measured cations, and the subscripts c, m, r and s refer to the minerals copiapite, melanterite, rozenite and szomolnokite, respectively. The variable m_T represents the mass of dissolved salt (mg), and V is the volume of deionized water used to dissolve the sample (L). Whole number coefficients represent the number of moles of each species in the ideal mineral formulas, and decimal coefficients represent the mean mole percent of iron in each of the two mineral suites as it was determined in chemical analyses of the dissolved salt solutions. Eq. 4 is based on the assumption that the ratio of iron to total cations is the same in melanterite, rozenite and szomolnokite. Moles of lattice water were calculated by subtracting the total mass of anions and cations from the actual mass of dissolved salt (eq. 6). The computer calculations consider only those minerals that were shown by XRD analysis to be a common constituent of the two suites (i.e. some mixture of copiapite, melanterite, rozenite and szomolnokite), and the computed mineralogy for each sample was forced to include only those minerals that had been detected in its XRD analysis. The set of equations were solved iteratively to a convergence criterion of $< 10^{-4}$ mol.

The computer-aided calculations, which are summarized on the right-hand side of Table 1, indicate that three of the melanterite–rozenite–szomolnokite salt samples, and eight of the copiapite-rich salt samples, were composed of a single mineral. Such a high percentage of single mineral salts is unlikely in light of our own XRD analyses (left-hand side of Table 1) as well as previous studies by Huggins et al. (1983) and Weise et al. (1987). Thus the approximate computer calculations are interpreted to indicate that a single abundant phase dominated the composition of that particular salt sample. The large differences in mass between the various mine drainage minerals makes serious errors in the mass-balance calculations unlikely. The growth of a single abundant phase is believed to be strongly influenced by the metastability of the environment adjacent to the mineral accumulations (Huggins et al., 1983), and may be encouraged by the highly concentrated solutions from which the salts precipitate (see Olyphant et al., 1991, p.226).

TREND OF CATION DISTRIBUTIONS IN ON-SITE WATERS

The (moles iron)/(total cation moles) ratio (= "mole percent iron") is used here to compare cation distributions in the field-collected water samples with the cation distributions produced by the dissolution experiments. These simple comparisons are based on iron because the difference between the mole percent iron in the two mineral suites was greater and more consistent than the variation of most other elements (Table 2). In addition, iron was present in every salt sample and consistently accounted for the largest fraction of cations. Aluminum concentrations in dissolved samples of the two salt suites have a greater level of statistical uniqueness (Table 2), but the occurrence of aluminum is not guaranteed by the theoretical mineral formulas.

Seasonal trends

Fig. 4 shows the temporal trends of mole percent iron in samples of groundwater collected at sites *12* and *2g*A (Fig. 2). The samples were collected over a 16-month period that included the entire 1988/1989 water year. Values of mole percent iron tended to decrease with depth during dry periods (e.g., late autumn of 1988), but a crossover occurred during the spring wetup of 1989 when mole percent iron observed in the sample from 0.5-m depth plummeted to 62%. The excursion was short lived, however, and values of mole percent iron in the shallow samples remained above 73% throughout the drying season. Values of mole percent iron in the samples collected from a depth of 2.4 m at site *12* varied somewhat cyclically between 72% and 84% with the highest values occurring at the same time that mole percent iron was declining at 0.5-m depth. The values of mole percent iron in samples collected at a depth of 4.3 m (saturated zone) at site *12* had a very limited range (64–70%) that was less than the minimum observed in any of the dissolved salt samples.

Values of mole percent iron observed in samples of storm runoff captured

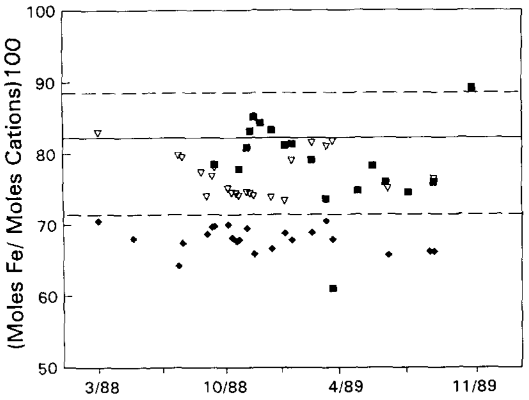

Fig. 4. Temporal trend of mole percent iron in the samples of groundwater collected from 0.5-m depth (*squares*) at site *2g*A, and 2.4-m (*triangles*) and 4.3-m (*diamonds*) depth at site *12*. Median value (*solid line*) and range (*dashed lines*) of mole percent iron in dissolved samples of the copiapite-rich suite are shown for comparison.

from the interfluve and at the watershed outlet are plotted vs. time in Fig. 5. The mole percent iron in samples collected at the watershed outlet ranged widely from a minimum of 51% to a maximum of 90%, and the values observed in samples captured by the sheetwash collector exhibited a similar range of 55–87%. The surface water samples exhibited their lowest values of mole percent iron at about the same time that the shallow groundwater samples did (late winter 1989). This was also the period of time when the concentrations of total dissolved solids (TDS) in storm runoff and shallow groundwater were at their minimal values. The mole percent iron in samples

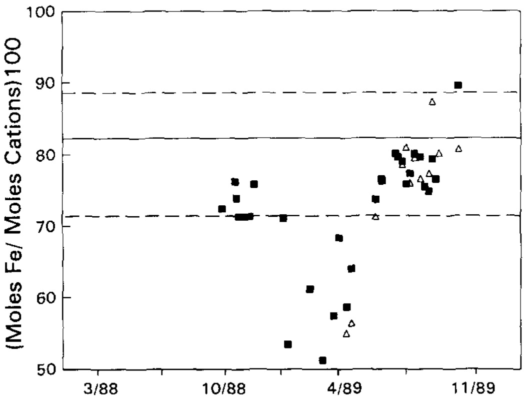

Fig. 5. Temporal trend of mole percent iron in samples of storm runoff collected at the watershed outlet (*squares*) and from a portion of an undissected interfluve surface (*triangles*). Median value (*solid line*) and range (*dashed lines*) of mole percent iron in dissolved samples of the copiapite-rich suite are shown for comparison. At both sample sites the mole percent iron in captured runoff increased from low winter season values (< 70%) to copiapite-like values (70–90%) in late summer.

of storm runoff collected at the watershed outlet progressively increased from 51% to 80% during the drying season of 1989, and mole percent iron in samples of sheetwash similarly increased from 55% to 81% (Fig. 5). The concentration of TDS in sheetwash also increased during this period (from 1,600 to 27,700 mg L^{-1}). During the period August–November 1989 samples of storm runoff captured at the interfluve site and the watershed outlet had values of mole percent iron that fluctuated between 70% and 80%. Values in this range also occurred in samples of storm runoff captured at the watershed outlet towards the end of the previous drying season (September–November 1988; Fig. 5).

Storm-period trends

Sixteen samples of storm runoff were collected during a 24-min long thunderstorm that occurred on July 18, 1989. The total storm rainfall was 152 mm and total storm runoff was 72 mm. Seven of the runoff samples were collected at the watershed outlet in order to study the temporal trend of runoff chemistry. Values of mole percent iron in those samples remained relatively constant (74–77 mole% Fe). Measured concentrations of TDS also remained approximately constant throughout the storm (3700–6000 mg L^{-1}). Nine samples of storm runoff were collected at 10–30-m intervals along the main channel that drained the instrumented watershed. The samples were collected during the period of peak flow. Measured values of mole percent iron increased from 73% near the sheetwash collector to 80% at the watershed outlet. A sample of runoff was also collected in the watershed headwaters from a reach of the channel that crossed the remnants of a soil cover that was applied during a previous reclamation attempt. The sample of runoff from the remnant soil cover had a mole percent iron of only 60%.

DISCUSSION

The findings of this study tend to support our hypothesis that hydrated iron sulfate minerals are the source of acidity in storm runoff from the study watershed. For example, laboratory dissolution of hydrated iron sulfate minerals sampled from the interfluve and gully surfaces produced aqueous solutions similar to samples of storm runoff. Also, samples of storm runoff collected at the watershed outlet and from the interfluve surface had values of mole percent iron that were largely within the range of dissolved copiapite-rich salts. During late summer and autumn the mole percent iron observed in storm runoff approximated the median mole percent iron in dissolved copiapite-rich salt samples (~80%, Table 2). The implication is that copiapite-rich salts were the main source of solutes in overland flow.

The low values of mole percent iron observed in samples of storm runoff captured during the recharge season correlated with the smallest concentrations of TDS and were lower than the mole percent iron values determined for either of the dissolved salt suites. This may reflect a decreased availability of hydrated iron sulfate minerals at the refuse deposit surface and the possible existence of another, less abundant, or less soluble source of dissolved solids. During winter and spring, most precipitation infiltrated the refuse surface and soil water movement was downwards toward the water table. As a consequence the processes responsible for the precipitation of soluble salts at the surface were probably inhibited.

Surprisingly, the melanterite–rozenite–szomolnokite mineral suite, which appeared abundantly on interfluve surfaces, did not seem to affect the cation distributions in samples of surface runoff. A possible explanation for this apparent anomaly is that the relative contribution of the melanterite–rozenite–szomolnokite suite to the TDS in overland flow was suppressed by a more abundant supply of copiapite-rich salts immediately below the deposit surface and within the interstices of the near-surface fragments. It is also possible that the consistently low pH of surface runoff (< 2.6) caused cations from coal and clay minerals to be dissolved, producing an aqueous chemistry similar to that of copiapite-rich salt samples. A third possibility is that during rainstorms, the fine-grained crystals of the melanterite–rozenite–szomolnokite suite dissolved more rapidly than the copiapite-rich suite. In numerous excavations of the refuse we observed an abundance of copiapite-rich salts to depths of $\sim$0.25 m. Accumulation of copiapite-rich salts may have resulted from oxidation and/or precipitation of solutes produced by dissolution of melanterite–rozenite–szomolnokite salts. The relative merits of these possible explanations cannot be tested with the data gathered to date, but are central to understanding the process of salt-generated acid drainage.

As previously noted (p. 324), the temporal trends of mole percent iron in samples of storm runoff collected on July 18, 1989 had a very limited range. Samples of runoff collected along the channel during the same storm also contained relatively invariant cation distributions. The limited range of mole percent iron values (74–77%) probably reflected an overwhelming influence of copiapite-rich salts on solute supply.

A set of curves has been constructed to estimate the percentages of a copiapite-rich suite and a melanterite–rozenite–szomolnokite suite that are necessary to produce the chemical range observed in samples of storm runoff collected at the instrumented watershed (Fig. 6). The mixing curves are based on a fixed mole percent iron of 93% for the melanterite–rozenite–szomolnokite suite, and a range of 72–90% for the copiapite-rich suite. These values were observed in the dissolved salt solutions (Table 2). Fig. 6 shows that the mean mole percent iron that occurred in samples of storm runoff during the

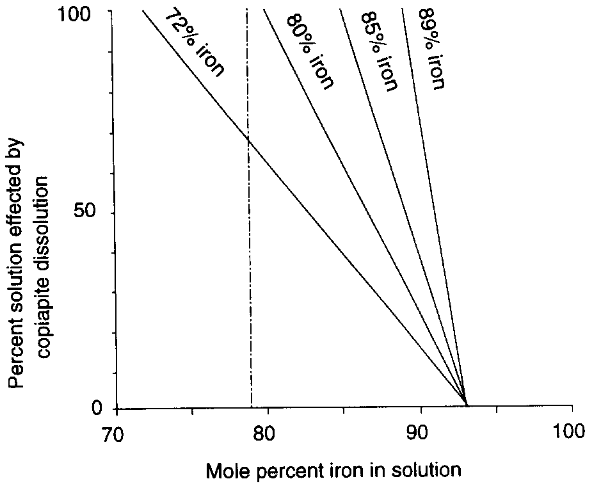

Fig. 6. Hypothetical mixing curves for solutions of dissolved copiapite-rich and melanterite–rozenite–szomolnokite mineral suites. The curves are based on the range of mole percent iron values observed in samples of the copiapite-rich salt (72–89 %), and the median mole percent iron observed in the melanterite–rozenite–szomolnokite suite (93%).

study period (78%) requires that a minimum of 68% of the total iron in solution would have been supplied by the copiapite-rich suite. The remaining 32% could have been provided by dissolution of a melanterite–rozenite–szomolnokite suite. Dissolution of a copiapite-rich salt could account for all of the iron observed in samples of storm runoff from the study watershed. These estimates of relative solute supply from a copiapite-rich suite and a salt consisting of melanterite, rozenite and szomolnokite are similarly suggested for runoff from the interfluve surface where the melanterite–rozenite–szomolnokite salts appeared abundantly while the copiapite-rich suite seemed scarce. The mixing curves also support our suggestion that low values of mole percent iron measured in samples of storm runoff collected from the interfluve surface during the recharge season (50–60%), and from the remnant soil cover at the head of the watershed, were not entirely due to dissolution of the same copiapite-rich or melanterite–rozenite–szomolnokite salts.

The mole percent iron in samples of groundwater collected from depths of 0.5 and 2.4 m fall almost entirely within the range of values observed for the dissolved copiapite-rich suite (Fig. 4). The similarity to cation distributions in the copiapite-rich suite is suggestive of a source–product relationship. Such an inference is consistent with our field observations indicating that interflow to lower portions of the more deeply incised gullies may have provided a solute source for precipitation of copiapite-rich salts. These findings are also consistent with our hypothesis that the source of solutes for precipitation of the copiapite-rich mineral suite in capillary pathways of the shallow unsaturated zone was upwardly moving groundwater. The steady decline in mole percent iron at 2.4-m depth between June and November 1988, to values that were similar to the saturated zone average of 69%, may indicate that water was moving upward from the water table during the period of prolonged drought.

The pronounced increase of mole percent iron in samples of unsaturated groundwater at 2.4-m depth during the winter recharge period of 1989 (Fig. 4) may have been a response to downward flushing of iron-rich waters observed in the shallow subsurface during the preceding autumn. The mass of dissolved salt necessary to alter the chemistry of pore water having concentrations of >120 g L^{-1} TDS must be relatively large, however, as the increase of mole percent iron that occurred in samples collected from 2.4-m depth was not obvious in samples collected from the saturated zone at site *12*.

CONCLUSIONS

Mine drainage studies have historically emphasized the oxidation of gangue minerals and this is understandable as weathering of metals is the ultimate source of the acidic solutions. Superimposed on the long-term effects of chemical weathering is the precipitation and dissolution of weathering byproducts such as the hydrated iron sulfate minerals, which many times are the direct cause of short-term (seasonal and weather-related) variability in mine drainage constituents. Thus, understanding the dynamics of weathering byproducts is important to a complete understanding of mine drainage phenomena.

Use of dissolved salt solutions to estimate salt mineralogy and to establish source–product relations with samples of groundwater and storm runoff is a simple approach that may be used in other mine drainage situations. Successful applications depend on the appropriateness of assumptions concerning comparable mineral solubilities, heterogeneities that affect the spatial distribution of salts within the watershed, and an accurate assessment of the watershed hydrology. Correct identification of source–product relationships in other studies may be complicated by the presence of several soluble mineral phases or other significant cation exchange mechanisms. In this study we have shown that the solutes produced by two different salts could be distinguished by their mole percent iron and that the established source–product relationships could be subsequently used to explain observed variability in mine drainage chemistry.

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REFERENCES

Bayliss, P., 1986. Quantitative analysis of sedimentary minerals by powder X-ray diffraction. Powder Diffraction, 1(2): 37–39.

Chen, P.Y., 1977. Table of key lines in X-ray powder diffraction patterns of minerals in clays and associated rocks. Ind. Dep. Nat. Resour., Occas. Pap. No. 21, 67 pp.

Ehlers, E.G. and Stiles, D.V., 1965. Melanterite–rozenite equilibrium. Am. Mineral., 50: 1457–1461.

Huggins, F.E., Huffman, G.P. and Lin, M.C., 1983. Observations of low-temperature oxidation of minerals in bituminous coals. Int. J. Coal Geol., 3: 157–182.

Jambor, J.L. and Traill, R.J., 1963. On rozenite and siderotil. Can. Mineral., 7: 751–763.

Nordstrom, D.K., 1977. Hydrochemical and microbiological factors affecting the heavy metal chemistry of an acid mine drainage system. Ph.D. Dissertation, Stanford University, Stanford, CA, 210 pp.

Nordstrom, D.K., Jenne, F.A. and Ball, J.W., 1979. Redox equilibria of iron in acid mine waters. Am. Chem. Soc., Symp. Ser., 93(3): 51–79.

Olyphant, G.A., Bayless, E.R. and Harper, D., 1991. Seasonal and weather-related controls on solute concentrations and acid drainage from a pyritic coal-refuse deposit in southwestern Indiana, U.S.A. J. Contam. Hydrol., 7: 219–236.

Weast, R.C. (Editor-in-Chief), 1973. Handbook of Chemistry and Physics. Chemical Rubber Publishing Company, Cleveland, OH.

Weise, R.G., Powell, M.A. and Fyfe, W.S., 1987. Spontaneous formation of hydrated iron sulfates on laboratory samples of pyrite- and marcasite-bearing coals. Chem. Geol., 63: 29–38.

Zodrow, E.L. and McCandlish, K., 1978. Hydrated sulfates in the Sydney coalfield, Cape Breton, Nova Scotia. Can. Mineral., 16: 17–22.

Zodrow, E.L., Wiltshire, J. and McCandlish, K., 1978. Hydrated sulfates in Sydney Coalfield of Cape Breton, Nova Scotia, II. Can. Mineral., 16: 63–70.