

Technical Communication

Acid Mine Drainage Flowing from Abandoned Gas Wells

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Abstract. In northwestern Pennsylvania (USA), numerous abandoned natural gas wells are producing artesian flows of Fe-contaminated water. The origin of the polluted water has been generally assumed to be brines from the gas-producing sands. We sampled 20 artesian discharges where iron staining was conspicuous. The waters were not brines, but were more characteristic of acid mine drainage (AMD). The dominant cations were Fe, Ca, and Mg, while the dominant anion was sulfate. The study area has a long history of coal mining in the lower Allegheny formation; however, the coal beds are generally at higher elevations than the discharges. We propose that AMD formed in the coal mines is infiltrating into lower aquifers, moving outside the lateral limits of mining, and using abandoned gas wells as conduits to the surface. While flowing through the underlying sandstones, the AMD chemistry is modified by contact with siderite, the dominant carbonate mineral in this stratigraphy. This would suggest that current remediation strategies that emphasize plugging the pollution-producing gas wells may be ill-advised because the source of the polluted water is more shallow than currently assumed.

Key words: Acid mine drainage; historic gas production; Pennsylvania; siderite

Introduction

Hundreds of kilometers of streams in northwestern Pennsylvania are polluted by artesian flows of Fe-contaminated water. Many of the discharges can be traced to century-old abandoned gas wells that originally tapped gas reserves in Devonian Bradford Sands, 300 – 500 m below the surface. This region also contains shallow coalbeds (0-30 m below the surface) and hundreds of abandoned surface and underground mines that commonly produce acid mine drainage (AMD). Because the artesian discharges are usually located outside the lateral extent of local coal mines and below the elevation of mined coal seams, the origin of the pollution has been assumed to be the gas-producing sands. Remediation activities have emphasized plugging of the wells, which is believed to permanently isolate the deep sources of pollution.

We investigated the chemical composition of 20 artesian flows where iron staining was conspicuous. Our results indicate that these polluted discharges are a result of downward flow from local surface coal mines, not upward flows from gas-producing aquifers. The abandoned gas wells act as conduits that transfer polluted water between near-surface aquifers, not the deeper brine aquifers that they originally accessed. The results call into question remediation strategies that emphasize plugging of the wells.

Methods

Alkalinity was measured in the field by titration to pH 4.5 using 1.6 N H₂SO₄. The pH was measured

using a Hanna HI 9023 meter. Water was collected in acid-cleaned polyethylene bottles for anion (500 ml) and trace metal (125 ml) analysis. Samples for trace metal analysis were filtered with a 0.45 µm filter and acidified with 2% HNO₃. Aluminum (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), sulfur (S), silica (Si), and strontium (Sr) concentrations were determined by Spectro-Flame Modula, End-on-Plasma, Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at the University of Pittsburgh using EPA QA/QC protocol SW846. Total blanks were analyzed to measure contamination from sampling and preservation techniques. Sulfate was estimated from sulfur concentrations. Chloride and acidity (hot peroxide method) were analyzed by G&C Laboratories (Summerville, PA). Acidity and alkalinity were expressed as ppm CaCO₃, while all other parameters were expressed as ppm.

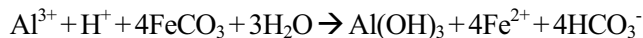
Results and Discussion

Chemical results are shown in Table 1. The gas-producing strata are commonly pumped and yield alkaline brines with >10,000 ppm Cl, >10,000 ppm Na, and 5 – 50 ppm Fe (Poth 1962). None of the artesian flows were brines. All of the waters had concentrations of Cl and Na less than 100 ppm. Two samples were alkaline and the presence of Cl and Na suggested a minor influence of brine. The remaining 18 samples were acidic with chemistries dominated by SO₄, Ca, Fe, and Mg. The geochemistry is indicative of pyrite oxidation and the formation of AMD (Rose and Cravotta 1998; Younger et al. 2002).

Table 1. Chemical analyses of samples from artesian discharges in Clarion and Jefferson Counties, Pennsylvania; concentrations of analytes are in ppm, acidity is as ppm CaCO₃, Bal. represents the cation/anion balance = the sum of the anions subtracted from the sum of the cations, divided by the sum of the cations.

Site ID	Acid.	pH	Ca ²⁺	Mg ²⁺	Na ⁺	Fe ²⁺	Mn ²⁺	Al ³⁺	K ⁺	Si ⁰	HCO ₃ ⁻	Cl ⁻	SO ₄	Bal.
M25D	-84	6.1	16	5	66	13	<1	<1	4	4	134	63	45	-4.9
S33D	-77	5.9	12	5	64	10	<1	<1	3	3	114	63	33	-1.6
ES1	27	5.6	57	23	39	40	3	<1	5	4	68	70	283	-9.4
M30D	36	5.5	72	27	30	47	4	<1	5	4	84	15	360	-1.9
M33D	46	5.4	81	33	33	52	5	<1	5	4	83	25	385	3.0
LH05D	82	6.1	48	28	7	67	5	<1	5	4	50	1	322	2.2
M70D	111	6.0	115	70	7	87	14	<1	6	5	61	6	657	5.0
L05	117	5.5	158	44	33	98	6	<1	6	5	95	19	707	0.0
TO2	123	5.4	164	84	21	84	10	<1	5	4	60	13	827	5.4
M19D	125	5.6	87	36	13	83	5	<1	5	5	40	4	481	3.3
WR1	128	5.8	191	85	36	81	17	<1	7	7	95	10	928	3.3
S45	133	5.7	65	43	8	89	6	<1	5	4	52	2	455	2.8
LC19	176	5.5	76	59	9	113	13	<1	6	4	46	3	601	3.2
LC20	197	5.2	76	61	10	109	13	<1	6	4	68	3	587	2.5
S37D	234	5.6	59	57	7	146	9	<1	5	5	43	4	595	3.5
H1	241	5.9	185	149	11	131	21	<1	8	6	54	2	1,254	2.3
WR2	244	4.7	197	102	24	115	29	<1	8	8	45	11	1,139	0.3
TO1	286	5.8	88	83	8	162	13	<1	5	4	36	3	809	2.4
LC40D	322	5.5	119	95	6	196	13	<1	7	5	44	5	1,012	-1.1
T1	358	5.9	105	89	4	215	14	<1	6	5	31	5	977	0.7

Local coal mines typically produce AMD with pH 3-4, 500-1,000 ppm SO₄, 10-100 ppm Al, 5-30 ppm Mn, and 1-40 ppm Fe (Table 2). The artesian discharges had: similar concentrations of acidity, sulfate, and Mn; higher pH and higher concentrations of bicarbonate and Fe; and substantially lower concentrations of Al. The differences in the contaminated waters can be explained by reaction of the low-pH AMD with siderite, FeCO₃. Dissolution of siderite should increase pH, generate HCO₃⁻, release Fe²⁺, and promote the hydrolysis and precipitation of Al. The net reaction is shown below.



The reaction does not affect net acidity because acidic aspects of H⁺ and Al³⁺ are replaced by Fe²⁺. Siderite dissolution should not affect concentrations of SO₄ or Mn.

In our study area, siderite is the dominant carbonate mineral in the shallow aquifers lying beneath the coal-bearing stratigraphy (Leggette1936). We propose that polluted artesian flows result from the infiltration of AMD from higher elevation coal mines into underlying siderite-containing aquifers. Typically, clays and claystones that lie beneath coal beds act as aquitards and confine AMD to the mined strata. In this area, mining often fractured the coal's underlying strata, allowing AMD to flow into and through

underlying aquifers that extend beyond the lateral extent of mining. Abandoned gas wells with missing or corroded casings pierce these aquifers and can act as conduits for polluted groundwater to up-well to the surface under the hydrostatic pressure supplied by the higher elevation surface mines (Figure 1).

Our findings are relevant to stream remediation efforts where contaminated artesian flows are commonly plugged. The discharges result from shallow flows of AMD associated with near-surface coal mines, not deep brine-filled sands. Plugging these shallow artesian flows may redirect water to

Table 2. Chemical characteristics of several spoil discharges from unreclaimed hilltop surface mines in northwestern PA

Site ID	pH	Cond.	Acid.	Fe	Mn	Al	SO ₄
HR25D	3.5	670	82	0.5	5.5	9.2	332
HR27D	3.2	1,875	358	0.5	5.5	9.2	1,269
HR40D	3.1	1,228	365	34.2	10.7	38.8	774
LC60D	3.3	1,258	268	21.2	12.6	28.6	792
LC57D	3.3	1,956	396	1.4	26.7	55.8	1,285
LC47D	3.4	1,653	600	4.6	13.8	98.1	1,125
LC46D	3.6	1,554	398	2.9	14.3	57.5	1,005
LC45D	3.3	2,143	481	2.7	24.6	70.0	1,415
LC37D	3.6	2,240	316	2.1	26.3	40.1	1,582
R63D	3.7	780	153	0.9	5.5	21.5	423
R64D	3.8	1,000	176	0.3	6.5	30.3	621

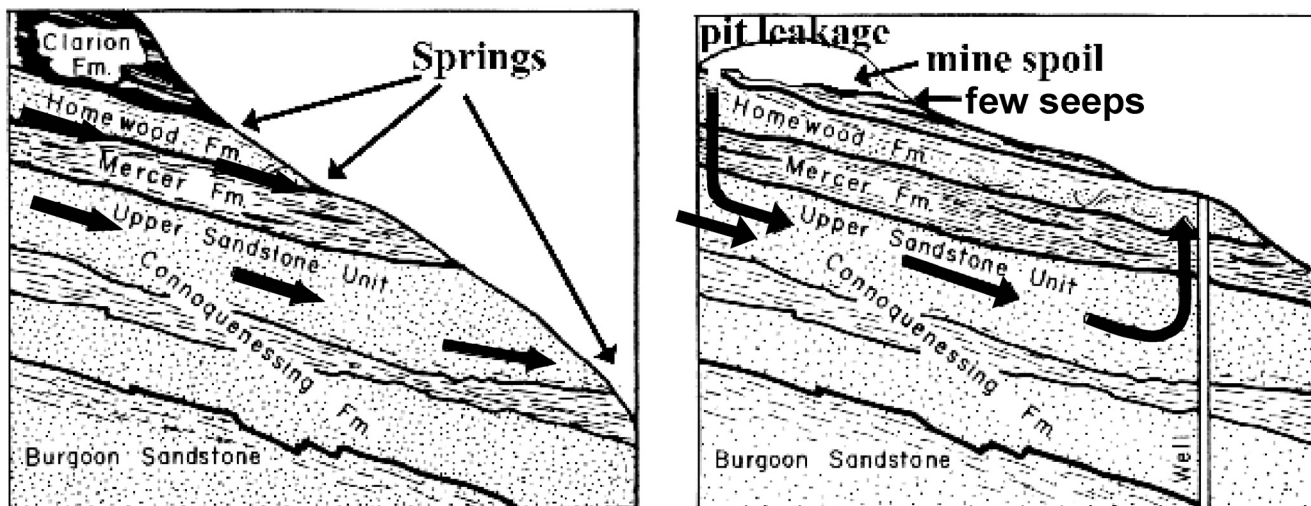


Figure 1. Generalized hydrogeologic cross sections for: a) an undisturbed area where ground water flow and discharges are controlled by strata porosity and aquitards; and b) an area disturbed by historic mining and gas drilling, where mine water infiltrates into underlying aquifers, flows outside the lateral extent of mining, and is able to flow by artesian pressure to the surface through abandoned wells (modified from Merritt and Emrich (1970)).

another well, spring, or fracture. If plugging transfers pollution from a point source to a non-point source, remediation will be greatly complicated.

It is interesting to note that the geochemical differences between the flows from the artesian flows (Table 1) and surface mines (Table 2) result in different treatment strategies and capabilities. The highly acidic, Al-contaminated drainages from the surface mines are difficult to treat with passive methods because of the tendency of Al solids to foul any alkaline substrate used (typically limestone aggregate). The acidic Fe-contaminated artesian flows are reliably treated with passive techniques that involve contact with limestone (anoxic limestone drains) followed by aerobic ponds and wetlands (Hedin et al. 1994). Flow through a siderite-containing aquifer appears to be a natural method for transforming problematic AMD into treatable AMD.

Classically, the geochemistry of AMD is explained by the balance between acidic products of pyrite oxidation and alkaline products of calcite and dolomite dissolution (Rose and Cravotta 1998; Younger et al. 2002). Siderite dissolution is generally ignored since it does not affect acidity but it can affect metal concentrations. Mine discharges with similar geochemistry have been observed by the authors in Ohio, West Virginia, Tennessee, Kentucky, Alabama, southern Wales, and northern England. Siderite's influence on mine drainage geochemistry is likely more significant than generally considered.

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