Geochemistry of Extremely Alkaline (pH > 12) Ground Water in Slag-Fill Aquifers

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Abstract

Extremely alkaline ground water has been found underneath many shuttered steel mills and slag dumps and has been an impediment to the cleanup and economic redevelopment of these sites because little is known about

and

OH^- in equilibrium with $Ca(OH)_2$. Where the alkaline ground water discharges in springs, atmospheric CO_2 dis-

Introduction

Extremely alkaline ground water has not been exten-sively studied, and there are only a few distinctive geological settings (High 1985). In a small area of northern Jordan, for example, pH in wells and adits is as high as 12.5, apparently due to the hydration of portlandite formed by the subterranean combustion of organic matter in a bituminous marl formation (Khoury et al. 1985). The pH also can exceed 10 in hypersaline evaporative lakes, such as Mono Lake in California or lakes in the Rift Valley of eastern Africa. Human activities can also produce high pH water.

Reaction with fly ash leachates commonly produces pH values in excess of 10 (Mattigod et al. 1990), and the dissolution of concrete can drive pH above 12 (Berner 1988).

Human activities have also produced the extremely alkaline ground water found around steel mills and slag dumps. The wetlands of the Lake Calumet region of southeast Chicago (87°36′

wastes also were used, including fly ash, solid industrial
wastes, demolition debris, and household trash (Colton

samples for this study and to assess the feasibility of re-cycling the entire steel slag pile for its iron content. Ground water was sampled as it entered the sides of the

depending upon the alloy being made. Steel slag gener-
ally is composed of large amounts of metal mixed with

in the lower zone. In the upper zone, magnetite and mackinawite appear along with the ferric iron minerals maghematite (γ-Fe_2O_3), hematite (Fe_2O_3), and magnesioferrite ($MgFe_2O_4$). Hausmannite (Mn_3O_4) and hauerite (MnS_2) were found in both weathered zones, and wurtzite (ZnS) was found in the upper zone. The calcium silicate portion of the slag is composed of rankinite ($Ca_3Si_2O_7$), larnite (Ca_2SiO_4), and wollastonite ($CaSiO_3$). Tridymite (SiO_2) and calcite ($CaCO_3$) are present in both weathered zones, and portlandite ($Ca(OH_2)$) is present in the lower zone. Tridymite is the stable form of quartz at the high-temperature and
.01n7707T(n-2572l46e1h3)-507i1257.54-25e5gh-t42n the   33.461156.955uJ-4611556.99Tc.9(a)5

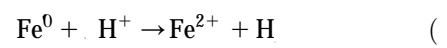metals oxidize through corrosion reactions that increase pH and produce dihydrogen (H_2):

$$Fe^0 + \; H^+ \rightarrow Fe^{2+} + H \qquad\qquad ($$

pH	12.2	11.2	12.5	12.2	
Temperature (°C)	13.6	14.5	17	8.7	
Eh (V)	−0.27	0.25	−0.045	−0.24	
TDS (mg/kg)	5100	170	2400	1900	
Dissolved oxygen (mmolal)	<0.01	0.55	<0.12		
NVOC (mmolal C)	6.8	0.33	0.92	1.83	
Major ions (mmolal)					
Calcium	0.27	0.82	27	18	18
Magnesium	0.010	0.005	<0.001	<0.002	0.20
Potassium	0.61	0.69	1.2	0.59	0.59
Sodium	78	0.57	2.2	2.5	2.7
Chloride	3.4	0.093	2.1	7.9	
Sulfate	20	0.14	0.055	0.22	
Alkalinity ($CaCO_3$)	19	1.2	27	16	
Modeled OH^-	12	1.6	53	33	
Modeled CO_3^{2-}	13	0.33	0.58	<0.02	
Minor ions (μmolal)					
Ammonia	210	15	360	39	
Nitrate\nitrite	—[2]	47	52	150	
Fluoride	53	53	270	240	
Phosphate	—[2]	<1.3	0.10	0.57	
Aluminum	30	12	5.2	2.1	20
Arsenic	9.5	<1.7	<0.53	<1.7	<3.3
Barium	0.30	0.23	2.7	2.2	2.0
Boron	69	<3.7	8.3	30	31
Cadmium	<0.14	<0.14	<0.04	<0.14	<0.10
Chromium	0.46	0.31	0.83	0.35	0.40
Cobalt	<0.19	<0.19	0.32	<0.19	<0.12
Copper	0.54	0.52	0.36	0.55	0.60
Iron	9.1	<0.16	0.7	<0.16	15
Lead	<0.36	<0.36	0.14	<0.36	<0.30
Lithium	6.1	4.9	<0.58	6.6	7.9
Manganese	0.09	<0.05	0.15	<0.05	0.55
Molybdenum	0.49	<0.24	0.06	0.39	0.27
Nickel	<0.41	<0.41	0.85	<0.41	0.65
Silicon	2700	61	<7.8	22	36
Strontium	0.64	1.5	37	9.5	9.6
Tin	<0.59	<0.59	<0.34	<0.59	<0.93
Titanium	0.17	<0.10	0.73	<0.10	0.21
Vanadium	2.6	0.20	0.10	0.29	0.27
Zinc	34	8.9	3.5	3.5	9.6

[1]Unfiltered.
[2]"—" indicates no result, excess interference from sulfate on IC.

Distribution of Metals

Understanding the fate in alkaline ground water of the major metals and steel additives found in slag, such as Cr, Cu, and V, is important to understanding the controls on the water's quality and toxicity. At high pH, Fe and Mn released from the weathering slag are likely to precipitate as oxide, hydroxide, sulfide, or carbonate minerals. With the exception of the 9.1 μmolal Fe^{2+} at site 2, the concentrations of dissolved Fe and Mn observed in the ground water were <0.7 μmolal. Formation of new Fe and Mn solids in the weathered slag was confirmed by XRD analyses, which detected the oxides hematite (Fe_2O_3) and hausmannite (Mn_3O_4) and the sulfides mackinawite (FeS) and hauerite (MnS_2). Which secondary minerals form at the site likely depends on local redox conditions, the availability of sulfide, and the kinetic rates of the reactions. The relative lack of Fe and Mn (<11% by oxide weight) in the weathering rind analyzed by Vythoulkas (1997) suggests that at his site these metals are mobile over distances of at least a few centimeters.

Three of the other major components in the slag, Al, Zn, and Si, are soluble at high pH. Al and Zn were observed at concentrations between 2 and 60 μmolal in the water at each site; Si varied from below detection limits at site 4 to 2.7 mmolal at site 2 (Table 2). These metals were also present in particulate matter, as indicated by the analysis of the unfiltered sample from site 7. The total concentrations of Al, Zn, and Si in this sample were 10, 3,

the concentration of dissolved silica slowly increased and the pH slowly decreased by the dissolution reaction:

$$SiO_2 + H_2O \leftrightarrow H^+ + H_3SiO_4^- \qquad (10)$$
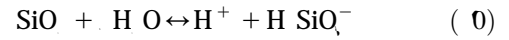
In the top of the sand underlying the slag at the Indiana site, Bayless and Schultz (2003) found pitted quartz fragments, also an indication of quartz dissolution by high-pH water. Therefore, the secondary quartz may slowly dissolve over time after its initial crystallization in the weathering rind.

Even though the concentrations of trace metals in the slag are up to 0.7 wt%, the concentrations of trace metals in the water generally occurred near or below the detection limits. Of the trace metals listed in Tables 1 and 2,

and 2 times higher, respectively, than the dissolved concentrations. In high-pH solutions, aluminum minerals such as gibbsite $(Al(OH)_3)$, kaolinite $(Al_2Si_2O_5(OH)_4)$, and feldspars are undersaturated and were not found within the weathered slag. Clay minerals were found precipitating within the sand below the slag at an Indiana site (Bayless and Schultz 2003). Wurtzite (ZnS) forms in the presence of sulfide ions and was observed by XRD analysis of the weathered slag at site 4.

The presence of quartz in the slag weathering rinds examined by Vythoulkas (1997) suggests that silica crystallizes in place as the slag dissolves. Geochemical models and a remediation experiment discussed subsequently provide evidence that the water at each site is undersaturated with respect to quartz. When quartz-containing dolomite aggregate was added to a sample of site 3 water,

reflecting the compatibility of the metals in the calcite crystal structure.

Mixing of Alkaline Ground Water with Surface Water

The evolution of water chemistry at site 7, where the spring discharge mixes in contact with the atmosphere

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