

Chemical Characterization of Acid Tunnel Drainage

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Abstract

Acid tunnel drainage of groundwater seepage through pervious rocks and joints has been released without care to public water bodies during maintenance immediately after tunnel excavation. The drainage water and seepage water are suspected of chemically corroding the tunnels and of being toxic to organisms in the natural environment.

This paper describes the results of water quality measurements, ICP spectrochemical analysis and ion chromatography to characterize the chemical variation of the drainage water and the seepage water. We collected 18 samples of drainage water and seepage water from five tunnels during maintenance in eastern Japan and determined the quantities of four elements (Ca^{2+} , Fe, Cl^- and SO_4^{2-}) by either ICP spectrochemical analysis or ion chromatography. The samples were found to contain both hydrochloric and sulfuric acids. The $\text{Cl}^-/\text{SO}_4^{2-}$ ratios were as high as those of hot springs around Quaternary volcanoes. In addition, concentrations of both Ca^{2+} and Fe were found to be proportional to those of hydrogen ion. It is suggested that acid drainage and seepage readily dissolved both Ca^{2+} and Fe from the concrete, steel supports and rocks.

Keywords: acid tunnel drainage, ICP spectrochemical analysis, ion chromatography

1. Introduction

Contamination of surface drainage systems by acid drainage water has become an environmental problem issues (Blowes et al., 2003). The flow of acid mine drainage water into surface streams, rivers and lakes has sometimes caused those water bodies to have low pH (pH 2 to pH4). In addition, the high concentrations of sulfate and metals contained in such acidic water are toxic to many organisms in the natural environment. Acid tunnel drainage water of groundwater seepage through pervious rocks and joints has been released without care to public water bodies during the tunnel maintenance stage just after excavation, too (Photo. 1). Acid drainage water from tunnels is also suspected of causing this problem.

High acidity gives water a greater capacity to dissolve minerals and metals from rocks and materials. Strongly acid groundwater seepage led to chemical attack on the lining concrete of the Mikuni Tunnel (Suzuki and Suwa, 1971).

This paper describes the results of water quality measurements and the quantification of four elements (Ca^{2+} , Fe, Cl^- and SO_4^{2-}) by either ICP spectrochemical analysis or ion chromatography, to characterize the chemical variation of acid tunnel drainage water and seepage water from five tunnels

during maintenance in eastern Japan.



Photo. 1 Acid drainage water from a tunnel

2. Method

2.1 Water quality measurement in situ

We measured temperature, potential hydrogen (pH), electrical conductivity (EC) and oxidation-reduction potential (Eh) with a combination probe at 18 spots of seepage or drainage from five tunnels during maintenance in eastern Japan (Fig. 1). We measured for at least 5 minutes at each spot, until the readings stabilized (Photo. 2).

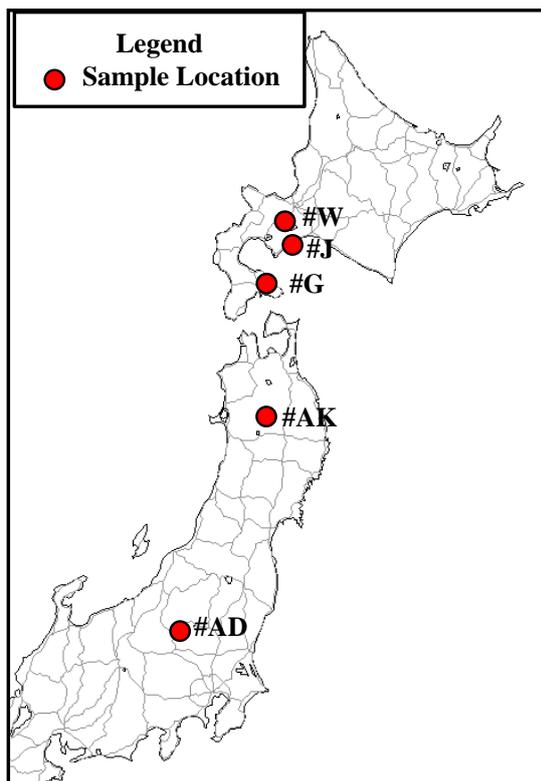


Fig. 1 Tunnel locations for groundwater sampling in eastern Japan



Photo. 2 A water quality measurement device (temperature, pH, EC, Eh)

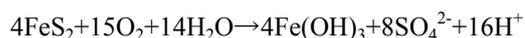
As readings are dependent on solution composition, water temperature and the type of sensor used, they needed to be normalized for mutual comparison. The Eh sensor uses a silver/silver-chloride reference electrode in place of the standard hydrogen electrode. Readings from the Eh channel displayed in Volts were normalized to the standard hydrogen electrode values as a standard

reference electrode. Readings of electrical conductivity (EC) were also standardized to the conductivity of a substance at 25°C.

Determination of groundwater origin is an important aspect of hydrological investigations. An Eh-pH diagram can be used as a first approximation to characterize natural waters after Baas Becking et al. (1960). They collected more than 6,200 pairs of Eh and pH values, and charted the distributions of Eh and pH of natural water bodies in an Eh-pH diagram (Fig. 2). The diagram showed two distribution sets of natural acid waters.

One is geothermal water. Its distribution set was delineated in both ranges from 1.2 to 9.5 in the pH values and from +0.7 to -0.185 V in the Eh values in the Eh-pH diagram of Baas Becking et al. (1960). Using a database of groundwater geochemistry, Asamori et al. (2002) reported that acid groundwater with pH of < 4.8 mainly occurs in currently active volcanic regions and is distributed from several kilometers to about 20 km from Quaternary volcanoes. Groundwater is contaminated with volcanic gases such as hydrogen chloride or sulfur dioxide. Hydrogen chloride is highly soluble in water and is emitted as hydrochloric acid (HCl), a very strong acid.

The other is oxidized mine water. Its distribution set was shown in both ranges from 2 to 9 and from +0.8 to around +0.17 V in the Eh values in the Eh-pH diagram of Baas Becking et al. (1960) (Fig. 2). This peculiarity is directly attributable to the presence of pyrite (FeS₂). Acid drainage can occur wherever rocks containing sulfide minerals are exposed to the atmosphere. The net reaction for the oxidation of pyrite which may be written as



The greater the amount of pyrite oxidized, the lower is the pH of the water. Similar reactions can be written for other common sulfide minerals, such as chalcopyrite (Cu₂S), pyrrhotite (Fe_{1-x}S), sphalerite (ZnS) and galena (PbS). Acid waters may contain great amounts of heavy metal elements such as As, Pb and Se, which are toxic to many organisms.

We compared our results with those of two distribution sets of acid waters bodies in the Eh-pH diagram of Baas Becking et al. (1960) and attempted to characterize their origins in the inorganic aqueous environments.

2.2 Sampling

We collected 18 groundwater samples at seepage or drainage sites from five tunnels between November 2012 and December 2013 to determine the quantities of four elements (Ca²⁺, Fe, Cl⁻ and SO₄²⁻) by either ICP spectrochemical analysis or ion chromatography. The samples were filtered using

filter paper with 1-micrometer pores to remove any solid substances. Two 500-ml polypropylene bottles that had been rinsed with concentrated nitric acid, tap water and pure water were filled with the sampled water. To one of the two bottles, we added 1-ml concentrated nitric acid per 100-ml water, to keep the metals dissolved for ICP spectrochemical analyses.

2.3 Ion chromatography

Chemically suppressed ion chromatography using a Dionex DX-320J, Ion Pac AS14 and AERS-500 system was used for the analysis of sulfate (SO_4^{2-}) and chloride (Cl^-) in 11 groundwater samples from three tunnels.

We divided the samples into sulfuric acid or hydrochloric acid by a graph with both $\text{Cl}^-/\text{SO}_4^{2-}$ ratio and $\text{Cl}^- + \text{SO}_4^{2-}$ concentration to differentiate the water by origin. The sample with the high ratio was suggestive of containing a large amount of hydrochloric acid that originated in geothermal environments. Hydrochloric acid is known to be more chemically corrosive to concrete materials than sulfuric acid is (Makita and Sakamoto, 1973).

2.4 ICP spectrochemical analysis

Calcium (Ca^{2+}) and iron (Fe) were analyzed by direct aspiration of ground water samples into an Inductively Coupled Plasma atomic emission spectrometry device (ICP-AES). Two different linear concentration standards were prepared: from 0.01 to 0.50 mg/L for iron, and from 0.10 to 5 mg/L for calcium. We compared the results of these concentrations with maximum concentrations determined by the equation that expresses the relationship between hydrogen ion and iron and between hydrogen ion and calcium hydroxide to estimate the amount of both iron and calcium ions dissolved chemically from lining concrete or steel supports of tunnel.

3. Results and Discussion

3.1 Results of water quality measurements

The results of temperature, potential hydrogen (pH), electrical conductivity (EC) and oxidation-reduction potential (Eh) are given in Table 1. The pH values range from 3.3 to 5.6. The specific conductivity ranges from 68 to 413 micro-S/cm. The Eh values range from 0.448 to 0.740 V. The pH values of the acid drainage water are below 5.8, a value that is specified by *The Water Pollution Prevention Law of Japan* as the minimum allowable pH value for drainage in terms of protecting human life from water pollution in public water bodies.

Fig. 2 shows an Eh-pH diagram modified from Baas Becking et al. (1960). An attempt was made to distinguish between the water that had leached from the oxidized pyrite and that which had contaminated the geothermal environment.

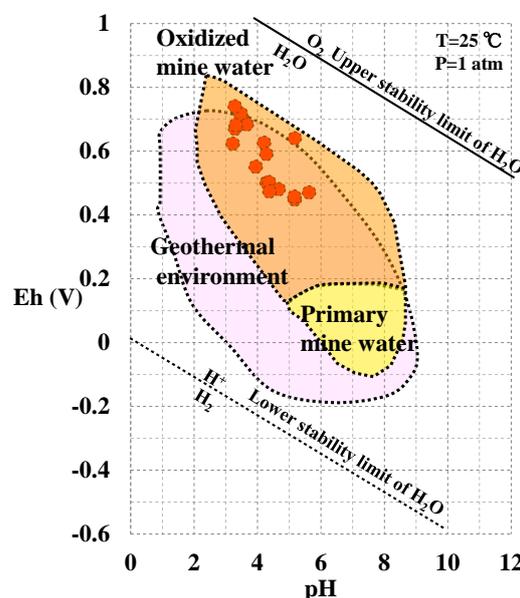


Fig. 2. An Eh-pH diagram modified from Baas Becking et al. (1960)

Table 1 Results of water quality measurement, ICP spectrochemical analysis and ion chromatography

RY; Rhyolite, DA; Dacite, ND; Neogene deposits

Sample	Tunnel	Geology	Date	Occurrence	Temp. (°C)	pH	Eh (V)	EC (uS/cm)	H ⁺ (mol/L)	Ca ²⁺ (mol/L)	Fe (mol/L)	Cl ⁻ (mol/L)	SO ₄ ²⁻ (mol/L)	Cl ⁻ +SO ₄ ²⁻ (mol/L)	Cl ⁻ /SO ₄ ²⁻
#1	#AD	ND	2012/11/5	drainage	9.7	3.5	0.698	208	3.55E-04	1.43E-04	4.96E-05	-	-	-	-
#2	#AD	ND	2012/11/5	drainage	10.3	3.6	0.698	182	2.82E-04	1.14E-04	2.67E-05	-	-	-	-
#3	#AD	ND	2013/1/13	seepage	6.9	4.0	0.550	126	1.12E-04	2.80E-05	8.57E-07	-	-	-	-
#4	#AD	ND	2013/1/13	seepage	5.9	4.3	0.501	127	5.13E-05	6.40E-05	1.64E-05	-	-	-	-
#5	#AD	ND	2013/1/13	seepage	7.7	3.3	0.670	413	5.01E-04	7.38E-05	3.22E-05	-	-	-	-
#6	#AD	ND	2013/12/17	seepage	6.3	4.2	0.626	136	6.17E-05	4.91E-05	3.16E-06	3.25E-05	3.92E-04	4.25E-04	0.083
#7	#AD	ND	2013/12/17	seepage	4.4	4.3	0.590	121	5.25E-05	7.26E-05	2.37E-05	3.16E-05	3.72E-04	4.04E-04	0.085
#8	#AD	ND	2013/12/17	seepage	6.0	4.7	0.480	107	2.14E-05	1.68E-04	1.66E-05	3.77E-05	3.53E-04	3.90E-04	0.107
#9	#AD	ND	2013/12/17	seepage	6.4	5.2	0.448	96	6.61E-06	1.44E-04	8.32E-06	3.04E-05	3.03E-04	3.33E-04	0.101
#10	#AD	ND	2013/12/17	seepage	7.5	3.2	0.623	360	6.03E-04	7.17E-05	1.71E-05	3.54E-05	8.60E-04	8.96E-04	0.041
#11	#AD	ND	2013/12/17	seepage	6.8	4.4	0.502	181	4.27E-05	4.08E-05	3.99E-05	3.66E-05	6.51E-04	6.88E-04	0.056
#12	#AD	ND	2013/12/18	drainage	6.8	3.7	0.683	235	2.14E-04	1.04E-04	2.38E-05	3.20E-04	5.40E-04	8.60E-04	0.593
#13	#AD	ND	2013/12/18	drainage	6.6	3.5	0.718	321	3.31E-04	1.13E-04	4.06E-05	5.83E-04	5.98E-04	1.18E-03	0.974
#14	#AK	ND	2012/11/8	seepage	10.8	5.2	0.457	82	6.76E-06	1.24E-04	1.46E-06	-	-	-	-
#15	#G	ND	2013/12/3	drainage	9.8	3.3	0.681	393	4.79E-04	1.76E-04	4.03E-05	4.55E-04	1.20E-03	1.65E-03	0.379
#16	#G	ND	2013/12/3	drainage	7.6	3.3	0.740	412	5.13E-04	1.90E-04	2.38E-05	2.71E-04	1.19E-03	1.46E-03	0.229
#17	#J	RY	2013/11/22	drainage	5.0	5.2	0.640	68	6.61E-06	1.86E-04	1.96E-07	7.49E-05	3.51E-04	4.26E-04	0.213
#18	#W	DA, RY	2012/8/28	drainage	28.2	5.6	0.470	127	2.34E-06	1.68E-04	-	-	-	-	-

All pairs of pH and Eh values were plotted in an oxidation range. A negative correlation was recognized between pH and Eh. However, an oxidized mine water area is wholly overlaid on a geothermal environment water one in the pH range from 2 to 9. The result of the attempt is that no samples of the geologically distinct environments could be differentiated by their Eh-pH characteristics.

3.2 Results of ion chromatography

We determined chloride (Cl^-) and sulfate (SO_4^{2-}) concentrations of 11 samples by ion chromatography to characterize their sources in the inorganic aqueous environments.

In 11 samples, the separation between peaks of chloride (Cl^-), and sulfate (SO_4^{2-}) showed good resolution. As seen in Table 1, the chloride concentrations range from 3.04×10^{-5} to 5.83×10^{-4} mol/L. The sulfate concentrations range from 3.03×10^{-4} to 1.65×10^{-3} mol/L.

Both concentrations show that the concentrations of chloride plus sulfate ($\text{Cl}^- + \text{SO}_4^{2-}$) concentrations range from 3.33×10^{-4} to 1.65×10^{-3} mol/L, and the $\text{Cl}^-/\text{SO}_4^{2-}$ ratios vary from 0.083 to 0.974. The concentrations of $\text{Cl}^- + \text{SO}_4^{2-}$ are approximately proportional to those of hydrogen ion (H^+) (Fig. 3).

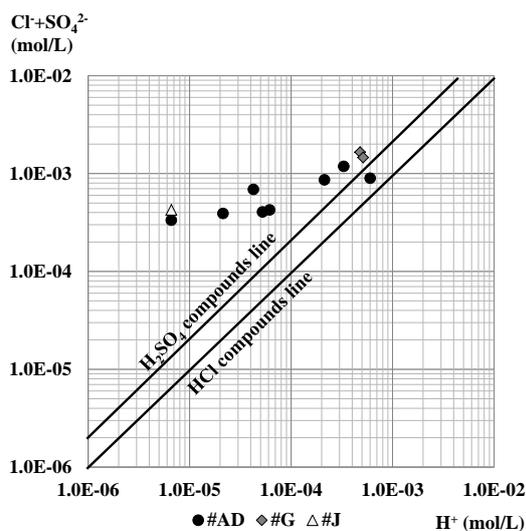


Fig. 3. Correlation between $\text{Cl}^- + \text{SO}_4^{2-}$ and hydrogen ion concentrations

The positive correlation between these concentrations suggests that most of the $\text{Cl}^- + \text{SO}_4^{2-}$ might come from hydrochloric or sulfuric acids. As the samples contained appreciable hydrochloric acid, they might be groundwater contaminated with volcanic gas in a geothermal environment. It was also proven that some of the ratios were as high as those of hot springs in geothermal environments determined by Tokumitsu and Matsushita (1979) (Fig. 4).

However, the ratios of seepage or drainage at eight spots from Tunnel #AD have a wide variety of acids in acidity and components. The pH values are from 3.3 to 5.2. The sample with the highest pH has roughly triple the chloride and sulfate ($\text{Cl}^- + \text{SO}_4^{2-}$) concentration of the sample with the lowest pH. However, the components are considered to be mixed acids of hydrochloric and sulfuric acids. The highest Cl^- concentration is 20 times the lowest one. The degree of chemical corrosion to the tunnel is assumed to be different at each spot.

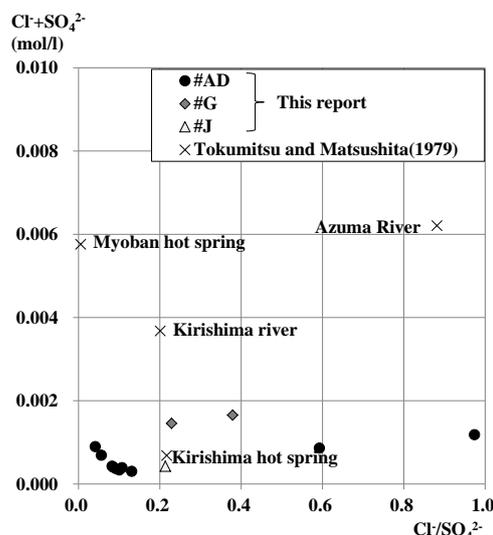


Fig. 4. Relationship between $\text{Cl}^-/\text{SO}_4^{2-}$ ratios and $\text{Cl}^- + \text{SO}_4^{2-}$ concentrations

3.3 Results of ICP spectrochemical analysis

We determined the dissolved Fe and Ca^{2+} concentrations of 18 samples from five tunnels by ICP atomic emission spectrometry (ICP-AES) to estimate the effect of chemical attack resulting from the seepage and drainage of acidic water.

As seen in Table 1, the dissolved Fe concentrations range from 1.96×10^{-7} to 4.96×10^{-5} mol/L. The concentrations of Fe increased with those of hydrogen ion along a maximum dissolved Fe line, a line that was based on the reaction between iron and hydrogen ion (Fig. 5a). Consequently, the Fe is considered to have readily dissolved from steel supports or rocks by the acid.

The dissolved Ca^{2+} concentrations range from 2.80×10^{-5} to 1.90×10^{-4} mol/L. The concentrations of Ca^{2+} are roughly proportional to those of hydrogen ion along the maximum dissolved Ca line, which is based on the reaction between calcium hydroxide ($\text{Ca}(\text{OH})_2$) and hydrogen ion (Fig. 5b). Calcium hydroxide is a major component of lining concrete. The calcium is considered to be readily leachable from the lining concrete. Many cracks and dissolution and pop-out were observed in the lining concrete of one of the tunnels (Photo. 3).

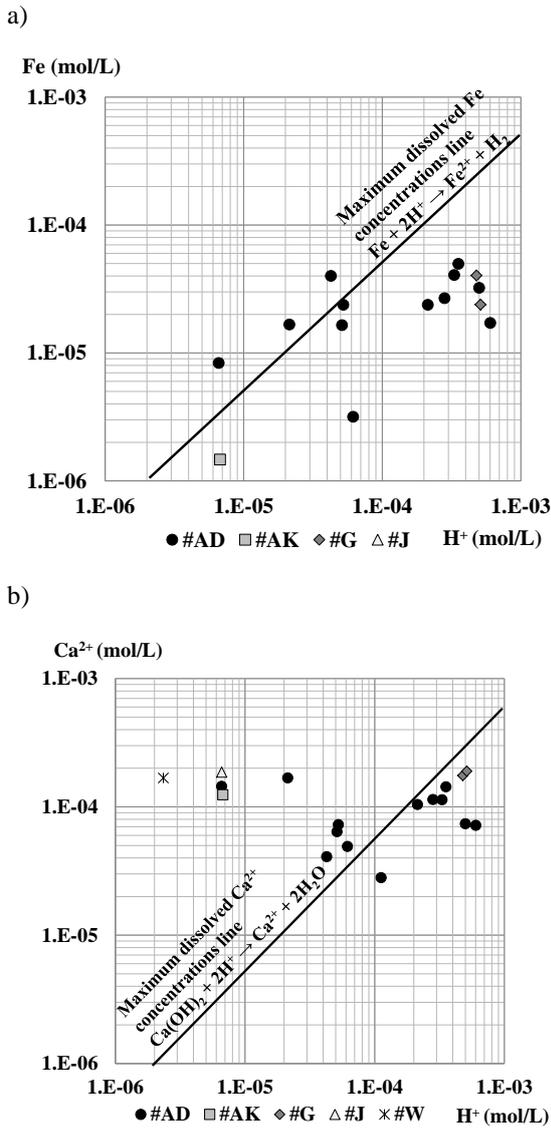


Fig. 5 Correlations of both Ca²⁺ and Fe concentrations with hydrogen ion ones



Photo. 3 Dissolution of borehole core drilled at lining concrete

Some Ca²⁺ concentrations are above the maximum dissolved Ca line when hydrogen ion concentrations were less than 1.0×10^{-4} mol/L. The calcium is considered to be added by solution of gypsum (CaSO₄ · H₂O).

We concluded that the acid drainage water or seepage water from the tunnel caused chemical corrosion and readily dissolved Ca²⁺ and Fe from the tunnel materials.

4. Conclusions

In this paper, we used iron chromatography to determine that acid tunnel drainage water and seepage groundwater contain both hydrochloric and sulfuric acids. The Cl⁻/SO₄²⁻ ratios were as high as those of hot springs around Quaternary volcanoes. Our ICP spectrochemical analyses revealed that the concentrations of both Ca²⁺ and Fe were proportional to those of hydrogen ion and that calcium and iron had been readily dissolved from lining concrete, steel supports and rocks.

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