Mineral-water interaction and hydrogeochemistry in the Samkwang mine area, Korea

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The abandoned Samkwang mine area was chosen as the research site for radioactive waste disposal in Korea. The study site chiefly consists of Precambrian granitic gneiss, which is considered as potential host rock of a radioactive waste repository. In this study, the chemical composition and residence time of groundwater collected at different depths and locations in the mine adits and boreholes nearby the mine were investigated. The factor analysis of hydrochemical data was applied to illustrate mineral-water reaction processes controlling the chemical composition of groundwater. Three chemical types of groundwater were recognized: Ca-HCO$_3$ type of shallow groundwater and Ca(Mg)-SO$_4$(HCO$_3$) type of shallow and deep groundwater in the mine, and Na-HCO$_3$ type of borehole groundwater. Tritium level indicates that the deep and borehole groundwater is older water recharged before 1950’s, and that shallow groundwater is younger water recharged after 1950’s. Thermodynamic equilibrium states between major minerals and water samples were calculated in the term of the activities of chemical constituents. The results of this study show that groundwater chemistry in the study area was evolved through the dissolution of calcite, chlorite, albite and sulfides, and the precipitation of clay and oxide minerals. The results of this study would be useful for the assessment of hydrochemical and mineralogical effects on the fate of radionuclides along groundwater pathways in the abandoned mine as a potential radioactive waste repository.

INTRODUCTION

The abandoned Samkwang mine area that chiefly consists of the granitic gneiss was chosen as the study site for the site-specific research program related with the disposal of the radioactive wastes in Korea.

The crystalline rocks such as granite and gneiss have been considered as the suitable host rocks of radioactive waste repositories. In many countries such as Sweden, Canada and United States, a number of hydrogeochemical investigations of granite and gneiss areas were carried out to determine whether such rock masses are suitable for the radioactive wastes disposal in safety respect (Fritz et al., 1979; Frape et al., 1984; Brookins, 1984; Nordstrom et al., 1985, 1989a, 1989b; Grimaud et al., 1990; Bottomley et al., 1990). Abandoned mines can be considered as a suitable disposal site of radioactive waste. Abandoned mines can provide the opportunity for direct sampling of groundwater from fracture pathways and understanding of underground environment. The Stripa mine that consists of granite of Precambrian age is an abandoned iron ore mine located in Sweden, and was selected as a potential candidate site for radioactive waste disposal. The groundwater chemistry of the mine area was investigated by many researchers to find out the suitability of the mine for a safe disposal of radioactive waste (Nordstrom et al., 1989a, b, c; Clauer et al., 1989; Fontes et al., 1989). In Korea, there were no such studies on groundwater chemistry except the study of acid mine drainage in an abandoned mine.

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The hydrogeochemical studies included the chemical evolution of groundwater and water-rock interaction in the crystalline rocks. The water-rock interaction in the underground environment may cause the dissolution of primary minerals and precipitation of secondary minerals (fracture-filling minerals in the crystalline rocks) (Steefel and Cappellen, 1990). The result is that as the groundwater moves along a flow path, its composition changes. The evolution of groundwater system has a great effect on the sorption behavior of radionuclides that could be released from radioactive wastes to geologic environment (Davis and Kent, 1990).

The purpose of the study is to characterize the chemical composition and the residence time of groundwater from boreholes and groundwater discharged at different depths and locations in the Samkwang mine area. The factor analysis and thermodynamic equilibrium analysis of hydrochemical data were also applied to illustrate dominant processes contributed to chemical evolution of groundwater. The work was a part of the hydrogeologic research program related with the disposal of the radioactive wastes in Korea.

**Samkwang mine site**

The Samkwang mine is located about 180 km south of Seoul (Fig. 1). The mine was exploited from 1933 to 1996. Electrum has predominantly been produced from the underground adits. The mine has eight levels of adits of which the maximum depth is about 220 m below 0-level (Fig. 2). The total length of main tunnel is about 2.7 km. Thus, the mine is very useful to collect deep and shallow groundwater samples of different flow paths as well as fracture-filling materials, and to understand water-conducting fracture system. A borehole of 200 m deep and three boreholes of 50 m deep were drilled adjacent to the mine for the investigation of fracture-fillings and hydraulic properties. Several horizontal boreholes in the mine were also drilled for prospecting of gold veins.
GEOLOGY

The geological map (Daehung sheet, 1:50,000 in scale) of the Samkwang mine area was made by Um and Lee (1963). The study area is mainly composed of the Yugu granitic gneiss assigned to Precambrian Kyeonggi gneiss complex (Fig. 1). The Yugu granitic gneiss covers most of the study area and frequently displays banded structure of biotite-rich mafic minerals and felsic minerals. The gneiss is medium- to coarse-grained. The Ungogri formation of the Daedong Supergroup overlies unconformably on the Precambrian gneiss and is locally distributed in the western part of the study area. The formation mainly consists of Early to Middle Jurassic sedimentary rocks. In the Samkwang mine area, there are a number of subparallel gold-silver-bearing hydrothermal quartz veins which were formed by fissure-filling of NE- and NW-trending fractures in granitic gneiss. Younger felsic and mafic dykes intruded into the gneiss. The Daehung talc mine is located in the northern part of the study area.

Mineral composition of gneiss and ores

The gneiss consists mainly of quartz, plagioclase, K-feldspar, biotite, muscovite, sericite and chlorite. Sericite and chlorite are the alteration products of plagioclase and micas. Accessory minerals of gneiss are zircon, monazite, calcite, opaque minerals, clay minerals and sulfide minerals. The microprobe analysis of feldspar shows the composition of Or_{30–1.0} Ab_{30–53} and An_{46–1.0} in mole percent. Most of feldspars are consider-

ably altered to sericite and chlorite, and are partly weathered to clay minerals.

Ore minerals associated with electrum are pyrite, chalcopyrite, arsenopyrite, sphalerite, pyrrhotite, galena, marcasite and argentite (So et al., 1988). Talc ore of the Daehung mine is composed mainly of talc, chlorite and carbonates.

Fracture-filling minerals

Even though various minerals fill the fracture and fractured zone, Chlorite and illite are the most common minerals found in the fault and shear zones. Calcite, gibbsite and Fe-oxides are also found as whitish and reddish coatings on the fracture of the borehole cores and the mine adits. The fracture fillings in gneiss cores of the borehole G1 were identified as kaolinite, smectite and illite by X-ray diffraction analysis. The XRD analysis also showed that darkish fillings collected from faults and shear zones in the mine adits were chlorite and illite. However, gibbsite and aluminum oxide were only recognized by optical inspection because they occur as very soft and soluble precipitates.

Sampling and Analysis

Twenty-five water samples were collected from the mine adits, boreholes and stream. The flux of groundwater at each sampling point in the mine was estimated from the amount of dripwater collected in the measuring bottle for 10 minutes.

The water samples include dripwater (0-, 6-, and 8-series samples) from the roof of 0-level,
6-level, and 8-level galleries, water from horizontal borehole (P-series samples) in the mine, groundwater from vertical boreholes (G1 and G2) and five stream waters (S-series samples) within the study area. The sampling sites are shown in Fig. 1. The sampling locations in the mine are shown as vertical section in Fig. 2. The groundwater samples from borehole G1 of 200 m deep below the ground surface were collected at three different levels of 50, 150 and 185 m. A borehole G1 is located outside the mine. A sampling device for groundwater consists of cylinder-type of a 30 cm long with head and bottom caps, which can be automatically closed at the depth of interest.

At each sampling site, pH and temperature of water samples were measured with portable ion meter (Orion model 290A). An electrical conductivity of water samples was measured by using portable conductivity meter (Orion model 142). Alkalinity as the concentration of bicarbonate was titrated by using 0.05 N HCl solution. All water samples for chemical analyses were filtered by 0.45 µm Millipore membrane filters. The 60 ml water samples for chemical analysis of cations were acidified to pH < 2 using HNO₃ solution. Major cations were determined by Shimadzu (ICPS-1000 III model) inductively coupled plasma-atomic emission spectrometer (ICP-AES). Anions of water samples were analyzed by Dionex 4500i ion chromatography. The reliability of chemical analyses was supported by the calculation of charge imbalance (below 5%) for the analyses.

Tritium (³H) levels of water samples were measured by liquid scintillation counting of an Instagel-water cocktail after the enrichment of 600 ml distilled water sample to 60 ml (Calf et al., 1976). Results are reported in tritium unit (TU). The precision is about ±0.5 TU.

**RESULTS AND DISCUSSION**

**Groundwater discharge into mine adits**

In the underground of the mine, groundwater is mainly discharged from fractures developed around quartz veins, fractures within dykes and water-conducting NE fracture set. Most faults and shear zones that are filled with dark clays and rock fragments are under dry condition. The discharge in the mine adits is restricted to very narrow area of about 5 m width at the points 01, 02, 61, 63, 81, C and E, and 10~20 m width at the points 03, 04, 05, A, B and D. The flux of groundwater shows the range of 8~3,000 ml/min (Table 1). The whole area except sampling sites in the mine adits is under dry or damp condition indicating no water discharge. It indicates that groundwater flow in the mine adits is strictly controlled by effective flow paths (water-conducting fractures) among fracture network of the crystalline rock mass.

**Water chemistry**

The chemical data of water samples from the Samkwang mine area are summarized in Table 1. Three chemical types of groundwater in the study area were recognized; calcium-bicarbonate(Ca-HCO₃), calcium-magnesium-sulfate-bicarbonate(Ca-Mg-SO₄-HCO₃) and sodium-bicarbonate(Na-HCO₃) types. The major ion compositions of surface water and groundwater are shown in the Piper diagram (Piper, 1944) (Fig. 3).

The shallow groundwater except the points 01 and 02 samples in the 0-level of the mine are of the Ca-HCO₃ type with Ca²⁺ concentration of 14~25 mg/l and HCO₃⁻ concentration of 50~97 mg/l. The groundwater of Ca-HCO₃ type shows electrical conductivity of 135~223 µS/cm and pH of 8.0~8.5. The water samples (P1, P2 and P3) from horizontal borehole in the 0-level and 6-level adits are also of Ca-HCO₃ type with electrical conductivity of 153~235 µS/cm.

Deep groundwater of 61 and 81 locations and shallow groundwater of 01 and 02 locations in the mine are of Ca(Mg)-SO₄(HCO₃) type with high electrical conductivity of 710~1,004 µS/cm. The content of Ca²⁺ shows the range of 77~132 mg/l. Mg²⁺ concentration ranges from 29 to 62 mg/l. HCO₃⁻ concentration is within a range of 107 to 253 mg/l. SO₄²⁻ concentration shows the range of 237 to 377 mg/l. The deep groundwater (61 and
Table 1. Summary of chemical compositions including tritium levels of the water samples from the Samkwang mine area

| Sample No. | *EC (µS/cm) | pH  | Temp. (°C) | Na⁺ (mg/l) | K⁺ (mg/l) | Mg²⁺ (mg/l) | Ca²⁺ (mg/l) | HCO₃⁻ (mg/l) | CO₂⁻ (mg/l) | Cl⁻ (mg/l) | NO₃⁻ (mg/l) | F⁻ (mg/l) | Si⁻ (mg/l) | **an/cat | ³H (TU) | ***Q (ml/min) |
|------------|-------------|-----|------------|------------|----------|------------|------------|-------------|-------------|------------|-------------|-----------|----------|----------|--------|----------|----------------|
| S1         | 66          | 6.86| 22.8       | 3.2        | 1.1      | 1.4        | 2.6        | 14.0        | 0           | 3.9        | 3.7         | 0.4       | —        | 4.1      | 0.984   | 9.6      |
| S2         | 80          | 7.03| 24.5       | 3.2        | 1.2      | 1.5        | 3.3        | 13.5        | 0           | 5.4        | 3.9         | 0.2       | —        | 4.1      | 1.028   | —        |
| S3         | 57          | 7.06| 21.5       | 3.8        | 0.3      | 1.3        | 5.0        | 17.4        | 0           | 4.0        | 4.4         | 2.7       | 0.04     | 4.5      | 1.013   | 10.3     |
| S4         | 92          | 7.19| 23.5       | 4.0        | 0.2      | 2.6        | 8.7        | 14.4        | 0           | 20.9       | 4.9         | 3.0       | 0.17     | 4.7      | 0.96    | 8.5      |
| S5         | 179         | 6.93| 20.3       | 8.0        | 2.8      | 4.1        | 19.5       | 42.7        | 0           | 21.5       | 12.9        | 13.2      | —        | 4.9      | 1.003   | —        |
| G11        | 154         | 8.77| 12.0       | 29.4       | 1.2      | 1.2        | 4.5        | 85.6        | 2.53        | 6.6        | 3.1         | 0.02      | 0.7      | 5.5      | 0.938   | 1.0      |
| G12        | 148         | 8.83| 14.5       | 36.0       | 0.5      | 1.2        | 4.3        | 104         | 3.53        | 6.7        | 3.3         | 0.1      | 0.5      | 5.4      | 1.034   | ND       |
| G13        | 207         | 9.20| 15.5       | 42.0       | 1.5      | 1.5        | 4.6        | 110         | 8.73        | 6.2        | 3.8         | 0.1      | 0.5      | 5.7      | 1.052   | ND       |
| G2         | 177         | 7.33| 17.9       | 11.1       | 1.5      | 4.2        | 30.5       | 67.1        | 0           | 27.6       | 10.6        | 16.8      | 0.2      | 6.1      | 1.061   | 9.1      |
| O1         | 839         | 8.15| 14.2       | 6.5        | 1.3      | 61.8       | 104        | 143         | 0           | 367        | 2.1         | ND       | 0.33     | 3.3      | 1.048   | 12.4     |
| O2         | 710         | 8.24| 13.4       | 5.4        | 1.6      | 59.6       | 77.1       | 253         | 0           | 237        | 3.0         | 1.3      | 1.2      | 3.8      | 0.977   | 11.6     |
| O3         | 198         | 8.00| 13.6       | 5.2        | 1.3      | 11.6       | 25.4       | 97.3        | 0           | 29.4       | 5.9         | 0.1      | 0.09     | 4.0      | 1.044   | 12.4     |
| O4         | 223         | 8.31| 14.5       | 5.3        | 1.2      | 9.5        | 22.0       | 85.4        | 0           | 21.8       | 6.0         | ND       | 0.11     | 4.4      | 1.055   | 10.5     |
| O5         | 143         | 8.15| 15.2       | 4.1        | 1.0      | 4.9        | 18.0       | 67.1        | 0           | 16.6       | 3.9         | 0.4      | 0.09     | 5.3      | 0.969   | 7.6      |
| P1         | 153         | 8.49| 15.6       | 4.8        | 1.0      | 6.4        | 17.2       | 75.1        | 1.16        | 17.5       | 4.2         | 0.3      | 0.15     | 6.1      | 0.966   | 11.9     |
| P2         | 235         | 8.12| 14.3       | 6.7        | 0.7      | 3.6        | 19.8       | 75.4        | 0           | 16.8       | 4.0         | ND       | 0.12     | 6.7      | 1.033   | 9.0      |
| P3         | 183         | 8.20| 16.0       | 8.7        | 0.8      | 8.2        | 19.5       | 97.0        | 0           | 18         | 4.3         | ND       | 0.12     | 7.5      | 0.979   | 9.0      |
| S1         | 1004        | 7.91| 16.6       | 29.1       | 3.1      | 39.2       | 132        | 119         | 0           | 377        | 36.4        | 5.7      | 7.45     | 6.5      | 0.975   | 2.4      |
| S2         | 321         | 7.83| 16.7       | 14.8       | 1.2      | 17.0       | 53.0       | 168         | 0           | 92.2       | 4.5         | ND       | —        | 7.3      | 0.984   | 2.0      |
| S1         | 715         | 7.84| 18.0       | 22.2       | 1.9      | 28.9       | 94.2       | 107         | 0           | 249        | 31.0        | 0.6      | 8.06     | 7.4      | 0.978   | 2.0      |
| A          | 177         | 8.33| 9.7        | 4.5        | 1.0      | 4.6        | 25.0       | 72.2        | 0           | 29.2       | 3.5         | 2.1      | —        | 6.5      | 0.958   | 12.8     |
| B          | 135         | 8.45| 10.3       | 3.1        | 0.8      | 4.7        | 14.0       | 53.5        | 0.76        | 6.3        | 3.3         | 0.8      | —        | 6.1      | 1.008   | 10.6     |
| C          | 143         | 8.50| 11.2       | 4.2        | 0.8      | 3.6        | 15.0       | 50.4        | 0.80        | 9.4        | 3.1         | ND       | —        | 7.2      | 1.032   | 17.1     |
| D          | 141         | 8.28| 12.2       | 3.8        | 0.6      | 5.6        | 15.0       | 63.2        | 0           | 10.6       | 2.8         | ND       | —        | 5.2      | 1.037   | 10.8     |
| E          | 152         | 8.05| 11.8       | 4.7        | 1.1      | 8.2        | 16.5       | 82.4        | 0           | 18.7       | 3.4         | 0.1      | 0.13     | 5.0      | 1.062   | 12.4     |

*EC: Electrical conductivity.
**an/cat: Charge balance of anions and cations.
***Q: Discharge amount of dripwater in the mine.
81 samples) is also characterized by high Cl\textsuperscript-- concentration of 31~36 mg/l and F\textsuperscript-- concentration of 7.5~8.1 mg/l.

The well was drilled at the discharge area in different hydrogeologic divide from the mine. The groundwater from borehole G1 are characterized as alkaline Na-HCO\textsubscript{3} water. The water shows Na\textsuperscript{+} concentration of 29~42 mg/l and HCO\textsubscript{3}-- concentration of 86~110 mg/l. The pH and ion concentration of groundwater from the borehole show increasing trend with depth.

The electrical conductivity (below 100 \(\mu\)S/cm) and pH (below 7) of surface water shows lower level than those of groundwater. However, high electrical conductivity of S5 sample might be due to mixing with mine water.

**Residence time of groundwater**

Tritium (\(^3\)H) is the radioactive isotope of hydrogen having 12.4 years of half-life and can be measured in tritium unit. 1 TU is defined as one atom of \( ^3 \)H in 10\(^{18}\) atoms of \( ^1 \)H. Tritium is derived: (1) naturally from the atmosphere by cosmic-ray radiation involving the interaction of nucleons with nitrogen, oxygen and argon, (2) artificially from the testing of thermonuclear devices in the period of 1952–1962. The tritium concentrations in precipitation before 1952 were shown about 10 TU (IAEA, 1967).

As a result of thermonuclear tests the tritium values increased dramatically reaching a peak of several thousands TU around 1963, and since then the levels have decreased steadily to several tens TU. The attraction of tritium as a hydrological tool is its use in distinguishing between recent water (recharged after 1950’s) and older water (recharged before 1950’s).

Tritium level indicates that the groundwater in the Samkwang mine area can be grouped into older water recharged prior to 1950’s and younger water recharged after 1950’s. Most groundwater sampled in the 0-level adit and G2 borehole show tri-
tium content of 7.6–17.1 TU (Table 1). The groundwater is younger water recharged post-bomb (after 1950’s). The groundwater of borehole G1 and deep groundwater from 6- and 8-level adits contains very low tritium (less than 2.4 TU), suggesting older groundwater recharged prior to 1950’s.

**Factor analysis**

The statistical approach such as multivariate analysis was used to characterize hydrochemical processes through data reduction and classification. Factor analysis can be performed to identify the most important factors contributing to the data structure and similarities between the factors. When factor analysis is applied to chemical data of groundwater, dominant processes can be identified as common factors that is sets of variables having strong associations with one another (Usunoff and Guzman-Guzman, 1989; Ritzi et al., 1993; Suk and Lee, 1999).

Factor analysis proceeds as follows: the correlation matrix, i.e., the array of correlation coefficients for all possible pairs of variables, is calculated. Then, the matrix is diagonalized and its principal components (eigenvectors) are obtained. The so-called factor I will be related to the largest eigenvalue and able to explain the greatest amount of variance in the data set. The second factor (orthogonal and uncorrelated to the first one) explains the greatest of the remaining variance, and so forth (Johnson and Wichern, 1992).

In this study, factor analysis was applied to identify the dominant processes controlling major chemical components of groundwater. The variables for factor analysis were Na⁺, K⁺, Mg²⁺, Ca²⁺, HCO₃⁻, SO₄²⁻ and pH. The calculation was performed using SAS package (SAS Institute Inc., 1996). The correlation matrix between the eight variables is shown in Table 2. The principal component analysis was adapted as extraction method of factors (Harman, 1979). The three factors are extracted to represent the contributions influencing chemical composition of groundwater. The varimax orthogonal rotation method was applied.

The results of factor analysis are summarized in Table 3. The most significant three factors indicate that three factors explain about 89.7% of total sample variance. The variance explanation of three factors shows 52.7% of factor 1, 20.9% of factor 2, and 16.1% of factor 3. The communalities of variables, which can explain the variance degree of variables by three factors, are higher than 0.765. Table 3 shows that the variables of Mg²⁺, SO₄²⁻, Ca²⁺ and HCO₃⁻ have high positive loadings on factor 1, and that the variables of Cl⁻ and K⁺ have high positive loadings on factor 2. The factor loadings of pH and Na⁺ show high positive value on factor 3.

The groundwater of calcium-bicarbonate type and calcium-magnesium-sulfate type can be explained by factor 1. The contents of Ca²⁺, Mg²⁺ and HCO₃⁻ in mine water could be principally controlled by carbonate mineral-water equilibrium:

<table>
<thead>
<tr>
<th>pH</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>HCO₃⁻</th>
<th>SO₄²⁻</th>
<th>Cl⁻</th>
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<tr>
<td>pH</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Na</td>
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<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>-1.440</td>
<td>0.321</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.073</td>
<td>0.025</td>
<td>0.426</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>0.002</td>
<td>0.180</td>
<td>0.621</td>
<td>0.878</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.471</td>
<td>0.326</td>
<td>0.310</td>
<td>0.748</td>
<td>0.506</td>
<td>1.000</td>
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</tr>
<tr>
<td>SO₄²⁻</td>
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<td>0.199</td>
<td>0.567</td>
<td>0.921</td>
<td>0.975</td>
<td>0.590</td>
<td>1.000</td>
</tr>
<tr>
<td>Cl⁻</td>
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<td>0.727</td>
<td>0.319</td>
<td>0.686</td>
<td>0.100</td>
<td>0.605</td>
</tr>
</tbody>
</table>

Table 2. The matrix of correlation coefficients among the chemical constituents for the groundwater samples
\[
(Ca_{1-x}Mg_x)CO_3 + H_2O + CO_2 \rightarrow (1-x)Ca^{2+} + xMg^{2+} + 2HCO_3^-.
\]  

(1)

A part of magnesium in groundwater would be also leached from Mg-rich minerals like chlorite that is a common mineral in gneiss and shear zone.

The potential sources of SO_4^{2-} include atmospheric sulfur deposition, the dissolution of sulfate mineral such as gypsum (CaSO_4·2H_2O) and the oxidation of sulfide minerals. Because gypsum was not found in gneiss or fracture-fillings, the SO_4^{2-}-rich mine water seems to be influenced by the oxidation of sulfide minerals. Thus high sulfate contents of deep mine water and shallow mine water of the points 01 and 02 could be originated from these sulfides. This can be expressed by the oxidation of pyrite (FeS_2) to ferric hydroxide:

\[
4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-}.
\]  

(2)

The reaction (2) results in the decreasing of \(pH\) and the increment of sulfate concentration in groundwater. The hydrogen ions liberated from the oxidation of pyrite will attack the vein calcite that commonly occurs together with sulfides. The concentration of Ca^{2+} and HCO_3^- in groundwater would be increased by calcite dissolution. Then, \(pH\) of groundwater would increase up to the range of 7.8–8.2. That is, the \(pH\) of mine water is buffered by the hydrogen production and consumption reactions.

The constituents, K and Cl in groundwater are grouped into factor 2. The deep groundwater of 61 and 81 samples shows higher Cl concentration (31 and 36 mg/l) than that (below 6 mg/l) of shallow groundwater from 0-level mine adit. During water-rock interaction, the major elements released into the solution behave in two different modes (Grimaud et al., 1990): (1) their concentrations are quickly limited by the precipitation of a sparingly soluble mineral phase in which they are immobilized. They are called as the controlled elements. The Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^- and Al(OH)_4^- (or Al^{3+}) ions as well as \(H_4SiO_4\) behave like controlled elements, and (2) their concentrations steadily increase during the evolution of the groundwater. Then they remain in the solution phase and are called as the soluble elements. The Cl ion is typical soluble element. The element of this type makes it possible to indicate the degree of reaction progress of the dissolution. Cl concentration can be used as an adequate indication for the evolution of water, assuming that Cl was derived from breakage and leaching of fluid inclusions (Nordstrom et al., 1989a). K-feldspar and illite that are major minerals of granitic gneiss in the Samkwang mine area may be major source minerals of K.
The variables (Na, pH) of the factor 3 are closely related to evolution process of Na-HCO₃ type water. The incongruent dissolution of albite written in the following ways leads the increment of Na⁺ content and pH of groundwater:

\[ 2\text{NaAlSi}_3\text{O}_8 + 9\text{H}_2\text{O} + 2\text{H}^+ \rightarrow 2\text{Na}^+ + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{Si(OH)}_4. \]  

The reaction (3) results in the consumption of hydrogen and the release of sodium. The variables (Na and pH) of factor 3 can be explained by the reaction (3).

**Thermodynamic calculation**

Aqueous speciation computed with WATEQ4F program (Ball and Nordstrom, 1992) was used to better define possible chemical reactions in the aquifer system and to assess the state of equilibrium between groundwater and minerals present. The WATEQ4F program is an equilibrium speciation code, which can calculate complexes, activity coefficients and equilibrium with minerals and gas pressures, all as a function of temperature and for all kinds of hydrochemical conditions. The calculation procedure of speciation using the program has a following order: (1) input of chemical data of water, (2) calculation of ionic strength, (3) activity of ions and complexes, (4) molar concentration of complexes, and (5) new molar concentration for all species. The calculation procedure can be converged using Newton-Raphson iteration. The equilibrium calculation between water and minerals was supported by thermodynamic data of equilibrium constants in the program. Equilibrium thermodynamics can only indicate the potential for such phase transfers. In reality, a number of kinetic reasons exist that may cause systems to behave differently than predicted (Nordstrom and Ball, 1989; Busby et al., 1991). However, the saturation index can be useful for examining potential secondary phases and the dissolution of the mineral of interest in aquifer system. The saturation index (SI) can be expressed in terms of ion activity product (IAP) and equilibrium constant (K) as follows:

\[ \text{SI} = \log \frac{\text{IAP}}{K} = 0; \text{equilibrium state} \]
\[ \text{SI} = \log \frac{\text{IAP}}{K} < 0; \text{under saturation state} \]
\[ \text{SI} = \log \frac{\text{IAP}}{K} > 0; \text{over saturation state} \]

Figure 4 shows the saturation states of water samples with respect to primary and secondary minerals as a function of the activities of major constituents. The saturation indices and activities of constituents were calculated by using WATEQ4F program. All water samples except a surface water sample are under-saturated with albite (Fig. 4(a)). This means that albite can dissolve continuously in groundwater environment of the mine and boreholes. Calcite and chlorite are equilibrated with the mine water and borehole groundwater, and are in the dissolution state with respect to surface water (Figs. 4(b), (c) and (d)). The change of saturation state indicates that the chemical composition of groundwater has been evolved from dissolution condition to equilibrium condition in respect to calcite and chlorite. All water samples are oversaturated with respect to muscovite and biotite (Figs. 4(e) and (f)).

The saturation states of water samples for the secondary minerals such as kaolinite, smectite and illite found in the mine area were also calculated. The surface water and the mine water are over-saturated with respect to kaolinite (Fig. 4(g)). However, Na-HCO₃ water is in equilibrium condition with kaolinite. The Na-HCO₃ groundwater of borehole G1 is under redissolution condition with respect to smectite and illite (Figs. 4(h) and (i)). In case of smectite and illite, surface water in over-saturated condition had been evolved into groundwater composition of re-dissolution condition by way of equilibrium state.

**SUMMARY AND CONCLUSIONS**

The hydrogeological and geochemical characteristics of the groundwater in the Samkwang mine area, Korea...
Fig. 4. Equilibrium states between major minerals and water samples as a function of the activities of main constituents in water. Open circles indicate surface water, solid triangles drip water in the mine, plus symbols groundwater of horizontal boreholes in the mine, solid circles groundwater of a vertical borehole (G1). The concentration of aluminium to calculate IAP of water samples with respect to minerals was assumed as 0.01 ppm.
Samkwang mine area, Korea

...area, which is the research site for a radioactive waste disposal are conclusively summarized as followings:

1. Three chemical types of groundwater, i.e., Ca-HCO₃, Ca(Mg)-SO₄(HCO₃) and Na-HCO₃ type are recognized in the study area. Tritium levels of groundwater indicate that Ca(Mg)-SO₄(HCO₃) type in the deep adits and Na-HCO₃ type in G1 borehole groundwater were recharged prior to 1950's, while a post-bomb recharge water is present in the shallow mine adit.

2. The factor analysis of chemical data shows that the variables (Mg, Ca, SO₄ and HCO₃) of factor 1 are mainly controlled by dissolution and oxidation reactions of carbonate minerals and sulfide minerals. The oxidation of pyrite (FeS₂) and dissolution of calcite result in high Ca, HCO₃ and SO₄ concentrations of Ca(Mg)-SO₄(HCO₃) type groundwater, and pH buffer of the range of 7.8–8.2. The constituents (Cl and K) of the factor 2 may be related to the leaching of fluid inclusion and the dissolution of illite. The high Cl and F concentrations of deep groundwater would be closely related to the mineralization zone. The variables (Na and pH) of factor 3 result from the incongruent dissolution of albite by the assumption of hydrogen ion. The Na-HCO₃ water of G1 borehole would be controlled by the incongruent dissolution of albite.

3. The thermodynamic saturation states between major minerals and water samples, and mineralogical evidences indicate that the groundwater chemistry in the study area was evolved through the dissolution of calcite, chlorite, albite and the precipitation of clay minerals.

4. The results of this study would be useful for safety assessment on the abandoned mine as a radioactive waste repository in the following areas: (1) the understanding of potential pathways of radionuclide transport, (2) the hydrochemical effect on the fate of radionuclides in groundwater system, and (3) the effect of potential secondary minerals that can react with radionuclides.

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