1b Risk assessment and management

PREDICTING THE OCCURRENCE OF ACID ROCK DRAINAGE THROUGH A GEOCHEMICAL STREAM SEDIMENT SURVEY

Joo Sung Ahn* · Sang-Woo Ji · Yong-Chan Cho · Seung-Jun Youm · Gil-Jae Yim
Geologic Environment Division, Korea Institute of Geoscience and Mineral Resources, Korea

*Corresponding Author
Tel. 82-42-868-3227
Fax 82-42-868-3414
E-mail: jsahn@kigam.re.kr
Address: Geologic Environment Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Korea

Abstract
During large constructions of roads or structures, unexpected acid rock drainage (ARD) can be caused by local mineralization containing sulfides in the geology. The potential of ARD occurrence of a certain area sometimes must be assessed before initiation of any engineering earth works. However, it is difficult to assess the entire area through collecting rock samples and predicting the potential by laboratory tests, such as the acid-base accounting method. In this study, a new prediction protocol using a geochemical exploration survey technique of stream sediment is proposed. Sediment samples were collected at the case study area where a large development is expected in the future, and the contents of some major and heavy metal elements were compared according to the major geologies of the sampling points. The modified geoaccumulation indices (I_{geo}) of Fe, Pb and As could indicate a possible zone of pyrophyllite mineralization, which may cause the occurrence of ARD at the study area. Using the enrichment index of the three elements relative to the median values of the area, a high potential zone of ARD could be designated, which was in agreement with the laboratory ARD prediction tests of the rock samples. In the other areas with different mineralization processes, other metallic elements can be selected as indicators of the ARD potential. Likewise, the potential of the occurrence of ARD at an area can be assessed by evaluating the geochemical distributions and drawing the indicator elements for ARD through a stream sediment survey.

Keywords Acid rock drainage · Stream sediment · Geochemical survey · Geoaccumulation index

Introduction

Acid mine drainage (AMD), which results primarily from surficial oxidation of pyrite in the mining sites of coal or base metals, is a significant environmental issue because of its impacts on water quality and stream biota. The increased acidity and metal concentrations can also be caused by the exposure of pyrite-bearing rocks to air and water in large construction sites, in which case it is generally called acid rock drainage (ARD). For example, construction along Interstate Highway 99 exposed sulfidic rock within a fresh roadcut on Bald Eagle Mountain at Skytop in central Pennsylvania, USA (Hammarstrom et al. 2005). The cut exposed pyrite veins associated with an unmined, sandstone-hosted, zinc-lead deposit. The excavated rocks were crushed and used locally as road base and fill. Within months, acidic (pH < 3), metal-laden seeps and surface runoff from the crushed rock piles and roadcut raised concerns about surface- and ground-water contamination and prompted a halt in road construction and the beginning of costly remediation. Similar cases have also been reported in the construction sites of highways, tunnels and buildings in Korea. Depending on the extent of the ARD generation, additional countermeasures were applied to cope with the ARD, or the construction was stopped. The most notorious bedrocks were suggested as black shale, coal seams and locally mineralized rocks at a few places in the country (Lee et al. 2005).

Methods used to predict the acid generation potential of specific materials are classified as either static or kinetic (USEPA 1994). Factors affecting the selection of the sampling regime and analytical method include an existing knowledge of the geology, costs and length of time available to conduct the test. The acid–base account (ABA) is one of the most commonly used methods in the assessment of mine waste materials for acid forming characteristics (Schumann et al. 2012). The ABA method involves static laboratory procedures that evaluate the balance between acid generation processes (primarily oxidation of sulfide minerals) and acid neutralizing processes (dissolution of alkaline carbonates, displacement of exchangeable bases, and weathering of silicates). The values arising from the ABA method are often referred to as the maximum potential acidity (MPA) and the acid neutralizing capacity (ANC). The difference between the MPA and the ANC is the net acid producing potential (NAPP). If the NAPP is positive, then the potential exists for the material to form acid. In order to evaluate the potential of ARD for a certain area where a large construction or development is planned, a new approach is required because it may be difficult to collect a sufficient amount of samples to cover the entire evaluation area, and it may be difficult to designate areas of high potential from the results of individual rock samples.

In this study, a new protocol to predict the occurrence of ARD at a certain area is suggested through collecting and analyzing stream sediment samples of the area. A stream sediment survey, one of the geochemical exploration surveys, is based on the theory that sediment samples represent the geological characteristics of the upper basin, and as a final result, an abnormal or mineralized zone can be assigned. The survey technique is also applied in geochemical mapping and environmental studies. Basically, ARD in a construction site can be generated when mineralized rocks are exposed. Through a stream sediment survey, the potential for the occurrence of ARD can be evaluated by finding an area where mineralized rocks are possibly present. For the study, a stream sediment survey was conducted in a case study area, and the possible factors indicating the ARD occurrence potential were selected. The predicted area of ARD was compared with the laboratory test results of the rock samples. The full descriptions can be found at the study by Ahn et al. (2015).

Study area

The case study area is located in the north-end part of Busan, the second largest city in Korea. The selected area is currently well outside of the main city with a relatively low population (presumably less than 1,000) and consists mostly of agricultural lands and low mountains. However, a new town and an industrial complex have been developed to the right north boundary very recently, and a main road to northbound cities is across the area with heavy traffic. Because of the expansion of the city, there is a high possibility for development in the future.

The geology of this area is composed of Cretaceous sedimentary rocks, andesitic rocks, various intruding igneous rocks and Quaternary alluvium in streams and valleys (KIGAM 1978). Black or dark-grey shale is distributed in small parts as xenoliths in andesitic rocks, which erupted due to the late volcanic activity. Acidic plutonic and hypabyssal rocks intruded the above rocks. Pyrophyllite deposits of lens type containing pyrite minerals were developed in andesitic rocks via hydrothermal replacement. Although several mines had been explored, all were closed in early 1990s and only ruins are left at two sites (IG and YC mines). In particular, fine-grained waste materials in a space of ca. 40,000 m^2 were left at IG mine, and acid leachate by pyrite oxidation continuously flows into the nearby stream. A largely mineralized zone of pyrophyllite is presumed to be in the area of andesitic rocks, and an evaluation of the potential of ARD is necessary due to the ongoing development of the area.

Materials and method

The drainage of the area is closely related to the structural line, and it has a general trend of north to south with numerous tributaries that are nearly perpendicular to this main trend (Fig. 1). Considering the stream distributions, 30 sampling points were selected, and a stream sediment sample was collected at each point. Each sample represents the composite material taken from 5-15 points over a stream length of 50 m. The required data were recorded at each sampling site in the field, including GPS position, basic water chemistry (pH and conductivity), possible contamination sources and land-use. A minimum of 100 g of samples was obtained by wet sieving through an 80-mesh sieve (< 180 µm). The samples were dried at 40°C and pulverized to a fine powder. A 0.1 g portion of each sample was digested using HF, HNO_3, and $HClO_4$ solutions at 130°C for 24h. The digested product was evaporated to dryness under 220°C, and then the residue was dissolved in dilute HNO_3 solution. The concentrations of the selected major and trace elements (Fe, Al, Mn, Cu, Pb, Zn, As and Cr) were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). The total sulfur contents were analyzed using an elemental analyzer (LECO CS230).

For rock sampling, 15 samples were collected at the sites of the representative andesite rocks and alteration zones, including waste rocks of the IG mine. The ABA test was performed to evaluate the potential for ARD of the rock samples in the laboratory.

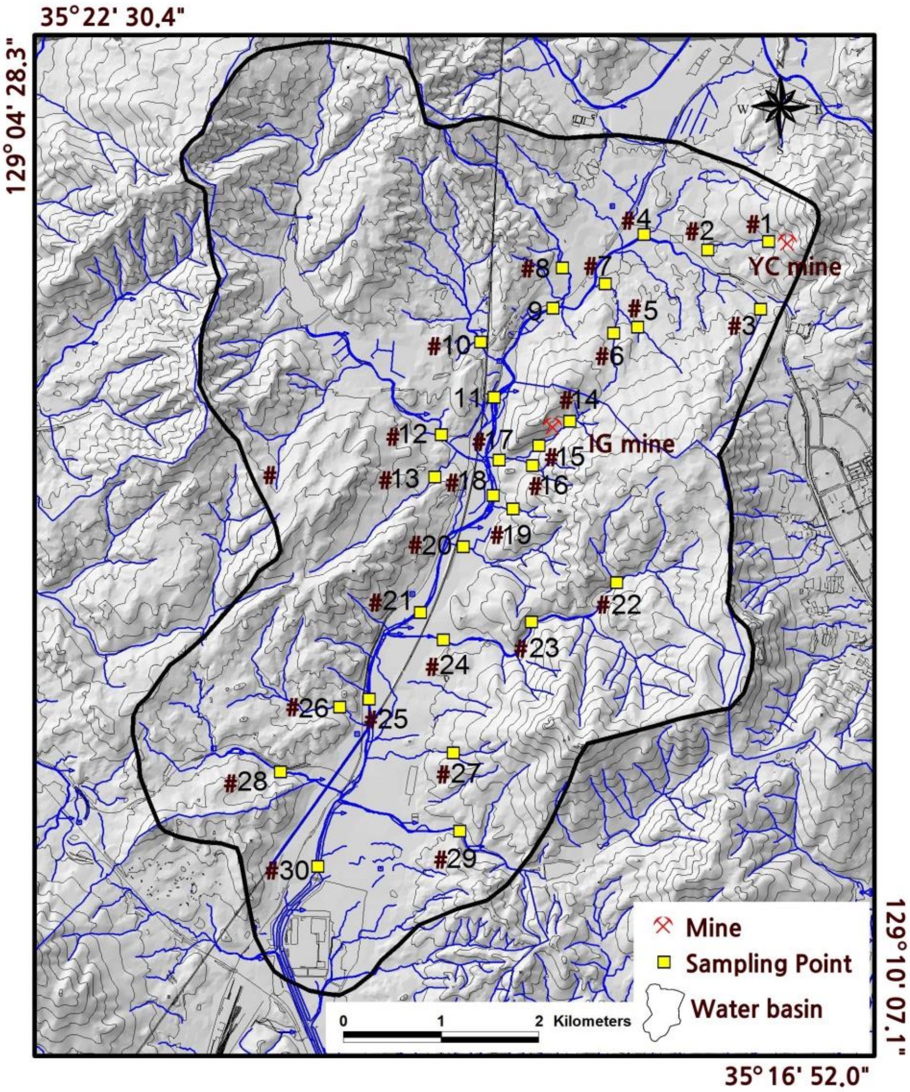

Fig. 1 Distributions of streams and sampling locations of sediments

Results and discussion

Stream sediment survey

The results of the chemical analysis of the stream sediments are summarized in Table 1. Median values of all samples are Fe 5.14%, Al 7.24%, Mn 0.18%, S 0.035%, Cu 25 mg/kg, Pb 88.0 mg/kg, Zn 200 mg/kg, As 10.5 mg/kg and Cr 25 mg/kg. The sediment collected at an adjacent stream from the waste rock dump of IG mine (#15) has maximum or relatively enriched contents of Fe 10.4%, Al 7.71% and S 0.694%, which indicates precipitation of Fe- and Al-hydroxides and sulfates derived by acid drainage. However, heavy metals, such as Cu, Pb, Zn and Cr, are not enriched. On the contrary, As is relatively enriched in the stream and in the upstream and down-stream areas (#14, #16 and #17). In the SS#1 sample collected downstream of the YC mine, the As content is relatively high at a value of 63 mg/kg, along with relatively high contents of Al and Pb. Regarding Pb, it was not high at #15, but it exhibited a maximum value at the #1 point and relatively high values (110-130 mg/kg) in the stream sediments of the IG mine (#14, #16 and #17). Based on the results, it is believed that the enriched contents of Fe, Al, Pb and As has occurred at streams affected by the ARD in pyrophyllite mineralization. The water samples of those streams exhibit acidic pH (3.19-3.74) and high EC values (510-750 µS/cm), indicating characteristics of strong acidic drainage from the closed mines. The stream of the SS#29 sample is located downside of a munitions factory and is also identified as being under agricultural activities, and heavy metals of the sample have relatively high contents of Zn 350 mg/kg and Cr 560 mg/kg. The contents of Zn are also high in samples of sites #8, #12, #25 and #28. These sites correspond to alluvium geology and are affected by agricultural activities, which results in enriched heavy metals.

The sediment samples have been classified by corresponding geology, such as andesite, granitic and alluvium, and their concentrations were compared to distinguish the effects of mineralization and agricultural activities on the major elements and the heavy metals. It is believed that the bedrock geology and mineralization effects are more pronounced in areas of andesitic and granitic rocks and that agricultural activity exerts more pronounced effects in areas of alluvium. Considering the distributions and median values of concentrations, Fe, Mn, Pb and As were high in the streams of andesite, and S and Cu are enriched in the alluvium areas. There were no significant differences in Al and Zn between the andesite and alluvium areas, and these elements seem to be affected by both geology and agricultural activities.

Table 1 Geochemical data of the stream sediment samples

Sample	Fe %	Al %	Mn %	S %	Cu mg/kg	Pb mg/kg	Zn mg/kg	As mg/kg	Cr mg/kg	pH[a]	EC[a] µS/cm
SS#1	2.82	7.16	0.01	0.080	14	210	64	63	8	3.19	510
SS#2	3.42	5.90	0.06	0.026	17	67	99	11	18	4.86	105
SS#3	5.34	6.92	0.10	0.021	6	52	76	< 2	15	6.89	69
SS#4	4.31	7.10	0.10	0.028	21	73	190	6	18	7.37	164
SS#5	10.1	5.59	0.32	0.012	9	60	110	8	16	7.32	61
SS#6	3.55	6.08	0.14	0.013	10	55	85	5	11	7.16	73
SS#7	5.93	7.19	0.18	0.030	34	85	160	6	27	7.11	95
SS#8	4.29	6.41	0.18	0.021	25	110	420	< 2	41	7.24	115
SS#9	4.24	7.48	0.12	0.031	24	89	170	5	21	7.53	193
SS#10	3.01	7.12	0.12	0.025	26	77	180	< 2	21	7.30	169
SS#11	3.88	8.25	0.12	0.039	29	87	220	5	21	7.56	188
SS#12	4.94	7.46	0.31	0.051	23	90	270	5	28	7.77	110
SS#13	1.78	4.36	0.06	0.014	15	65	110	20	13	7.48	65
SS#14	6.01	7.96	0.28	0.014	28	110	310	96	140	6.35	160
SS#15	10.4	7.71	0.14	0.694	37	83	110	87	38	3.68	513
SS#16	5.89	7.63	0.37	0.014	25	130	230	99	18	6.74	63
SS#17	8.75	8.00	0.27	0.353	38	110	150	56	33	3.74	750
SS#18	5.64	7.38	0.20	0.151	34	84	210	13	22	6.42	333
SS#19	5.49	6.90	0.20	0.040	35	98	280	12	23	7.97	90
SS#20	6.76	8.68	0.25	0.038	39	97	210	13	37	7.65	93
SS#21	4.13	8.50	0.19	0.225	46	90	320	11	20	7.40	199
SS#22	6.05	7.87	0.37	0.061	22	120	280	10	26	6.71	60
SS#23	6.14	7.46	0.28	0.044	24	110	230	12	39	6.72	79
SS#24	5.33	6.53	0.19	0.043	42	93	230	10	36	7.15	99
SS#25	3.55	7.56	0.14	0.106	39	82	270	6	25	8.19	187
SS#26	3.10	6.37	0.11	0.028	19	76	180	< 2	25	7.14	83
SS#27	6.24	7.47	0.18	0.030	23	68	140	3	60	7.69	158

SS#28	3.42	6.82	0.15	0.045	38	120	290	5	35	7.61	227
SS#29	3.78	6.29	0.17	0.101	39	120	350	< 2	560	6.85	562
SS#30	5.72	7.29	0.17	0.022	17	49	170	< 2	38	7.23	209
Min	1.78	4.36	0.01	0.012	6	49	64	3	8	3.19	60
Max	10.4	8.68	0.37	0.694	46	210	420	99	560	8.19	750
Average	5.13	7.11	0.18	0.080	26.6	92.0	204	23.6	47.8	6.80	193
Median	5.14	7.24	0.18	0.035	25.0	88.0	200	10.5	25.0	7.20	136

[a]pH and electric conductivity of the corresponding water sample

It was difficult to find distinct differences among the areas of different geologies by comparing the raw contents of major and heavy metal elements. Therefore, a modified geoaccumulation index was used. The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing current and preindustrial concentrations. Originally used with bottom sediments (Förstner and Müller 1981), the index is computed using the following equation:

$$I_{geo} = \log_2(C_n/1.5B_n)$$

where C_n is the measured concentration of the element n in the pelitic sediment fraction (< 2 µm), and B_n is the geochemical background value in the fossil argillaceous sediment (average shale). The factor 1.5 is used because of the possible variations of the background data to lithogenic effects. This work used a modified geoaccumulation index to perform the calculations. The modification was as follows: C_n denotes the total concentration of a given element in the sediment samples tested, while B_n denotes the concentrations of the elements in the Earth’s crust (Wedepohl 1995). Stream sediments reflect the average geogenic composition of a catchment basin which is a part of the surface layer of the Earth’s crust. The concentrations of the elements in the shale accepted by Förstner and Müller (1981) were much higher than those in the upper continental crust suggested by Wedephol (1995). Considering these matters, the element concentrations in the upper crust were adopted as reference values. The modification has also been employed using the crust values or soil background values in the assessment of the metal pollution of soils (Loska et al. 2004; Li et al. 2014). A value of the index of less than zero means the soil is practically uncontaminated, and higher values are gradually classified as moderately, heavily and extremely contaminated situations.

The calculated index of each element by geology is shown in Fig. 2. Among the elements, Al, S and Cr exhibit less than zero values in most of the samples, suggesting no contamination of these elements is present. In contrast, indications of Mn, Cu and Zn contamination were found in all geologies, all exhibiting greater than zero values, and there is no significant difference among the geologies. Lithological enrichment can be pronounced in an andesite area, and artificial contamination can be due to agricultural activity in alluvium area. Therefore, Mn, Cu and Zn are affected by both sources in the study area. In the case of Fe, an index value greater than zero occurs in the andesite area, and Pb and As also exhibit values greater than zero in all geologies, with higher median values in the andesite area, which exhibit different characteristics compared to the other elements. Among these elements, Fe is directly related with the oxidation reaction of pyrite, and Pb can be related with the oxidation of various sulfide minerals. Arsenic is generally one of the associated elements of pyrite and can be released by pyrite oxidation (Pokrovski et al. 2002). Thus, the enrichment of Fe, Pb and As in the andesite area can indicate the mineralization of pyrophyllite as opposed to anthropogenic contamination and can be used in evaluation of the potential of ARD in the area. Likewise, the factors indicating the ARD generation potential can be assigned by obtaining and interpreting the geochemical data of the stream sediments in the study area. Of course, at the other areas where different mineralization processes have occurred, other metallic elements can be selected as indicators for ARD generation, and the geochemical meaningfulness should be assessed.

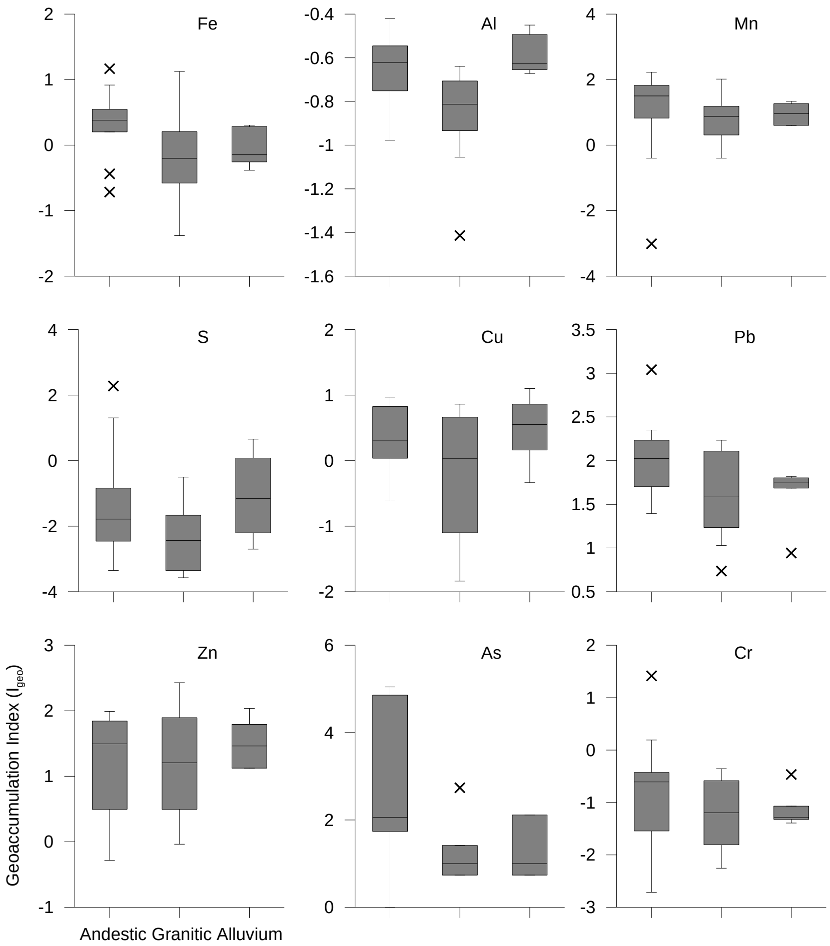

Fig. 2 Boxplots of the geoaccumulation indices in stream sediments according to geologies

ARD potential of the study area

In the study area, ARD can be generated at the zones of pyrophyllite mineralization. The above analysis indicates that the elements of Fe, Pb and As are indicators of the mineralization, and the potential for ARD can be evaluated by the relative enrichment of these elements in the stream sediments. The enrichment can be calculated by averaging the ratio of indicator element concentrations in samples to their baseline values. As a baseline for the evaluation of the enrichment of the elements, the median values of the study area are used, and the enrichment index (EI) of the three elements is calculated as follows,

$EI = [Fe/Fe_{back} + Pb/Pb_{back} + As/As_{back}] / 3$
Fe_{back} : 5.14 %, Pb_{back} : 88 mg/kg, As_{back} : 10.5 mg/kg

Through calculation of the enrichment index, the potential for ARD can be quantitatively evaluated at each of the sampling points. The calculated ARD potential value of each sampling point and the calculated potential of the entire study area using the Kriging method are shown in Fig. 3. There is low potential at the zone of values of less than zero, and there will be very high potential at the zone of values of greater than two. The maximum value of 4.02 is found at the stream of the IG mine where acid drainage occurs, and the values are higher than two are found at nearby streams. At the points of #22, #23 and #24, the potentials are greater than one, which agreed with the results from the laboratory test of the rock samples (data not shown). Generally, andesite rocks located southeast from the IG mine have high potential for ARD. Currently, there is no ARD generation at the zones; however, land use and development of the area can initiate the generation of ARD.

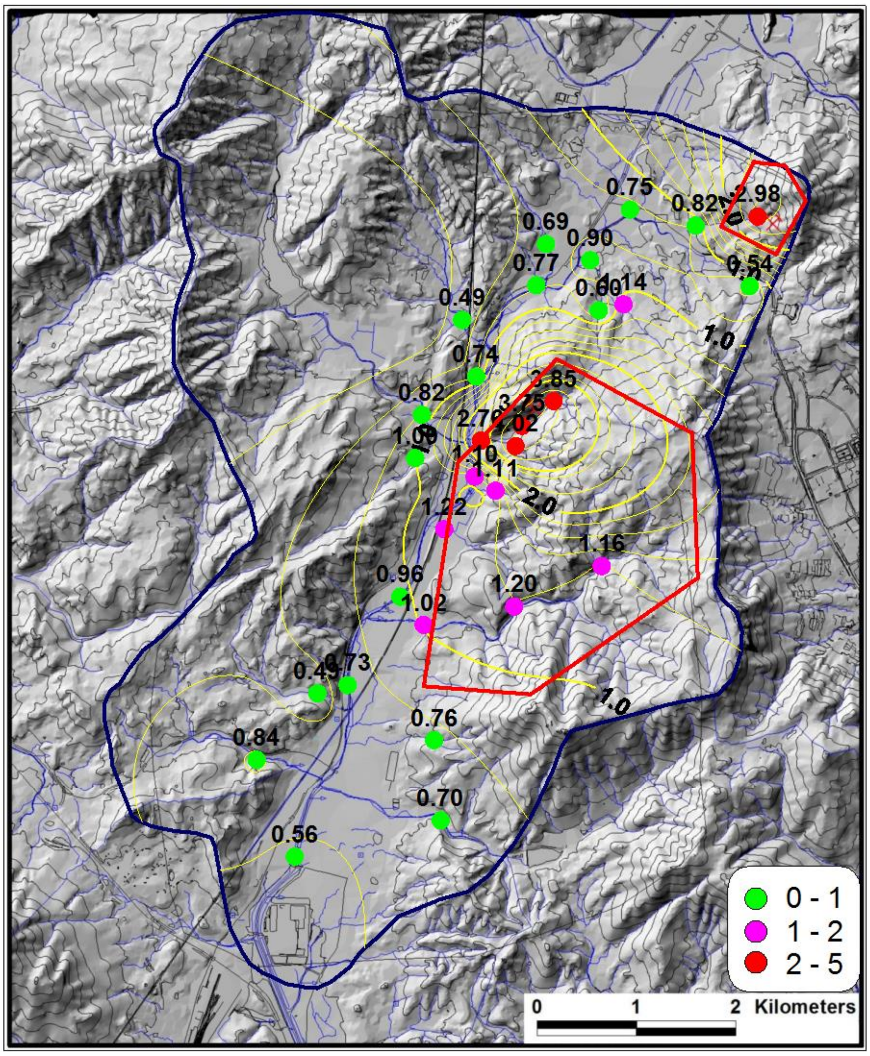

Fig. 3 Enrichment index of indicators and potential for ARD occurrence in the study area
(Zones with a red line have high potential for ARD)

Conclusion

A new method to evaluate the potential for ARD in a certain area using a technique of stream sediment survey was proposed. As applied in the study area, values greater than 2 of the enrichment index of the indicator elements were found at the samples of nearby streams around the IG and YC mines, where acid drainage occurs. There were also high values at the basins of andesite rocks, where the ABA and NAG test results of rock samples exhibited high ARD potential, thus raising attention to possible ARD generation in these rocks. Currently, ARD is not observed, but excavation or exposure of bedrocks may initiate ARD in the zones. The method of using the enrichment index of the indicator elements for evaluating the ARD potential proposed in this study can be applied in an area where direct sampling of rocks is impossible. If available, the established data of the sediments from a previous geochemical mapping project can be used, which removes the need to perform some of the evaluation procedures, thereby reducing the time to perform the evaluation. In summary, the proposed procedure of determining the ARD potential involves the following steps: 1) elucidation of the mechanism of ARD generation in the study area, 2) evaluation of the geological and land-use characteristics and the distribution of the elements by geologies, 3) determining the indicator elements for ARD and evaluation of the meaningfulness of the geochemical reaction, and 4) calculating the enrichment index of the indicator elements and mapping the ARD potential.

Acknowledgements
This research was supported by the Basic Research Project (15-3414) of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Science, ICT and Future Planning of Korea.

Reference

Ahn, JS, Ji SW, Cho YC, Youm SJ, Yim GJ (2015) Assessment of the potential occurrence of acid rock drainage through a geochemical stream sediment survey. Environ Earth Sci 73:3375-3386

Förstner U, Müller G (1981) Concentrations of heavy metals and polycyclic aromatic hydrocarbons in river sediments: geochemical background, man's influence and environmental impact. Geojournal 5:417-432

Hammarstrom JM, Brady K, Cravotta CA (2005) Acid-rock drainage at Skytop, Centre County, Pennsylvania, 2004. USGS Open-File Report 2005-1148, p 45

KIGAM (1978) Geological map of Korea, Donrae and Weolnae sheets 1:50000. Korea Institute of Geoscience and Mineral Resources

Lee GH, Kim JG, Lee JS, Chon CM, Park SG, Kim TH, Ko KS, Kim TK (2005) Generation characteristics and prediction of acid rock drainage (ARD) of cut slopes. Econ Environ Geol 38:91-99 (in Korean with English abstract)

Li Z, Ma Z, van der Kuijp TJ, Yuan Z, Huang J (2014) A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. Sci Tot Environ 468-469:843-853

Loska K, Wiechula D, Korus D (2004) Metal contamination of farming soils affected by industry. Environ Int 30:159-165

Pokrovski GS, Kara S, Roux J (2002) Stability and solubility of arsenopyrite, FeAsS, in crustal fluids. Geochim Cosmochim Acta 66:2361-2378

Schumann R, Stewart W, Miller S, Kawashima N, Li J, Smart R (2012) Acid-base accounting assessment of mine wastes using the chromium reducible sulfur method. Sci Tot Environ 424:289-296

USEPA (1994) Acid mine drainage prediction. US Environmental Protection Agency, EPA 530-R-94-036, p 48

Wedepohl KH (1995) The composition of the continental crust. Geochem Cosmochim Acta 59:1217-1232