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Geochemical Application for Environmental Monitoring and Metal Mining Management

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1. Introduction

Metal mines have been increasing continuously due to high growth rate of population and rapid development of industry throughout the world. Various kinds of metal ores are supplied into industries. Precious metals such as gold, platinum and silver have been utilized for ornamental purposes due to their beauty, rarity and durability whereas industrial ores are demanded by many sectors. These ores usually occur in different geological conditions which lead to diversity of depositional characteristics. Multiple elements occur naturally in the same mineral deposits; some of these elements, particularly heavy metals, may in turn have potential impact to the environment. Therefore, heavy metals are the most crucial aspects for toxicity. However, these metals have several chemical binding forms which just a few forms appear to contaminate environment.

Moreover, Acid Mine Drainage (AMD) is another environmental concern. AMD appears to have been accelerated during mining processes when metal sulfides in mineralized rocks and solid wastes are exposed to oxygen and water allowing rapid oxidizing reaction. Oxidation of metal sulfide has potential to produce sulfate which may turn into sulfuric acid. Subsequently, it may be dissolved by rain and leading to acidity drainage. AMD can also cause heavy metal leaching from waste rock and tailings; consequently, some toxic metals (e.g., lead, zinc, copper, arsenic, selenium, mercury and cadmium) may contaminate runoff and groundwater. AMD with high metal concentrations may in turn yield severe toxicological effects on aquatic ecosystems. Biota will be affected primarily and subsequently toxic levels would be increased through food chain. Although, some heavy metals such as copper and zinc are required with small quantities for normal metabolism, their high concentrations become toxic and can cause malfunctioning of human organs.

Geochemical exploration has been carried out by mining geologists for investigation and evaluation of mineral deposit, metal ore in particular. It can also be applied to environmental impact assessments and monitoring. Moreover, mineralogical and chemical characteristics are one among many scientific tools that will lead to identification of potential sources of such problems. Appropriate prevention and mining plans can be designed based on these data. Unfortunately, most mining geologists always apply geochemistry for exploration and mining without concern of environmental impacts; on the other hand, most environmental scientists have little knowledge on geology and mining

materials, mining designs and processes. Environmental protection should be carefully planned in order to eliminate and/or minimize any short- and long-term environmental impacts that may occur. Otherwise, serious problems may occur that may be very difficult to remediate and extremely cost enormously.

This chapter will review standard procedures for evaluation of AMD potential of rock waste and tailing generated from mining activity. Digestion techniques for analysis of heavy metals are also considered to give basic knowledge for environmental monitoring and impact assessment. Some cases studies in Thailand will be given for better understanding.

2. Mining wastes

Mine operations may include 3 principle activities which are mining, mineral processing/dressing and metallurgical extraction/refining. All of these activities usually produce wastes that are unwanted and non-economic value. Solid mining wastes and other related wastes may be generated from each activity were summarized by Lakkopo (2002) as shown in Table 1.

Dusts, ashes and other atmospheric emissions may be routinely monitored by environmental scientists who have experienced in other industrial plants. Slag and waste water can also be tested before suitable processes of treatment and disposal will be designed by environmental engineers. Therefore, heterogeneous geological materials including overburden soils and rocks appear to be the most crucial solid wastes due to lack of geological knowledge of both environmental scientists and engineers. Geologist and mining engineer should share their opinion for environmental plans. However, top soils may have been utilized as construction materials during mining activities and reclamation at the mining end. Although, these top soils may contain some natural contaminants, particularly heavy metals in this case, they would have low impact to the environment. This is because they have been undertaken naturally erosion and weathering processes for several hundreds or thousands of years then transportation of contaminant have been taken place slowly ever since. Moreover, quantities of these top soils are usually much lower than waste rocks and tailings. Rocks usually have stable chemical forms of minerals but mining processes such as blasting, grinding and milling will reduce their sizes and increase surface of reaction. Consequently, chemical reactions would be activated rapidly leading to metal leach out form these rocks. On the other hand, tailings are the other solid waste left after ore and metal extractions which usually involve with chemical additives as well as alteration of the natural chemical bonding. This waste type should then be concerned for environmental monitoring plan.

Activities	Mining Wastes
Open pit and underground mining	Waste rocks, overburden soils, mining water, atmospheric emissions
Mineral processing, coal washing, mineral fuel processing	Tailing, sludge, mill water, atmospheric emissions
Pyrometallurgy, hydrometallurgy, electrometallurgy	Slag, roasted ores, flue dusts, ashes, leached ores, process water, atmospheric emission

Table 1. Summary of mining activities and their solid, gaseous and liquid wastes (modified after Lakkopo, 2002)

Waste Rocks: Large amount of waste rocks may have been removed from mining site, particularly for quarrying and excavation, to access to the ore body. These waste rocks are eventually remained in the site and surrounding areas after the mining end (see Fig. 1). Subsequently, they may become sources of environmental impacts. Although, mining design can reduce quantity of waste rocks; for example, mining excavation generates very less amount of waste rocks in comparison with open-pit mining. Geologic setting and ore formation are however the main factor for the mine planning; the open-pit mine may be economically more suitable in many cases. Besides, some waste rocks can be used for construction within the mining site; however, they must be tested prior to appropriate utilization. Otherwise, unexpected threats may occur.

Various types of waste rocks situated within ore deposits usually have different compositions that would be characterized for both mineralogical and geochemical constituents. Apart from heavy metals contained in these rocks, Acid Mine Drainage (AMD), a potential threat, may be activated and lasted for long period of time. AMD actually lowers pH of water; subsequently, the low pH drainage may flow over waste dumps including waste rocks and tailings and may in turn leach some heavy metals and contaminate surrounding area. Surface water and ground water would be crucial pathways of such contamination to ecosystem and food chain. However, most of these threats can be protected and prevented by good environmental management and monitoring plans.

Tailings: During the mineral processing (dressing), ore minerals and their host rocks have to be ground and milled prior to separation; besides, chemical additives may be added during the processes. Although, most of these chemicals are usually recovered and reused in the process, some of them may still remain in these tailings. Some chemical additives can be decomposed naturally within short period but many of them may be bound strongly and long lasted within the tailings. Moreover, these tailings may contain concentrate non-economic minerals such as silicates, oxides, hydroxides, carbonates and sulfide that have never been collected throughout the dressing process. Therefore, these modified ingredients may partly be toxic and harm ecosystem. Tailings are similar to slurry, a mixture of fine-grained sediment and water that have been disposed into tailing pond (see Fig. 2).



Fig. 1. Huge amount of rock waste generated from a gold mine in Thailand: left photo is waste dumping site; right photo shows placing process based on geochemical properties of each type of waste rock

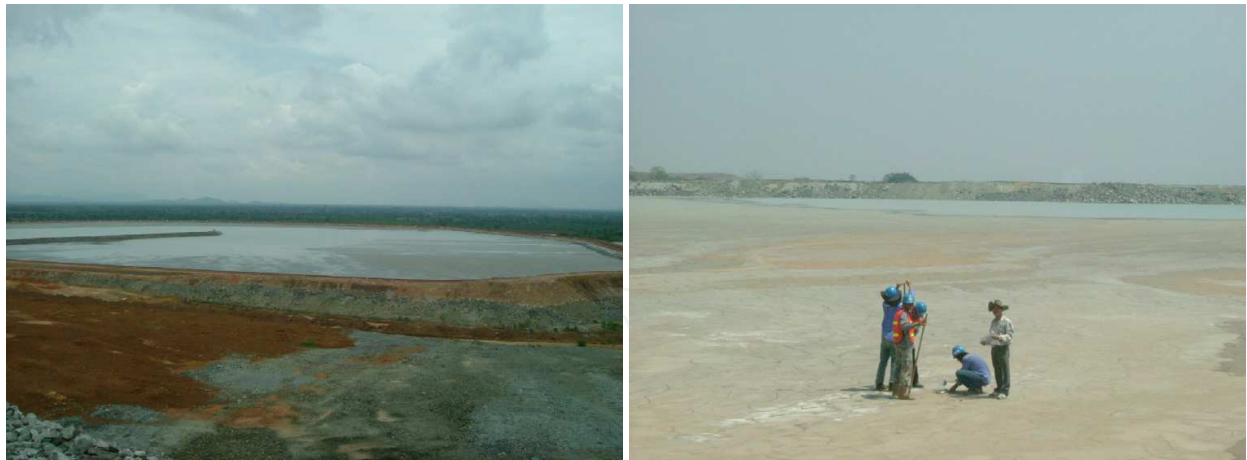


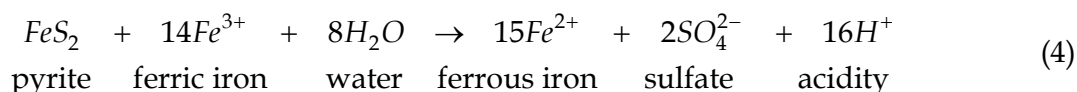
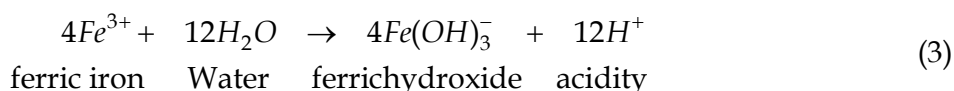
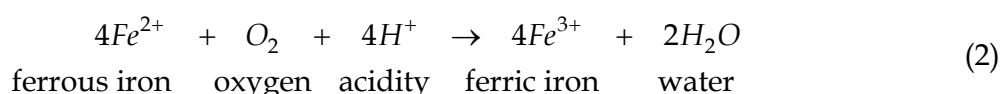
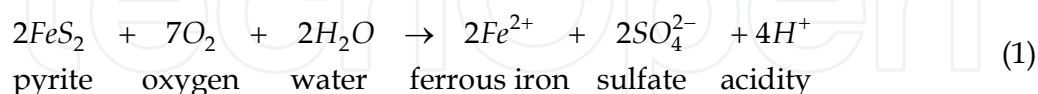
Fig. 2. Tailing pond (left photo) for disposal of slurry-like waste produced from gold dressing and sample collection (right photo), a routine monitoring program which has to be carried out regularly

Due to tailings comprise both solid wastes mixing with water during the operation period of mine and they will become drying after the mining end, redox reaction would be taking place and may in turn change stability of some elements which can be leached out to the environment by accident. Moreover, their property may also cause AMD. Therefore, routine monitoring plans for both water and tailing must be designed and continuously followed up. Monitoring data should be used for protection at the end and may be very useful for development of the mineral processing.

3. Acid mine drainage

Acid Mine Drainage (AMD) is the problem of acid drainage, traditionally referred in Australia and North America as Acid Rock Drainage (ARD). It seems to be a significant environmental impact of mining activities especially in opencast mines. It may damage long after the operation has ended because process and reaction have taken time. Runoff passing through the sourcing area can then give rise to severe threat. Moreover, AMD potentially dissolves and leaches out some toxic metals from the heap, mining waste dump and even natural soil and rock prior to contamination of surface water and groundwater. AMD is usually generated by the oxidation of sulfides in mining wastes; consequently, water supply from the area would be sulfide-rich drainage with acidic leaching property that may lead to mobilization of metals. Sulfides bound up in the waste rocks and tailings usually have various forms. Mineral sulfides are crystalline substances that contain sulfur combined with metal or semi-metal without oxygen. The most general form is "pyrite" (FeS_2), moreover, other forms also include $\text{Fe}_{1-x}\text{S}_x$, Fe_3S_4 , FeS , CuFeS_4 , ZnS , PbS , HgS , CoAsS etc. After these sulfide minerals are exposed to the air and water, the sulfide ions are oxidized into soluble sulfates as well as toxic metal ions and hydrogen ions may in turn be released into the environment. Initial factors for acid generation are: 1) sulfide minerals in the solid wastes (e.g., rocks and tailings); 2) water or a humid atmosphere; 3) an oxidant (usually oxygen in the form of O_2). Therefore, processes of acid generation and metal release would be taken place together during the formation of AMD which are closely related to oxidation of pyrite and precipitation of Fe hydroxides. There are four common chemical reactions represent AMD formed from pyrite. The first equation shows that an important oxidant of pyrite is

oxygen. Ferrous iron is released and sulfur is oxidized and changed to sulfate. This equation shown 2 moles of acidity generated from each mole of pyrite. The second equation is the conversion of ferrous iron to ferric iron. It consumes one mole of acidity. The third equation is a hydrolysis reaction which splits the water molecule; consequently, moles of acidity are generated as by-product. The fourth reaction is the oxidation of additional pyrite by ferric iron. The ferric irons generated in reaction steps 1 and 2 are cycle and propagation of the overall reaction. They take place very rapidly and continue until either the ferric iron or pyrite are depleted. In this reaction, iron is the main oxidizing agent instead of oxygen.



Many procedures have been developed to assess the acid forming characteristics of mine waste materials. The most widely used methods are Acid-Base Accounting (ABA) test and the Net Acid Generation (NAG) test. These procedures are described below.

3.1 Acid-base accounting

Characterization of rock types and geologic setting in the mine should be initially concerned prior to determination of capacity acid drainage generation of these rocks (Environment Australia, 1997). Acid-Base Accounting (ABA) is the most commonly-used static procedure that has been used for estimation/qualification of the acid generation potential of mine wastes (Ferguson & Erickson, 1988). This procedure was developed at West Virginia University in late 1960s. ABA tests are designed to measure the balance between potentially acid-generating potential, particularly oxidation of sulfide materials and acid neutralizing potential in sample such as dissolution of alkaline, carbonates, displacement of exchangeable bases and weathering of silicate. The values arising from ABA are referred to the Maximum Potential Acidic (MPA) and the Acid Neutralizing Capacity (ANC), respectively. After MPA and NAC have been determined for a sample, both values are compared with set criteria. Two methods of combination commonly used are: 1) The difference in value between MPA and ANC or Net Acid Producing Potential (NAPP) where $\text{NAPP} = \text{MPA} - \text{ANC}$; 2) The ratio of ANC to MPA (ANC/MPA). NAPP is a theoretical calculation commonly used to indicate where a waste material has potential to produce acidic drainage. NAPP values represent balance between capacity of acid generation and capacity of acid neutralization. Unit of NAPP is also expressed as $\text{kg H}_2\text{SO}_4/\text{t}$ in MPA and ANC. In addition, ANC/MPA ratio is also considered for assessment of acid generation from mine waste material. The main purpose of ANC/MPA ratio is to indicate relatively

safety margin of material. Safe values for prevention of acid generation are reported with different ANC/MPA values ranging from 1 to 3. The higher ANC/MPA value indicates high probability of the material that may remain circum-neutral in pH and should not be problematic by acid rock drainage. Both NAPP value and ANC/MPA ratio are usually used together for placement planning of rock waste and other overburdens (Skousen et al., 1987). Sulfur and ANC data are often used in combination with ANC/MPA ratio as presented in Fig. 3.

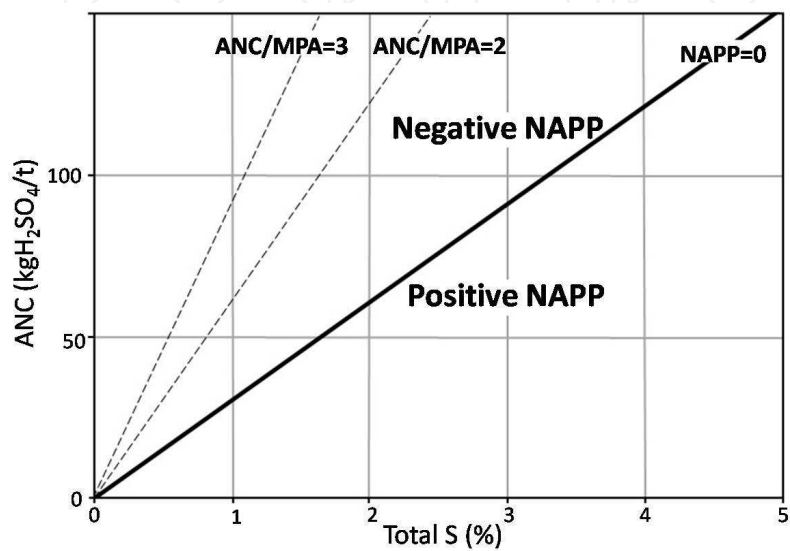


Fig. 3. Plots of all parameters considered in Acid-Base Accounting (ABA)

Maximum Potential Acidic: MPA is the maximum amount of acid that can be produced from the oxidation of sulfur-containing minerals in the rock material. It can be measured and calculated from the sulfur content. Total sulfur content of a sample is commonly determined by the LECO high temperature combustion method or other appropriate methods. For instant, it is assumed that all sulfurs occur as iron-sulfide (or pyrite; FeS_2) and this iron-sulfide reacts under oxidizing condition to generate acid according to the following reaction:



According to the stoichiometry, the maximum amount of acid that could be produced by a sample containing 1%S as pyrite would be 30.6 kilograms of H_2SO_4 per ton of material. The MPA is calculated from the total sulfur content as:

$$\text{MPA (kg H}_2\text{SO}_4/\text{t)} = (\text{Total \%S}) \times 30.6$$

Acid Neutralizing Capacity: ANC is calculated from the amount of acid neutralizer in the sample and it is expressed in metric tons/1000 metric tons of material. Acid generated from pyrite oxidation will be partly reacted by acid neutralizing minerals contained within the sample. This inherent acid buffering is resulted in term of the ANC. Most of the minerals which contribute the acid neutralizing capacity usually are carbonates such as calcite and dolomite. The modified Sobek method is the most common method used to determine ANC. This method is determined experimentally by reaction of a known amount of standardized acid (hydrochloric acid, HCL) with a known amount of sample and then the mixed solution sample is back-titrated by sodium hydroxide (NaOH). The amount of acid consumed

represents the inherent acid neutralizing capacity of the sample. Calculation will be carried out and expressed in terms of kg H₂SO₄/t.

3.2 Net acid generation

Net Acid Generation (NAG) test was developed as an assessment tool for acid producing potential of sample for longer than 20 years ago. The NAG test is usually used in association with NAPP. It is direct method to measure ability of sample to produce acid via sulfide oxidation. Hydrogen peroxide (H₂O₂) is used to activate and complete oxidation process of the sulfide minerals contained in the sample. H₂O₂ added during the NAG test leads to simultaneous reactions of acid generation and acid neutralization. Then pH measurement of solution has to be carried out after the completion of reaction. The acidity of solution under the NAG is a direct measurement of net acid generation of sample. Shu et al. (2001) studied the effect of lead/zinc mine acidity on heavy metal mobility using both NAG test and ABA method. They concluded, based on their results that NAG test, direct measurements of ANC from acid produced from oxidized sulfide, yields more accurate than that of ABA method. This is because prediction of acid forming potential from the total pyritic sulfur content as done for ABA method may overestimate amount of acid generation due to uncompleted acidification of pyritic sulfur. However, classifications of waste rock have generally used NAPP estimation based on ABA method in combination of NAG pH testing. Schematic classification is present in Fig. 4. Three types of west rocks from mining activity can be grouped as No Net Acid Forming (NAF), Potentially Net Acid Forming (PAF), and Uncertainly Net Acid Forming (UC). Definitions of these groups are given below.

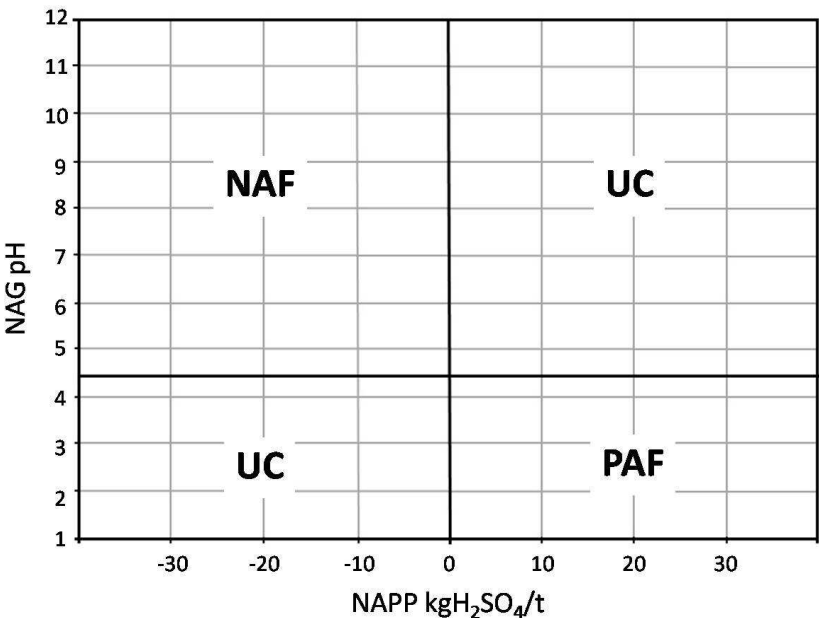


Fig. 4. NAG pH plot against NAPP for classification potential of net acid formation of waste rock

No Net Acid Forming (NAF): either there is minimal or no sulfides present or the neutralization potential exceeds the acid potential. This type of waste rock gives a negative NAPP and NAG pH greater than or equal to 4.5.

Potentially Net Acid Forming (PAF): the acid potential exceeds the neutralization potential. These rocks are described as potentially acid forming. They may generate AMD if they are exposed to sufficient oxygen to allow sulfide oxidations. Geochemical tests usually yield positive NAPP and NAG pH below 4.5.

Uncertain Net Acid Forming (UC): uncertain classification is obtained when there is an apparent conflict between the NAPP result and NAG pH; for example, NAPP is negative but NAG pH lower than 4.5 or NAPP is positive but NAG pH higher than 4.5. However, further testing work would be performed for such rock types to determine proportion between NAF and PAF if they occur.

Recently, this classification has been using widely for geochemical study of waste rock and assessment of acid forming potential. Tran et al. (2003), for an example, also used NAG together with NAPP tests to figure out key criteria for construction design of waste rock dumps to avoid AMD. They collected samples from 2 sites in which have different temperatures. NAG and NAPP tests were applied to classify PAF, NAF and UC materials prior to placement control of waste rocks within the dumps. They succeeded to have reduced AMD load that may be generated from both dumps.

4. Heavy metals

As mentioned earlier, heavy metals contained in mine wastes, particularly rocks and tailings, may in turn become contamination to water systems around the dumping site. Analyses of these solid wastes must be very crucially considered for environmental protection plan during the mining operation. In fact, these heavy metals usually have different forms appeared in these rocks and tailings. Some forms are quite stable and durable to natural reactions such as weathering and erosion; however, some forms may be leached and available to contamination. Moreover, their stable chemical bonds may have been destroyed during the mining process, mineral dressing and metal extraction. Therefore, placement and dumping of these solid wastes should concern about these geochemical characteristics. Several standard procedures have been proposed for analyses of heavy metals contained in geological materials such as soils, stream sediments and rocks. These methods were initially engaged for geochemical exploration searching for potential area of mineral deposits. Although, they can also be applied for environmental purpose, some assumption must be taken into consideration as well as limitation of selected method must be understood clearly before interpretation will be carried out. Some methods are designed for total concentrations of element contained in the samples; on the other hand, some of them are planned for partial portions of these elements reliable for specific concern. However, some methods have been developed for environmental impact assessment. In this section, some selective standard procedures are described for suitable application of mining waste and related fields.

4.1 Total digestion

Whole-Rock Geochemical Analyses: this method is designed for analysis of total chemical concentrations contained in the rock materials. This method may not be suitable to the environmental concern because major and minor compositions of these rocks are usually non toxic and they are quite stable. However, their trace compositions may have partly impact after accumulation and transportation have taken place for some periods of time, particularly due to AMD. Moreover, these whole-rock analyses are very useful for

geological classification as well as mining operation. Placement and disposal may be designed based on this classification in cooperation with other testing methods. Rock powdering using appropriate crusher and miller must be done prior to further analyses. Subsequently, the powdered rock samples may be fused to glass beads or pressed as pellet for X-ray Fluorescence (XRF) analyses of 9 major oxides (i.e., SiO₂, TiO₂, FeO_t, MnO, MgO, CaO, Na₂O, K₂O and P₂O₅) and perhaps some trace elements (e.g., Ba, Zn, Sr, Rb, Zr, Co, Cr, Ni, Y and V). Rock standards should be used for calibration at the same analytical condition. Moreover, loss on ignition (LOI) should also be measured by weighting rock powders before and after ignition at 900° C for 3 hrs in an electric furnace. Trace and rare earth elements may be additionally analyzed using advanced instruments such as Inductively Coupled Plasma (ICP) Spectrometer, Atomic Absorption Spectrometer (AAS) and other spectrometric techniques. Rock samples have to be digested totally without remaining of rock powders. About 0.1000 g (± 0.0001 g) of powdered samples are weighted and then dissolved in a concentrate HF-HNO₃-HClO₄ acid mixture in sealed Teflon beakers. The digested samples were diluted immediately and added mixed standard solution to all samples. Proportion of these concentrate acids is usually adapted in laboratory as well as time of digestion. Hotplate has been engaged traditionally but it may take long time. Alternatively, microwave has been applied to shorten the digestion time. This method is total digestion which most elements including toxic elements and non toxic ones are dissolved for analyses. However, these contents do not clearly reflect environmental impact. Microwave-assisted acid solubilization has been proved to be the most suitable method for the digestion of complex matrices such as sediments and soil. This method shortens the digestion time, reduces the risk of external contamination and uses smaller quantities of acid (Wang et al., 2004). However, there are different procedures required for appropriate sample types. Some standard digestion techniques are usually used for soil, sediment and sludge; for example, EPA 3052, EPA 3050B and EPA 3051 are described below.

EPA 3052: This method is an acid digestion of siliceous matrices, and organic matrices and other complex matrices (e.g., ashes, biological tissues, oils, oil contaminated soils, sediments, sludges and soils) which they may be totally decomposed for analysis. Powdered sample of up to 0.5 g is added into 9 ml of concentrated nitric acid and usually 3 ml hydrofluoric acid for 15 minutes using microwave. Several additional alternative acids and reagents have been applied for the digestion. These reagents include hydrochloric acid and hydrogen peroxide. A maximum sample of 1.0 g can be prepared by this method. Mixed acids and sample are placed in an inert polymeric microwave vessel then sealed prior to heating in the microwave system. Temperature may be set for specific reactions and incorporates reaching 180 ± 5 °C in approximately shorter than 5.5 minutes and remaining at 180 ± 5 °C for 9.5 minutes to complete specific reactions. Solution may be filtered before appropriate volume is made by dilution. Finally, the solution is now ready for analyses (e.g., AAS or ICP). More details should be obtained from EPA (1996).

EPA 3050: Two separate procedures have been proposed for digestion of sediment, sludge and soil etc. The first procedure is preparation for analysis of Flame Atomic Absorption Spectrometry (FLAA) or Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) whereas the other is for Graphite Furnace AA (GFAA) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Appropriate elements and their detection limits must be concerned and designed for selection of both methods (EPA, 2009). Alternative determination techniques may also be modified as far as scientific validity is proven. This method can also be applied to other elements and matrices but performance need to be

tested. It should be notified that this method is not a total digestion for most types of sample. However, it is a very strong acid digestion that may dissolve most elements that could cause environmental impact. In particular, silicate-bonding elements are unlikely to be dissolved by this procedure. About 1-2 g (wet weight) or 1 g (dry weight) sample is dissolved by repeated additions of nitric acid and hydrogen peroxide. For GFAA or ICP-MS analysis, the digested solution is reduced in volume while heating then the final volume is made to 100 ml. This method may refer to EPA 3050B. On the other hand, for ICP-AES or FLAA analyses, hydrochloric acid (HCl) is additionally poured into the previous digested solution; consequently, the solubility of some metals may be increased which may refer to EPA 3050A. After filtering, filter paper and residue are dissolved by additional HCl and then filtered again. Final digested solution is diluted to 100 ml (EPA, 2009).

A simplified procedure of EPA 3050B has been suggested as following detail. Powdered sample (e.g., soil, sediment and sludge) is mixed in 10 ml of 1:1 HNO_3 , then sample is covered with a watch glass. Subsequently, the sample is heated to $95 \pm 5^\circ\text{C}$ and refluxed for 10 to 15 minutes without boiling. When the sample is allowed to cool, 5 ml of concentrate HNO_3 is added and covered and refluxed for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3 , repeat this step (addition of 5 ml of HNO_3 conc.) over and over until no brown flame will be given off by the sample indicating the complete reaction with HNO_3 . The solution has to be evaporated to approximately 5 ml without boiling or heating at $95 \pm 5^\circ\text{C}$ for 2 hrs. After the sample had been cooled, 2 ml of water and 30 ml of 30% H_2O_2 are added into the sample. In addition, 1 ml of 30% H_2O_2 has been continuously added with warming until the generated sample appears to have no further change. The sample has to be heated until the volume reduces to about 5 ml. Finally, the sample is then diluted to 100 ml with D.I. water after cooling. Particulates in the solution must be removed by filter (Wattman No.41). The sample is now ready for analyses of ICP or AAS.

EPA 3051: is an alternative to EPA 3050 procedure which is a rapid acid digestion of multielement for analysis. Leaching levels must be designed. In case, hydrochloric acid is required for digestion of certain elements; therefore EPA 3050A would be applied. Otherwise, EPA 3051 may be considered. After 0.5 g of sample is placed in a digestion vessel, 5 ml of 65% HNO_3 is added and the vessel is closed with a Teflon cover. Then, the sample will be heated at $170 \pm 5^\circ\text{C}$ for approximately 5.5 minutes and remained at $170\text{--}180^\circ\text{C}$ for 10 minutes to accelerate the leaching process by microwave digestion system. Heating temperature and time may be adjusted as appropriate to each microwave system produced by various manufacturers. After cooling, the solution must be filtered by membrane filter of $0.45\ \mu\text{m}$ pore diameter. Finally, the filtered solution is further diluted in 50 ml volumetric flask. The sample is now ready to be analyzed by ICP and AAS.

It has to be notified that EPA 3050 and 3051 methods usually are not total digestions; undigested materials will be remained after acid is added into the sample. However, most of the chemical bonding forms potentially environmental impact appear to have been dissolved. Silicate bonding in particular is a stable form and unlikely to be removed; it actually has no impact. Both methods are suitable for mining wastes that can be used for environmental monitoring and protection plans. In addition, Aqua Regia, mixture of hydrochloric acid and nitric acid, may also be applied for digestion. It is quite similar to EPA 3050A method. Gold can be dissolved in this mixed acid which the method is usually applied for stream sediment collected for mineral exploration.

4.2 Sequential extraction

In the environmental field, determination of total metal concentrations in mining wastes does not give sufficient information about the mobility of metals. Metals may be bound to particulate matter by several mechanisms such as particle surfaces absorption, ion exchange, co-precipitation and complexation with organic substances. For example, not all of heavy metals in soil are available for plant uptaking, only the dissolved metals content in soil solution is moveable enough for plant to absorb. Therefore, heavy metals speciation in form of water soluble fraction and free weak acid soluble fraction out of total heavy metal content are the maximum amount of heavy metals possibly uptaken by plant. However, actual bioavailability of heavy metals by each species of plant must be determined from the plant itself. This will lead to protection and reclamation plans after the mine close. Chemical extraction is played an important role to define metal fractions, which can be related to chemical species, as well as to potentially mobile, bioavailable, or ecotoxic phase of sample. The mobile fraction is defined as the sum of amount dissolved in the liquid phase and an amount which can be transferred into the liquid phase. It has generally accepted that ecological effects of metals are related to such mobile fractions rather than the total concentration.

Sequential extraction procedures are operationally defined as methodologies that are widely applied for assessing heavy metal mobility in sediment. It is also used for the fractionation of trace metal within sediment (Quevauviller et. al., 1993 ; Ure et. al., 1993) and allows for the study of the bioavailability and behavior of metals fixed to the sediment (Pazos-Capeáns et al. 2005). BCR has been applied to characterize the metal fraction of a variety of matrices, including sediment with distinct origin, sewage sludge, amended soils and different industrial soil (Mossop & Davidson, 2003).

There are many methods to determine the different forms of metals. BCR three-step sequential extraction procedure is one of them, which was proposed by the Standards, Measurements and Test Programme (SM&T-formerly Community Bureau of Reference, BCR) of the European Union. It has been applied for the determination of trace metals (e.g., Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) binding various forms. It is strongly recommended to quantify the fractions of metal characterized by the highest mobility and availability applied for sample which the total concentration is high enough. This procedure provides a measurement of extractable metals from a reagent such as acetic acid (0.11 mol/l), hydroxylammonium chloride (0.1 mol/l) and hydrogen peroxide (8.8 mol/l), plus ammonium acetate (1 mol/l), which are exchangeable, reducible and oxidizable metals, respectively. There are many researchers have studied about this procedure and results indicated that this procedure gave excellent recoveries for all six elements (e.g., Cu, Cr, Cd, Zn, Ni and Pb). The concentration of metal extracted by the various reagents above gave a good reproducibility on species bonded to carbonates, Fe/Mn-oxides, and the residual fraction. Characters of each fraction are simplified and shown in Fig. 5 which summary of these fractions are given below and details were described by Serife et al. (2003).

BCR 1: is an exchangeable, water and acid-soluble fraction. This fraction represents amounts of elements that may be released into the environment if the condition becomes more acidic. Acetic acid is applied for this extraction. The extracted solution includes water-soluble form, easily exchangeable (non-specifically adsorbed) form and carbonate bonding form which are vulnerable to change of pH and sorption-desorption processes. In addition, plants can uptake this fraction easily; consequently, this metal form may in turn contaminate into food chain. It is therefore the most dangerous form for the environment concern.

BCR 2: is a reducible fraction. It theoretically represents contents of metals bond to iron and manganese oxides/hydroxides. These oxides/hydroxides are excellent cleaners of some trace metals that have been weathered and transported from the initial sources. They are thermodynamically unstable under anoxic conditions (Panda et al., 1995). Hydroxylamine hydrochloride is used for this extraction. Levels of extraction in this step should be effected by efficiency and selectivity of reagents used in the previous BCR 1. Therefore, this fraction may be too high if the carbonates have not been completely dissolved or too low if parts of the iron and manganese hydroxides have already been extracted.

BCR 3: is an oxidisable fraction or organic bound. Hydrogen peroxide and ammonium acetate are applied for this extraction. Metals can bond to various forms of organic matter. The complexities of natural organic matter are well recognized, as the phenomenon of bioaccumulation in certain living organisms. These organic matters can be degraded naturally under oxidizing conditions in waters leading to release of soluble metals. An oxidizing condition may have occurred during exposure to the atmosphere either by natural or artificial processes.

BCR 4: is defined as final residue. The final fraction can be calculated as the difference between metal contents extractable from Aqua Regia method (using nitric and hydrochloric acids) and metal contents released from the previous sequential extractions. Metal contents of all three previous fractions are considerable as more mobile and bioavailable than the residual fractions (Tack & Verloo, 1995; Ma & Rao, 1997). The residual metals appear to have relation with mineral structures that are the most difficult to be extracted (Kersten & Förstner, 1991).

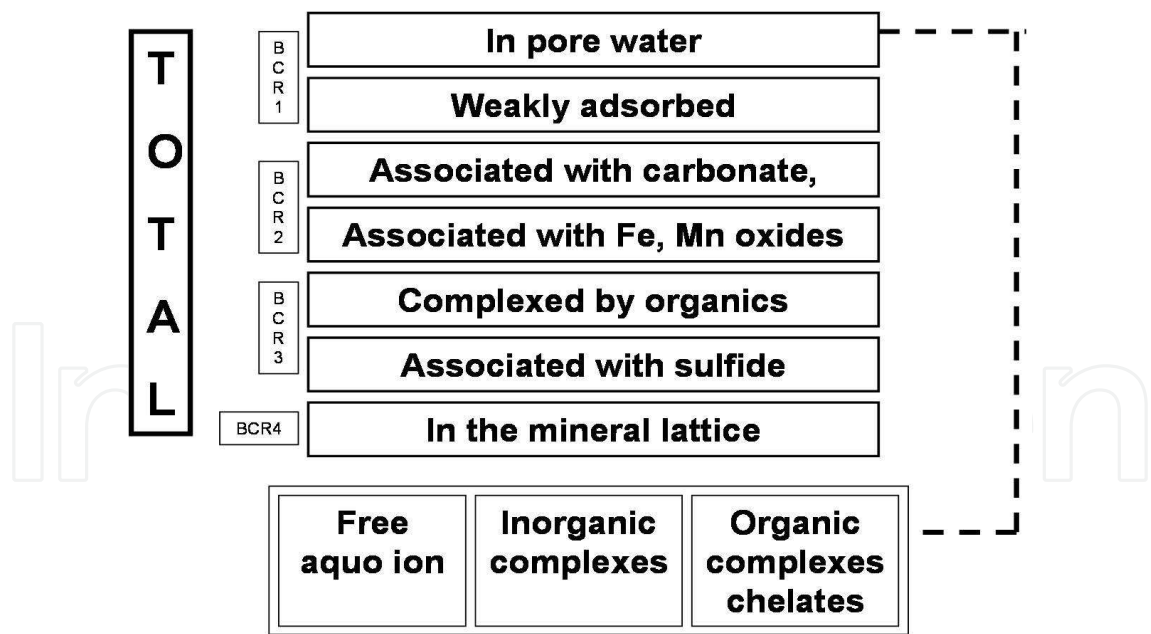


Fig. 5. Chemical fractions of metals in sediments and their characters.

5. Case study in Thailand

Geochemical investigations as mentioned above were applied to the environmental aspects of Akara Gold mine in Pichit Province of Thailand (i.e., Changul et al., 2010 a and b;

Sutthirat et al., 2011). Although, obvious environmental impacts have never been directly evidenced, some concerns have been raised by some sectors. Waste rocks from particular mining pit and tailings from tailing pond were characterized based on their geochemistry. Apart from AMD assessment, investigation of the geochemical characteristics, including their heavy metal contents and the potential of each of these metals to leach, is the first step to develop the best practice for environmental protection. Results of these studies are summarized below.

5.1 Waste rocks

Six types of waste rocks including volcanic clastic, porphyritic andesite, andesite, silicified tuff, silicified lapilli tuff and sheared tuff were collected under supervision of mining geologists. Whole-rock geochemistry, particularly their major compositions (rock powders analyzed by XRF), can be used to differentiate these rocks clearly as shown in Fig. 6; moreover, some trace elements and rare earth elements, using EPA 3052 digestion and analyzed by ICP-OES, were applied for determination of their geneses and evolutions (Sutthirat et al., 2011). Although, these may not be related to environmental aspect they should be initial investigation, at least to distinguish types of waste rock clearly before further testing program will be designed.

Subsequently, nitric leaching of these rocks was experimented following the EPA 3051 method. Amounts of leachable elements were then compared with the total digestion. Almost linear relationship between both forms of at least eight heavy metals was observed (Fig. 7). Except for As, the nitric recoverable levels of the heavy metals were slightly lower than the total concentrations. In conclusion, the maximal leaching potential (%) of these heavy metals were calculated as 30.5 - 63.2% for As, 80.4 - 81.9% for Ag, 0 - 92.8% for Cd, 63.6 - 87.6% for Co, 91.1 - 100% for Cu, 87.9 - 99.7% for Mn, 85.3 - 93.5% for Ni and 0 - 82.8% for Pb, respectively. Three of the six rock types, i.e., porphyritic andesite, silicified tuff and silicified lapilli tuff, are of the greatest concern because they contain a high heavy metal load (proportional concentration) each with a high maximal acid leaching potential. In the worst case scenario, over 50% of the total heavy metal load would be leached by a very strong acid passing through these rocks and impacting the environment, consequently; however, this case is unrealistic and unlikely to happen.

Acid Base Accounting (ABA) and Net Acid Generation (NAG) tests were applied for evaluation of acid generation potential of these waste rocks (Changul et al., 2010a). Experimental results reveal silicified lapilli tuff and shear tuff are potentially acid forming materials (PAF); on the other hand, the other rocks, i.e., volcanic clastic, porphyritic andesite, andesite and silicified tuff are potentially non-acid-forming (NAF). Among these waste rocks, shear tuffs appear to be the most impact to the environment, based on their highest potential of acid forming. Therefore, great care must be taken and focused on this rock type. Finally, they also finally concluded that AMD generation from some waste rocks may be occur a long time after mine closure due to the lag time of the dissolution of acid-neutralizing sources. In addition, environmental conditions, particularly the oxidation of sulphides which is usually activated by oxygen and water, are the crucial factor. Consequently, waste rock dumping and storage must be planned and designed very well that will lead to minimization of risk from AMD generation in the future. Surface management system and addition storage pond should be installed to control the over flood and runoff direction away from the rock waste dump. Environmental monitoring plan including water quality should be also put in place.

5.2 Tailings

Tailing samples were also systematically collected and analyses for chemical composition and mineral assemblages (Changul et al., 2010b). Consequently, these tailings have little differences of chemical compositions quantitatively from place to place but their mineral assemblages could not be clearly distinguished. They suggested that these end-processed tailings were mixed between high and low grade ores which may have the same mineral assemblages. Variation of chemical composition appeared to have been modified slightly by the refining processes that may be somehow varied in proportion of alkali cyanide and quick lime in particular. Moreover, content of clay within the ore-bearing layers may also cause alumina content in these tailings, accordingly. Total heavy metals in the tailing samples were analyzed using solution digested following the EPA 3052 method. Toxic elements including Co, Cu, Cd, Cr, Pb, Ni, Zn etc. range within the Soil Quality Standards for Habitat and Agriculture of Thailand. Only Mn contents are higher than the standard.

Potential of acid generation of these tailings was tested on the basis of Acid-Base Accounting (ABA) and Net Acid Generation (NAG) tests. Tailing samples appear to have high sulfur content but they also gave high acid neutralization capacity; therefore, they were generally classified as a non-acid forming (NAF) material. However, they still suggested that oxidizing process and dissolution should be protected with great care. Clay layer may be placed over the pound prior to topping with topsoil for re-vegetation after the closure of the mining operation. Native grass is suitable for stabilization of the surface and reduction of natural erosion. In addition, water quality should also be monitored annually.

Mining and environmental management programs usually require considerable data for best practice of mining operation and environmental monitoring. The management techniques include the sampling and classification of waste rock types.

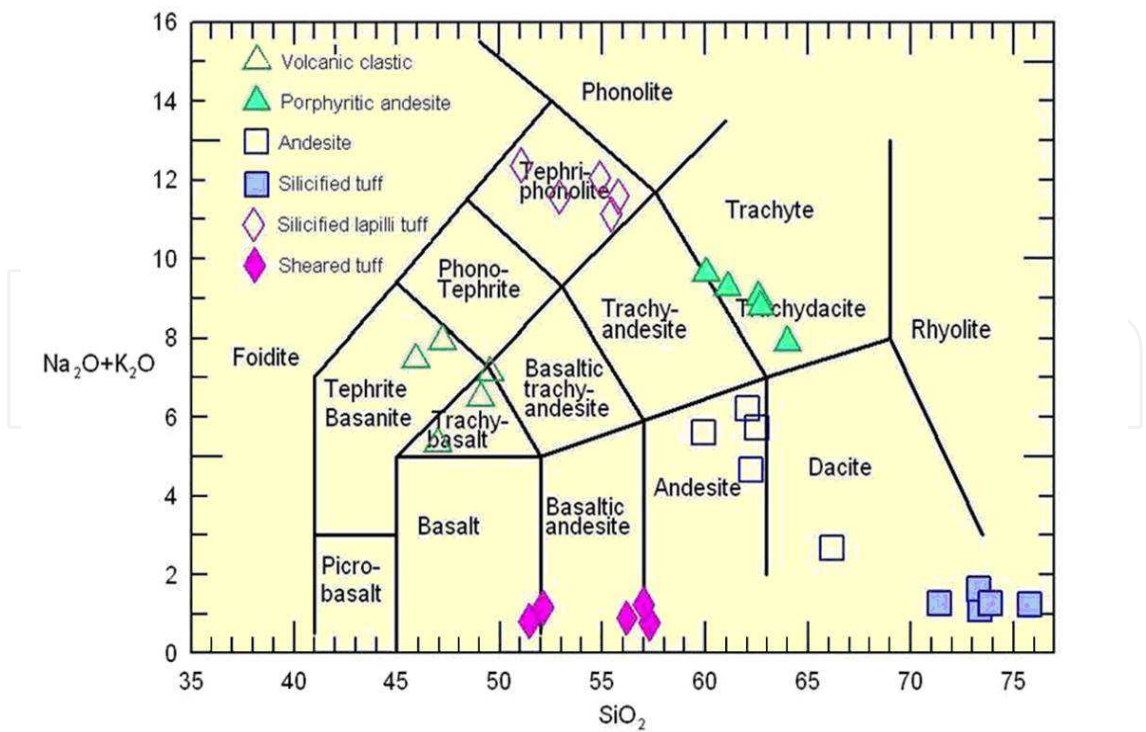


Fig. 6. Alkali-silica discrimination diagram of Le Bas et al. (1986) applied for whole-rock geochemical analyses of waste rocks from the Akara Gold Mine, Thailand

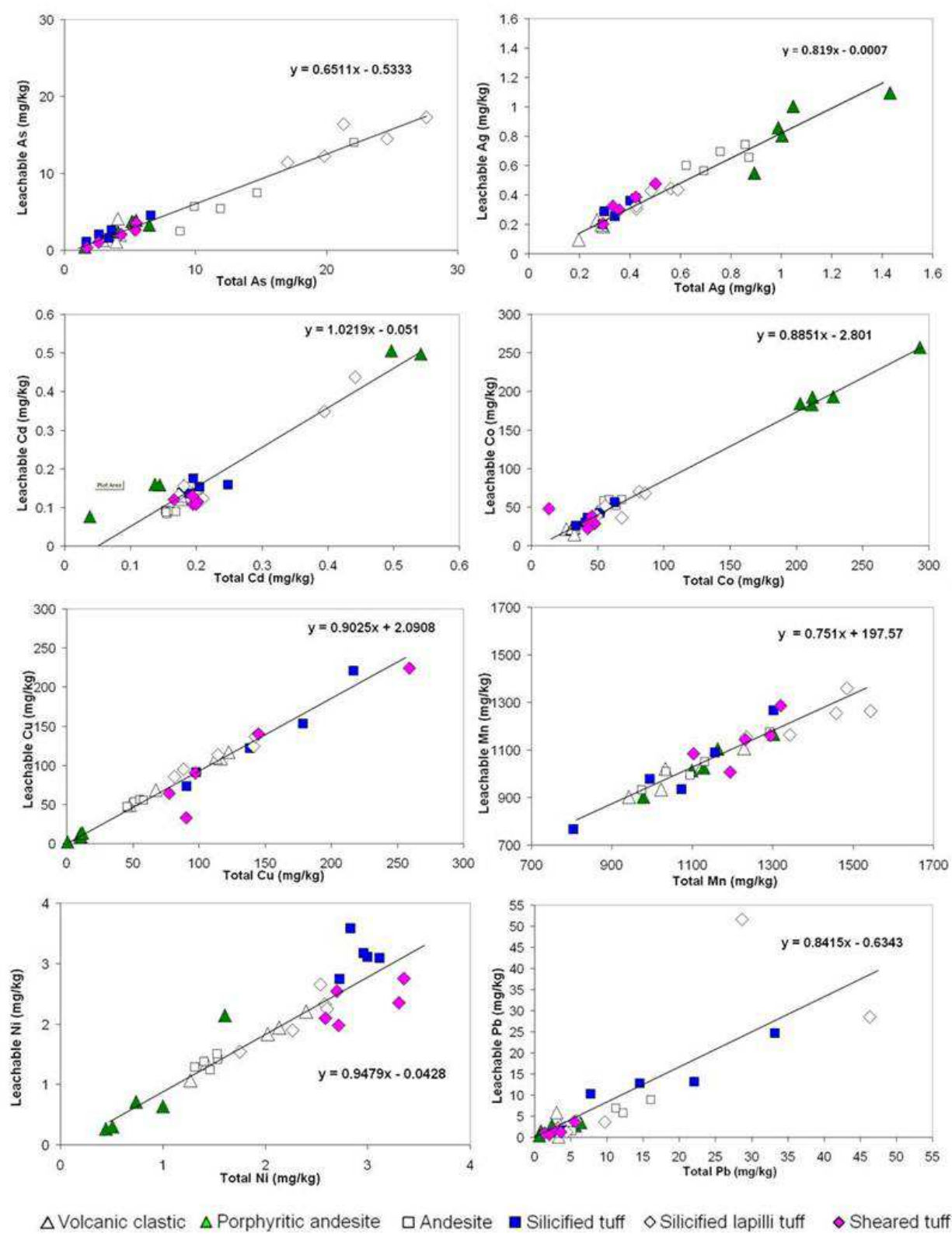


Fig. 7. Correlations between the total and nitric-leachable concentrations of eight heavy metals from various waste rocks from Akara Gold Mine, Thailand, showing linear regression relation

6. Conclusions

Solid mining wastes including host rocks and tailings must be managed during the whole period of operation. Some of them can be utilized for construction and other activities; however, some of them may also cause severe environmental impacts. Moreover, unexpected occasions can be happened individually even routine monitoring program has been carried out during all time of the operation. Therefore, all concerns must be taken into account since mining plan is developed initially. All mining wastes generated from each step of operation should be tested and put into the long term monitoring plans. Besides, all types of top soil and host rock must be sampled systematically for analyses of AMD and heavy metals prior to waste categorization and placement design. Dealing with natural materials, both rock and top soil in this case, variety of chemical composition may lead to complexity. Many of these chemicals are stable and unable to leaching out; however, just in case of some leachable form exiting, it may turn to harmfulness and difficulty of operation. Protection and prevention should therefore be planned well to keep mining operation moving smoothly and clearly to be inspected.

Regarding to rock waste and top soil, both AMD and heavy metal have become the most concerns for mining and environmental management. Some materials are unlikely to cause AMD but they contain high amounts of heavy metals that seem to be well leachable. These materials must be placed away from AMD potential wastes. Otherwise, mixing up of both types can threaten the surrounding area leading to widely land contamination. Neutralizer should be provided during the placement process. Limestone has been used as natural neutralizer which is easy to find and quite cheap. Liners should also be provided particularly for waste materials trending to have potentials of acid generation and/or heavy metal contaminants. Both natural and artificial materials can be used in individual cases, based on nature of the site and characteristics of mining waste. Cares must be taken very well during operation as well as monitoring program must be carried out regularly. It would also be notified that unexpected events can occur all the time; therefore, detailed investigations have to be initiated anytime whenever unusual signature is reveled either by regular monitoring or accident finding.

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