

## Investigating acid mine drainage potential and alteration properties of Zn-Pb wastes from Görgü (Malatya, Türkiye) region

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**Abstract:** Acid mine drainage (AMD) is one of the main causes of environmental threats resulting from mining activities, yet efficient characterization and prediction of AMD potential of wastes play an important role in preventing AMD. In this study, the chemical and mineralogical properties of fresh waste samples, collected from waste ponds of the Görgü (Malatya) zinc-lead ore processing plant, were determined and the results were used to explain its AMD potential. Alteration properties of the wastes in water was investigated by monitoring certain properties of the prepared suspension with respect time. Additionally, pyrite concentrate particles were added into the suspensions at certain proportions to evaluate its effect on the AMD generation and alteration. Analysis and test results showed that the raw waste was rich in carbonate and poor in pyritic sulfur, and hence did not have the AMD generation potential. The pH, electrical conductivity, and metal ions concentrations of the suspension medium were determined at regular intervals, and obtained data were found very beneficial to explain the time-dependent behavior of waste in water. After the depletion of liquid in the suspension, the remained solid residuals were chemically and mineralogically analyzed to compare with raw waste. It was concluded that sufficient aeration and stirring of suspension is required for noticeable alteration of the waste.

**Keywords:** degradation of waste ore, acid mine drainage, static tests, pyrite

### 1. Introduction

Air, soil, and water pollution may occur because of industrial activities. From an environmental point, water and soil pollution by heavy or toxic elements is as important as air pollution. Water pollution is the main pollution that threatens the ground and surface water resources due to its potential to spread to very large areas. Utilization of huge mining machines and increased exploitation led to the opening of large and deep mine pits, which attracted public attention. As the awareness for environmental protection has increased, the exploitation of natural resources is now required to be conducted in such a way as to minimize the environmental impact. Assessment of the negative effects of mining activities and minimizing or eliminating these effects is possible with environmental planning studies.

The concept of Acid Mine Drainage (AMD) was put forward and discussed in developed countries earlier, and now has been adopted by all countries. It is one of the main environmental threats resulting from mining activities. AMD is frequently encountered in sulfide ores and coal mines. The largest contribution of AMD to streams and lakes is from the numerous abandoned mined lands that were mined and left without reclamation (Skousen et al., 2019). AMD can cause direct and indirect environmental problems and its economic consequences can be surprisingly large. In addition, a high level of heavy metal contamination is possible in case of collapse or flooding of tailings ponds for various reasons (e.g. landslides, earthquake, excessive precipitation). Since the handling (or management) of wastes depends on their properties by law, wastes should be characterized well. Determining the type and amount of wastes, predicting their long-term behaviour, and taking all precautions are very necessary. The AMD risk of untreated sulfide wastes is high when they are left exposed to the atmosphere and do not contain enough amount of neutralizing materials. Their risk can be predicted by AMD tests and their handling strategy can be set according to their risk level. The waste

ponds can be designed according to the risk level, and the utilization of solids or reuse of water in the ponds can be decided accordingly.

On the other hand, static AMD tests determine the total acid generating and neutralizing potentials of the sample, but do not consider the differences between the reaction rates of different minerals in the ore, which produce or neutralize the acid. During the contact of ore with water and air, the quality of water change over time that cannot be identified solely by static tests (Matsumoto et al., 2018). In AMD studies, in order to determine the impact of materials, different analyzes are performed regularly on AMD liquid samples taken from streams, seeps, or pools (Skousen and Jacobs, 2014). The most important analyzes include pH, EC, dissolved oxygen amount, reduction-oxidation (redox) potential, salinity, total dissolved solids (TDS), and turbidity of the liquid (Skousen and Jacobs, 2014). Sulfide containing ores can be used in, and hence, can affect large structures (e.g. dam body), which require large amounts of rockfill and concrete (Petrilakova et al., 2014; Goto et al., 2016). Such studies are especially important in observing the behavior of sulphurous wastes in waste ponds, which can be designed according to the risk level. The utilization of solids or reuse of water in the ponds can be decided according to the results.

Türkiye hosts a range of significant zinc-lead deposits belonging to the Tethyan Metallogenic Belt (Santoro et al., 2013; Santoro et al., 2014). Zinc-lead deposit located in Görgü (Malatya) region is one of the important operating metallic deposits in Türkiye. The mined ore is subjected to various ore preparation and concentration processes to obtain zinc and lead concentrates separately. The waste material accumulated in ponds is sold on demand to be used as landfill material.

This study aimed to determine to AMD potential of the zinc-lead concentrate waste as well as its alteration (or degradation) properties in water under environmental conditions. The alteration (or degradation) properties of mine wastes and their effect on the environment under environmental conditions were not studied in the literature largely. In this context, the chemical and mineralogical properties of the waste were determined by various methods, including X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Inductively Coupled Plasma (ICP), Atomic Absorption Spectroscopy (AAS), and elemental analysis. A range of static AMD tests, including Acid Base Accounting (ABA), Net Acid Generating (NAG), and British Columbia (BC) Research Initial Test, were performed. A set of waste-water suspensions were prepared in plastic containers by analogy with waste ponds and then, the change in certain properties of the medium, including pH, electrical conductivity (EC), and metal ion concentrations, were monitored with time. Knowing that pyrite is the most important mineral in AMD, the effect of the pyrite addition was evaluated in separate container tests.

## 2. Materials and methods

### 2.1. Materials

The zinc-lead ore samples were obtained from Görgü (Malatya) district located in the Central-Eastern region of Türkiye. The mine and mineral processing facilities are operated by ÇEVKUR Mining Ltd. a subsidiary of CVK Holding. The extracted ore is enriched first by gravimetric method followed by flotation. Approximately 200 kg of representative sample was taken from different parts of the fresh flotation waste pile. About 5 kg of pyrite mineral chunks was picked from Ergani Eti-Gümüş A.Ş (Elazığ) facilities.

The Isolab Laborgerate GmbH brand  $H_2SO_4$ , HCl, NaOH and Merck KGaA brand  $H_2O_2$  chemicals were purchased and used in the experiments. Distilled water produced by GFL 2102 Equipment (GFL mbH, Germany) was used in all experiments.

### 2.2. Methods

#### 2.2.1. Sample preparation

The waste samples taken from the piles were prepared for characterization, static AMD, and degradation tests as illustrated in Fig. 1. They were dried in an oven at 60°C for 3 days and the aggregates formed during drying were dispersed manually by wearing gloves. The sieving was done with a 300 µm sieve to remove any large foreign material. To ensure homogeneity, all samples were blended, and the sampling were carried out by sample reduction methods in order of coning-and-

quartering, riffle splitting and a rotating turntable coupled with a vibratory feeder. These representative 500 g samples were kept in sealed plastic bags until use. To obtain sufficiently pure pyrite mineral, the handpicked chunks were subjected to size reduction and concentrated by a shaking table.

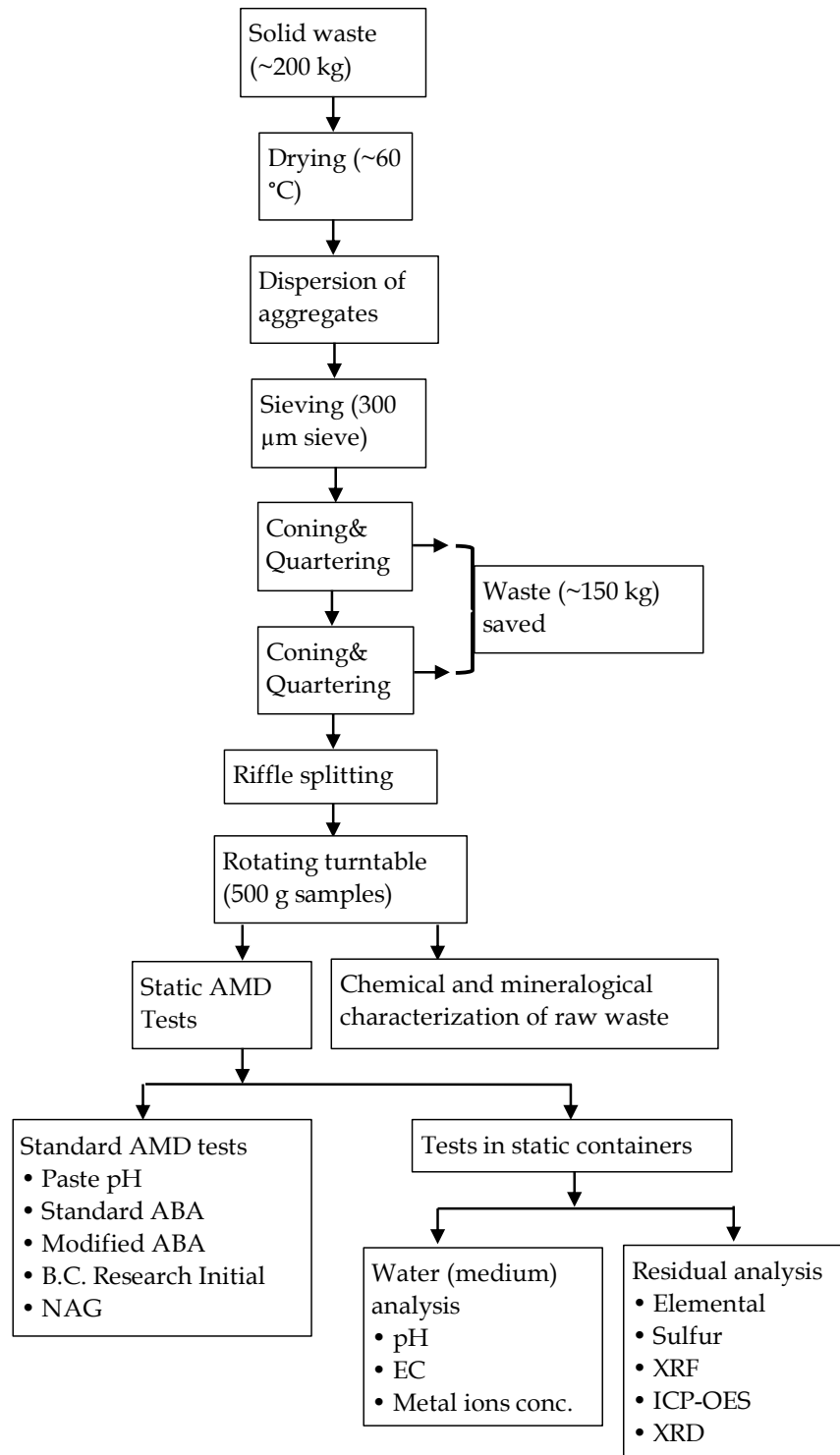


Fig. 1. Preparation of waste sample to the tests and characterizations

### 2.2.2. Sample characterization

Particle size distribution, elemental, XRD, XRF, ICP, and AAS analyzes were performed for the characterization of the samples. Particle size distributions of samples were determined by using Malvern Mastersizer 2000 Particle Size Analyzer (Malvern Instruments Ltd., United Kingdom) which

utilizes laser diffraction technique. Leco CHNS-932 (LECO Corporation, MI, USA) device in İnönü University Central Research Laboratory was used for the determination of C, H, N, and S elements. The total sulfur in the sample was obtained by elemental analysis, and was used in the AMD calculations. XRF and ICP-OES analyzes conducted by Bureau Veritas Minerals (Canada) were used to determine the major oxides and elements in the samples. Mineralogical analyzes were carried out by Rigaku Geigerflex D-Max/B (Japan) XRD instrument at Central Research Laboratory of İnönü University. In order to determine metal ions concentration in the suspension medium, Flame AAS devices in the Chemistry Department of İnönü University were utilized.

### 2.2.3. Sulfur analysis

Sulfur can be found in different forms, such as sulfate, sulfide (or pyritic), and organic forms (Çavuşoğlu and Karaca, 2017), and the form of sulfur is crucial for evaluating AMD generation over time (Matsumoto et al., 2018). While pyrite, pyrrhotite, marcasite, chalcopyrite, galena, and sphalerite are important sources of pyritic sulfur, minerals such as barite, gypsum, anhydrite, and jarosite are important sources of sulfate sulfur. The sulfur content is one of the most important parameters indicating the AMD potential of the ore. Because sulfide sulfur makes the main contribution to AMD formation, some researchers considers only the amount of sulfide sulfur in AMD calculations. Since there is no organic sulfur in the studied sample, it is assumed that the total sulfur consists of sulfate and sulfide sulfurs. Total sulfur was determined by the Leco CHNS-932 instrument, while the sulfate sulfur was determined according to the TSE 329 and ISO: 157-1966 standards. The percentage of sulfide sulfur in the ore was calculated from Eq. 1. In the calculation of Acid Production Potential (APP), which is utilized in ABA calculations, both, total and pyritic sulfur contents were used in Eq. 2 which states that 31.25 kg CaCO<sub>3</sub>/Mg of neutralizing material is required for each 1% sulfur neutralization in the sample.

$$\text{Sulfide (or pyritic)sulfur (\%)} = \text{Total sulfur (\%)} - \text{Sulfate sulfur (\%)} \quad (1)$$

$$\text{APP} = \text{Total or sulfide sulfur (\%)} \times 31.25 \quad (2)$$

### 2.3. Static AMD tests

The following static laboratory tests were carried out to determine the AMD potential of the ore. Since there are some minor differences for the same tests in the literature, the tests were performed as described in URL1 (The Mine Environment Neutral Drainage program, Report 1.20.1).

1. Paste pH
2. Standard Acid-Base-Accounting
3. Modified Acid-Base-Accounting
4. British Columbia (BC.) Research Initial Test
5. Net Acid Generation Test

### 2.4. Static tests of waste-water suspensions

500 g solid sample was mixed with 1000 cm<sup>3</sup> distilled water and placed in 2 dm<sup>3</sup> plastic containers to simulate waste ponds. The lids of the container were perforated systematically by small holes (~3 mm diameter) in such a way as to prevent rapid evaporation of liquid but to maintain contact of samples with air under laboratory conditions (Fig. 2). The containers were not disturbed but kept in place on the laboratory bench and no stirring (mixing) was performed. In order to examine the effect of pyrite mineral, certain amounts (by percent) of pyrite were added to certain wastes. The reproducibility of the experiments was confirmed by preparing two identical suspensions and carrying out parallel tests (Table 1). The investigations at this stage can be classified into three groups:

1. pH and EC measurements: After 24 hours of preparation, the pH and EC of the suspensions were measured regularly at least two times a week. The measurements were always made at the center of the suspension and continued until not enough liquid remained in the suspension for measurement.

2. Metal ions concentration: In order to determine the change of concentrations of some metal ions in liquid with time, 10 cm<sup>3</sup> of liquid was taken from the suspension each time. The first 10 cm<sup>3</sup> of liquid was taken after 24 hours following the preparation of suspensions and sampling was made once every 2 weeks. Liquid samples taken by plastic syringes were filtered into 20 cm<sup>3</sup> glass tubes with 45 µm pore

size disc filters. The tubes were sealed and kept closed until performing AAS analysis. Sampling continued until not enough liquid remained in the suspension for sampling.

3. Characterization of solid residuals: After completion, the remained solids were dried in an oven and analyzed by elemental, sulfur, XRD, XRF, and ICP methods. The changes in solid properties were determined by comparing the raw waste and residual samples.



Fig. 2. Static tests conducted in plastic containers

Table 1. Test suspensions prepared with 500 g solid and 1000 cm<sup>3</sup> water

Sample code	Solids	Remarks
500-1 ve 500-2	500 g waste	0% pyrite
475-1 ve 475-2	475 g waste + 25 g pyrite	5% pyrite
450-1 ve 450-2	450 g waste + 50 g pyrite	10% pyrite
400-1 ve 400-2	400 g waste ve 100 g pyrite	20% pyrite

### 3. Results and discussions

#### 3.1. Characteristics of waste and pyrite

Particle size distribution is one of the important parameters affecting the AMD potential of ores. As the particle size decreases, the specific surface area of the sample increases and hence the reaction rate of the samples with water and air, as well as the AMD formation rate will increase (Ergüler and Ergüler, 2015). The particle size distributions of the waste and pyrite samples were measured and mean sizes ( $d_{50}$ ) were obtained approximately 20 and 162  $\mu\text{m}$ , respectively. The waste has a very fine size, indicating that, if it has AMD potential, the generation could be fast. The XRD analyzes of the samples were performed to determine the mineral content of the waste. As seen in Fig. 3, the waste contains dolomite, calcite, quartz, and smithsonite minerals, and is mainly composed of carbonates. Pyrite mineral, which has the highest AMD formation potential, was not detected in the main peaks. The XRD analysis of the concentrated pyrite showed that it is not pure, but contains some quartz (Fig. 4).

Elemental analyzes of waste and pyrite samples were made, and the results are presented in Table 2. The waste and pyrite contain 0.149% S and 47.49% S, respectively. The results reveal that the waste is rich in carbonate minerals (with 8.668% C), but the pyrite does not contain any carbon. Considering that

the sulfur comes only from the pyrite mineral, it is calculated that the concentrated pyrite is 88.75% pure. It was conceived that, along with quartz, some other minerals could be found as impurities in the concentrated pyrite. Sulfate sulfur analysis was also performed to calculate the sulfide sulfur by percent in the waste and it was found that the waste contained 0.134% sulfate sulfur. When total sulfur (0.149%) content is considered, sulfate sulfur is much more than pyritic sulfur.

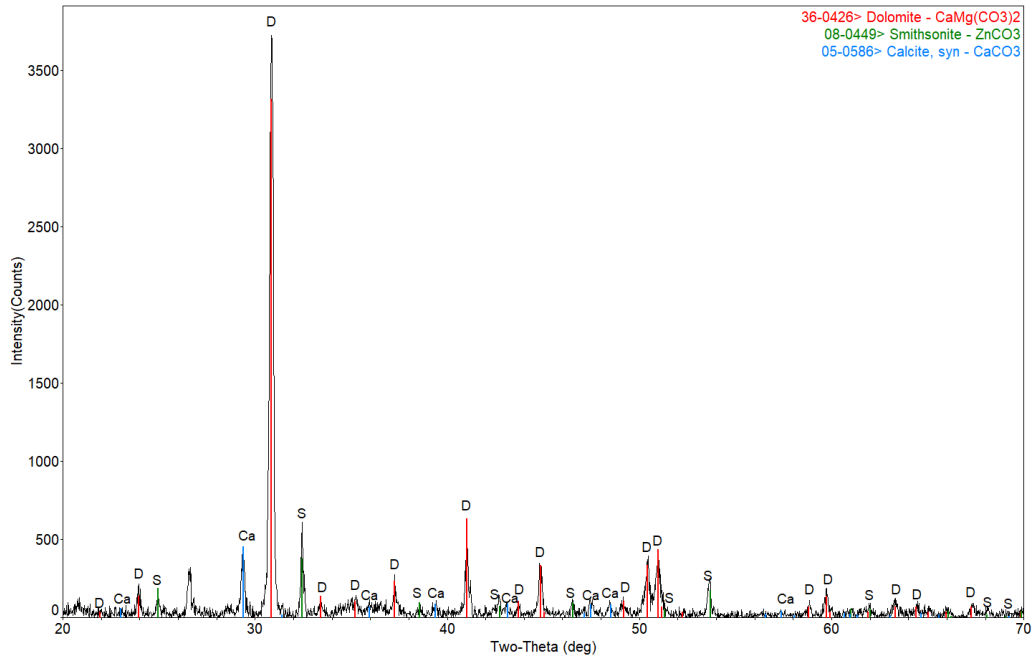


Fig. 3. XRD results of waste sample

Table 2. Elemental analysis of waste sample and concentrated pyrite

Material	% C	% H	% N	% S
Waste sample	8.668	0.119	-	0.149
Pyrite	-	-	-	47.49

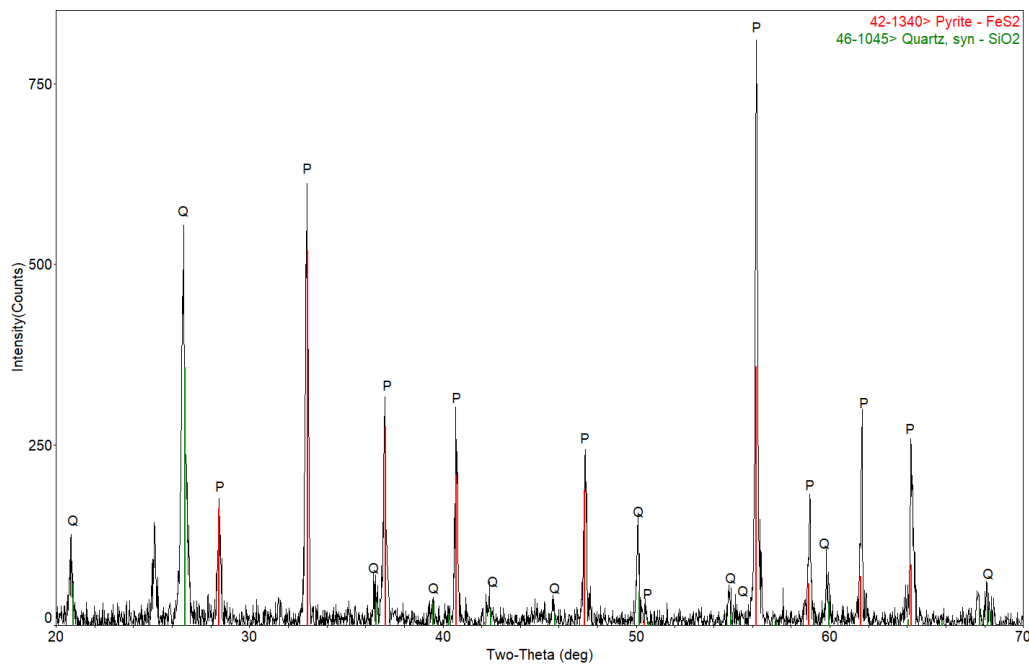


Fig. 4. XRD results of concentrated pyrite

Knowing that, heavy metals can transfer from the solid into the medium, the metal content of the sample is commonly determined in the AMD studies. For this purpose, the XRF and ICP-OES analyzes were performed on the sample and the results are presented in Tables 3 and 4, respectively. The XRF results showed that the sample had a high content of CaO (20.85%), MgO (9.63%), and SiO<sub>2</sub> (12.84%). The high percentage of loss on ignition (LOI 31.9%) indicates the presence of a significant amount of carbonate minerals (e.g. dolomite, calcite, etc.). It is obvious that the results of XRF are compatible with the XRD results. The detection of 4.63% Fe<sub>2</sub>O<sub>3</sub> and 4.91% Al<sub>2</sub>O<sub>3</sub> indicates, respectively, the presence of iron, mainly in oxide forms (e.g. FeCO<sub>3</sub>), and significant amount of clay minerals in the waste. It is also seen that the waste coming from the flotation circuit has low Pb (0.84%) and high Zn (7.70%) contents. It is seen that the XRF, XRD, and ICP-OES results are compatible as both revealed the complex structure of the waste. It has also been determined that there are significant amounts of heavy metals such as Zn, Pb, Al, Fe, Cr, Co, Cd, and Ni in the waste. In the case of AMD generation, the heavy metals can report into the medium and harm the environment. The Cu, As, Sb, Mo, W, and Bi elements remained under the detection limit of the instrument. All of the characterization methods (i.e. elemental, XRD, XRF, and ICP-ES) showed that the waste is poor in pyrite and sulfur, but rich in carbonates, which can lead one to consider that the ore may not generate the AMD.

Table 3. XRF analysis of waste sample

Pb, %	Zn, %	SiO <sub>2</sub> , %	Al <sub>2</sub> O <sub>3</sub> , %	Fe <sub>2</sub> O <sub>3</sub> , %	CaO, %	MgO, %
0.84	7.70	12.84	4.91	4.63	20.85	9.63
K <sub>2</sub> O, %	MnO, %	TiO <sub>2</sub> , %	P <sub>2</sub> O <sub>5</sub> , %	Cr <sub>2</sub> O <sub>3</sub> , %	Ba, %	LOI, %
1.52	0.31	0.59	0.19	0.01	0.60	31.90

Table 4. ICP-OES analysis of waste sample

Pb, %	Zn, %	Fe, %	Ca, %	Mg, %	Al, %	Mn, %	Ni, %
0.84	7.80	3.23	14.85	5.61	2.63	0.24	0.003
Na, %	Cu, %	Cr, %	Co, %	P, %	Cd, %	K, %	S, %
0.16	0.003	0.008	0.001	0.08	0.024	1.34	0.46

### 3.2. Static AMD test results

#### 3.2.1. Paste pH

In order to determine the paste pH of the waste, 10 g sample was weighed and the measurement was conducted as explained in the methods section (2.3). The measurable pH of the waste was 8.01 and the pH increased slowly with the addition of more distilled water. The value of paste pH is interpreted in different ways in the literature (Demirel, 2015). Gül (2014) and Miller and Murray (1988) stated that rocks can generate AMD if the pH of the paste is below 4, but Morin and Hutt (1997) stated that AMD is possible at the paste pH below 6. The paste pH test of the concentrated pyrite was carried out in the same way; the pH was read as 3.37 which increased slightly with the addition of more distilled water. As expected, the pH of the pyrite paste was quite lower than the waste paste. As expected, the concentrated pyrite has a very high AMD potential than waste and can enhance the bacterial activity. On the other hand, the paste pH of the pyrite and waste mixture prepared in equal amounts was measured as pH 6.25 that is between the pyrite and the waste samples alone. Depending on the paste pH result alone, it can be concluded that the mixture does not have the potential to generate AMD and the waste can neutralize the acidic pyrite.

#### 3.2.2. Standard and modified ABA test

For ABA tests, APP and NP tests of the sample were carried out and then NNP values were calculated from the results. Total sulfur percent was utilized in Eq. 2 to calculate APP and 4.66 kg CaCO<sub>3</sub>/Mg was obtained. This result shows that the acid production of the waste is low and only 4.66 kg of CaCO<sub>3</sub> is

sufficient to neutralize one ton of the waste. For NNP calculations, first, the fizz test was performed as described in the references (URL1). Dropping 2 drops of 25% HCl on 0.5 g sample resulted in a strong fizz sound. In accordance with the standards, the test was continued by adding 80 cm<sup>3</sup> of 0.5 mol/dm<sup>3</sup> HCl solution on 2 g sample. Digestion is achieved by heating the suspension at 90 °C until the gas bubbling stopped. Afterwards, the suspension was back titrated with 0.5 N NaOH solution to pH 7.0 to calculate NP by Eq. 3. To reach pH 7.0, 28.7 cm<sup>3</sup> of 0.5 mol/dm<sup>3</sup> NaOH was consumed and the calculations showed that the NP of the sample was quite high (641.25 kg CaCO<sub>3</sub>/Mg). From APP and NP data, a net-neutralizing potential (NNP = APP - NP) and neutralizing potential ratio (NPR = NP/APP) were calculated. Although different site-specific cut-off values to assess acid-production risks are used, it is often assumed that NNP < 10 kg CaCO<sub>3</sub>/Mg and NPR < 1 indicate potential net acid-generating material. Since calculations resulted in NNP >> 10 kg CaCO<sub>3</sub>/Mg and NPR >> 1, it was concluded that the waste has no net acid generation potential.

$$\begin{aligned} \text{APP} &= \text{Total sulfur (\%)} \times 31.25 = 0.149 \times 31.25 = 4.66 \text{ kg CaCO}_3/\text{Mg} \\ \text{NP} &= \frac{50[aV_{\text{HCl}} - bV_{\text{NaOH}}]}{w} = \frac{50[0.5 \times 80 - 0.5 \times 28.7]}{2} = 641.25 \quad (3) \\ \text{NNP} &= \text{NP} - \text{APP} = 648.75 - 4.66 = 636.59 \text{ kg CaCO}_3/\text{Mg} \\ \text{NPR} &= \text{NP}/\text{APP} = 641.25/4.66 = 137.61 \end{aligned}$$

In the modified ABA test, 2 g of the sample was used due to strong fizz rate of the sample. Initially, 3 cm<sup>3</sup> of 1 N HCl stock solution was used and 2 more cm<sup>3</sup> of solution was added after 2 hours. A total of 15.3 cm<sup>3</sup> stock solution was used to lower the mixture to pH 2-2.5 range, and then 11.2 cm<sup>3</sup> of 0.5 N NaOH solution was used to increase the pH back to pH 8.3. The modified NP potential of the sample was calculated according to Eq. 3 and found to be 242.5 kg CaCO<sub>3</sub>/Mg. In the modified APP calculation, sulfide sulfur, instead of total sulfur, was utilized and 0.469 kg CaCO<sub>3</sub>/Mg was calculated. From the data, modified NNP and NPR values were calculated as 242.031 kg CaCO<sub>3</sub>/Mg and 517.0, respectively. As in the standard ABA test, it was again concluded that the waste has no net acid production potential since modified NNP >> 10 and NRP >> 3 were achieved.

When standard and modified ABA methods are compared, it is seen that the standard ABA test resulted in higher NNP, but lower NPR values than modified ABA tests. The reason for the differences is utilizing either total sulfur (in standard ABA) or pyritic sulfur (in modified ABA). Still, both tests revealed that the acid potential of the waste was low, but the neutralization potential was high.

$$\text{Modified APP} = \text{Sulfide sulfur (\%)} \times 31.25 = 0.015 \times 31.25 = 0.469 \text{ kg CaCO}_3/\text{Mg}$$

$$\text{Modified NP} = \frac{50x[(1 \times 15.3) - (0.5 \times 11.2)]}{2} = 242.5 \text{ kg CaCO}_3/\text{Mg}$$

$$\text{Modified NNP} = 242.5 - 0.469 = 242.031 \text{ kg CaCO}_3/\text{Mg}$$

$$\text{Modified NPR} = \text{NP}/\text{APP} = 242.5/0.469 = 517.0$$

### 3.2.3. BC research initial test

The BC Research Initial test was performed using a 10 g sample and 100 cm<sup>3</sup> of distilled water as described in URL1. H<sub>2</sub>SO<sub>4</sub> solution was added into the suspension by using a micropipette and the addition continued until the pH was stabilized at about 3.5 (until the pH remained stable for 4 hours). A total of 76.1 cm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> was added for stabilization. By using Eq. 4, it was calculated that one ton of waste could consume 372.89 kg of H<sub>2</sub>SO<sub>4</sub>. On the other hand, the acid production potential of one ton of ore was calculated according to Eq. 5, and 4.56 kg of H<sub>2</sub>SO<sub>4</sub> was achieved. Since the acid consumption of the ore is much higher than the acid production, it is concluded that the waste is not a net acid producer.

$$\text{Acid consumption} = \frac{\text{Amount of 1N sulfuric acid (cm}^3\text{)} \times 0.049 \times 1000}{\text{Sample weight, g}} \quad (4)$$

$$\text{Acid consumption} = \frac{76.1 \times 0.049 \times 1000}{10} = 372.89 \frac{\text{kg H}_2\text{SO}_4}{\text{Mg ore}}$$

$$\text{APP} = 0.149 \times 30.625 = 4.56 \text{ kg H}_2\text{SO}_4/\text{Mg ore} \quad (5)$$



Differing from BC Research Initial test, Lapakko (1994) took the endpoint pH of titration as 6.0 instead of 3.5 as described by Gül (2014). This test, also known as the Lapakko test, considers the drainage quality of water and calculates the amount of acid that the ore (ore waste) can neutralize between its original pH and pH 6. As indicated below, the waste consumed 5.9 cm<sup>3</sup> of acid to reach pH 6 and the acid consumption amount of 1 ton of waste was 28.91 kg of H<sub>2</sub>SO<sub>4</sub>. The Lapakko test showed that the acid consumption potential of the waste is higher than the acid production potential.

$$\text{Lapakko acid consumption} = \frac{5.9 \times 0.049 \times 1000}{10} = 28.91 \frac{\text{kg H}_2\text{SO}_4}{\text{Mg ore}}$$

### 3.2.4. NAG Test

The single addition NAG test is used in association with the NAPP to classify acid generating potential of the waste. The NAG test was performed using a 2.5 g sample in accordance with the standard procedure (URL1). After completion of 12 hours reaction between the sample and H<sub>2</sub>O<sub>2</sub>, the suspension was heated at 90°C for 2.5 hours and then left to cool at room temperature. Later, the pH and EC of the suspension were measured as 8.77 and 378.04 μS/cm, respectively. Since the pH value was above pH 4.5 (or 7.0 in some other references), NaOH titration of the suspension was not needed. The measurements were repeated for the filtrate (aliquot), after filtering the suspension, then a pH of 7.57 and EC of 267.11 μS/cm were measured. A separate test without peroxide addition was also performed for a better explanation and comparison of the results. Then, it was found that the suspension had a pH of 8.98 and EC of 182.74 μS/cm, while the filtrate had a pH of 7.33 and EC of 190.66 μS/cm.

Since the pH values remained above 4.0 (or 7.0) for all cases in NAG tests, it was concluded that the waste is not the net acid producer. It can be seen that the NAG test results are consistent with other static test results as summarized in Table 5. Considering that pyrite, pyrrhotite, arsenopyrite, and chalcopyrite minerals can reduce the suspension pH below 4.5, or sphalerite, galena, bornite, chalcocite, and covelin minerals can reduce the suspension pH 4.5-7.0 range (Stewart et al., 2003), it is understood that the waste does not contain these minerals sufficiently.

Table 5. Summary of static test results

Paste pH	Fizz rate	Standard ABA test		Modified ABA test		BC Research Initial test		NAG test
		NNP, kg CaCO <sub>3</sub> /Mg ore	NPR	NNP, kg CaCO <sub>3</sub> /Mg ore	NPR	kg H <sub>2</sub> SO <sub>4</sub> consumption by one ton ore	kg H <sub>2</sub> SO <sub>4</sub> production of one ton ore	NAG pH
8.01	Strong	636.59	137.61	242.031	517.0	372.39	4.56	Above 7.0

### 3.3. Static test results of waste-water suspensions

Dissolved metal ion concentration, pH, and EC of the medium are very important in terms of observing the behavior of sulphurous wastes in waste ponds. Low pH not only degrades drainage water quality but also multiplies the activities of acid-producing bacteria and hence increases the severity of AMD. EC is related to the concentration of ions in the liquid, but since conductivity depends on many factors, alone it does not indicate the quality of water. However, possible changes in the environment can be observed with EC measurements. Metal ions in water usually are not biodegradable and thus tend to accumulate in environment and living organisms, and then can have lethal effects when attain a certain concentration.

The liquid sampling as well as pH and EC measurements continued until the depletion of liquid in the containers which lasted for only 17 weeks due to liquid evaporation and samplings. For brevity, only average values were presented as the result.

#### 3.3.1. pH and EC

The pH values of the suspension medium measured over time for all samples are shown in Fig. 5. No steady variation was observed but pH fluctuated in the range of 8.6-7.6. While the initial pH values of the pyrite containing samples were low, it was seen that pH values approached without pyrite samples over time and stabilized approximately in the pH range of 8.1-8.2. It was considered that the fluctuation

was due to the complex structure of the samples, that is, the presence of many different minerals. These long-term data revealed that the reaction or alteration rates of different minerals making up the waste was not the same. It can be inferred that due to differences in the reaction rate of minerals with water and air, the equilibrium pH could be attained at longer period when homogenous stirring is not applied. Goto et al. (2016) studied the water/aggregate/pyrite mixture and monitored the effect of different amounts of pyrite on the pH, temperature, EC, and TDS of the medium with time for 30 days. They supplied continuous air into the medium by an air compressor at a pressure of 100 mbar without additional stirring. At the end of 30 days, the pH of the medium without pyrite remained at pH 8.2, while 5% pyrite-containing medium decreased to pH 3.0. The results show that oxygen or air plays a very important role in the oxidation of pyrite.

The average EC values measured against time are presented in Fig. 6, which showed an increase for all samples due to continuing transfer of ions from the solid surface into the medium. The increase rate was higher in the first three weeks after which a slower increase was attained. It is seen that similar EC values were obtained in the short and long periods from samples containing 5% pyrite and no pyrite, respectively. While the initial values of the samples were very close for all samples, the conductivity was slightly higher in the samples with 10% and 20% pyrite, which stabilized after 14 weeks. Similar results were obtained by Goto et al. (2016) who investigated the effect of different amounts of pyrite on the EC of the medium made up of water/aggregate/pyrite mixtures. They observed that the EC of the medium increased continuously for 20 days and then stabilized. However, the increase in the EC was higher with an increasing ratio of pyrite in the mixture.

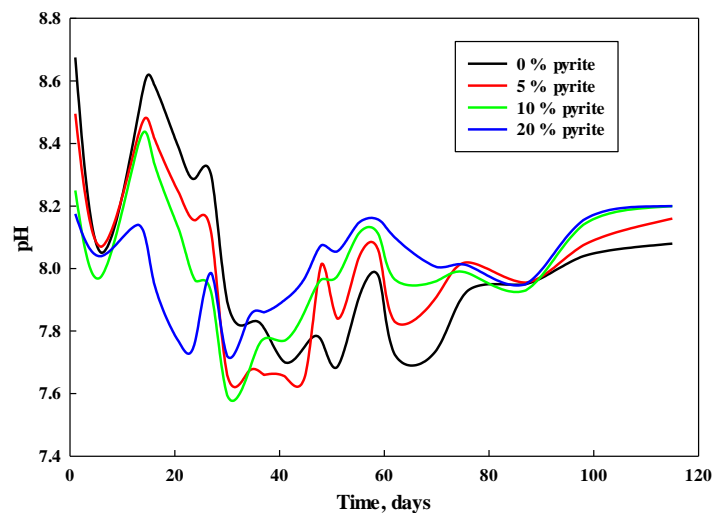


Fig. 5. Variation of waste-water medium pH with time

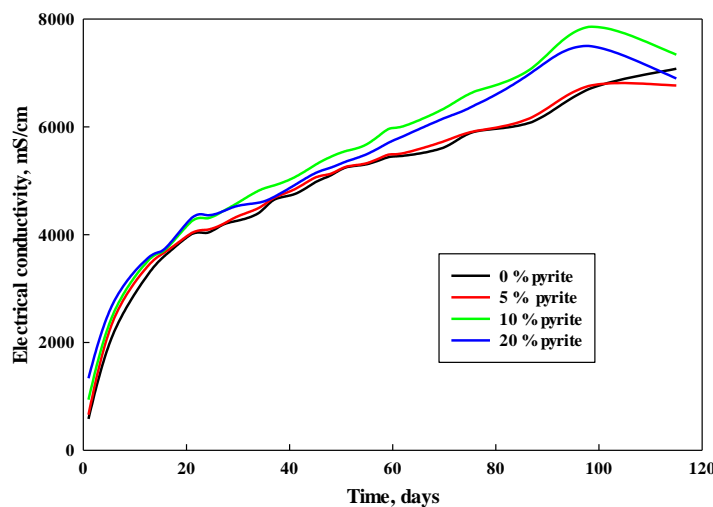


Fig. 6. Variation of electrical conductivity of waste-water medium with time

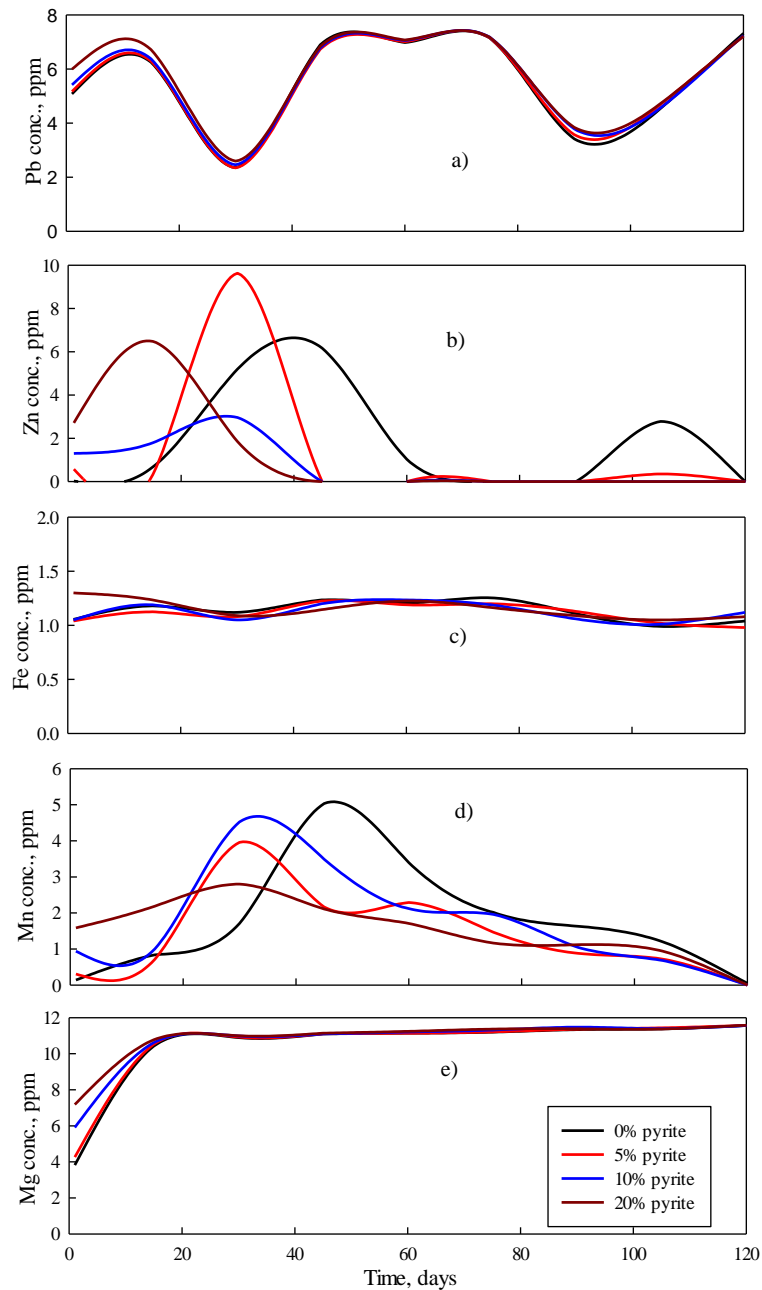


Fig. 7. Variation of metal ions concentration in the medium, a) Pb, b) Zn, c) Fe, d) Mn, and e) Mg

### 3.3.2. Variation of metal ion concentration in the medium with time

After the first 24 hours, 8 more liquid samples were taken regularly from each suspension to figure out the variation in metal ions concentration over time. Pb, Zn, Fe, Al, Mn, and Mg were analyzed as important elements that can be found in the sample and contribute to AMD generation. Since Al concentration remained below the detection limit of the device, it was always measured as zero by the AAS instrument. As seen in Fig. 7, there have been significant changes in the ions concentration over time. Although there are salient variations in Pb concentration, which represents 0.84% of the raw waste, it remained below 8 ppm (Fig. 7a) and pyrite addition did not affect the concentration. Significant changes were observed in the concentration of Zn with time, which constitute 7.80% of the sample, but the concentration remained below 10 ppm (Fig. 7b). On the other hand, no significant time-dependent change in Fe concentration remained below 1.4 ppm (Fig. 7c). Despite the addition of pyrite, the Fe concentration did not increase in the medium due to the stability of pyrite during the period of the study or re-precipitation under studied conditions. The fluctuation must be due to the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and dissolution-precipitation of the iron ions in the basic medium ( $\text{pH} > 7.6$ ). Similar to lead and zinc,

there is no steady change in Mn content that remained below 6 ppm (Fig. 7d). Unlike other metal ions, Mg concentration increased steadily for the first three weeks and then remained almost constant at about 11 ppm level (Fig. 7e). Mg is generally expected to result from the most dominant mineral, dolomite that contributes to the prevention of AMD generation.

The metal ions concentration in AMD is the result of a complex set of oxidation, hydrolysis, and precipitation reactions that start with the oxidation of minerals in the medium. In particular, carbonate minerals such as dolomite and calcite in the sample are expected to alter more rapidly in water than sulfide and silicate minerals. It is thought that the pyrite minerals, which make the most important contribution to the AMD generation, are not expected to decompose notably and contribute to AMD under the studied conditions and period. Wels et al. (2003) evaluated the AMD potential of mine wastes and concluded that the circulation of air in the waste had a great effect on the oxidation of pyrite and significantly increased the AMD generation. Moricz et al. (2012) determined that the presence of neutralizing minerals prevents acidity, slows down the oxidation of metallic minerals, and reduces metal ions concentration in the medium by precipitation.

### 3.3.3. Characterization of residuals in the containers

Elemental, sulfur, XRF, XRD, and ICP analyzes were performed on solid residuals that remained in the containers. Only the sample without pyrite was selected to be able to compare with raw waste. The C, H, N, and S contents of the sample are presented in Table 6, which shows a slight increase in C and H, but a noticeable increase in S contents in residual waste. Sulfur analysis (Table 7) indicates that the increase is mainly due to the stability of the pyritic sulfur. It can be inferred that the waste altered to an extent during the test, but the pyrite in the waste is not affected as much as other minerals. The XRF results of the residuals are given in Table 8 together with raw waste to express the changes in concentration of constituents in parenthesis. It was observed that while the concentration of  $\text{Fe}_2\text{O}_3$ ,  $\text{K}_2\text{O}$  and  $\text{TiO}_2$  increased by 1.27, 0.03, and 0.01%, respectively, and the concentration of other components decreased noticeably. The decrease was more pronounced for carbonates and most significant minerals, such as CaO (0.5%), MgO (0.23%), Zn (0.24%), and  $\text{SiO}_2$  (0.15%). The decrease in the LOI (2.0%) also indicates the alteration of carbonate minerals during the tests.

Table 6. Elemental analysis of waste sample and residual waste

Material	% C	% H	% N	% S
Waste sample	8.668	0.119	-	0.149
Residual waste in container	8.844	0.177	-	0.282

Table 7. Sulfur analysis of waste sample (before test) and residual waste

Total sulfur, %		Sulfide sulfur, %		Pyritic sulfur (calculated from difference), %	
Before	After	Before	After	Before	After
0.149	0.282	0.134	0.253	0.015	0.029

Table 8. XRF analysis of the residual waste (differences is given in the parenthesis)

Pb, %	Zn, %	$\text{SiO}_2$ , %	$\text{Al}_2\text{O}_3$ , %	$\text{Fe}_2\text{O}_3$ , %	CaO, %	MgO, %
0.83	7.46	12.69	4.79	5.90	20.35	9.40
(-0.01)	(-0.24)	(-0.15)	(-0.11)	(+1.27)	(-0.5)	(-0.23)
$\text{K}_2\text{O}$ , %	MnO, %	$\text{TiO}_2$ , %	$\text{P}_2\text{O}_5$ , %	$\text{Cr}_2\text{O}_3$ , %	Ba, %	LOI, %
1.49	0.30	0.58	0.18	0.01	0.57	29.90
(0.03)	(-0.01)	(0.01)	(-0.01)	(0)	(-0.03)	(-2.0)

Table 9. ICP-OES of the residual waste (differences is given in the parenthesis with respect to waste sample)

Pb, %	Zn, %	Fe, %	Ca, %	Mg, %	Al, %	Mn, %	Ni, %
0.80 (-0.04)	7.34 (-0.46)	5.06 (+1.83)	14.19 (- 0.66)	5.43 (-0.18)	2.63 (0)	0.23 (-0.01)	0.003 (0)
Na, %	Cu, %	Cr, %	Co, %	P, %	Cd, %	K, %	S, %
0.14 (0.02)	0.003 (0)	0.008 (0)	0.001 (0)	0.008 (0)	0.023 (-0.001)	1.23 (-0.11)	2.72 (+2.01)

The ICP-OES results of the residuals are given in Table 9 together with raw waste to express the changes in concentration of constituents in parenthesis. When examined, it was observed that while the concentrations of Fe (1.83%) and S (2.01%) increased, the concentrations of other constituents decreased. The decrease is generally in Ca (0.66%), Zn (0.24%), Mg (0.18%), and K (0.11%), which are the main constituents of the waste. In agreement with XRF results, ICP-OES results indicated the alteration of carbonate, but the stability of sulfide minerals in the static tests. The XRD analysis of the residual waste was carried out and the results are presented in Fig. 8. When Figs. 4 and 8 are compared, no significant changes are observed between the main peaks of raw and residual wastes. Considering that the alteration of minerals remained at a low level during the test, noticeable changes are not expected in XRD peaks. The limited alteration of the wastes in the container can be explained by; i) limited contact of the medium with air due to limited contact apertures (holes) on the container lid, ii) limited contact of solids with water due to the absence of stirring and iii) limited test duration (17 weeks) due to depletion of liquid in the containers.

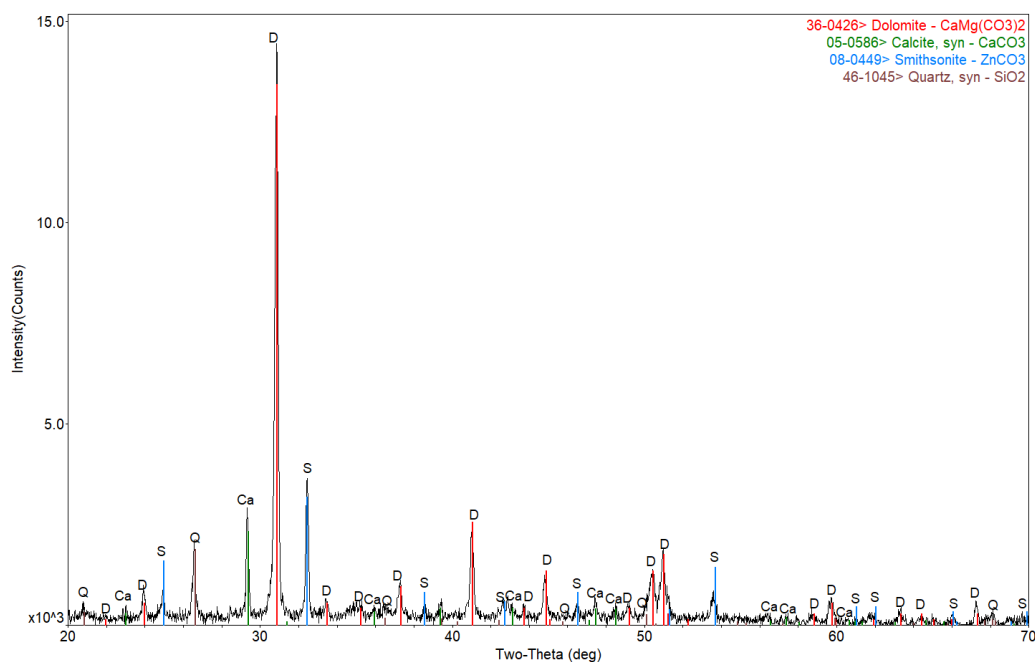


Fig. 8. XRD results of residual waste sample in the containers

#### 4. Conclusions

The chemical and mineralogical properties, and AMD potential of Görgü (Malatya) zinc-lead ore wastes were investigated by static tests. The following conclusions were withdrawn:

- The waste, which is very rich in carbonate minerals and very poor in pyritic sulfur content, does not have AMD generation potential.
- The paste pH, Standard and modified ABA, BC Research Initial, and NAG test results showed that the waste did not have a potential to generate AMD.
- The pH of the suspension medium varied between 8.6-7.6 irregularly for 15 weeks after which remained stable at pH ~8.0.

- The electrical conductivity of the medium over time increased from 1500  $\mu\text{S}/\text{cm}$  to 7500  $\mu\text{S}/\text{cm}$  because of continuing transfer of ions from the solid surface into the medium.
- Metal ions transferred from minerals into the medium because of alteration with time, but their concentration in the medium varied due to continuous dissolution and re-precipitation processes of the ions in the basic medium ( $\text{pH} > 7.6$ ).
- When the XRD analyzes of the raw and residual samples were compared, it was found that the alteration of minerals remained at a low level under the working conditions.
- Static AMD test showed that the waste material had no AMD potential and the addition of pyrite did not significantly contribute to its AMD potential.
- The limited alteration of the minerals in the static containers was explained in terms of; i) limited contact of the medium with air due to limited contact apertures (holes) on the container lid, ii) limited contact of solids with water due to the absence of stirring and iii) limited test duration due to depletion of liquid in the containers.

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