DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

IMMOBILIZATION OF METALS IN MINE TAILINGS AND THE EFFECTING FACTORS

by
Derya AKTAŞ

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IMMOBILIZATION OF METALS IN MINE TAILINGS AND THE EFFECTING FACTORS

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled "**IMMOBILIZATION OF METALS IN MINE TAILINGS AND THE EFFECTING FACTORS**" completed by **DERYA AKTAŞ** under supervision of **PROF. DR. GÖRKEM AKINCI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Görkem AKINCI
Supervisor

Prof. Dr. Ayşegül PALA
Thesis Committee Member

Prof. Dr. Osman Nuri AĞDAĞ
Thesis Committee Member

Prof. Dr. Ahmet ALTIN
Examining Committee Member

Prof. Dr. Nuri AZBAR
Examining Committee Member

Prof. Dr. Okan FISTIKOĞLU
Director
Graduate School of Natural and Applied Sciences

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IMMOBILIZATION OF METALS IN MINE TAILINGS AND THE EFFECTING FACTORS

ABSTRACT

Mining activities are important for economic development and sustainability. However, mining activities carried out without taking the necessary precautions pose a great danger to the environment and human health. One of these dangers is the formation of acid mine drainage in waste piles after mining activities. This formation is accepted as one of the main heavy metal sources today.

In this study, the determinant factors on the formation and control Acid Mine Drainage (AMD) were investigated in order to prevent metals' mobilization from mine waste. The use of binding materials to immobilize heavy metals is focused in the content of the thesis. In the first step, leonardite and compost were used as binding materials and the potential for AMD formation under the influence of *Thiobacillus sp.* was observed in short-term tests. Accordingly, it was revealed that the presence of *Thiobacillus sp*., independent of the binding material, caused an increase in metal mobilization. In the second step, long-term column tests were run, where triple super phosphate (TSP) and marble dust were used as binding materials. The results show that marble dust is more effective than TSP in controlling the monitoring parameters such as acidity, alkalinity, and pH in sequential leaches. The increase in the ratio of TSP in mine waste increased the mobilization of some heavy metals. In the last step, long term paste tests were applied by using marble dust, fly ash, cement, and bentonite as binding materials with different rates and by using waste samples with different metal, sulfur and carbonate contents. Different rates of binding material interaction of each waste sample revealed different immobilization results.

Keywords: AMD, binding materials, immobilization, heavy metal

MADEN ATIĞI SAHALARINDA METALLERİN HAREKETSİZLEŞTİRİLMESİ VE ETKİLEYEN FAKTÖRLER

ÖZ

Madencilik faaliyetleri ekonomik kalkınma ve sürdürülebilirlik açısından önemlidir. Ancak gerekli önlemler alınmadan yapılan madencilik faaliyetleri çevre ve insan sağlığı için çok büyük tehlike arz etmektedir. Bu tehlikelerden biri de maden faaliyetlerinden sonra ortaya çıkan atık yığınlarındaki asit maden drenajı (AMD) oluşumudur. Bu oluşum günümüzde temel ağır metal kaynaklarından biri olarak kabul edilmektedir. Bu çalışmada, ağır metallerin hareketsizliğini sağlamak için maden atıklarındaki AMD oluşum potansiyeli değerlendirilmiş ve oluşumları kontrol altına alınmaya çalışılmıştır. AMD'yi kontrol etmenin yöntemlerinden biri maden atığı içindeki ağır metallerin hareketsizliğini sağlamak amacıyla bağlama materyalleri kullanmaktır. Bu materyallerin etkisini gözlemlemek için AMD ölçüm yöntemlerinden faydalanılmıştır. Çalışmanın ilk adımında, leonardit ve kompost bağlama materyali olarak kullanılmış ve *Thiobacillus sp.*'nin etkisi altında AMD oluşum potensiyeli kısa süreli testlerde gözlemlenmiştir. Buna göre bağlama materyalinden bağımsız olarak *Thiobacillus sp.*'nin ortamdaki varlığı metal mobilizasyonu artışına sebep olmuştur. Çalışmanın ikinci adımında, kinetik test metotlarından biri olan uzun süreli kolon testleri işletilmiştir. Burada bağlama materyali olarak triple super fosfat (TSP) ve mermer tozu kullanılmıştır. Elde edilen sonuçlar, mermer tozunun asidite, alkalinite, pH gibi parametrelerin kontrolünde TSP'den daha etkili olduğunu; TSP oranındaki artışın bazı ağır metallerde mobilizasyona sebep olduğunu ortaya koymuştur. Çalışmanın son adımında ise yine uzun süre devam eden paste testler uygulanmıştır. Bağlama materyali olarak mermer tozu, uçucu kül, çimento ve bentonite farklı oranlarda ve farklı içeriğe sahip atık örneklerinde değerlendirilmiştir. Sonuç olarak her bir atık örneğinin farklı oranlardaki bağlama materyali etkileşimi farklı immobilizasyon sonuçları ortaya koymuştur.

Anahtar kelimeler: AMD, bağlama materyali, immobilizasyon, ağır metal

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ABBREVIATIONS

ABA:	Acid Base Accounting
AGP:	Acid Generation Potential
AMD:	Acid Mine Drainage
AP:	Acid Production
APP:	Acid Production Potential
ARD:	Acid Rock Drainage
ATSDR:	Agency for Toxic Substances and Disease Registry
BCR:	Community Bureau of Reference
Cd:	Degree of Contamination
DAP:	Diammonium Phosphate
EAF:	Exchangeable and Acid Soluble Fraction
EF:	Enrichment Factor
EPA:	Environmental Protection Agency
EPS:	Extracellular Polymer Substances
FTIR:	Fourier Transform Infrared
HCT:	Humidity Cell Test
HEI:	Heavy Metal Evaluation Index
HMTL:	Heavy Metal Toxicity Load
HPI:	Heavy Metal Pollution Index
ICP-OES:	Inductively Spectrometer
Igeo:	Geoaccumulation index
MABA:	Modified Acid-Base Accounting
NAG:	Net Acid Generation
NNP:	Net Neutralizing Potential
NP:	Neutralization Potential
NPL:	National Priorities List
NPR:	Neutralization Potential Rate
OF:	Oxidizable Fraction (bound to organics / Organic Fraction)
PCA:	Principal Component Analysis
PI:	Pollution index

RCA:	Recycled Concrete Aggregate
RF:	Reducible Fraction
RF:	Residual Fraction
SEM:	Scanning Electron Microscopy
SRB:	Sulfate Reducing Bacteria
TA:	Tannic Acid
TAD:	Total Acid Digestion
TKİ:	Turkish Coal Enterprises Institution
TSP:	Triple Super Phosphate
WPIi:	Water Pollution Index
XPS:	X-ray Photoelectron Spectroscopy

CHAPTER ONE
INTRODUCTION

It has needed raw materials to improve itself since human beings have existed (Qi, 2020). Even now, the majority of demand is met by the mining sector (UNEP, 2013; Probst et al., 2016; Kinnunen & Kaksonen, 2019). Manufacturing, including glass, paper, plastics, electronics, etc., cannot be done without minerals, elements, and other ores (Azapagic, 2004; Qi, 2020; Bellenfant et al., 2013) (Figure 1.1). Mining activities are a hindrance to the environment due to the destruction of land, the depletion of non-renewable resources, and the threat to the health and safety of the local population. Despite their significance in terms of both economic growth and sustainability, mining is detrimental to the environment (Azapagic, 2004; Kitula, 2006). In addition, mining and quarrying wastes, such as mine tailings, are produced in huge amounts during processing (Bellenfant et al., 2013; Edraki et al., 2014).

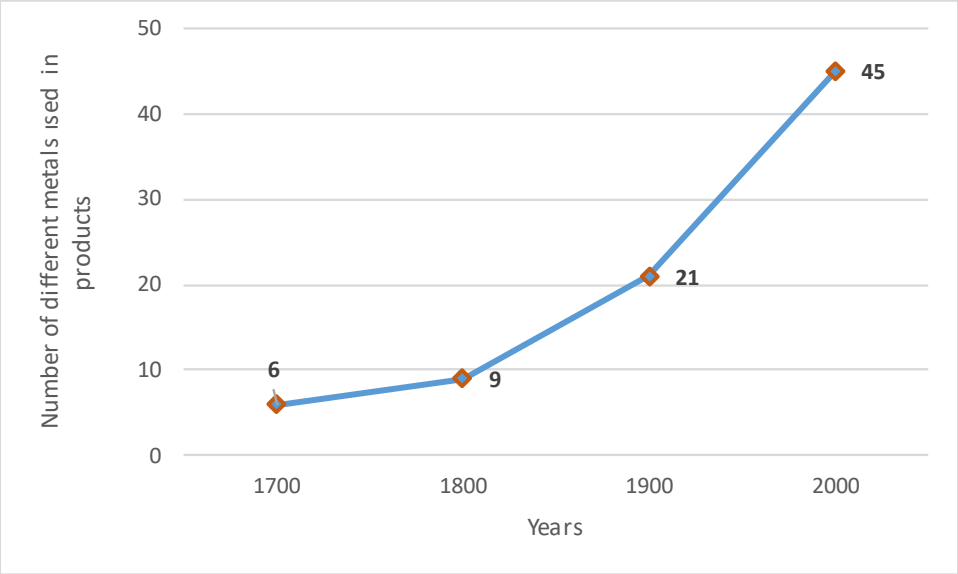


Figure 1.1 The rate of use of metals and elements in products through the ages (adopted from Bellenfant et al., 2013)

Mine tailings occur in years during ore processing and contain heavy metals and sulfide minerals. Although they are constructed over impermeable layers, a potential risk to the environment is always present because of causes such as earthquakes, soil

instability, wrong management of the site water (improper hydrological conditions), and possible damage to the impermeable membrane, etc. Therefore, mine tailings must be managed using a variety of approaches to reduce this potential risk.

Typically, mine tailings are dumped into streams near mines, where interactions with flowing water, air, and precipitation oxidize the sulfides, notably pyrite, to produce acid mine drainage (AMD). Consequently, these streams contain very toxic trace metals, including As, Cd, Pb, Zn, Cu, Hg, Sb, and Se. (Dinelli et al., 2001; Fernandez et al., 1986; Monterroso & Macias, 1998; Ritchie, 1994; Williams & Smith, 2000).

1.1 Characteristics of Acid Rock Drainage (ARD) and Acid Mine Drainage (AMD)

AMD is one of the most dangerous pollutants for the environment. Because of the risk of leaching surface and underground water, mining wastes, primarily coal and gold mining, are a major source of AMD. (Munnik et al., 2010). Environmental management and studies about AMD have great importance. (Moeng, 2018). AMD doesn't take its source from not only mining operations but also can arise from sulfide minerals such as tunnel construction, excavation operations, etc. (Simate & Ndlovu, 2014). Therefore, this process can be named in two different ways depending on its origin:

1) ARD (Acid Rock Drainage): It results from a natural geochemical process. In nature, oxidation happens spontaneously when rocks and soils containing sulfide minerals are exposed to weather impacts (rain, snow, wind, etc.). It is called as ARD (Jacobs, et al., 2014).

2) AMD (Acid Mine Drainage): It is a result of anthropogenic effects. The interaction of air and water oxidizes the by-products of mining operations (especially excavation, tunnel, and airport building). It is called as AMD. (Sainz et al., 2002).

AMD arises from surface and underground works, waste and physically processed rocks, tailings piles, and ponds (Durkin & Herrmann, 1994; Akcil & Koldas, 2006) (Table 1.1). The physically and chemically processed ore has a larger and more activated surface area than the virgin earth material, that's why, acid-generating minerals in the waste materials are more disaggregated and concentrated, AMD that flows from them may be more aggressive than that, which discharges from the mine itself. Another consideration is the potential long-term pollution problem. Production of AMD may continue for many years after mines are closed and tailings dams decommissioned (Johnson & Hallberg, 2005).

Table 1.1 The source of AMD (Akcil & Koldas, 2006)

Primary sources	Secondary sources
Mine rock dumps	Treatment sludge pounds
Tailings impoundment	Rock cuts
Underground and open pit mine workings	Concentrated load-out
Pumped/nature discharged underground water	Stockpiles
Diffuse seeps from replaced overburden in rehabilitated areas	Concentrate spills along roads
Construction rock used in roads, dams, etc.	Emergency ponds

AMD has low pH (<4), high electrical conductivity, high concentrations of dissolved heavy metals such as iron, aluminum, manganese, zinc, copper, etc., high concentrations of sulfate (SO_4^{-2}) (Tsukamoto et al., 2004). The acid produced dissolves salts and mobilizes heavy metals from mine workings. Dark, reddish-brown water and pH values as low as 2.5 persist at the site (Akcil & Koldas, 2006). Nordstrom et al. (2000) has been reported that total dissolved metal concentrations as high as 200.000 mg/L and dissolved SO_4^{2-} as high as 760.000 mg/L was to be in AMD.

AMD is not only associated with surface and groundwater pollution but is also responsible for the degradation of soil quality, for harming aquatic sediments and fauna, and for allowing heavy metals to seep into the environment (Adler & Rascher, 2007).

1.2 The Formation of AMD

AMD formation is based on oxidation of sulfide minerals such as pyrite (Table 1.2). It occurs by way of the microorganisms when these minerals contact both oxygen and water (Ali, 2011; Down & Stocks, 1977; Akcil & Koldaş, 2006). Though AMD production is basically correlated with the presence of air and oxygen of sulfide minerals, its formation depends on solid phase composition and microbial activity, too.

Table 1.2 Partial list of sulfide minerals (Skousen et al., 1998)

Some of the metal sulfide minerals
Pyrite (FeS_2)
Marcasite (FeS_2)
Pyrrhotite ($Fe_{(1-x)}S$)
Chalcocite (Cu_2S)
Covelite (Cus)
Chalcopyrite ($CuFeS_2$)
Molybdenite (MoS_2)
Millerite (NiS)
Galena (PbS)
Sphalerite (ZnS)
Arsenopyrite (FeAsS)

Pyrite is the most abundant mineral among the sulfide minerals. So, AMD formation will be explained through pyrite.

AMD has four sub-reactions (Singer & Stumm, 1970; Simate & Ndlovu, 2014; Akcil & Koldas, 2006):

1) The oxidation of sulfide to sulfate and ferrous ion (Eq 1.1) : If there is an increase in total dissolved solids and acidity of the water, Fe^{2+}, SO_4^{2-}, and H^+ ions are leached much more into the environment unless neutralized. In this manner, pH is decreased.

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1.1)$$

Penetration of oxygenated water is believed to occur through the expansion and contraction of pore-air due to diurnal and seasonal temperature changes. Therefore, erosion of the dumps or any other disturbance that would permit penetration of oxygenated water, For example, reworking of the dump poses a potential pollution problem.

2) Other sulfide minerals can lead to the dissolution of elements such as As, Cu, Cr, Ni, Pb, Co, and Zn:

These elements can be leached into underlying aquifers by percolating rainwater. As groundwater exudes into surface water bodies, ferrous iron undergoes oxidation. This reaction is pH dependent and proceeds slowly under acidic conditions (pH≈2-3). So, much of the ferrous irons is oxidized to ferric ions:

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (1.2)$$

This is dependent on the presence of *Thiobacillus ferrooxidans* bacteria (which are acidophilic and chemolithotropic), oxygen, and pH. As well as, when the pH is below 4, iron-oxidizing bacteria, especially those live in pH values between 2 and 4, highly enhance rates of Fe oxidation (Eq 1.2) by factors much more than 10^6. Thus, the oxidation of Fe^{2+} to Fe^{3+} is frequently called the rate-determining step in the acid generation process. If the process reaches pH values less than 4, a self-perpetuating cycle of Fe^{3+}-driven oxidation of pyrite and regeneration of Fe^{3+} through Fe oxidizers is started. In this case, it generates more acidity and Fe^{2+} until ferric iron or the pyrite waste is finished (Figure 1.2).

3) Neutralizing reactions: With mineral phases in rock, they often reduce the acidity, resulting in a groundwater plume at a slightly acidic pH but containing high concentrations of Fe^{2+} and SO_4^{2-}. If the pH is higher than 4, ferric iron precipitates as $Fe(OH)_3$ and jarosite.

$$4Fe^{3+} + 12H_2O \rightarrow 4Fe\,(OH)_3 \downarrow + 12H^+ \quad (1.3)$$

4) That do not precipitate as $Fe(OH)_3$ in Eq. 1.3 and the remaining Fe^{3+} from Eq.1.2 can be used to oxidize the remaining pyrite with the following equation. The oxidation of additional pyrite by ferric ion, Fe^{3+}:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe_{2+} + 2SO_4^{2-} + 16H^+ \quad (1.4)$$

As seen in Eq. 1.4, pH is further decreased by oxidation of the remaining pyrite.

The overall reaction is as below for stabile ferric irons (Eq 1.5) :

$$FeS_2 + 15/8O_2 + 13/2Fe^{3+} + 17/4H_2O \rightarrow 15/2Fe^{2+} + 2SO_4^{2+} + 17/2H^+ \quad (1.5)$$

These reactions, except for eq 1.2 and 1.3, assume that the oxidant is oxygen and the oxidized mineral is pyrite. But different sulfide minerals can have other ratios of metal sulfide and metals other than iron. Also, these minerals have different pathways, stoichiometries, and rates (Akcil & Koldas, 2006).

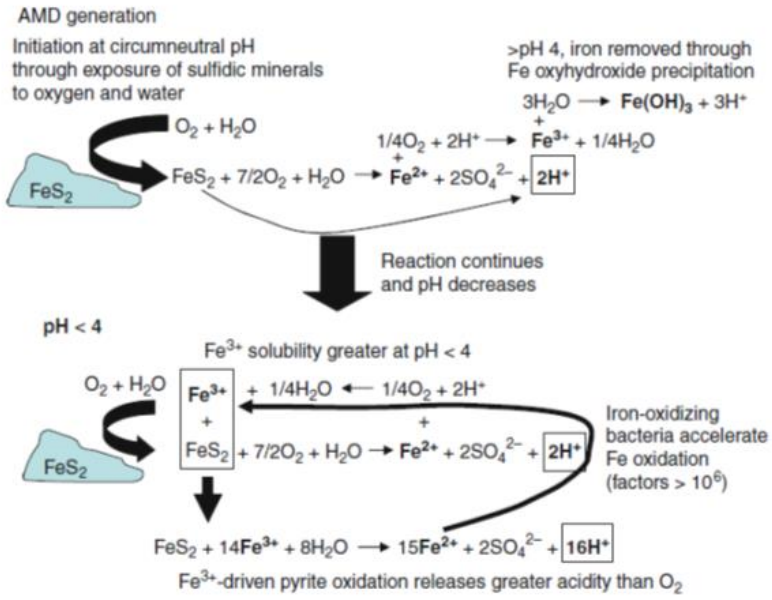


Figure 1.2 AMD generation from FeS_2 (Warren, 2011)

This is a self-sustaining reaction and, as such, renders tailings dumps as sources of AMD for a long time after mining operations have ceased (Nordstrom, 1979; Moses

et al., 1987; Ehrlich, 1996; Blowes et al., 1998). This is prevalent in gold and coal mines, which are considered to be the main long-term polluters (Pulles, 2003).

1.3 Factors Affecting AMD Generation

The main factors effecting the formation of AMD can be listed as below (Ferguson and Erickson,1988; Akcil & Koldas, 2006; Berghorn & Hunzeker, 2001) (Figure 1.3).

- Sulfide minerals (associated with metals)
- pH
- Temperature
- Oxygen content of the gas phase, if saturation is less than 100%
- Oxygen concentration in the water phase
- Degree of saturation with water
- Chemical activity of Fe^{3+}
- Surface area of exposed metal sulfide
- Chemical activation energy required to initiate acid generation
- Bacterial activity
- Pyrite morphology and occurrence
- Paleoenvironment

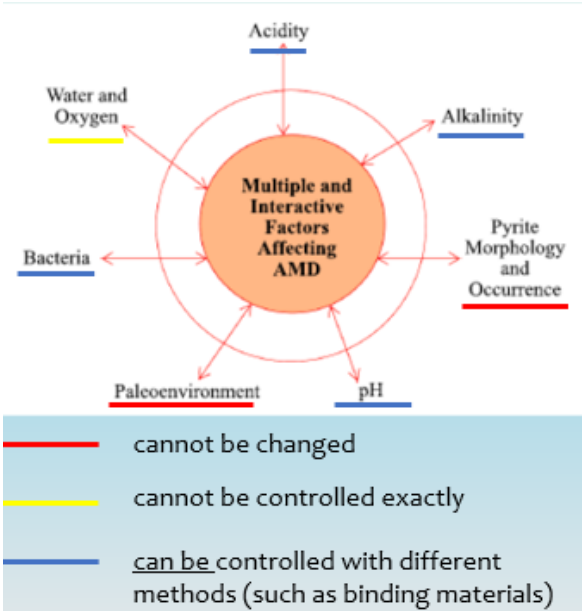


Figure 1.3 Factors affecting of AMD (adopted from Acharya & Kharel, 2020)

The higher permeability, which is one of the most important physical factors, of dumps, the more oxygen enters, and it occurs at a higher rate of chemical reactions, such as increasing temperature and oxygen input. *Acidithiobacillus ferrooxidans* which they have been mentioned mostly about oxidation of pyrite also may expedite to oxidation of sulfide minerals of antimony, gallium, molybdenum, arsenic, copper, cadmium, cobalt, nickel, lead and zinc. The most appropriate environmental conditions must be needed for the bacterium to participate in the oxidation of sulfide. For example, *A. ferrooxidans* is inactive when the pH of the ambient is more than 3.2. (Akcil & Koldas, 2006).

Kirby (2014) is classified AMD into five types according to pH:

"Type 1: pH < 4.5 with Fe, Al and Mn metals, and higher oxygen levels";

"Type 2: pH > 6.0 with higher levels of ferrous iron, Mn and dissolved solids";

"Type 3: alkaline, with low to moderate levels of Fe, Mn, and dissolved solids";

"Type 4: neutralized AMD (pH > 6.0), with high levels of suspended particles"; an

"Type 5: neutralized AMD with high levels of dissolved solids, and dissolved Ca and Mg (Acharya & Kharel, 2020). Type 1 is a basic model of AMD. As pH is lower in acidic waters, electrical conductivity (EC) generally increases because of leaching of metals that has arisen from the oxidation of pyrite and metal mobility eventuating at lower pH (Equeenuddin et al., 2010, Acharya & Kharel, 2020)".

A strong relationship has been found between pyrite morphology and AMD generation. Pyrite may be in different forms such as, framboidal, anhedral, or euhedral. One of them, Framboidal pyrites, produces more and more AMD as it breaks down. Non-framboidal iron disulfides have less activity, and they are not fast to decompose. They generate the lower capacity of acids (Caruccio et al., 1977). Fine-grained pyrites produce more acid when the compared coarse-grained pyrites (Acharya & Kharel, 2020).

The factors of Paleoenvironmental might be effect rock types and chemistry at a spatial scale. Brady et al. (2000) showed that stratigraphy and the amount of carbonates

at lateral spaces in open pit mining sites in Pennsylvania change rapidly owing to paleodeposition.

1.3.1 Bacterial Activity in the AMD Formation

The AMD generation begins generally with the initial phase of mining operations in sulfide-rich rocks and keeps going even if mining operations are terminated (abandoned) (Măicăneanu et al., 2013). AMD plays a part in the Sulfur cycle due to oxidation of sulfur in its structure. Sulfur occurs with three oxidation states of −2 (sulfide and reduced organic sulfur), 0 (elemental sulfur), and +6 (sulfate) with different pathways. Sulfur oxidizing bacteria catalyze H_2S to sulfur or sulfate with some reactions. If the environmental conditions are suitable, sulfate can be converted to sulfide by the Sulfate Reducing Bacteria (SRB). Figure 1.4 shows that redox reactions being via microorganisms in sulfur cycle (Bhandari & Choudhary, 2022).

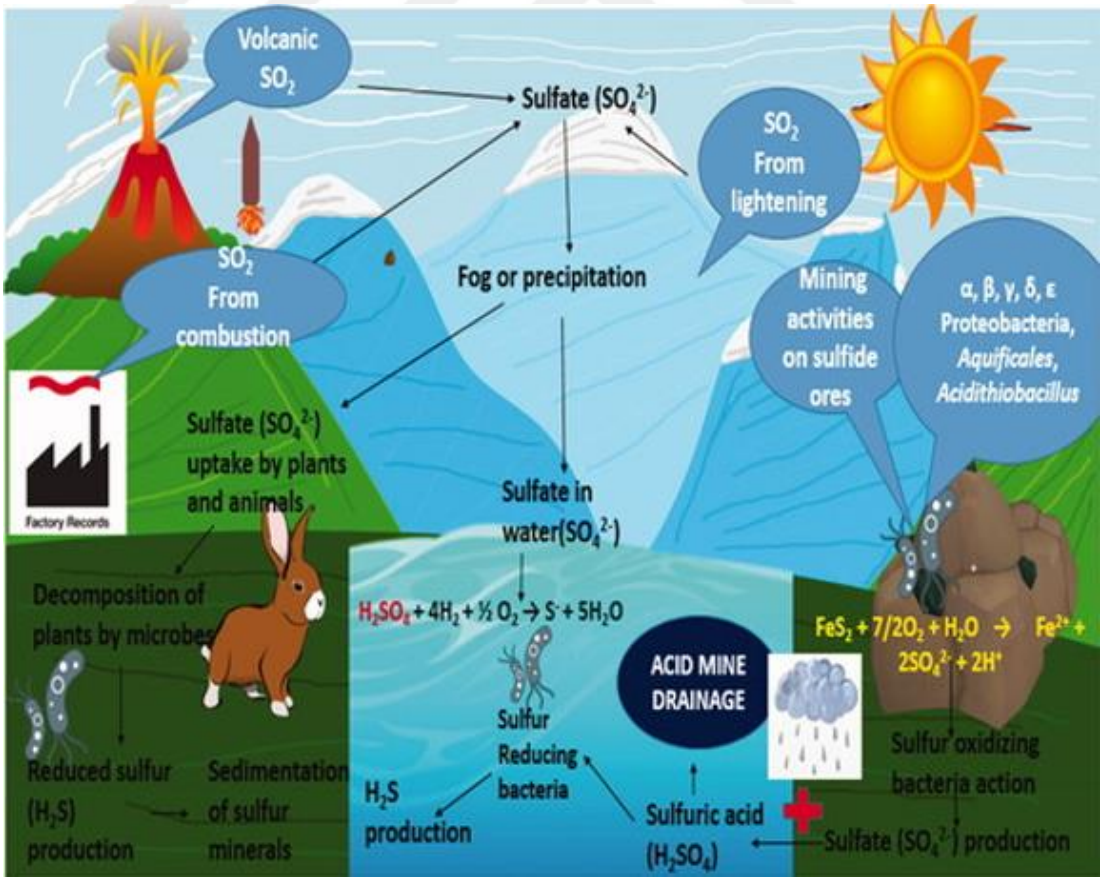


Figure 1.4 Sulfur cycle related with AMD (Bhandari & Choudhary, 2022).

Sulfur-oxidizing bacteria which dissolved to the sulfidic mineral leads to leaching of heavy metals like iron, nickel, lead, aluminum, copper, zinc, manganese, cadmium into the nature. (Johnson & Hallberg 2005; Kefeni et al., 2017). Acidophiles such as Acidithiobacillus are the most known oxidizing bacteria, having an important role in the dissolution of sulfide-containing minerals.

In publications before 2000, it is stated that AMD is a product formed by the atmospheric oxidation (by water and air) of pyrite and pyrrhotite (the most common sulfide minerals) in the presence of bacteria (*T. ferrooxidans*). Since the beginning of the 2000's, it was called *Acidothiobacillus ferrooxidans*. While the tests based on isolation from culture medium have been used to identify the iron-oxidizing bacteria, today, different species of iron oxidizing bacteria such as Legionella, Thiomanas, and Gallionella have been described by molecular phylogenetic techniques in addition to the originally identified *T. ferrooxidans* (Downing, 2014; Hao et al., 2010).

Pyrite is the mineral for which its mechanism is the best known and the production of AMD the most common (Tong et al., 2020). *T. ferrooxidans* and other iron-oxidizing bacteria is the oxidation of ferrous to ferric iron (Fe^{2+} to Fe^{3+}) (Eq 1.2). Fe^{+3} is an important oxidizing agent. When the ratio of Fe^{3+} /Fe^{2+} is 1:1,000,000, a redox potential greater than +0.4V is produced, which is quite enough for the dissolved of most base metal sulfides (Dutrizac & MacDonald, 1974).

Metal sulfide minerals (except pyrite) oxidize by interacting with oxygen, water, and microorganisms or dissolution of pyrite. But metals ions are released via oxidative decomposition (Kaur et al., 2018). It is shown in equation 1.6.

$$MS_x+(2x-0.5)H_2O+O_2 \xrightarrow{\text{Bacteria}} M^{+x}+ XSO_4^{-2}+2H^+ \quad (1.6)$$

Oxidation mechanism of metal sulfide minerals can be categorized in two groups: direct and indirect. In a direct mechanism, bacteria hold on to the mineral particle surfaces, and directly oxidize iron and sulfur. In this way, metal ions are released into the environment. In an indirect mechanism, bacteria in solution oxidize ferrous iron to

ferric iron and elemental sulfur to sulfate ions (Eq 1.7 and 1.8, respectively). Thereafter, the produced Fe^{+3} releases the sulfide mineral (Eq 1.9) (Simate & Ndlovu, 2014; Chen et al., 2021).

$$2Fe^{+2} + 0.5\ O_2 + 2H^+ \xrightarrow{\text{Bacteria}} 2\ Fe^{+3} + H_2O \quad (1.7)$$

$$S^0 + 1.5O_2 + H_2O \xrightarrow{\text{Bacteria}} SO_4^{-2} + 2H^+ \quad (1.8)$$

$$MS_x + Fe^{+3} \xrightarrow{\text{Chemical}} M^{+x} + XS^0 + Fe^{+2} \quad (1.9)$$

where *M* is a metal, and *X* is a whole number.

Some studies show that there is no direct action of microbial oxidation of metals sulfide minerals. Also, an indirect mechanism can be classified as a contact or non-contact action in itself. In contact action, microorganisms on the metal sulfide mineral's surface use extracellular polymer substances (EPS) to produce Fe^{+3}. In this manner, oxidizing of metal sulfide minerals consistently goes on. Microorganisms use incessantly Fe^{2+} as an electron donor and oxygen as an electron acceptor to catalyze of metal sulfide minerals in non-contact action (Rodríguez et al., 2003; Sand et al., 2001). In the presence of *Thiobacillus ferrooxidans*, the oxidation rate of metal sulfide minerals is 10^6 times faster according to chemical oxidation (So, it's called rate-determining step; in eq 1.2). (Xie et al., 2009).

1.4 Important AMD Accidents in Turkey and in the World

Although AMD may be handled at the mine to a limited extent, such as by neutralization at source using limestone, settling and tailings ponds, or wetlands, this method is never completely successful. Moreover, accidents are possible with the treatment technique. Moreover, accidents are possible with the treatment technique. Although all of the measures are taken by the site managers or other responsible person; a potential risk for environment is always present because of causes such as earthquake, soil instability, wrong management of the site water (improper hydrological conditions) and the possible damages in impermeable membrane, etc. So,

important AMD cases / accidents Turkey and in the world are given in this part of the study. Since 1960, 150 mining accidents have been recorded at the mine sites and these accidents are still being recorded (Wise Uranium Project, 2022). After the accidents, millions of cubic meters of mine waste containing heavy metals were released into the environment. These mine wastes have harmed numerous organisms by contaminating agricultural areas, basins, streams, and even the coastline. In fact, some accidents have resulted in human deaths, injuries, and missing persons. The accidents have caused millions of dollars in financial loss and damage. The environmental and financial repercussions of certain accidents continue to be felt today.

1.4.1 Important AMD Accidents in Turkey

On December 13, 2021, a waste storage facility belonging to a mine for iron ore in the Ayvalık area of the northwest province of Balıkesir collapsed. The company announced that concrete blocks had been placed around the garbage storage location to avoid a similar accident. As a result of the mine's collapse, heavy metals in the waste pile contaminated the stream water. The stream in issue served the region's irrigation requirements and supplied the Madra Dam, which was intended to supply Ayvalık with drinking water in the future (Kaya, 2022; Sputnik Türkiye, 2021; James, 2021).

On November 19, 2021, the cyanide waste storage ponds of a mining site in Şebinkarahisar, Giresun, where this is a lead-zinc enrichment plant collapsed during the second tailings dams restoration. According to the prepared report, a portion of the facility's waste dam No. 2 was demolished, and hundreds of tons of toxic heavy metals were dumped into dam No. 1 and then into the Darabul Stream; afterwards, they reached Kılıçkaya Dam. Also, it is reported that more than 4.500 tons of chemical waste is cleaned after being dispersed into the environment. The Ministry of Environment, Urbanization, and Climate Change said that the mine's operator had been fined the maximum amount of 12 million Turkish liras (836.000 USD) and had been forbidden from operating (NewsyList, 2021; Madencilik Türkiye, 2021; Cumhuriyet, 2021).

Another accident in Turkey occurred On March 25, 2022. The pipe leading to the wastewater pool of the nickel cobalt facility in the Gördes area of Manisa, which is claimed to use one thousand tons of sulfuric acid every day, burst. After the waste pipe burst and the wastewater mixed with the streams, the drinking water of Kalemoğlu village was cut off. It is unknown whether the hazardous tailings reach the Çiçekli Dam located near the area that both supplies water to the nickel mine and is also used for agricultural irrigation. The soil and water samples from where the wastewater was leaked were analyzed, and it was determined that the results were much greater than the standard values (Ekoloji Birliği, 2022; Bianet, 2022; Akdemir, 2022a; Akdemir, 2022b)

1.4.2 Important AMD Cases in the World

In April 1998, the breach of a tailings dam at a zinc mine in southern Spain triggered the greatest environmental pollution incident ever recorded in Spain (Grimalt et al., 1999; Galán et al., 2002; Gibert et al., 2011). The collapse of a tailing dam retaining wall caused the flow of about 4 million cubic meters of acid mine drainage and 2 million cubic meters of hazardous sludge containing heavy metals (Grimalt et al., 1999). A layer of sludge averaging 7 cm in thickness covered a total area of 4286 hectares (Kraus & Wiegand, 2006). Because of the fine particle size of the tailings (k_{80} < 45 μm), they were simply carried by flow wave in suspension. At the flow measuring station El Guijo, seven kilometers down the road from the tailings pond, the water level rose 3.6 meters within thirty minutes. Moreover, twelve hours later, the rise in water level at El Guigo was less than 0.2 meters (Eriksson et al., 2000). Large amounts of soil and sediment remained polluted despite the intensive cleaning procedures (building of barriers to contain the flood, removal of mud and dead animals, construction of a water treatment plant, etc.) taken immediately after the tragedy (Kraus & Wiegand, 2006; Simon et al., 2008). After 20 years, although there was a decrease in some metal concentrations (Al and Pb concentrations were increased while Cd, Cu, Fe, Mn, and Zn concentrations were decreased), it was observed that the spatial distributions in both 2002 and 2020 were the same. This means that the main source of pollution remains dam leakage (Santos et al., 2020).

One of the worst mining accidents in the world occurred on March 24, 1996, on the Philippine Island of Marinduque. A crack in the drainage tunnel of a big pit carrying mine tailings resulted in the release of hazardous mining waste into the Makulapnit-Boac river system at a rate of 5 -10 cubic meters per second, causing flash flooding along the river's beds. It was predicted that 1.6 million cubic meters of mining waste was discharged into the streams except for an unknown quantity of debris that reached the island's western coast within a few days following the spill (Cotter & Bridgen, 2006; David, 2002). Five villages, with a population of 4,400 people, were transferred to the other side of the Boac River because hazardous spills caused flash floods. One village, Barangay Hinapula, was flooded by mud water that was six feet deep, and 400 people had to move to higher ground. Their water supplies were polluted with dead fish, freshwater shrimp, and swine. Needed food, water, and medical supplies for the transferred people were delivered by helicopter. Twenty settlements, out of the province's total of sixty, were recommended to leave (Tauli-Corpuz, 2022).

The Kingston Fossil Plant retention pond collapsed on December 22, 2008 in eastern Tennessee, causing 4.1 million cubic meters of coal ash to flow 6 river kilometers upstream into the neighboring Emory and Clinch Rivers and 11 river kilometers downstream into the Watts Bar Reservoir. Approximately 2.3 million cubic meters of this material was dumped into the Emory River, flooding the navigation channel with up to 9 meters of fly ash and covering an area of approximately 120 hectares (300 acres) with fly ash. As a consequence of damage caused during the release, three houses were deemed unfit for residence. (U.S EPA, 2009; Ruhl et al., 2009; Stanley et al., 2013; Tennessee Valley Authority, 2009). All cleanup operations cost more than $1.1 billion and physically removed up to 90% of coal ash from the Emory River's most damaged areas (Flessner, 2015). The first coal ash leak resulted in no injuries or fatalities, but as a consequence of exposure to the poisonous coal ash, many workers of an engineering company hired by TVA to clean up the disaster acquired brain cancer, lung cancer, and leukemia, and by the tenth anniversary of the incident, more than 30 had perished (Rozhina et al., 2021).

The collapse of the Fundo tailings dam on November 5, 2015 is the biggest disaster of its kind in history and the worst environmental tragedy in Brazilian history (Almeida, 2016; Burritt & Christ, 2018) It happened due to the breakdown of the Fundo dam, a tailings dam for iron mining. On November 22, 2015, the breach discharged roughly 60 million m3 of waste into the headwaters of the Doce River basin, Brazil's fifth-largest watershed, (reaching the Gualaxo do Norte, do Carmo, and Doce rivers) that transported the muck 677 km down to the Atlantic Ocean (Segura et al., 2016). The amount of tailings led to a rapid rise in water turbidity, pollution of riverbed soils, loss of natural flora, including remnants of Atlantic Forest (a hotspot of biodiversity) and other locations legally listed as “permanent protection areas” (Vergilio et al., 2021; Omachi et al., 2018). In addition to environmental damages, the social consequences were severe, including the deaths of 19 people, contamination of the water supply, evacuation of the riverside population, restrictions on fishing activities and other water uses (such as irrigation), socioeconomic losses, and a sense of helplessness among the affected population (Hatje et al., 2017; Carmo et al., 2017; Vergilio et al., 2021).

The last known accident occurred in China on March 27, 2022. A dam was breached by a tailings pond belonging to Daoer Company in Wenquan Township. A section of the manufacturing area was submerged; a massive hole was created in the tailings pond, the dam body was flushed with a 70- to 80-meter gap, and mud build-up obstructed the local road. After preliminary inspection, the People's Government of Jiaokou County reported that a landslide occurred in a material storage yard of Daoer Company in the county, burying 7.5 m2 of arbor forest land, blocking more than 200 meters of seasonal ditches and rural roads, and washing away a portion of the surrounding walls of nearby companies. No victims were discovered. It is not yet known how much waste was released tailings after the accident (Petley, 2022).

The history of the major tailings dam disasters from 1960 to the present is shown in Table 1.3.

Table 1.3 The history of the major tailings dam disasters (2015-Present) (Wise Uranium Project, 2022)

Date	Location	Ore type	Type of Incident	Release	Impacts
2022, Mar. 27	Wenquan Township, Jiaokou County, Shanxi Province, China	bauxite	tailings dam failure	?	Part of the factory area was buried; a large pit was formed in the tailings pond, the dam body was flushed with a gap of about 70 to 80 meters, causing 7.5 mu [0.5 ha] of arbor forest land to be buried, more than 200 meters of seasonal ditches and rural roads were blocked, and part of the surrounding walls of adjacent enterprises were washed away.
2022, Jan. 20	Banjhiberana village, Thelkoloi area, Sambalpur district, Odisha (formerly Orissa), India	iron	breach of tailings pond wall holding iron slurry generated from beneficiation plant	?	at least 20-30 acres [8-12 hectares] of farmland were submerged under the iron ore slurry while two ponds were contaminated, causing a fish kill; a security guard is reported missing
2022, Jan. 8	Pau Branco mine, Nova Lima, Minas Gerais, Brazil	iron	After heavy rain, a slope failure involving three banks of the Cachoeirinha mine waste pile resulted in a release of mine waste into the Lisa water retention dam. The dam then overflowed on the whole length of the embankment, without compromising its stability.	?	The mud wave overflowing from the retention dam blocked the BR-040 highway. One person was injured.
2021, Dec. 24	Ulundi, KwaZulu-Natal, South Africa	anthracite coal	slurry dam failure	1,500 cubic metres of slurry, containing a variety of several toxic heavy metals and chemical compounds that include mercury, manganese, arsenic, copper and lead	the liquid coal waste poured into the Black Umfolozi and White Umfolozi River system, flowing through rural communities and the Hluhluwe-iMfolozi and iSimangaliso wildlife reserves, raising concern about the health of people, animals and the broader environment exposed to toxic and acidic wastes
2021, Nov. 26	San Antonio de María mine, Ananea, San Antonio de Putina province, Puno, Peru	gold	tailings dam (settling pond?) failure after heavy rain	?	the tailings wave destroyed approx. 400 meters of the national road that goes to the La Rinconada town center and spilled into three residential areas (Progreso, Central and Santiago)
2021, Nov. 18	Yedikardes village, Sebinkarahisar district of Giresun, Turkey	lead, zinc, copper	failure of tailings dam No.2	> 4,500 t	the tailings flowed into dam No. 1 and then into the Darabul Stream and reached Kiliçkaya Dam 5 km downstream (watch TEMA Foundation video on Youtube)
2021, July 27	Catoca mine, Saurimo, Lunda Sul, Angola	diamond	breach in spillway duct leads to massive spill of "rejected pulp"	?	Lova River polluted 100 km downstream; pollution of Tchicapa River rendered drinking water in the Muatova neighborhood in the city of Lucapa unsafe (view Sentinel Vision images)

Table 1.3 Continues

Date	Location	Ore type	Type of Incident	Release	Impacts
2020, July 2	Hpakant, Kachin state, Myanmar	jade	waste heap failure after heavy rain	?	a heap of mining waste collapsed into a lake, triggering a wave of mud and water that buried many workers; at least 126 people were killed
2020, May 1	San José de Los Manzanos, Canelas, Durango, Mexico	lead, zinc	tailings dam failure	6,000 m3	the tailings spilled on a nearby road and 8,000 m2 of land, reaching the San Bernabé stream after 5 km and the town of the same name
2020, Mar. 28	Tieli, Yichun City, Heilongjiang Province, China	molybdenum	No. 4 overflow well [decant tower?] of the tailings dam tilted, resulting in the release of supernatant water and tailings through a drainage tunnel, while the embankment itself remained intact	2.53 million m3	water and tailings flowed through surrounding area, reaching Yijimi river after 3 km, threatening the drinking water resource of 68,000 people in Tieli City; by Apr. 4, the pollution reached 208 km downstream
2019, Nov. 13	La Rinconada, Ananea, San Antonio de Putina province, Puno, Peru	gold	tailings dam failure	?	the tailings wave flowed over the Ananea-La Rinconada highway, killing one motorcyclist
2019, Oct. 1	Nossa Senhora do Livramento, Mato Grosso, Brazil	gold	tailings dam failure	?	tailings flowed 1-2 km, thereby disrupting a power line
2019, July 10	Cobriza mine, San Pedro de Coris district, Churcampa province, Huancavelica region, Peru	copper	tailings dam failure	67,488 m3 of tailings	tailings covered an area of 41,574 m2 and reached Mantaro River
2019, Apr. 22	Hpakant, Kachin state, Myanmar	jade	waste heap failure	?	3 workers killed, 54 workers are missing
2019, Apr. 9	Muri, Jharkhand, India	bauxite	failure of red mud tailings pond	?	spill of red mud over 35 acres and a nearby railway line, number of casualties still unclear
2019, Mar. 29	Machadinho d'Oeste, Oriente Novo, Rondônia, Brazil	tin	failure of inactive tailings dam after heavy rain	?	tailings spill damaged seven bridges, leaving 100 families isolated; no deaths or injuries reported
2019, Jan. 25	Córrego de Feijão mine, Brumadinho, Região Metropolitana de Belo Horizonte, Minas Gerais, Brazil	iron	failure of tailings dam No. 1	12 million m3	The tailings wave devastated the mine's loading station, its administrative area, and two smaller sediment retention basins (B4 and B4A); it then traveled approx. 7 km downhill until reaching Rio Paraopeba, thereby destroying a bridge of the mine's railway branch, and spreading to parts of the local community Vila Ferteco, near the town of Brumadinho; the slurry was then carried further by Rio Paraopeba; 259 people were killed, and 11 are reported missing.

Table 1.3 Continues

Date	Location	Ore type	Type of Incident	Release	Impacts
2018, June 4	Cieneguita mine, Urique, Chihuahua, Mexico	gold, silver	tailings dam failure	249,000 m3 of tailings and 190,000 m3 of embankment material	Dam failure results in tailings release travelling 29 km downstream; most of the tailings have been deposited along the course of the Cañitas River. The Federal Attorney's Office for Environmental Protection (PROFEPA) says that the tailings don't contain cyanide or any heavy metals. Three workers were killed, two wounded, and four are reported missing.
2018, Mar. 9	Cadia, New South Wales, Australia	gold, copper	tailings dam failure, mainly due to the existence of a low-density foundation layer in the vicinity of the slump.	1.33 million m3 of tailings	Embankment failure results in "limited breakthrough" of tailings material from the northern to the southern tailings dam. The breakthrough has been contained within the southern tailings dam.
2018, Mar. 3	Huancapatí (Huancapetí), Recuay province, Áncash region, Peru		collapse of embankment of tailings dam No. 2 after heavy rain	80,000 m3 of tailings	the incident has contaminated crops, the Sipchoc creek and the Santa river
2018, Feb. 17	Barcarena, Pará, Brazil	bauxite	overflow of red mud basin after heavy rain [the company, however, maintains that no overflow has occured at all!]	?	Highly alkaline and metal-laden liquids flooded the surrounding residential areas, rendering the drinking water supply in the area unusable.
2017, Sep. 17	Kokoya Gold Mine, Bong County, Liberia	gold	rupture of a section of the geo-membrane layer / overflow after heavy rain (?)	discharge of 11,500 m3 of slurry containing cyanide into Sien Creek, a major water source for residents in Saywehta Town	30 people became ill as a result of pollution of the creek due to the chemical spill, but this cause for the illnesses reported was later disputed

Table 1.3 Continues

2017, June 30	Mishor Rotem, Israel	phosphate	phosphogypsum dam failure	100,000 m3 of acidic waste water	The toxic wastewater surged through the dry Ashalim riverbed and left a wake of ecological destruction more than 20 km long
2017, Mar. 12	Tonglvshan Mine, Hubei province, China	copper, gold, silver, iron	a partial dam failure occurred at the northwestern corner of the tailings pond, opening a crevasse (gap) of approx. 200 metres	approx. 200,000 m3 of tailings	The tailings flooded the fish pond downstream of approx. 27 hectares. Two persons were reported dead and one was reported missing.
2016, Dec. 28	Satemu, Hpakant, Kachin state, Myanmar	jade	waste heap failure	?	approx. 50 workers missing
2016, Oct. 27	Antamok mine (inactive), Itogon, Benguet province, Philippines	gold	tailings flow through drain tunnel of underground mine after heavy rains	at least 50,000 t of tailings (an amount considered "negligible" by the company)	The leaked tailings flowed into Liang River, then Ambalanga river before reaching Agno river.
2016, Aug. 27	New Wales plant, Mulberry, Polk County, Florida, USA	phosphate	a 14 metre-wide sinkhole appeared in a phosphogypsum stack, opening a pathway for contamined liquid into the underground; the liquid reached the Floridan Aquifer, a major drinking water resource	840,000 m3 of contaminated liquid released (as of Sep. 17, 2016)	

Date	Location	Ore type	Type of Incident	Release	Impacts
2016, Aug. 8	Dahegou Village, Luoyang, Henan province, China	bauxite	failure of a tailings dam holding about 2 million cubic metres of red mud	?	village totally submerged in red mud, around 300 villagers evacuated, many farm and domestic animals killed
2016, Aug. 4	Ujina, Pica, Tamarugal Province, Tarapacá Region, Chile	copper, molybdenum	breakage in a tailings transport chute, allegedly caused by an earthquake that occurred in the area	4,500 cubic metres of tailings	the spilled toxic material ran into an ancestral grazing area, threatening four specimens of Vicuña, a protected camelid species, and the groundwater
2016, May 22	Ridder, Kazakhstan	zinc	failure of former "water discharge collector system" (decant tower?) at the Talovsky Tailings Dam	?	tailings slurry containing cyanide, zinc, lead, copper and manganese was discharged into the Filippovka River, later reaching Tikhaya River and Ulba River, and was to reach the Siberian city of Omsk 1,100 km downstream around June 2
2015, Dec. 14	Lamaungkone, Hpakant, Kachin state, Myanmar	jade	waste heap failure	?	1 worker killed, approx. 20 others missing
2015, Nov. 21	San Kat Kuu, Hpakant, Kachin state, Myanmar	jade	waste heap failure	?	at least 113 people killed
2015, Nov. 5	Germano mine, Bento Rodrigues, distrito de Mariana, Região Central, Minas Gerais, Brazil	iron	failure of the Fundão tailings dam due to insufficient drainage, leading to liquefaction of the tailings sands shortly after a small earthquake.	32 million m3	slurry wave flooded town of Bento Rodrigues, destroying 158 homes, at least 17 persons killed and 2 reported missing; slurry pollutes North Gualaxo River, Carmel River and Rio Doce over 663 km, destroying 15 square kilometers of land along the rivers and cutting residents off from potable water supply; the damage is at least US$ 6.7 billion

1.5 The Control of AMD and Treatment Methods

The acidity level, metal composition, and concentration of a specific AMD source are determined by the kind and amount of sulfide (acid-producing) and carbonate (acid-neutralizing) minerals present in the rock formations (Skousen, 2017; Skousen, 2019; Perry & Brady, 1995). Whether or not there is enough neutralization potential or base to neutralize the acid made by sulfide oxidation depends on how much carbonate is in the overburden. There are many kinds of substances in rocks that can neutralize acid, but only carbonates and some clays are found in enough amounts to neutralize acid-producing rocks. The balance between the acid production potential and acid neutralizing capacity indicates acidity or alkalinity that could come from total weathering (Skousen et al., 1998).

Three aspects are critical for comprehending AMD control prior to interfering on the land: 1) characteristics geochemically of mining debris or overburden (characterization of mine waste) 2) during operation and reclamation, the technique and accuracy with which overburden is handled and placed in the backfill or garbage pile 3) the field's hydrology after mining operations (Skousen, 2019; Sobek et al., 2000). To understand these factors, the tests mentioned above must be done before starting mining activities.

After determining the acid generation potential, the most appropriate treatment method is chosen for the area. AMD treatment techniques can be separated active and passive (Johnson & Hallbeg, 2005; Skousen et al. 2005). Also, Johnson & Hallberg (2005) have categorized the treatment technologies biological (based on biological activities) and abiotic (non-biological activities). Both treatment procedures attempt to reduce acidity, heavy metal concentrations, salinity, and sulfate, while increasing pH. (Taylor et al., 2005). Usually, passive treatment is chosen for abandoned and closed land while active treatment is used on mining sites that are still in operation. Some equipment (e.g., pumps, mixers) and chemicals are required for active treatment systems. Although it requires maintenance and power, it is preferable over passive therapy because to its more dependable outcomes. The primary benefits of active

treatment are effective contamination removal, precise process control, and suitability for small lands. The primary drawbacks of active treatment are the high expenses of investment, operation, and maintenance. Passive systems are based on biological, physical, and geochemical phenomena that occur spontaneously. It must be done extremely carefully since passive treatment approaches may fail if they are not selected appropriately. It is configured utilizing a neutralizing substance to ensure that it has a 25-year life without requiring any further inputs. In the majority of passive treatment methods, the neutralizing substance is dissolved and subsequently used to neutralize the acidity in AMD. Passive systems need large areas since neutralizing activities require residence time. As a consequence, it is more appropriate and cost effective for closed mine areas or complex and dynamic systems. (Skousen et al., 2000; Costello, 2003; Favas et al., 2016; Taylor et al., 2005; Trumm, 2010). Open limestone channels, anoxic limestone drains, dispersed alkaline substrate, aerobic wetlands, anaerobic "wetlands"/compost reactors, successive alkalinity-producing systems, permeable reactive barriers, and packed-bed iron-oxidation bioreactors are all examples of passive treatment. (Skousen et al., 2017; Favas et al., 2018). Active systems include neutralization with alkaline chemicals (adding caustic soda, lime, magnesium sulfate, e.g.), aeration, ion-exchange, adsorption, bio-sorption, etc. (Johnson & Hallberg, 2005; Favas et al., 2018; Masindi, 2017).

Passive treatment techniques are in-situ systems, such as wetlands and bioreactors, that may be naturally managed at their source (Sephton & Webb, 2017; García -Valero et al., 2020). The most often employed alkali materials in AMD neutralization and remediation are lime, sodium hydroxide, and limestone. However, these materials generate far too much sludge and are prohibitively expensive. Therefore, alternative materials should be sought and selected (cheap, readily available, and, if feasible, waste materials) (Gitari et al, 2018).

1.6 The Measurement Methods and Technics of AMD

Prediction of acid mine drainage (AMD) is crucial for predicting and preventing environmental damage caused by mining operations. Also, it is important governments

and state authorities are progressively implementing new rules and legislation to control mining waste management.

But, the prediction of AMD is difficult, expensive, and of uncertain reliability due to the fact that mineralogy and other elements impacting the production of AMD are quite varying from site to site (US EPA, 1994).

The goals of predictive testing are to (1) establish if a discrete amount of mining waste will produce acid and (2) estimate the drainage quality based on the recorded rate of acid generation. (California Mining Association, 1991; Geidel et al. 2000; Brady et al. 1994; Gautama & Hartaji 2004). Two crucial factors must be taken into consideration when assessing the acid production capability of a rock material: The first is how to collect samples for analytical testing in the field. The second consideration is which analytical test technique should be used. After selecting the sample technique, a suitable analytical technique (or methods) may be chosen (US EPA, 1994). To predict the behavior of a rock sample concerning AMD production, primarily two kinds of testing are used: Static and Kinetic tests. The static test evaluates both the total acid producing potential and the total acid neutralizing potential of a sample, while acid drainage is estimated as either the difference between the results or a ratio of the values. In contrast to kinetic testing, static tests may be performed rapidly and economically. The static test can only evaluate the possibility of acid drainage, but the kinetic test can determine the rate of acid production. Typically, kinetic tests model the processes happening at mining sites at a sped-up level. These tests are substantially more time-consuming and costly than static testing. The results of these tests are used to assess the acid-generating capacity of materials and also, they use to assess the economic study of mines in the exploration phase (Sobek et al., 1978; Brodie et al., 1991; Banerjee, 2014; Parbhakar et al., 2017; Duncan & Bruyensteyn, 1979; Lawrence et al., 1989; Lawrence & Scheske, 1997).

Table 1.4 presents some of the factors that influence the drainage features of waste management plants. The observed factors may be applicable for the other units, such as mining pits and underground workings.

Table 1.4 Sources on the potential for acid production in new and operating mines (US EPA, 1994)

Information Type	New Mine	Operating Mine
Mine Rock Classification	• Outcrop exposures • Exploration drill samples, logs • Geological sections • Core assays	• Outcrop and excavation exposures • Drill core • Production sampling • Core assays • Specific sampling from working areas and piles
Mine Rock Distribution	Mine planning	• Mine planning • Mine rock placement records • Pit and underground plans and exposures • Pile surveys • Pile drilling and sampling • Site personnel
Acid Generation, Leaching Potential	• Static testing • Short term leach extractions • Mineralogy • Site comparisons	• Observation of old cores • Field sampling • Static testing of distinct sub-units from working areas
Drainage Water Quality	• Kinetic testing • Background water quality	• Regular monitoring • Seep surveys • Kinetic testing • Leach extraction

To estimate the acid production potential, the following steps listed below (California Mining Association 1991, British Columbia AMD Task Force, 1989):

1. ‘Define in detail the geology and mineralogy of the mining area.
2. Design a sample strategy based on geological information (rock mass, etc.). Sampling to reflect compositional variation ranges within a rock unit.
3. Choose static or kinetic tests and assess acid formation potential.
4. Assess sample criteria and, if necessary, perform further kinetic tests.
5. Create a model as suitable.
6. Categorize geologic (lithologic) units as acid, non-acid forming, or unknown based on the results.’

1.6.1 Static Tests

Static tests are the laboratory testing of geological materials for chemical features such as total metal levels, pH, or total S by a study of rock or soil material's bulk concentrations. Static tests began to be used in the metal mining industry in the late 1970s, despite having been first designed for the coal mining industry. Sobek et al. (1978) produced a commonly used version of the static test, and additional modifications (Schafer & Associates, 1987) exist. The goals of the static test are to determine the sulfur content of a rock or soil sample and to calculate how much acid will be necessary to neutralize the sample. It can't be obtained time of any acid production with the results of the static tests, if at all, acid production, neutralization kinetics, or effluent water quality. Static tests are particularly useful when the acid production behavior of a mining waste is understood or confirmed by other experiments (Jennings & Jacobs, 2014).

1.6.1.1 Acid-Base Accounting Test (ABA)

The acid production (AP): It is calculated by multiplying the percentage of total sulfur or sulfide sulfur (depending on the test) in the sample by a conversion factor (Eq 1.10):

$$AP = 31.25 * \%S \tag{1.10}$$

According to formula, it is anticipated that each mole of sulfur will generate two moles of acid. AP unit is tons of acidity per ton of rock.

Neutralization potential (NP): It is detected with the amount of carbonate available to neutralize acid. Firstly, it is evaluated by a simple fizz test to determine the acid concentration to be used in the next phase. According to this information, sodium hydroxide is used to back-titrate the resultant solution to pH 7 in order to measure how much acid was used in the reaction between HCl and the sample. (Ferguson & Morin 1991, Lapakko, 1993). Laboratory tests for NP without accompanying mineralogical

characterization may often result in an overestimation of NP due to its inherent limitations for this method (Lawrence and Scheske, 1997; Paktunc, 1999).

Net neutralizing potential (NNP): It is the difference between the neutralizing and acid generating potentials. It is calculated by subtracting the acid formation potential from the neutralizing potential (Eq 1.11).

$$NNP = NP - AP \tag{1.11}$$

NNP levels below 20 (kg $CaCO_3$/ton) are most likely to cause in acid. Those with NNP levels over 20 were unlikely to produce acid. For NNP levels between -20 and 20, the acid production potential was difficult to estimate.

Balci & Demirel (2018) studied to predict AMD formation potential in the biggest and most important copper reserves in Turkey. They were used to acid-base accounting test (ABA), net acid generation (NAG) tests, leaching test, and detailed mineralogical research for the determination of AMD. ABA, NAG and long-term paste pH tests revealed that pH was less than 4 in ore wastes and ore-rich samples. The correlation between net neutralization potential and acid generating potential found that waste rocks with a low sulfur concentration were generally low potential sources of acid mine drainage (AMD). Concentrations of Fe, Cu, Zn, Ni, Pb, Cd, Co and As determined with leaching test were higher because of releasing from the rich waste in pyrite. These results were compatible with the static test (ABA and NAG). Ore-rich waste was the primary source of AMD and metal pollution in the area.

The formation of AMD was investigated by using static tests in Mutki Cu-Fe-Cr deposit (Bitlis, in Turkey) by Gücer et al., 2020 (Gücer et al., 2020). The tests were applied in the investigation were short-term contact leaching, ABA, and geochemical analyses. Short-term contact leaching tests showed that sulfide and oxide mineralization were related the high enrichment in toxic element concentrations (particularly such as Cr, Cu, Mn, and Zn) in ore-bearing samples. Net neutralization potential (NNP) and net potential ratio (NPR) values in ore samples were below –20

kg $CaCO_3$/t and 1, respectively. Leaching tests, paste pH (3.42–4.46), and sulfide-sulfur (3.9–13.4 wt%) (S content must be more than 3 for AMD generation) readings all indicated that the mineralization region had the potential to produce AMD.

The purpose of the investigation realized by Karagüzel et al. (2020) was to determinate the potential of AMD formation where it was in the lignite stripping material and open pit operating activities. AGP and NP was detected 12 kg $CaCO_3$ t^{-1} and 240 kg $CaCO_3$ t^{-1}, respectively. Also, the NP/AGP ratio was greater than 3. According to all of the results, investigators found that AMD formation will not come true in the short or medium duration.

1.6.1.2 Modified Acid Base Accounting

Unlike the ABA test, the result is obtained by using sulfide sulfur (Lawrence, 1990). In this test, NP is determined via a prolonged (24-hour) acid digestion at the room temperature (in ABA test, hydrochloric acid was boiled). When back titrating with sodium hydroxide to assess the acid used during digestion, 8.3 is utilized as the endpoint rather than 7.

If jarosite or other acid-producing sulfate minerals are available, this revised procedure may underestimate potential APP since it assumes sulfur present as sulfate is not acid-producing. For this reason, many prediction methods to detect AMD generation potential have been developed.

Pope et al. (2010) realized that the ABA test had some problems, such as the fact that the oxidation methods used to dissolve pyrite in the ABA test can react with organic material, which can lead to a false-positive study. Other assumptions in ABA test, such as the use of total S content to determine pyrite-related acidity, was incorrect for certain samples due to the presence of other types of S. They assumed that all of the measured sulfur exists as pyrite, that all pyrite was completely oxidized, and that the products were hydrolyzed to produce acid, $Fe(OH)_3$. During pyrite oxidation, two

moles of S in FeS_2 generate two moles of H_2SO_4, hence the S content (w%) could be used to determine acid produced (kgH_2SO_4/t) as follows (Eq 1.12) :

$$\text{Acidity generated (kg } H_2SO_4\text{ /t)} = \frac{S\ w\% * 10 * 2\ (moles H_2SO_4\ ) * 98{,}07\ (\frac{g}{mol})}{2\ (moles\ S) * 32{,}06\ (\frac{g}{mol})} = \text{S w\% * 30,06} \quad (1.12)$$

They used to a conversion factor of 30.06 to calculate acid generation in kg H_2SO_4/t from the S content in weight %. the results showed that there are a number of attempts that prevent the interpretation of these data. Because there is organic matter in coal measurement sequences, NAG pH and acid production potential of NAG could give wrong readings for acid generation (as in the example of Brunner coal). Additionally, this interference could be a certain NAPP-negative in Paparoa Coal Measures samples to have an incorrectly low NAG pH and the acid production potential could be overestimate since a part of the sulfur in these rocks did not exist as pyrite in Gore Lignite sample.

1.6.1.3 British Columbia Research Initial Test (BC)

The test that was developed by Duncan and Bruynesteyn (1979) is similar to the ABA test in terms of calculating APP based on total sulfur. To figure out NP, 1.0 normal sulfuric acid is added to the sample until the pH is 3.5. Coastech (1989) emphasizes that this method needs more complex equipment (i.e., an automated titrator) and more time than the ABA method. The samples are crushed to under 400 mesh. If it is found that a sample has the ability to generate acid, the B.C. Confirmation kinetic test may be performed.

1.6.1.4 Alkaline Production Potential: Sulfur Ratio (APP:S)

Caruccio et al. (1981) was developed the Sulfur ratio test and Coastech (1989) was modified the test. The APP:S test, like the ABA and B.C. beginning tests, employs total sulfur to estimate the total acid potential. Alkaline Production Potential is the same meaning with the acid consuming potential (NP in the previous tests). The value

is calculated by grinding a 500 mg sample to minus 23 micron, adding 20 mL of 0.1N HCl, and leaving the mixture to react at room temperature for two hours. The sample and solution are then titrated to a pH of 5 to assess the potential for alkaline production.

The alkaline production potential test results are presented with the total sulfur content test findings for the same samples. Several APP:S ratio samples are chosen for kinetic testing to identify which will produce acid. In this way, the acid generating potential of future samples from the different geologic units may be estimated based on the APP:S ratio without using kinetic tests. Like the other static tests, potential acid production may be overestimated by containing sulfate minerals.

Zumarán Farfán et al. (2004), were detected the potential of AMD generation by using Modified Acid-Base Accounting (MABA) and the Alkaline Potential Production/Sulfur Ratio (APP/S Ratio). Also, samples from a Brazilian coal mine were pre-evaluated using the MEND program (The program estimated AMD production potential) with daily monitoring of static methods. The following Total S and Pyritic S values were determined the sulfur content of the samples (RG and RF): RG = 5.91 and 4.450 % ; RF = 1.67 and 0.57 %, respectively. A mineralogical analysis using X-Ray Diffraction and Scanning Electron Microscopy revealed that the samples contain a larger quantity of acid generating sulfide minerals (pyrite) and very insignificant levels of acid consuming minerals. The final Net Neutralization Potential (Net NP) values obtained with the MBAB were RG = -147.2508 and RF = -47.2600 (t $CaCO_3$ eq/1000 t of material). The resulting Neutralization Potential Ratio (NPR) was RG = 0,0364 and RF = -0,0975. Considering the PPA/S Ratio, the following values for the Alkaline Potential Production (APP) were determined: RG = -11.3821, while RF = -15.0432 (mg eq $CaCO_3$/500 g of sample). The assessment of these values suggested that all tested materials had the ability to generate acid mine drainage.

1.6.1.5 Net Acid Production Test

Hydrogen peroxide is used to hasten the oxidation of sulfide in the Net Acid Production Test (Lawrence et al., 1988). In order to oxidize the metal sulfide minerals,

five grams of material are oxidized with 100 mL of 15 percent hydrogen peroxide. The reaction generates acid, which interacts with the sample's buffering minerals. After all observable indicators of reaction have ceased, the reaction is permitted to continue for one hour. The pH of the solution is measured and then adjusted to 7 via titration. This provides a number for the sample's Net acid or neutralizing potential.

This test differs from the above-described static tests in that it simulates the reaction of APP and NP and calculates a single result, NNP. This test has a potential limitation. If the level of oxidation in the field is larger compared to the test, acid generation may be underestimated by the test. It provides the potential for certain acid-producing trash to be misclassified as non-acid-producing.

Table 1.5 Summary of static test methods advantages, disadvantages, and costs (Lapakko, 1993)

Acid Base Accounting (Sobek et al, 1978)	MODIFIED Acid Base Accounting (Coastech, 1989)	BC RESEARCH INITIAL (Duncan and Bruynesteyn, 1979)	Alkaline Production Potential: Sulfur (Caruccio et al, 1981)	Net Acid Production (Coastech 1989)
ACID PRODUCTION DETERMINATION				
Acid Producing Potential = 31.25 * Total S	Acid Producing Potential = 31.25 * Total S	Total Acid Production = 31.25 * Total S	Total S used as indicator	300 mL H_2O_2 added to 5 g rock to directly oxidize sulfides present
NEUTRALIZATION POTENTIAL DETERMINATION				
-60 mesh (0.24 mm) Sample add HCl as indicated by fizz test, boil one minute than cool titration endpoint pH 7.0 cost: 34-110	-60 mesh (0.24 mm) Sample add HCl as indicated by fizz test agitate for 23 hours at room temperature pH 1.4 - 2.0 required after six hours agitation titration endpoint pH 8.3 cost: 34-110	-300 mesh (0.038 mm) Sample titrate sample to pH 3.4 with 1.0 N H_2SO_4 titration endpoint not applicable cost: 65-170	-0.023 mm sample 20 mL 0.1 N HCl to 0.4g solid for 2 hours at room temperature titration endpoint pH 4.0 cost: 34-110	particle size not presented acid produced by iron sulfide oxidization dissolves buffering minerals titration endpoint pH 7.0 cost: 25-68
ADVANTAGES AND DISADVANTAGES				
simple and short time1,3 no special equipment and easy interpretation[1] many samples can be tested[3]	simple, short time, no special equipment, and easy interpretation[1]	simple and fairly short time[1,3] no special equipment and easy interpretation1 many samples can be tested[3]	simple, short time, and no special equipment[1]	simple, short time, no special equipment, and easy interpretation[1]
does not relate to kinetic[2]assumes parallel acid/ alkaline release[2,3] if APP and NP are close, hard to interpret and different particle size not reflected[3]	does not relate to kinetic[2] assumes parallel acid/ alkaline release[2,3] if AP and NP are close, hard to interpret and different particle size not reflected[3]	assumes parallel acid/ alkaline release, different particle size not reflected, and if APP and NP are close, hard to interpret[3]	moderate interpretation	limited reproducibility[4] uncertain if extent of sulfide oxidation simulates that in field

1 = Coastech 1989, as referenced in Lapakko 1993
2 = Bradham and Caruccio 1990, as referenced in Lapakko 1993
3 = Ferguson 1984, as referenced in Lapakko 1993
4 = Lawrence 1991, as referenced in Lapakko 1993

1.6.2 Kinetic Tests

Kinetic tests differ from static tests in that they aim to simulate the natural oxidation processes that occur in the field. Kinetic testing has been established as a laboratory technique to better estimate the potential of acid drainage from rocks, sediments, and soils that are capable of producing acid (Downing, 2014). These tests use a larger sample amount and require much more time to complete than static tests. They reveal the rate of sulfide mineral oxidation and, therefore, acid generation, as well as the drainage water quality.

Kinetic test is used to evaluate the influence of various factors on the acid-generating capacity. (e. g., inoculating with bacteria, change the temperature). The sample particle size in these tests must be less than a specified sieve size (e.g., minus 200 mesh).

It is advantageous to supplement kinetic testing with an awareness of empirical data describing the sample. Examples include surface area analysis, mineralogy, and metals. Such information may influence the interpretation of test results and is crucial for conducting geographical and temporal comparisons between samples based on test data.

All of the kinetic test protocols include the following components (Downing, 2014):

- Samples subjected to periodic leaching
- Drainage sample collection for analysis
- Calculation of acid production and neutralization
- Calculation of acid production and neutralization
- Calculation of metal release rates
- Estimating of water quality

Two factors are crucial when utilizing kinetic tests: 1) If the sample was permitted to react before to testing (e.g., during storage), oxidation products may have formed-

This would be removed in the initial water rinses. 2) If the test duration is insufficient, neutral drainage may result in an inaccurate acid potential prediction.

1.6.2.1 Humidity Cell Tests

Standard and Modified Humidity Cell Tests that developed by Sobek (1978) are used to assess the acid production rate. Tests are done in a chamber simulating a box with ports for air intake and outflow. The modified humidity cell consists of samples that have been crushed and resembles a column. No standard exists for either humidity cell test.

Based on the sample, it may be necessary to prolong the time of the test. Monitoring sulfate and dissolved metal concentrations is essential for tracking both the oxidation process and metal mobility.

Sapsfort et al. (2009) were studied to determine AMD potential of a waste mine sample in Avoca, County Wicklow, Ireland. The results reported in this work showed that sulfide oxidation rates were sensitive to the particular characteristics of the weathering environment and could vary by an order of magnitude within humidity cell tests and across tests of the same material and also, they said that protocol modifications could vary the sulfide oxidation rate by an order of magnitude in some situations. It was suggested that the operation of humidity cells (and related tests) and the use of the resulting data should only occur after a thorough assessment of the project-specific data needs.

Maest & Nordstrom (2017) investigated by using a modified humidity cell test (HCT) the production of acid mine drainage in three projects that they had different geology and mineralization. HCT results revealed that fast sulfide oxidation predominates between 40 and 200 weeks of testing. Also, early flush releases and rapid sulfide oxidation rates in HCTs showed that it could be related with the field conditions. But it was inadequate to estimate the formation of AMD with leachate concentrations, loads, or rates of reaction from the laboratory test results.

1.6.2.2 Soxhelet Extraction Tests

This test mimics geochemical weathering by recirculating fluid through a sample using a soxhelet extraction equipment. In the unit, the sample is put in a thimble, and the solution is cycled from a reservoir. The standard test by Singleton & Lavkulich (1978) and the modified test by Sobek et al. (1978) were described. In the standard test, the sample is leached for six weeks using a 70 °C solution of acetic acid or distilled water (The time of the procedure can be variable. The modified test uses only distilled water at 25°C.

The settings of Soxhelet extraction tests are stricter than those of other kinetic experiments. However, it is a quicker test and may be beneficial for mimicking long-term patterns in weathering in a very brief test period. The disadvantages of the test include the need for costly equipment and the overall difficulty of the test.

It was studied the effect of using phosphate on Fe immobilization to prevent the formation of acid mine drainage by Spotts & Dollhopf (1992). Using the Soxhlet humidity cell leaching method, the ability of four different phosphate compounds to stop acid formation from pyritic coal overburden was tested. Two apatite ores (Comineo ore and Texas Gulf ore) were applied at a rate of 30 kg/t apatite [$Ca_5(PO_4)_3OH$], and two phosphate industry wastes (Cominco waste and Stauffer sludge) were applied at rates of 10, 30, and 50 g/t apatite by weight. According to leachate data, when apatite phosphate materials were added to acid-producing coal overburden, cumulative levels of Fe, acidity, and SO_4 were lower than when the control was used. All of the reductions were statistically significant at the 95% confidence level, except for those reached for Fe by samples treated with Cominco ore at a rate of 30 g kg^{-1} apatite application.

Table 1.6 Summary of some kinetic test methods, advantages, disadvantages, and costs (Lapakko, 1993)

HUMIDITY CELLS (Sobek et al., 1978)	SOXHELET EXTRACTION (Singleton and Lavkulich, 1978; Sullivan And Sobek, 1982)	COLUMN TESTS (Bruynesteyn and Hackl, 1982; Hood and Oertel, 1984)
SUMMARY OF TEST METHOD		
-2.38 mm particle size 200g of rock exposed to three days dry air, three days humidified air, and rinsed with 200 ml on day seven Cost: 425-850	Particle size not presented T=70°c (Singleton and Lavkulich, 1978) T=25°c (Sullivan and Sobek, 1982) water passed through sample is distilled and recycled through sample Cost: 212-425	Variable particle size Columns containing mine waste are leached with discrete volumes or recirculating solutions Cost: dependent upon scale
ADVANTAGES		
Models ap and np well and Models wet/dry[3] Approximates field conditions and Rate of acidity per unit of sample	Simple, Results in short time, and Assessment of interaction between AP and NP[3]	Models ap and np, Models effect of different rock types, Models wet/dry, and Models different grain size[3]
DISADVANTAGES		
Moderate to use, Results take long time, and Some special equipment Moderate ease of interpretation[1,3] Large data set generated	Moderate to use and Need special equipment[1] Moderate interpretation[1,3] In developmental stage and Relationship to natural processes not clear[3]	Difficult interpretation, Not practical for large number of sampled[3] Large volume of sample[2] Lots of data generated, Long time, and Potential problems: uneven leachate Application, channelization[2,3]
BC RESEARCH CONFIRMATION (Duncan and Waiden, 1975)	**BATCH REACTOR (Haibert et al., 1983)**	**FIELD TESTS (lidgerand Lapakko, 1985)**
SUMMARY OF TEST METHOD		
400 mesh particle size 15-30g added to bacterially active solution at ph2.2 to 2.5, t=3fpc If pH increases, sample is non-acid producer; If pH decreases, 1/2 original sample mass is added in each of two increments Cost: 170-340	200 mesh particle size Sample/water slurry is agitated 200g/500 ml[1] Cost: 425-850	Field scale particles 800 to 1300 metric ton test piles constructed on liners flow and water quality data collected tests began in 1977 and are ongoing Cost: initial construction is expensive, subsequent costs are comparable
ADVANTAGES		
Simple to use, Low cost, Assesses potential for biological leaching	Able to examine many samples simultaneously and relatively simple equipment	Uses actual mine waste under environmental conditions can be used to determine drainage volume mitigation methods can be tested
DISADVANTAGES		
Moderate to use, Longer time needed, And some special equipment needed difficult interpretation if pH change is small, Does not model initial ap step, and long time for pH to stabilize[3]	Subject to large sampling errors and lack of precision[4]	Expensive initial construction long time

1 = Coastech 1989, as referenced in Lapakko 1993
2 = Bradham and Caruccio 1990, as referenced in Lapakko 1993
3 = Ferguson 1985, as referenced in Lapakko 1993
4= Babij et al. 1980, as referenced in Lapakko 1993

1.6.2.3 Column Tests

For column tests, waste or material is placed in a cylinder or similar apparatus. The wetting and drying cycles are produced by introducing water to the column and then permitting it to dry. Each cycle might continue anywhere from a few days to a week or more, but the average duration is three days. When packing the column, care must be given to prevent piping at the sample-wall contact. The additional water is collected and examined in order to ascertain the present oxidation rate, metal release, sulfate formation, and other characteristics.

Column test equipment, such as humidity cells, is a very basic item of equipment. It may be readily adjusted to evaluate other control options, such as the addition of limestone, the impact of bacteria, and water saturation (Humphreys, 1990). According to the findings of the study, column tests of well-sorted tailings material larger than 0.5 centimeters in diameter properly match field test situations (Bradham & Caruccio, 1990). There were no reports of waste rock material tests. As discussed before, the drawbacks with column-type testing are that it takes a long time, costs a lot, and can lead to channeling.

A sample of paddy soil contaminated with AMD, which is often used in irrigation, was run by using the column test to observe the effects of AMD generation by Pan et al. (2021). In column test, the influence of continuous AMD flooding on pH, redox potential Eh, and the movement of Cu and Cd in contaminated paddy soil was examined to assess the degree to which AMD affects contaminant levels in such procedures. Over a period of 60 days, the dynamic variations of Cu and Cd concentrations in pore water were monitored using simulated AMD, and the regulating parameters pH, Eh, and the presence of Fe, dissolved organic carbon, and sulfate were observed. During the experiment simulating AMD generation in columns, the soil pH raised while Eh reduced. The pH of the soil stabilized after 60 days. The contents of Cu and Cd in the pore water were inversely linked with pH and sulfate. According to BCR results, the fraction of exchangeable Cu concentration increased throughout the flooding of AMD. Cu concentration increased from 0.29 mg/g to 0.41 mg/g, but Cd

concentration dropped from 9.2 mg/g to about 7.2 mg/g. Despite anaerobic conditions, the release of Cu and Cd under AMD flooding can increase potential environmental risks since the release could cause the formation of metal sulfide deposits.

1.6.2.4 British Columbia Research Confirmation Test

This test was first developed by Duncan & Bruynesteyn (1979) to verify the findings of the B.C. Initial (static) Tests; particularly, it is designed to evaluate whether bacteria can catalyze sufficient reactions to meet their acid needs. If the bacteria in the sample survive, there is a high probability that acid drainage will be produced in the waste unit being evaluated (British Columbia AMD Task Force, 1989). If insufficient acid is generated, the solution's pH will reach the natural pH (above 3.5), indicating that the sample is non-acid generating. If the solution is below 3.5, there is a strong likelihood that the sample is an acid generator.

This test's initial acidification of the sample shows conditions that vary greatly from those in a typical waste unit. The test does not assess mineral/bacterial responses above pH 2.5 (2.8 as described above). Reactions above these levels may have a significant role in deciding whether acid drainage is produced (Lapakko, 1993). In addition, the test discredits neutralization potential and sulfide oxidation rates (British Columbia AMD Task Force, 1989).

Hesketh et al., (2010) were detected the formation of AMD via microbial activities to applying modified British Columbia Research Confirmation Test. The biokinetic experiments conducted in this study augment the findings of conventional static testing, yielding valuable information about microbial activity and its significance in the kinetics and processes of AMD production.

The modified test offered information on the potential and probability of acidification following microbial colonization, and also the relative rates of acid-consuming and acid-producing activities. A sample of copper sulfide flotation tailings was used in the biokinetic test. When the results were evaluated, they were obtained

more stable information compared with static tests. Under non-acidic situations, the biokinetic experiments demonstrated the low AMD potential of the low sulfide tailings sample. In addition, they exhibited the distinct timescales of acid-consuming and acid-generating processes. Samples containing sulfide produced acid over time on disposal. Due to the different time scales of acid neutralization and formation, the observed acidification could be overestimated compared to that predicted by the static test. When bioleach assays with and without pH control were compared, it was found that low sulfide tailings could cause a small amount of leaching and consequently, AMD generation under acidic conditions, the gangue composition inhibited the establishment of these conditions in the absence of external acid addition.

1.6.2.5 Batch Reactor (Shake Flask) Tests

Similar to the British Columbia Confirmation test, a mine sample and water are mixed in a flask for the Batch Reactor test. Typically, the solution is distilled water, although nutrients may be supplied. The sample size and volume of the solution are selected by the user. Coastech (1989) did studies using 250 grams of waste and 500 milliliters of distilled water. The flasks are continually shaken throughout the test. At regular intervals, water samples are collected to measure water quality parameters like pH, sulfate, and metals in solution. During extended tests, sampling for water quality analysis may need the addition of water to maintain volume. This situation may complicate the interpretation of the data. The test results are used to determine the rate of sulfide mineral oxidation and the release of pollutants. Different variables, such as pH and temperature, may be checked continuously using the batch reactor, which is quite easy. As test parameters, the effect of microorganisms and control methods may be used.

The method's principal limitation is that the period of the test cannot exceed the lag period before acid production (Lapakko, 1993). Also, the amount of water in the flask could stop acid formation and bacteria might not be able to adapt to the test conditions (British Columbia AMD Task Force, 1989).

1.6.2.6 Field Scale Test

Similar to the On-site Rock Piles reported by the B.C. AMD Task Force, Field Scale Testing utilizes huge amounts of material to build test cells under ambient environmental settings, often at the mining site at issue. These tests are substantially different from those done in a laboratory under controlled conditions. Depending on the amount of available space, the sample size might range from 1 to 1 000 metric tons. Typically, the particle size of the test sample is not lowered to better simulate field conditions. The sample is placed on an impermeable liner to collect solutions, and a container is utilized to gather the leachate. An aliquot has been evaluated for pH, sulfate, dissolved metals, and other parameters, and the volume of the solution has been measured.

The rate of sulfide oxidation, acid production, neutralization, and metal dissolution as indicated by analysis of the leach solution must be separated from climatic factors. This is required because climatic factors, particularly precipitation, dictate the flushing rate but have no impact on the reaction rate or the following chemical composition of the leachate. (British Columbia AMD Task Force, 1989).

Field-scale tests have the benefit of being done under the same environmental conditions as the waste or other units they are mimicking. In addition, they enable monitoring of the impact of microorganisms and management methods. Field testing has the disadvantage of requiring longer test periods. In contrast to previous kinetic testing, field tests do not accelerate environmental conditions, which tend to evaluate the potential for acid production more rapidly. Therefore, field testing will offer information on the acid generation potential of a mining waste unit for as long as it is conducted prior to waste emplacement. For some operations, this time period may be longer than ten years, and test results may be used to improve the design of reclamation (Lapakko, 1993).

1.7 The Application Binding Materials to Control of AMD

One of the main causes the mobilization of heavy metals is the decrease in pH due to AMD formation.

Metal(loid) ions may be stored in the soil through sorption/desorption process, precipitation/dissolution process, oxidation/reduction process, methylation/demethylation, and complexation processes, and they can be released by plant uptake, leaching, and volatilization (Bolan et al., 2014). Firstly, heavy metals accumulate inclination in sediments and soils and have a prolonged persistence period. Secondly, they are pervasive in sediments and soils originating from both natural and human sources, with routes including inheritance from parent rocks, application of water, and fluvial deposition of missions from dust and mining. (Getaneh & Alemayehu, 2006). These metals can enter the food chain via uptake by plants and animals (or human) (Aslibekian & Moles, 2003; Grzebisz et al., 2002; Patel et al., 2005).

Immobilization of pollutants may be accomplished primarily by adsorption, precipitation, and complexation processes that redistribute toxins from the solution phase to the solid phase. Consequently, their bioavailability and environmental transmission are limited (Amstaetter et al., 2010). Biochar, organic compounds (such as biosolids-especially alkaline stabilized- and animal manures), liming materials (such as red mud, lime), and phosphate compounds (such as diammonium phosphate, DAP, KH_2PO_4) used to achieve for the metal(loid)s immobilization (Liu & Zhao, 2007; Basta & McGowen, 2004; Cao et al., 2003; Ruttens et al., 2010; Castaldi et al., 2005; Yang et al., 2020; Gibert et al., 2005).

The last years, to lower the high cost, to minimize maintain and to be available substantial matter for AMD treatment started to use low-cost waste materials, such as fly ash and recycled concrete aggregate (RCA), (Jones & Çetin, 2016).

Lately, scientists began to research use of nanotechnology materials such as nano zero-valent iron in the AMD. The propose is to increase the adsorbent's surface area when in contact with the heavy metal solution (Mokgehle & Tavengwa, 2021; Wang, et al., 2021).

1.7.1 The Case Studies with Binding Materials to Control of AMD

Li et al. (2022) reported that green polyphenol tannic acid (TA) that was an organic compound when it was used as a passivator inhibited pyrite oxidation. In addition to chemical experiments, to observe morphological changes of pyrite before and after TA passivation was used to scanning electron microscopy (SEM) and then to investigate in depth the interaction mechanism between TA and pyrite was utilized Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Experimental findings showed that TA passivation coating could offer excellent antioxidant protection for pyrite, and the suppression performance of TA improves as TA concentration increased. The construction of TA coating was mostly due to the chelation of TA with Fe ions on pyrite to produce TA-Fe complexes, that could effectively cover the surface of pyrite and prevent oxidation. So, Therefore, it was predicted that this research would give a low-cost and easy method for controlling AMD.

Garcia Valero et al. (2020) studied the neutralization of AMD and precipitation of metals by using sandstone, marl, and calcareous crust. For the experimental set up, using a 5/10 alkaline material(g)/AMD(mL) ratio, a batch test was designed and to optimize the procedure, three particle sizes (2–10, 10–20, and 20-30 mm) of each material were utilized, and water samples were taken during the neutralization period. The results showed that all of the examined alkaline materials (marl, sandstone, and calcareous crust) could be utilized for AMD rehabilitation owing to their high capacity to raise pH and reduce metal(loid) content by precipitation. The levels of Fe, Cu, Zn, As, Cd, and Pb in AMD treated with marl were lower than those reported for sandstone and calcareous crust. The removal percentage was shown in the Table 1.7.

Table 1.7 The removal percentage of the experimental set-up

	Removal percentage					
	Fe	Cu	Zn	As	Cd	Pb
Marl	100	99	69	29	70	100
Sandstone	98	98	62	0	68	100
Calcareous Crust	100	92	40	0	60	100

Also, marl and sandstone exhibited the lowest contact time with AMD for complete neutralization, enabling rapid precipitation of metal(loid)s. In contrast, while calcareous crust contains 98% carbonates, it required a longer contact time to accomplish neutralization and metal precipitation than marls and sandstone owing to its more compact structure and tougher consistency.

Sephton & Webb (2017) investigated the use of Portland cement in different ratios to control the production acid mine drainage. After adding of the cement, leachate from the cemented columns exhibited a decrease in acidity of 85 and 100 percent compared to the control columns for w/c ratios of 0.8, both 1.0 and 1.2, respectively. The columns including with greater w/c ratios (1.0, 1.2), the cement reached to the column bases and drastically reduced permeability. Due to the larger covering of the waste rock by the cement and the prolonged contact time between the leachate and cement, these columns did not produce any acid drainage (pH 7-8, Fe, Al, Mn, Zn and Cu concentrations rarely above detection limits). The other columns with a w/c ratio of 0.8, the cement slurry was mostly maintained in the top 30-50% of the waste rock, leaving a significant portion of the waste rock below uncoated with cement. Leachate drained rather rapidly from these columns. The investigators thought that it was most likely through a limited number of channels through the cement plug, carrying relatively minor amounts of acidity and metals from uncemented waste rock under the cement.

Kalombe et al. (2020) designed a batch jet loop reactor pilot plant to evaluate treatment of acid mine drainage (AMD) using coal fly ash. They were obtained that the concentration of main pollutants (sulfate, Al, Fe, Ca, and Mg) and minor contaminants in treated AMD may be greatly reduced (between one and four orders of magnitude) when compared to untreated AMD. Also, maximum pH of 9 could be

attained in the pilot plant by treating AMD with just fly ash, and pH could be raised to 12 with the addition of a little quantity of lime. This study demonstrated that 98.4% sulfate can be removed along with the majority of toxic metals after 30 minutes of contact time during the treatment of AMD with fly ash at a liquid-to-solid ratio of 5:1 and 0.25 percent (w/v) of lime in a pilot plant with three jet loop reactors operating in parallel.

Jones & Cetin, (2016) assessed the effectiveness of two distinct waste forms (Four different RCA materials and three different fly ash materials) were evaluated in remediating acid mine drainage. Results of the Column leach tests indicated that recycled concrete aggregates (RCAs) and one of the very alkaline fly ashes could be effectively increase the pH and lower Cr, Cu, Fe, Mn, and Zn levels in AMD. The column leach tests showed that RCAs and one of the very alkaline fly ashes were able to raise the pH and lower the levels of Cr, Cu, Fe, Mn, and Zn in AMD. In addition, sulfate concentrations in AMD reduced considerably after treatment with RCAs, but they raised following treatment with fly ashes. X-ray fluorescence spectroscopy was used to quantify the effect of CaO and LOI in the remediation materials on the sorption capacity of metals from the AMD. It was found that materials with high CaO and LOI concentration and little unburned carbon have a larger ability for absorbing Cr, Cu, Fe, and Zn.

Alkaline phosphate wastes (APW) were added to coarse tailings from an abandoned mine to prevent the formation of AMD in the laboratory by Hakkau and the others. (Hakkou et al., 2009). According to the laboratory column experiment, the addition of 15% APW to Kettara coarse tailings neutralized the acidic mine effluents effectively. Additionally, the modifications substantially decreased the metal concentrations in the leachate compared to the original Kettara coarse tailings.

Fahruddin et al. (2021) investigated the use of a bacterial consortia to remove sulfate and decrease lead (Pb) concentrations in acid mine drainage by adding compost to the bioreactors. At the end of the study, it was seen that pH and overall bacterial growth were increased while the treatment of non-sterile compost in acid mine

drainage decreased the initial heavy metal concentration of Pb by 84% and the sulfate content by 72%. Whereas the adding of sterilized compost was not efficient compared to the adding of nonsterile compost. It only decreased Pb levels by 63% and sulfate levels by 54% due to the fact that non-sterilized compost served as a source of organic material for sulfate-reducing bacteria.

CHAPTER TWO
THE AIM OF THE STUDY

Mining operations may be dangerous for the environment because they damage the land, use up nonrenewable resources, and put the health and safety of the people in the area at risk, even though they are important for economic growth and sustainability. In particular, the mine tailings that are not kept under control may pose a significant hazard to the environment and human health as they are produced in very large quantities after operations. Even though the tailings are washed with recirculated water after the chemical extraction of the metals, it is not possible to obtain a precise and final stability of the metals due to the rainwater pH, oxygen and carbon dioxide entering the piles, the possible development of Thiobacillus sp. in the waste material, and the tectonic movement of the piles. These factors can lead to AMD generation.

AMD is characterized by low pH, high electrical conductivity and sulfate concentration, and increased amounts of toxic heavy metals. The formation of AMD happens naturally. But it occurs a slower rate due to limited oxygen or water. After the mining activities, large amounts of sulfide minerals are abruptly produced and their surface area exposed to oxygen is considerably increased, resulting in a rapid rise in the rate of this process. This process of AMD dissolved the metal’s salts (due to a decrease in pH) and it causes to be released the toxic heavy metals such as Arsenic, Mercury, Cadmium, and Uranium into surface and ground waters. Once a metal reaches to aquatic environment, it is not degraded; rather, it tends to accumulate in sediments, soil, air, and water. Based on its chemical form, it may decrease and increase its toxicity, bioavailability, and solubility.

Despite the fact that there are currently a variety of strategies for controlling AMD's effects, these technologies are costly and difficult to maintain. A type of AMD control strategies is to use binding materials to immobilize the metals in the waste. However, selection of binding materials and the dosage of use are depending to many factors related to the material itself and the waste, as well as the cost of the material. The factors effecting the immobilization of elements in tailings are previously studied by

the researchers, however, studies covering the broad range of factors are not present in the literature.

That's why, the aim of this thesis is selected as investigating a large range of factors effecting element immobilization in mine tailings in order to define their importance on elemental immobilization. With this aim, the research stages are defined as follows to reveal the effects of wide range of factors on metals' immobilization in mine tailings:

1. The effect of initial elemental concentrations and their chemical fractionations in mine waste
2. The effect of *Thiobacillus sp*. in the medium
3. The effect of waste acid production and neutralization potential
4. The effect of organic and inorganic based binding materials: their properties and the doses.

These goals are investigated by using short term flask tests, long term kinetic column tests and long-term paste tests. The data from each test processed statistically to identify the major factors.

Finally, the indexes evaluating the leach quality are applied to select high performing binding materials and an economical evaluation on binding materials is presented.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Sampling

In this study, 3 different waste samples were used. Two of the waste samples were collected from lead-zinc (Pb-Zn) mining in Balya / Balıkesir and the other was taken from the boron (B) mining in Emet / Kütahya.

3.1.1 The waste samples of used in experimental set ups

3.1.1.1 Abandoned Open Bit Mining Balya

Balya mine, one of the world's oldest mines, with a history of more than 1200 years. It is known that the "Christian" mine at Balya was in operation throughout the Romans. The first authorized business in the region was established by "Balya Mining Enterprises" between 1839 and 1849. The mining operation rights taken by a German man named "Reiser" were transferred to a company called "Laurium". Laurium had legal operational rights over a 17.5 km^2 area for mineral exploration, business, and slag usage. A French man named "Riol" had got a "Management Privilage" for 99 years for mining and business. It is reported that 97.96% Pb, 0.11% Sn, 0.01% Bi, 0.54% Cu, 0.03% Fe, 0.004% Ni, and 0.01% As are present in the galena deposits at the site (Kovenko, 1940).

In 1892, a French company called "Societe des Mines de Balya Karaaydin" (Balya-Karaaydin Mining Corporation) was established. This company was the longest-lasting company in this mine. The company didn't confine its operation in Balya. It gained mining claims for coal in Mancilik and manganese mixed with lead, zinc, and iron in Patlak. The company obtained electricity by burning coal in its power plant, which was established in Balya in 1901, and shared the excess of it with the local government, so the city was enlightened (Journal of Mining Turkey, 2013).

Before the First World War, the Balya-Karaaydin Mining Corporation was one of the biggest mining companies in the world. It is known that there are two flotation units and one smelter unit established at Balya (Figure 3.1). In 1913, the plant worked at its maximum capacity and produced 13.890 t of lead (Pb) and an approximately equal amount of zinc (Zn). The plant, which stopped operations during the first war, started operations again at the end of the 1920s (Akyol, 1982). Between 1869 and 1939, the "Societe Anonyme Ottomane de Mines de Balya-Karaaydın" produced approximately 400,000 tons of metal lead in two flotations and a smelting plant at the Balya Pb-Zn mine (Öngür, 2003).

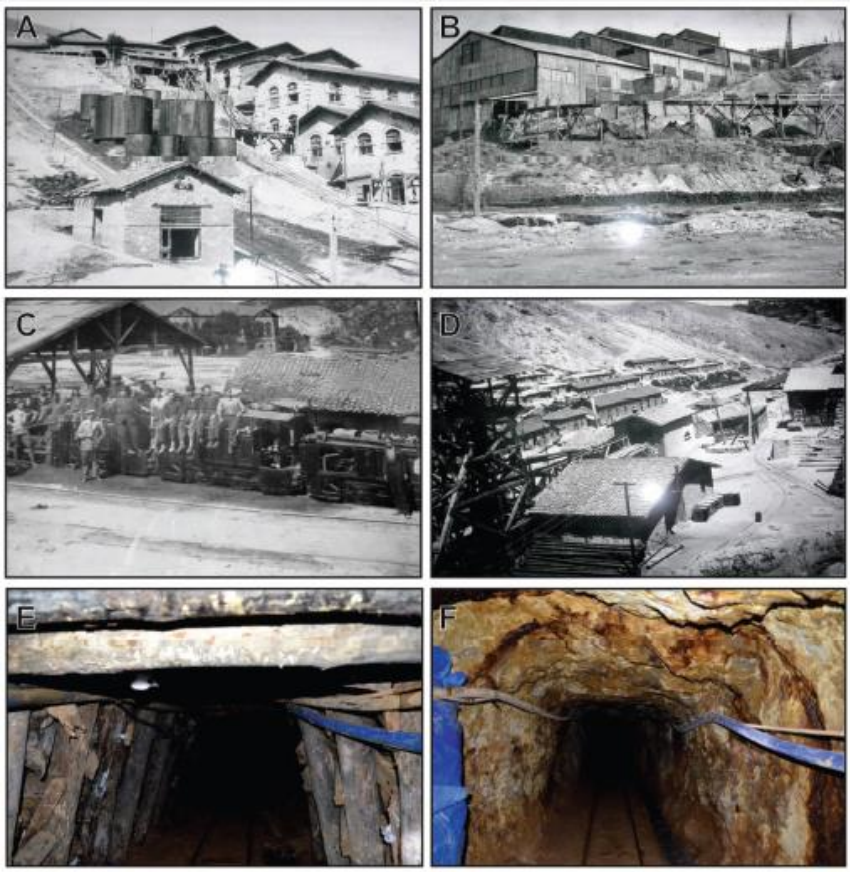


Figure 3.1 A) French flotation plant (1937), B) French smelting plant (1904), C) Railway used for ore transportation (1901-1937), D) French buildings and miners (1937), E, F) Former French Sarısu production galleries (restored by Esan Eczacıbaşı Company) (Baştürk & Aydoğan, 2022)

In 1960, the Turkish company 'Rasih and Ihsan Mining' first got a mining license and then, in 1970, was entitled to a business license for 10 years. The company gave the tailings that remained from the French and contained economically valuable

minerals to Mutlu Turker Smelting Company by royalty. The company established a lead-zinc flotation unit with a 50 ton/day capacity in the area. After all, in 1979, Rasih and Ihsan Company forfeited its license, and the area was given to Etibank by the state (Journal of Mining Turkey, 2013).

In 1997, Gurmin Company was assigned to reconnoiter the region. The company conducted some research on the area but could not find any satisfactory results that were worth working on and stopped activities (Öngür, 2003). On May 12, 2002, Eczacıbaşı Esan purchased the not operated area by tender, and the field studies started on May 29, 2002. At the beginning of 2007, Eczacıbaşı Esan began its investment activities and commenced operations in 2009. Today, Eczacıbaşı Esan goes on operating the mine next to the abandoned area.

*Reserve and tenor amount in Balya***:** The ore deposits in the Balya region are spread over an approximate 8 km^2 area. This area is grouped under three main zones: Balya, Daridere, and Bahcecik. The reserves in Balya are estimated at 3.260 million tons, with a tenor of 2.7% Pb, 7.2% Zn, and 0.3% Cu (Mineral Research and Exploitation, Akyol 1982). Minor components are pyrrhotite, marcasite, bismuth, sulfosalts, arsenopyrite, tetrahedrite-tennantite, bornite, argentite, heyrovskite, hematite, magnetite, pyrolusite, orpiment-realgar, and native tellurium. The primary cations in the galena fraction from the Balya deposit (Table 1) consist of 97.96% Pb, 0.11% Sn, 0.01% Bi, 0.54% Cu, 0.03% Fe, 0.004% Ni, and 0.01% As (Kovenko, 1940).

Table 3.1 Heavy metal loads of different waste rock dump samples (Kovenko, 1940)

Element	**The chemical composition of ore deposits (%)[a]**	**The primary cations in the galena fraction % Ag g/t**	**Waste Rock Dump (WRD)[b]**				
			1	**2**	**3**	**4**	**5**
Pb%	2.7	97.76	5.47	13.31	5.30	5.35	5.40
Zn%	7.2	NA	4.18	5.27	5.54	2.43	2.26
Fe%		0.13	8.17	16.59	7.17	12.9	13.52
Cu%	0.3	0.54	0.172	0.330	0.225	0.199	0.194
Mn%		NA	0.13	1.19	0.25	0.13	0.12
As%		0.01	0.30	0.44	0.27	0.34	0.33
Cd%		NA	0.028	0.034	0.034	0.015	0.014

a: Akyol (1982); b: metallurgical waste

Mine wastes in the area: The smelting and flotation wastes in the area are about 1–2 km northeast of Balya town, in the north-eastern and southern parts of Hastane Hill. Flotation wastes spread to the northeast of Hospital Hill from the north and continue along Maden Stream until they reach the Balya-Gönen road. Flotation and smelting wastes are observed on the southern part of Hospital Hill between the abandoned structures of the former business and Maden Stream. It was estimated that the remaining waste from previous operations amounted between 3.000.000 and 3.500.000 tons. They were located in Hastane Hill, in the old French flotation facility, and in the area of Mutlu Battery Inc. is established (Baştürk & Aydoğan, 2022). (Figure 3.2)

Figure 3.2 showed images of the areas where the waste samples used in this thesis were collected.

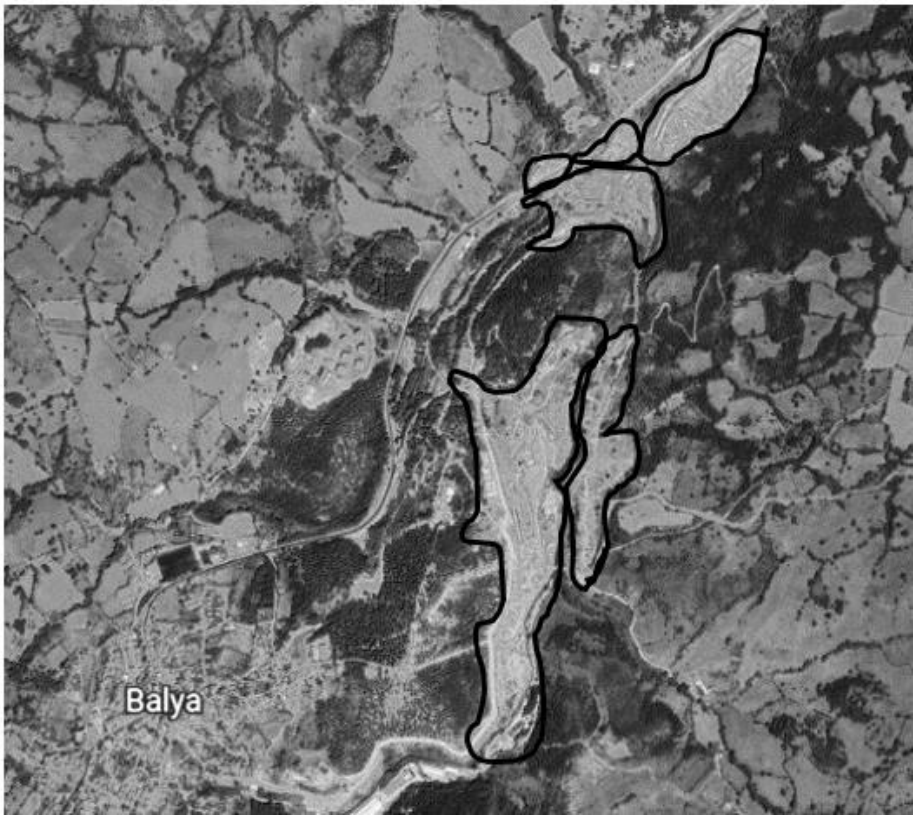


Figure 3.2 The total sampling area collected all of the waste samples

Figure 3.3 The images of the area where they were collected of waste samples in the abandoned Balya mine area

The first waste sample collected from Balya in April 2016 was used both in the flask test and the column test. The coordinates of the location map (39° 45.13'N - 27° 35.29'E) where the sample was collected and the satellite imagine of the sampling point are shown in the Figure 3.4 and Figure 3.5, respectively. The other Balya waste samples were used in paste test experimental set up were collected sample was collected 2019 August.

Figure 3.4 The sampling point the Balya waste sample used in flask and column test

3.1.1.2 The Boron Mining in Emet

The world's total boron reserve is estimated to be 885 billion tons, with the most significant reserves located in Turkey, the United States, and Russia. Turkey is the world's largest producer of borate-based goods. In about 1860, foreign companies started boron mining in Turkey, one of the world's largest suppliers of boron today. The mining operation rights were then given to the government sector, namely Etibank. Today, it is reported that Turkey has 72.20 percent of the world's boron reserves, and the Emet Stream Basin contains the country's most significant borate resources (Tokatlı et al., 2016; Etimaden, 2019; Önal & Burat, 2008).

Tincal (Na Borate) and Colemanite (Ca Borate) are the primary boron minerals in Turkey. At the Emet Colemanite Concentration facility, which has an annual capacity of 600.000 tons, 27% B_2O_3-containing colemanite ore is processed to generate a 43% B2O3-containing concentrate at a rate of 300.000 tons per year. In the production of boron compounds, separating boron minerals from clay minerals is one of the most significant problems. Another environmental issue is the continuous increase in the quantity of borogypsum. Boron waste is the output of the Emet Boric Acid Factory's H_3BO_3 (boric acid) synthesis process between $Ca_2[B_3O_4(OH)]22H_2O$ (colemanite ore) and H_2SO_4 (sulfuric acid) (Çelen, et al., 2019; Kunt, et al., 2015).

There are 12 million m^3 of solid waste and 6.5 million m^3 of wastewater containing 3 g/L of B_2O_3 (boron oxide) in the existing tailings dams (Önal & Burat, 2008).

The Emet waste was used only in the flask tests. The samples were taken from the concentrator plant where boron ores were processed. The waste was disposed at the tailing storage site at the northern part of the area.

3.1.2. Sampling of Binding Materials Used in the Experimental Set Ups

3.1.2.1 Binding Materials Used in Flask Tests

In the set up that microorganisms were studied, leonardite, which was used as inorganic binding material was made a request from Konya/Ilgın Department of Turkish Coal Enterprises Institution (TKİ), while the material was originally mined from Afşin-Elbistan zone of Turkish coals. Compost produced from municipal solid waste was taken from ISTAC that it was used as organic binding material. The microorganisms *Thiobacillus thiooxidans* (11478) used in the experimental procedure was obtained from DSMZ collection (German Collection of Microorganisms and Cell Cultures). It was reproduced by taking it from the DEU environmental engineering microbiology laboratory.

3.1.2.2 Binding Materials Used in Column Tests

Two different binding materials, one of which was strap material from marble dust and the other of which was Triple Super Phosphate (TSP), were used in the columns. While marble dust was from the DEU department of Mining Engineering, TSP was purchased from any flower store.

3.1.2.3 Binding Materials used in paste tests

In paste test experiments, four different binding materials were used: marble dust, ash, cement, and bentonite. Marble dust, bentonite, and cement were taken from the DEU department of Mining Engineering, the DEU department of Environmental Engineering, and the DEU department of Civil Engineering, respectively. Fly ash was from Seyitömer Thermal Power Plant.

3.2 Sample Preparation

3.2.1 The Preparing of Waste Samples and Binding Materials Used with Flask Test

Both waste samples (Balya waste sample + Emet waste sample) and binding materials were sieved to 1mm. *Thiobacillus thiooxidans* (11478) used in the experimental procedure was cultivated by the liquid media-Medium 271 (DSMZ, 2014).

Medium 271: 1 l of basal medium consists of 2 g of $(NH_4)_2SO_4$, 0.5 g of NO_2HPO_4, 0.5 g of $MgSO_{4x}7H_2O$, 0.1 g of KCl, and 0.01 g of $Ca(NO_3)_2$. The pH was adjusted to 2.0 with dilute H_2SO_4 (1 mol/l). As the substrate was used elemental sulfur. For 1 l of media, 10 g of sulfur was sterilized in screw-capped tubes in a water bath on 3 days for 3 h at 90-100 °C. Before use, the sterilized sulfur was layered onto the surface of autoclaved liquid basal medium. The sterilization was operated under 121 °C for 15 minutes by using Alp CL-40L Autoclave. The cultures were inoculated for maintaining subcultures in 500 ml 40 flasks. The flasks were being incubated in shaking incubator under 30°C with 170 rpm speed for 15 days.

3.2.2 The Preparing of Waste Samples and Binding Materials Used in Column Tests

Sample preparing and storage: Mine waste samples were dried for analysis at room temperature (25 °C). Approximately 2000 g of samples were prepared to fill a single column for EPA Method 1627. Fine gravel is collected from the DEU department of Civil Engineering Laboratory as a natural soil. It was again and again rinsed with water until no sand or other contaminants were left, and then was dried at 70°C overnight.

Sample crushing and splitting: Before loading, all of the mine waste samples were crushed until the largest pieces were no bigger than 3/8 inch (9.52 mm, or about 1 cm).

Sample sieving: Waste samples were passed through a 3/8-inch mesh to ensure that no particle sizes greater than 3/8 inch were added to the column. In order to measure

the particle size distribution of the waste sample, at least five dry sieves were utilized. (Table 3.2):

Table 3.2 Used sieve no and opening in the experiment

Sieve No	Opening, mm
5	4
10	2
18	1
35	0.5
60	0.25

Reconstruct samples into particle size distribution parts based on the weight percentages indicated in Table 3.3 using sieved sample portions According to Table 3.3, real values used in the columns was showed in Table 3.4.

Table 3.3 Particle size distribution of reconstructed samples

Sieve No	Percent of Sample (by weight)	Weight, g
3/8" - 5	40	800
5-10	25	500
10-18	15	300
18-35	15	300
35-60	5	100
Less than 60	5	100
Total	100	2000

Table 3.4 Particle size distribution of reconstructed samples (g, weight)

Sieve No	% of Sample (by weight)	Weight, g	**COLUMNS**				
			C1	**C2**	**C3**	**C4**	**C5**
			Control column- Fine Gravel	Balya mine waste	1% TSP + Balya mine waste	2% TSP + Balya mine waste	1% marble dust + Balya mine waste
3/8’’- 5	**40**	800	800	800	8+792	16+784	8+792
5-10	**25**	500	500	500	5+795	10+790	5+795
10-18	**15**	300	300	300	3+797	6+794	3+797
18 - 35	**15**	300	300	300	3+797	6+794	3+797
35 - 60	**5**	100	100	100	1+799	2+798	1+799
Less than 60	**5**	100	100	100	1+797	2+798	1+797
Total	100	2000	2000	2000	2000	2000	2000

Figure 3.5 and Figure 3.6 show that sieve analysis for the particle size distribution and the sieve analysis portions of the mine waste sample before mixing.

Figure 3.5 Sieve analysis for the particle size distribution

Figure 3.6 Before mixing the sieve analysis portions of the mine waste sample

3.2.3 Preparation of Waste Samples and Binding Materials Used in Paste Tests

The waste samples studied in paste tests were collected from different point and depth in Balya / Balıkesir mine area in 2019 August. These samples were collected from different points and depths were mixed and 5 different samples were obtained. The sample of No5 was formed by putting together different quantities of the other four samples (No1, No2, No3, and No4) These mixtures were prepared considering

the total sulfur, pyritic sulfur, total carbonate, neutralization potential, and acid production potential of each sample. These tables were shown in Appendix 1, Appendix 2, Appendix 3, Appendix 4, Appendix 5, and Appendix 6.

Firstly, all of the waste samples before mixing (Figure 3.7) were dried at 60 °C separately (Figure 3.8). After the drying process, a riffle splitter (Figure 3.9) that can be separated homogeneously solid samples into two half was used to obtain homogeneous mixing Then, all of the waste samples and binding materials were sieved to 1 mm before being mixed in the desired quantity.

Figure 3.7 Before mixing the waste samples

The abbreviation of the binding materials and ratios used in the tables is as follows:

Binding Material	Ratio (%)	Sample Number
MD: Marble Dust	1	1
A: Ash	2	2
C: Cement	5	3
B: Bentonite	10	4
		5

An example for reading

A 3.2 : Sample no 3 added binding material of 2% ash

- The ratio of binding material
- The number of samples
- The name of binding material

Figure 3.8 Dried the waste samples at 60 °C

Figure 3.9 The use of a riffle splitter for homogenous mixing

3.3 The Experimental Set Up

3.3.1 The Experimental Set Up in The Flask Test

Leaching capacities of metals in the Balya and Emet waste samples were investigated by using binding materials and *Thiobacillus thiooxidans* presence/absence by applying EPA 1310 B Extraction Procedure (Standard leach test) and EPA 1320 Multiple Extraction Procedure (Dynamic leach test). Kinetic tests were carried out in two stages for the waste samples and binding materials prepared according to section 1.2.1. In the second stage, the EPA 1320 Multiple Extraction Procedure was applied, which is a long-term kinetic test while in the first stage, EPA 1310 B Extraction Procedure which is a short-term kinetic test was applied. Tests were conducted with control tests by using different waste and binding ratios, and in the presence and absence of *Thiobacillus thiooxidans*. Experimental sets were represented in Table 3.5.

A culture containing 10 ml of 5×10^6 cfu/ml of bacteria was added to experimental sets carried out the with the presence of *Thiobacillus thiooxidans* (not exceeding the amount of liquid that must be present in the system). The procedure was carried out using different ratios of the binding materials. For 10 g dry matter; waste/binding

material ratios were as follows: 10/0 (control), 9.5/0.5, 9/1, 8/2; 10/0 (control), 9/1 for the for EPA 1310 B and EPA 1320 procedures, respectively.

10 experimental sets were applied for only one sample by using one kind of the waste/binding material. Total 40 experimental sets were applied for two different mine samples and two different binding materials.

Table 3.5 Experimental sets for EPA 1310 B and EPA 1320, in the absence or presence of *Thiobacillus thiooxidans* and their ratios

EPA 1310 B Extraction Procedure		**EPA 1320 Multiple Extraction Procedure**	
Thiobacillus thiooxidans	*Thiobacillus thiooxidans*	*Thiobacillus thiooxidans*	*Thiobacillus thiooxidans*
Absence	**Presence**	**Absence**	**Presence**
Waste/Binding Material (g/g)			
10/0 (Control)	10/0 +*T.Thiooxidans* (Control)	10/0 (Control)	10/0 +*T.Thiooxidans* (Control)
9.5/0.5			
9/1	9/1+ *T.Thiooxidans*	9/1	9/1+*T.Thiooxidans*
8/2			

3.3.2 The Experimental Set up in the Column Test

3.3.2.1 Column Design

The column design was based on U.S. Environmental Protection Agency (EPA) (2011) Method 1627 for kinetic test procedure. Method 1627 was a kind of field-based kinetic experiment, and it was a simulated weathering test that offers data that may be used to predict the quality of mine drainage that may result from mining operations and weathering. Method 1627 was designed for use in assessing likely hydrologic effects and improving a cumulative hydrological impact assessment. The method was applied by a column with which to generate data used to design and implement best management practices and treatment processes.

Column Apparatus and Materials: Columns were made up of vertical tubes that can hold a sample with particles no bigger than 0.9525 cm (3/8 inch) and move gases and water or store them. To prevent air entrapment, imitate varied groundwater conditions,

and maximize contact with the particle surface area, water and/or gases were pumped into and drained from the bottom of the column.

The column was made of polycarbonate with an inner diameter of 5.08 cm (2 inches). (Figure 3.10). It was made of a clear material so that the movement of samples could be seen with the naked eye during the weathering and leaching processes and when samples were being added to the column.

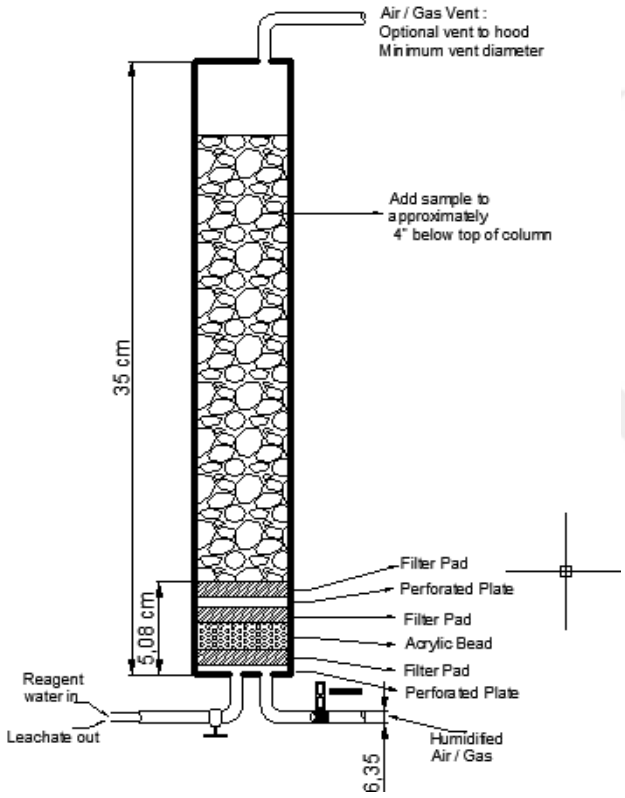


Figure 3.10 Leaching column

Column: 5.08 cm ID, clear, rigid, polycarbonate

Column seals: Columns were sealed at the bottom and had a cap that could be removed and had a hole in it where gases could be measured and let out. (5.08 cm, clear, rigid, PC).

Column Ports: Ports were built into the top and bottom of the column to let mixed gases and water in, collect leachate, and let gas out.

- Air/gas introduction and venting ports: Polypropylene, thread 0.635 cm (1/4”) NPT, Tube ID 0.635 cm (1/4”).
- Leachate drainage port: Nylon, threaded 0.635 cm (1/4”) NPT, Tube ID 0.9525 cm (3/8”).

Column Tubing and Clamps: Column ports were linked to tubing that was directed to permit gravity flow of water into the column, drainage of water from the column, as well as the introduction and exhaustion of gases. Tubing sizes were 0.635 cm (0.25”) (gas mixture) and 1.27 cm (0.5”) (reagent water).

- Vinyl tubing: It was used for tubing that does not need to be clamped (e.g., manifold, gas lines, and tubing from gas source to humidified gas reservoir). 0.635 cm (¼-inch) ID and 0.9525 cm (3/8-inch) OD, 0.15875 cm (1/16-inch) wall thickness.
- Rubber tubing: It was used for tubing that has to be clamped (e.g., water introduction and drainage tubing, tubing from humidified gas reservoir to column). Thick wall, rubber latex tubing. 0.635 cm (1/4”) ID, 1.11125 cm (7/16”) OD, 0.238125 cm (3/32”) wall thickness.
- Plastic tubing clamps: It was used on latex tubing for quick, total shut off of gases or fluids. Fits 0.3175 cm- 1.27 cm (1/8- to 1/2”) tubing.
- Fixed jaw clamps: It was used on latex tubing to adjust gas flow.
- Nylon Tees: It was used to connect tubing. Tube ID 1.27 - 0.635 cm (1/2”and 1/4”).
- Couplers: It was used to connect tubing. Tube ID 0.635 cm (1/4”), nylon or PVDF.

Column Lining: The bottom (up to about 5% of the total column height) was made up of various layers of filters and support materials to allow for consistent entry of water and gases into the column. Reagent water and gas mixtures were pumped through the plates, beads, and filter material and into the sample through ports at the bottom of the column. These layers consist of two PC perforated plates and three filter

material layers. (aquarium filter media, and a 3.81 cm (1.5”) layer of 0.79375 cm (5/16”) diameter acrylic beads.

- Perforated Sheets: PVC, Natural, 0.47625 cm (3/16”) thickness, 0.47625 cm (3/16”) hole diameter, staggered rows
- Plastic Beads: PVC, 1.27 cm (1/2”) diameter
- Filter Pads: 0.20128992 m^2 (312 square inches). They were prepared circles to provide three filter pads to line column.

3.3.2.2 Gas Mixture

Using flow meters and a 10-liter glass bottle, gases were mixed at a ratio of 90% air to 10% CO_2. To obtain air mixing, filtering apparatus is used after the compressor. Filter systems were designed by using yard filter, $Ba(OH)_2$, $Ca(OH)_2$, carbon filter, and spun filter.

Gas introduction: Once mixed, gases were pumped into the reagent water in the reagent water reservoir through a porous stone under the surface of the water. The humidified gas mixture was introduced continuously through the column at a ratio of 9:1(Air:CO_2) and it was at the same temperature as the column (20-25°C ±3°C). (Figure 3.11).

- *Gas monitoring*: Continuous gas flow was set up to keep constant positive pressure, and flow meters were used daily to maintain positive flow and a CO2 content of at least 10% in the outflow gas.
- *Tubing clamps*: Tubing clamps were used to control gas flow through the tubing into the columns. A flow meter was used to maintain a flow rate of approximately 1 L/minute
- *Rotameters*: Capable of regulating a flow rate of about 1 liter per minute. Between the gas source and the reagent water reservoir, as well as between the reagent water reservoir and each column, rotameters were used.

- *Tubing connectors*: Threaded, barbed elbows, 0.3048 x 0.635 cm (0.12 x 0.25”), it was used to connect rotameters to inlet and outlet tubing.

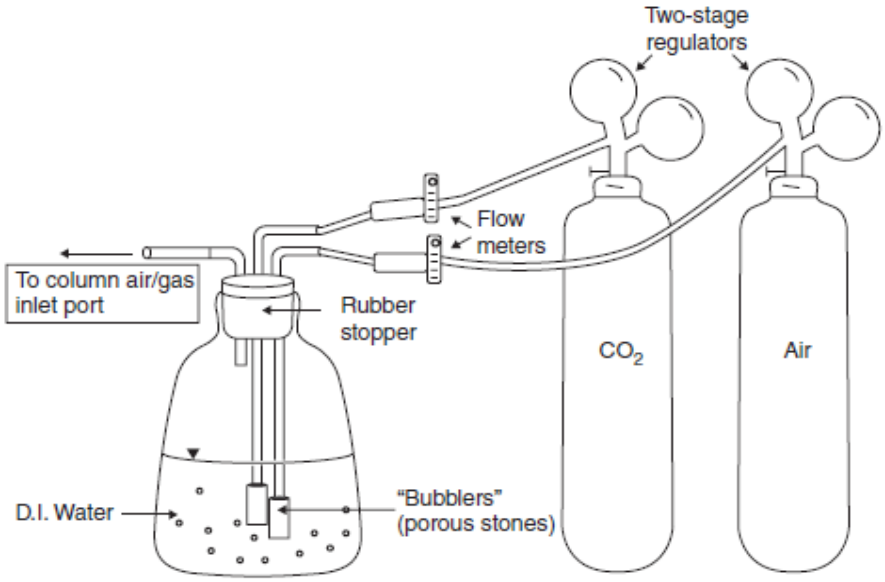


Figure 3.11 Humidified air/gas apparatus according to Method 1627 (U.S. EPA, 2011)

Reagent Water Reservoir: A water bottle was half filled with reagent water. The bottle was sealed with a rubber stopper that has ports for the introduction and release of the mixed gases.

- *Glass bottle*: The volume of the glass bottle was 10 liters.
- *Rubber stopper*: 2-hole, with third hole drilled into stopper at a distance sufficient to allow bungee cord to secure stopper in place once tubing is inserted.
- *Ridged tubing*: The inner dimeter was 0.79375 cm (5/16-inch). ID extruded ridged tubing was put into stopper holes to support flexible tubing. Ridged tubing was connected inlet and exit tubing.
- *Gas outlet port*: Tubing was inserted through and immediately below the rubber stopper into the remaining reservoir headspace.

3.2.3.3 Filling the Columns and Start Up

After the sieving and weighing, the columns are filled with the different binding materials and their different ratios. The columns were defined by the following abbreviations:

C1 (Control column): The control column material was fine gravel.

C2: C2 column was only filled with unrefined Balya mine waste.

C3: TSP was used as a binding material by adding at the ratio of 1% to Balya mine waste sample.

C4: TSP was used as a binding material by adding at the ratio of 2% to Balya mine waste sample

C5: Powderized marble was used as a binding material by adding at the ratio of 1% to Balya mine waste sample.

Columns were filled with the own sample so as to leave a minimum of 10 cm (approx. 4') space from top of the sample up to column height (Figure 3.12).

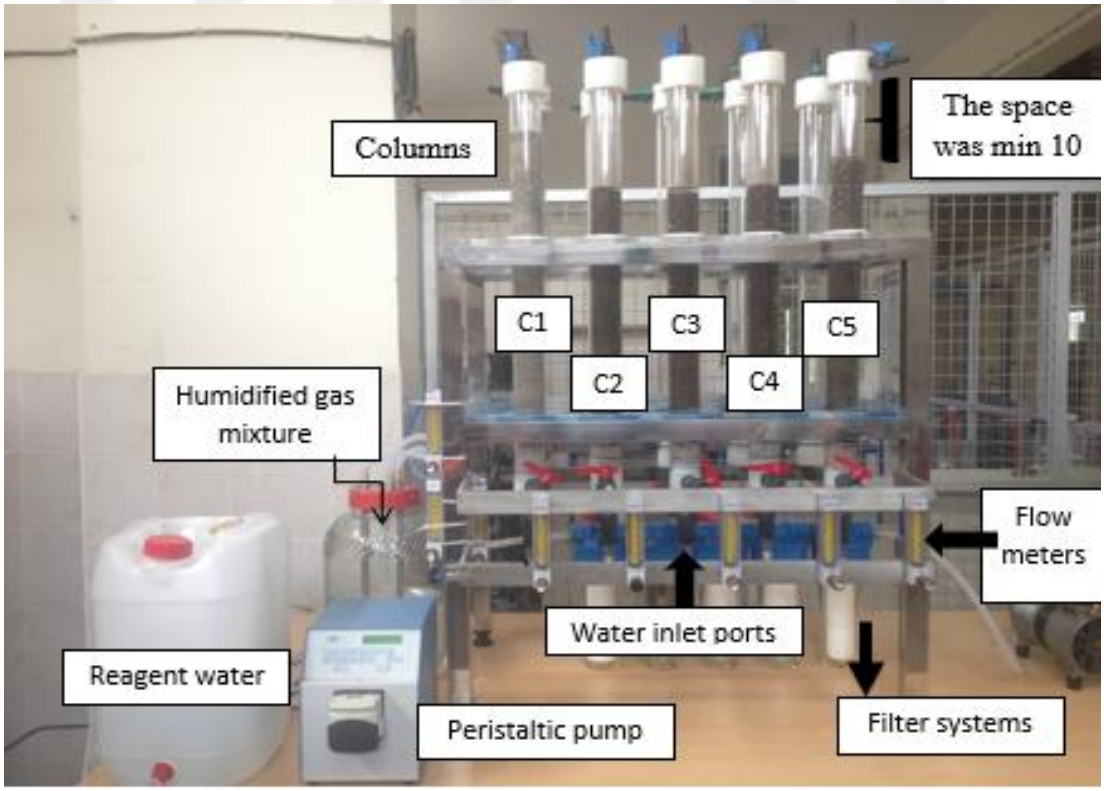


Figure 3.12 Columns designed according to EPA 1627 and experimental set up

Initial Column Flush: The reagent water was introduced through the water inlet port until the column was full and all visible pore spaces were saturated. It waited approximately 1 hour prior to collecting and analysing the initial flush water for conductivity to sit the reagent water in the column. The electrical conductivity measurement was repeated hourly, and it was continued until the difference between two measurements was less than 20%. The flush water samples from collected the columns were not poured, they were put away in containers separately and analysed after that (0. Week). During this time, the addition of the reagent water was continued to inlet ports to fulfil the volumes that were lost. The volume of the reagent water and flush water was recorded at every turn. These volumes were also recorded during each weekly saturation period.

Humidified Air Cycles: After the last initial flush sample had been drained from the column, the humidified gas mixture was introduced continuously via the gas input port at the bottom of the column. During the humidified air cycle, the column stayed stationary for six days. A 9:1 mixture of humidified air and carbon dioxide. Gas flow was controlled and maintained at approximately 1.0 L/minute using a combined flow meter. Each saturation cycle was followed by a repetition of this cycle.

Saturation Cycles: After each humidified air cycle, reagent water was introduced via the water inlet port to just above the surface of the sample. After addition the reagent water, clamp the water inlet tube was shut to ensure that the water collected at the end of the saturation period had been in sufficient contact with the sample. The contact time was 24 hours. The volume of added the reagent water was recorded each weekly.

3.3.2.4 Leachate Collection and Experiment

Following each 24-hour saturation cycle, the water/leachate was drained from the column and collected for analysis. Leachate was drained from the column through the water inlet tubing by disconnecting the tubing from the water source. The total volume

added to and collected from each column were measured and recorded prior to water analysis.

The EPA 1627 method required the measurement of pH, conductivity (EC), alkalinity, acidity, and dissolved metals.

3.3.3 Experimental Set Up in the Paste Taste

The experimental set up was planned as continuous and intermittent (Table 3.6; Figure 3.13) in the centrifuge tubes. In a continuous set up, pH and EC were measured every week while they were detected every three weeks in an intermittent set up. In addition, the liquid fraction (supernatant) was taken after centrifugation at 7000 rpm for 5 minutes in both setups, and the liquid volume was measured. The supernatants are then kept at +4 °C. The experiment of intermittent set up was designed at 3 weeks intervals. The first measurement was obtained 3 weeks later, and then measurements were continued at 3 weeks intervals through 15 weeks in mine samples. Liquid fraction (supernatant after centrifugation) of mine samples were collected in a single container. The measurements were performed by the gathering of liquid fraction every 3 weeks for 15 weeks in that container.

Table 3.6 The experimental set up

Continuous Set up					**Intermittent Set up**				
control	No dose	No bm	5 samples	5	**control**	No dose	No bm	5 samples	5
w*/bm**	4 doses	4 bm	5 samples	80	**w/bm**	4 doses	4 bm	5 samples	80
			Total	85				Total	85

* w: waste / ** bm: binding material

Figure 3.13 Continues (right) and intermittent (left) experimental set up

A flask (centrifuge tube) whose volume was 50 ml was used in the experimental set up. 15 g sample was put into the flasks, and 30 ml of distilled water was added. While the control group did not contain any binding material, 1%, 2%, %5 and %10 ratios of binding materials were added to the experimental sets (Table 3.7) The total number of experiments were 85 (5 for the control group and 80 for binding material added).

Table 3.7 Binding materials and doses used in experimental set up

		Dosages			
Binding materials	**Control (%0)**	**1%**	**2%**	**5%**	**10%**
Marble dust Fly ash Bentonite Cement	Original waste sample	14.85 g w* + 0.15 g bm**	14.7 g w + 0.3 g bm	14.25 g w + 0.75 g bm	13.5 g w + 1.5 g bm

*w: waste / **bm: binding material

3.4 Analytical Methods

3.4.1 pH in Waste Samples and Binding Materials

Waste samples and binding materials were determined by using HANNA HI22II a portable device with the method EPA 9045C (US EPA, 1995). Waste sample-water ratio was prepared as 5:20. The solution was stirred continuously for 5 minutes and after waiting 15 minutes for the solution to stabilize, the measurement was performed.

3.4.2 pH in Leach

The leaches in the paste test and column test were analysed by using the same device, HANNA HI22II with the method EPA 150.1. In this method, the glass pH probe was submerged directly into the leaches collected from columns, flasks, and the other experiments, and then the results were recorded.

3.4.3 Conductivity in Leach

All of the leach samples were measured using HANNA HI22II a portable device (the same as with measuring pH) according to the method EPA 120.1. The EC probe was immersed directly into the samples as leaches.

3.4.4 Sulfur Fractions (Pyritic S) and Acid Production Capacity

To detect the sulfur content in the samples was determined with the method modified by Sobek (1978). After waste samples were homogenized, they were sieved to <60 mesh (<0.25 mm) The sample The experiment was carried out in three steps and 0.5 g of waste sample was weighed for each step. The samples in each step were named by A-B-C.

- The sample A was kept for the total sulfur analysis without any process (0.5 g). the amount of used sample for the marble dust was 1 g.

- The sample B was treated with HCl. It was placed on glass filter paper that tared before and washed with 50 ml of 40% HCl. After washing, the liquid that was at the bottom was put into a different container. The sample on the glass filter paper was rinsed twice with 50 ml of dH_2O and 3 drops of AgNO3 was added to filtrate. At the end of the process, if turbidity or sediment was noticed in the water, the washing procedure was repeated with 50 ml of dH_2O until the turbidity was eliminated. When the water turned clear, the glass filter paper was left to dry at room temperature for 24 hours. At the end of the period, the sample on the glass filter paper was dried at room temperature. After that, the sample on the filter paper was weighed and stored airtightly until analysis.
- The sample C was treated with HNO_3. The sample was kept for 24 hours in 50 ml of hno3 solution prepared at a ratio of 1:7. At the ending of the time, the sample was filtered through glass filter paper. Care was taken to ensure that no samples were left in the container throughout this period. The sample on the glass filter paper was washed with 50 ml of dH_2O. 1-2 drops of Nessler's reagent were dropped into the filtrate, and it was observed whether a yellow color was formed. This process was continued until the yellow color was removed. At the end of the period, the sample on the glass filter paper was dried at the room temperature. As in B sample, the sample on the filter paper was weighed and stored airtightly until analysis.

According to the obtained analysis results, pyritic sulfur and inert carbon were calculated in the below formula:

Pyritic Sulfur (percentage or ppm) = B - C
Inert Carbon (percentage or ppm) = A - B

3.4.5 Inorganic Carbon and the Carbonate Neutralization Potential

The same method referred for pyritic sulfur in section 3.4.4 was applied to detect inorganic carbon. To detect the carbonate Neutralization Potential was used Sobek test method (Sobek et al., 1978).

The waste samples and binding materials were ground and sieved to pass 60 mesh (<0.25 mm). The quantity and concentration of HC1 added to each beaker was determined by the fizz test.

According to the observations in the fizz test, the normality and amounts that should be added to the samples are shown in Table 3.8. Approximately 0.5 g of sample was put on a piece of aluminium foil. One or two drops of HCl solution prepared with a 1:3 ratio was put on each sample and was determined the bubbling or fizz rate. 2 g of sample was weighed. According to the fizz test result, the needed volume and normality of HCl (0.1N or 0.5N-exact concentration known) solution in the Table 3.8 was added on each sample. The sample was heated, but it didn't boil. Every 5 minutes, it was stirred until the reaction was done. When no bubbles were seen rising through the suspension and the sediment settled uniformly on the bottom of the flask, it was concluded that the reaction was complete. The sample was diluted with dH_2O until the total volume was 125 ml. The sample was boiled for 1 minute and allowed to cool at room temperature. After that, the sample was titrated by using 0.1N or 0.5N NaOH (exact concentration known) to pH 7. The pH was measured in pH 7 until it stayed stable for 30 seconds. If NaOH consumption was less than 3 ml of NaOH, the procedure was repeated with the higher HCl concentration.

Table 3.8 Volume and normality of HCl used for each fizz test

Fizz Rating	**HCl**	
	ml	normality
None	20	0.1
Slight	40	0.1
Moderate	40	0.5
Strong	80	0.5

The carbonate NP value was derived from the carbonate C concentration. The value was multiplied by a factor of 83.3, which was calculated as follows:

100.06 (mole weight of calcite) / 12.01 (mole weight of carbon) * 10 ($tCaCO_3$=1000t) = 83.3

Neutralization potential was detected according to the below equation 3.1:

$$\text{Neutralization potential (NP)} = \text{Inert C} * 83.3 \quad (3.1)$$

3.4.6 Siderite-Corrected Acid Neutralization Potential

This method was used to eliminate siderite ($FeCO_3$) to obtain pure inert carbon. (Bureau of Mining Regulation and Reclamation, 2021). The similar procedure of neutralization potential mentioned in section 4.4.5 was applied to calculate siderite corrected neutralization potential. Then, it was followed by a different procedure and continued from the last step of NP.

After the titration step, the sample was boiled by putting it into glass beads (covered with watch glass) and cooled at room temperature. The sample was filtered with Whatman No 40. 5 ml of 30% H_2O_2 was added to the filtrate. The boiling process was repeated for 5 minutes by putting glass beads into the erlenmeyer and covering it with the watch glass. After cooling, the sample was again titrated with 0.1 N or 0.5 N NaOH (exact concentration known) to pH 7. Similar to the neutralization potential procedure, the experiment was repeated with a higher HCl concentration if less than 3 ml of NaOH was consumed. During the experiment, a blank was prepared for each volume and normality in the fizz test.

- Constant (C) = (volume [ml] acid in blank) / (volume [ml] base in blank);
- ml acid consumed = (volume [ml] acid added) - (volume [ml] base added x C);
- ANP = (Tons $CaCO_3$ equivalent / thousand tons of material [T/kT]) = (volume [ml] of acid consumed) x (25.0) x (N of acid).

3.4.7 Evaluation of AMD Potential

The acid production potential (APP): The acid production potential (APP) was calculated from the total sulfur concentration using the following formula (Acid Mine Drainage Prediction, 1978):

$$AP = 31.25 \times \% S \quad (3.2)$$

The net neutralization potential (NNP) was calculated two different ways: (Acid Mine Drainage Prediction, 1978)

a) NNP = NP – AP

If the NNP is lower -20 (kg $CaCO_3$/ton), the potential exists for the sample to generate acid. If it is much more 20 (kg $CaCO_3$/ton), then there may be lower risk. When the NNP is between -20 and 20 (kg $CaCO_3$/ton), prediction of the acid potential is more difficult. It can be applied static tests.

b) NPR = NP/AP

The ratio of a sample's neutralization potential and acid production potential is greater than 3:1, experience indicates that there is lower risk for acid drainage to develop (Brodie et al., 1991). For ratios between 3:1 and 1:1, referred to as the zone of uncertainty, additional kinetic testing is usually recommended. Those samples with a ratio of 1:1 or less are more likely to generate acid (Nordstrom, 1979).

Also, the risk of AMD occurrence is considered in materials having sulfur concentration above 0.3% in mass. In addition, any sample having Sulfur above 1% in mass should be evaluated for its AMD production potential according to EPA and EU criteria.

3.4.8 Total Acid Digestion (TAD)

Total acid digestion procedure was preferred to measure heavy metal concentration. EPA Method 3050B (US EPA, 1996) was applied to detect total acid digestion by using Perkin Elmer SPB 50-48. Waste samples were sieved by using No10 sieve (2mm) before the added to flask. In the first step, 0.5 g of waste samples and binding materials was placed in 50 ml falcons and 5 ml HNO_3 was added at a ratio of 1:1. The samples for the digestion were kept at 120 °C for 15 minutes. Meanwhile, the end of black smoke output should be observed. At the end of the time, the samples were left

to room temperature. In the second step, 2.5 ml of concentrated HNO_3 was added to the samples and kept at 120 °C for 20 minutes. If steam output is still visible at this level, step 2 is repeated without added HNO_3 until there is no longer any steam output. While the samples were left to cool, the device temperature were decreased at 95°C. After the cooling, without added any solution, samples were digested 95°C for 60 minutes. After the samples were at room temperature, 1 ml dH_2O and 1.5 ml concentrate H_2O_2 were added to samples, respectively. Then, they were waited at the same temperature for 90 minutes. If foam production is noticed at this stage, 5 ml of H_2O_2 is added gradually until a total amount of 5 ml has been supplied (1 ml for each). If not like this, 5 ml of H_2O_2 was added. In the third step, 5 ml of HCl were added and the samples were boiled at 95°C for 15 minutes. Then, cooling process were started for the samples. Cooled samples were diluted to 50 ml and filtered through 0.45 µm filter paper. The samples were stored at +4 °C before the analyses. An inductively spectrometer (ICP-OES) Thermo Scientific iCAP 6000 Series was used to detect to heavy metal concentration (As, Ba, Cd, Total Cr, Cu, Hg, Mo, Ni, Pb, Se, Zn, Sb, Al, Na, K, Fe, and Ca).

3.4.9 Sulfate in Leach

Sulfate analyses were performed using turbidimetric method (APHA, 2017) (4500-SO_4^{-2} /E) with a device called pg instruments T80+. In this method, 10 ml of Buffer A (Table 3.8) solution was added to 50 ml of sample and was stirred at a constant speed for 5-10 second and at the same time, approximately 0.2 g of $BaCl_2$ was added to sample. As soon as $BaCl_2$ was put in the sample, 1 minute was started to pass. At the end of the period, the sample was read as mg/L from the U.V instrument.

Table 3.9 The formula of tampon A solution

Quantity	Chemical	Description
30 g	$MgCl_2$ (Magnesium Chloride)	First, these substances were dissolved in some water, and then the total volume was adjusted to 1000 ml (V_{total} = 1000 ml).
5 g	$CH_3COONa.3H_2O$ (Sodium Acetate)	
1 g	KNO_3 (Potassium Nitrate)	
20 ml	CH_3COOH (Acetic acid)	

3.4.10 Determination of Chemical Distribution in Samples: The BCR Sequential Extraction Procedure

Chemical distribution in the waste samples was detected by using the technique which is called The BCR sequential extraction method is developed by European Commission for Standards, measurement, and Testing (ECTS&T) (Rauret et al., 1999; Dean, 2003; Guven & Akinci, 2008). This technique allows to emerge 4 fractions (exchangeable and acid soluble, reducible, organic, and residual fraction) that they're bound of metals. CH_3COOH (0.11 mol/L acetic acid), $NH_2OH{\cdot}HCl$ (0.5 mol/L hydroxylamine hydrochloride), and ammonium acetate (CH_3COONH_4) solutions was used to detect for exchangeable and acid soluble, reducible, and bound to organics, respectively. The residual fraction was calculated by subtracting the sum of these three fractions from the total amount of metal (Figure 3.14).

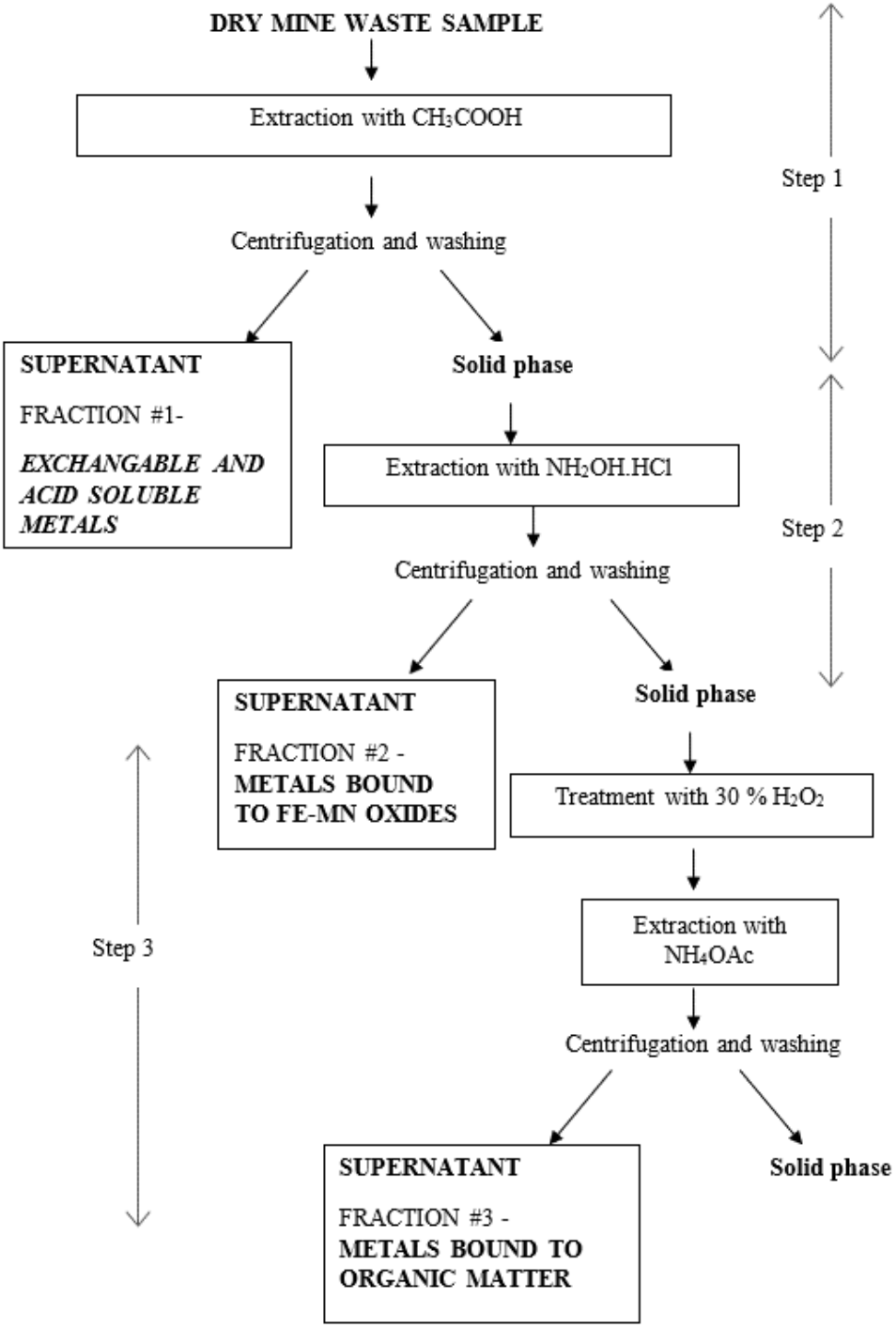


Figure 3.14 The BCR sequential extraction scheme (Guven, E.D., 2008)

3.4.11 Determination of Leaching Quantity: EPA1310 B Method

EPA 1310 B used for the determination how much it was leached from the metals at pH 5 ± 0.2 for 24 h. 100 g of sample was extracted with 1600 ml of the deionized water. pH was adjusted with by using glacial acetic acid and the samples were shaken

in the incubator at sufficient agitation to obtain well mix for 24 h. The supernatant was filtered from 0.45 µm, and the extract was stored at 4 °C until the analyses (US EPA, 2004) (Figure 3.15).

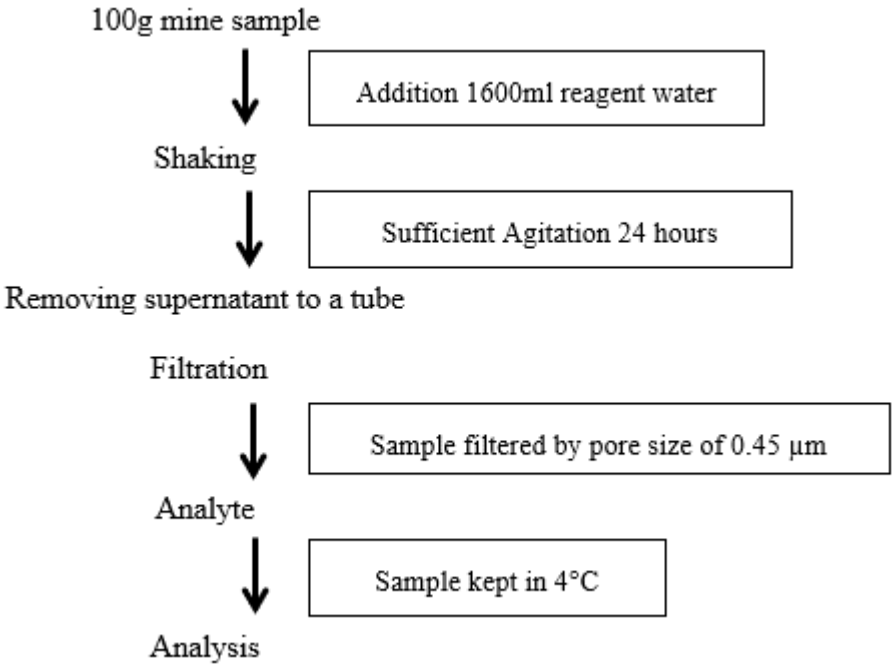


Figure 3.15 EPA 1310 B extraction procedure flow chart

The results of both EPA 1310 B and BCR methods was performed by using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Thermo Scientific iCAP 6000 Series). Also, it was used to detect to heavy metal concentration (As, Ba, Cd, Total Cr, Cu, Hg, Mo, Ni, Pb, Se, Zn, Sb, Al, Na, K, Fe, and Ca).

3.4.12 EPA 1320 Method

The procedure of EPA 1320 conducted with being filtered liquid part of sample used in the EPA 1310 B extraction procedure. In this method, the filtered liquid part was shaken with water pH 3 (60/40: H_2SO_4/HNO_3) for 24 hours. The water quantity used in this procedure was 20 times of filtered liquid part's weight. After 24 hours, sample was taken for detecting metal mobilization. Then, the same process went on 8 additional times. The aim of the EPA 1320 Multiple Extraction Procedure was to determinate metal leaching from the waste under acidic conditions (US EPA, 1986).

3.4.13 Alkalinity

EPA 310.1 Method was preferred to determine waste samples' alkalinity. The pH of 50 ml sample was determined and titrated to pH 3.9. Then, the alkalinity was calculated using the following formula.

$$\text{Alkalinity (mg/L)} = \frac{A*N*50000}{Sample\ Volume(ml)} \quad (3.3)$$

where, A was the amount of H_2SO_4 consumed up to pH 3.9. N was normality of the used acid in the experiment (Because the alkalinity in the samples was less than 1000 mg/L, 0.02N H_2SO_4 was utilized).

3.4.14 Acidity

EPA 305.1 Method was used to determine waste samples' alkalinity. The pH of 50 ml sample was detected. If the pH is over 4, 0.02N H_2SO_4 is added until it falls below 4 and the consumption is recorded. If the pH is under 4, this procedure is not required. Then, 10 drops H_2O_2 were added to the sample and was boiled for 5 minutes. After the sample was cool, it was titrated to pH 8.2 with 0.02 N NaOH and consumption were recorded. The calculation of acidity was below:

$$\text{Acidity (mg/L } CaCO_3\text{)} = \frac{[(A*B)-(C*D)]*50000}{Sample\ Volume\ (ml)} \quad (3.4)$$

where, A was the consumption of NaOH; B was the normality of NaOH (0,02N); C was the quantity of adding H_2SO_4; D was the normality of H_2SO_4.

3.4.15 Organic Matter

Standard Methods were used for determining the organic matter content of waste sample and binding materials (APHA, 2017).

3.5 Statistical Methods

The results of both microbiological studies and flask tests were evaluated to PCA (Principal Component Analysis) and correlation analysis by using SPSS 24.0 (IBM Inc., Chicago, Ill., USA).

3.6 Pollution Indices

3.6.1 Pollution Indices in Waste Samples

3.6.1.1 Comparison of the Total Acid Digestion (TAD) Results of the Waste Samples and Binding Materials with SQuiRTs Chart and Earth's Crust Level

Total metal concentrations in waste samples were compared with earth's crust level and SQuiRTs Chart. SQuiRTs Chart (Screening Quick Reference Tables) is a table which is developed by NOAA (National Oceanic and Atmospheric Administration). It enables to evaluate screening concentrations in different media (water, soil or sediment.). In this way, pollution risks emerged from contaminated soil, water or sediment can be detected.

In the chart, while concentrations in the first column (Background) belongs to U.S Geological Survey, the concentrations in the second column (Dutch Standards) had been obtained from the name of article is Ecotoxicological Serious Risk Concentrations for soil, sediment and (ground) water: updated proposals for first series of compounds where has been published in National Institute of Public Health and The Environment in Holland. The concentrations in the third column were acquired from EPA (ECOTOX/Ecological Soil Screening Levels (Eco-SSLs)).

3.6.1.2 Pollution Index (PI)

Pollution index (PI) is used to assess contamination level of the heavy metals. The pollution index is calculated by taking the average of the ratios for each element

concentration (ppm) of interest to its tolerable level in soil for plant growth (ppm) (Eq. 3.5)

$$PI=\Sigma\ Cn/Bn \tag{3.5}$$

where, Cn is the metal concentration of the waste samples in the examined environment, Bn tolerable level in soil for plant growth (Nishida, 1982). Bn data is based on ECOTOX.

3.6.1.3 Enrichment Factor (EF)

The Enrichment Factor (EF) is one of the indicators used to assess the pollution indices. It can be used to distinguish the metal pollution where from originating either anthropogenic activities or natural sources.

It is calculated by dividing one metal concentration against a reference metal concentration (Eq 3.6).

$$EF = (Metal/RE)_{soil} / (Metal/RE)_{background} \tag{3.6}$$

where, RE is reference element which chosen is. The most used reference elements are Si, Sr, K, Sc, Mn, Ti, and Al (Malkoc et al., 2010). Al was chosen as the reference element in this calculation. Also, element concentrations in earth's crust level were used in the formula for the background values.

3.6.1.4 Geoaccumulation Index (Igeo)

Geoaccumulation index (Igeo) that been one of the pollution indices which compares the current and pre-industrial concentrations of the metals in the soil (Iqbal & Shah, 2011). It is defined by the following relationship (Eq 3.7):

$$Igeo=\log_2 C_n/1.5B_n \tag{3.7}$$

3.6.1.5 Contamination Factor (Cf)

One of the indices used to assess natural or human-caused soil pollution was the contamination factor. The Cf proposed by Hakanson was described mathematically (Eq 3.8):

$$C_f = C_n / B_n \quad (3.8)$$

where, Cn was concentration of the nth element and Bn was earth's crust level of nth element (Hakanson, 1980).

3.6.1.6 Pollution Load Index (PLI)

Pollution load index (PLI) was an effective, simple, and comparable method for estimating the level of heavy metal contamination in a soil sample (Eq 3.9).

The index described by Tomlinson, et al. (1980) was calculated as follows (Angulo, 1996):

$$\text{PLI} = \sqrt[n]{CF1 * CF2 * CF3 * \ldots . CFn} \quad (3.9)$$

Where C_f was a contamination factor of the element; n was the number of metals.

3.6.2 Metal Pollution indices in Leaches

3.6.2.1 Heavy Metal Pollution Index (HPI)

The heavy metal pollution index is a rating scale that demonstrates the cumulative impact of each heavy metal on the overall quality of water (Sheykhi & Moore, 2012; Kumar et al., 2019). It was developed by Prasad and Bose. Each HM is allocated a grade based on its relative importance and defined as inversely proportionate to its suggested standard value (Prasad & Bose, 2001). HPI is computed as the following:

$$HPI = \frac{\overset{i=n}{\Sigma\,(Qi*Wi)}}{\underset{i=1}{\overset{i=n}{\Sigma\,Wi}}} \quad (3.10)$$

$$\text{Qi} = \sum_{i=1}^{n} \frac{|Mi-Ii|}{Si-Ii} * 100 \quad (3.11)$$

where, HPI is the heavy metal pollution index; Qi is the sub-index of the heavy metal; Wi is the unit weighting of the heavy metal and n is the is the number of heavy metals mentioned.

3.6.2.2 Heavy Metal Evaluation Index (HEI)

HEI, like HPI, represents the total surface water quality in terms of HMs concentration and is calculated using the following formula (Al-Ani et al., 1987; Edet & Offiong, 2002; Ameh, 2013) (Eq 3.12):

$$\text{HEI} = \sum_{i=1}^{n} (Mi\ /MACi) \quad (3.12)$$

where, Mi and MACi represent the parameter's measured value and maximum allowable concentration, respectively. MACi values was obtained from Siegel (Siegel, 2002).

3.6.2.3 Degree of Contamination (Cd)

The degree of contamination considers both the number of parameters that exceed the upper allowed limit or guidance values of potentially hazardous components, as well as the concentration of these parameters that exceed these limits. Briefly, Cd represents the cumulative negative effect of HMs on surface water (Backman et al., 1998; Kumar et al., 2019). It is computed as the below equation (Eq 3.13; 3.14)

$$C_d = \Sigma Cfi \quad (3.13)$$

$$Cf_i = (Mi\ /MACi) - 1 \quad (3.14)$$

where, Cf_i is the contamination factor for the i-th parameter. Mi and MACi are aforementioned in HEI.

3.6.2.4 Water Pollution Index (WPIi)

This index offers a relative value for the permitted minimum level of a specific heavy metal (Thukral et al., 2005) and is calculated as below (Eq 3.15):

$$\text{WPI} = \frac{Mi - Mini}{Ri} \tag{3.15}$$

where, Mi is the measured value and Mini is the minimum acceptable limit that was obtained from US EPA. (US EPA, 2018). Ri is the range of the acceptable limit for specific heavy metal that data was taken from (Cotruvo, 2017).

CHAPTER FOUR
EXPERIMENTAL RESULTS

4.1 The Factors of Effecting the Metal Mobilization of Flask Test

4.1.1 The Properties Waste Sample and Binding Materials

Table 4.1 demonstrated that the contents of pH, organic matter, total Sulfur, and carbonate were waste and binding materials in flask tests. Emet waste sample was alkaline characteristic while leonardite and compost had a neutral pH. The pH of a Balya sample was somewhat acidic. Balya waste sample had the highest concentration of total sulfur. The compost and leonardite were rich in organic materials. The Emet sample has the lowest carbonate concentration among the others.

Table 4.1 General characterization waste samples and binding materials

Waste/Binding material	**pH**	**Organic Matter % dm**	**Total Sulfur % dm**	**Carbonate kg $CaCO_3$/t dm**
Balya waste	6.04	0.6	7.40	58.9
Emet waste	8.76	12	0.06	38.4
Leonardite	7.47	45	1.67	63.2
Compost	7.76	36	0.98	55.6

The results of the sieve analysis were showed in Table 3.2. As seen in Table 4.1, all of the wastes and binding materials had different particle size distributions. Compost was formed entirely of particles smaller than 1 mm, while leonardite consisted mostly of particles with a 2 mm diameter. 45% of Balya waste sample was larger than 4 millimetres, and the particle size distribution of Emet waste sample was similar to that of Balya waste sample.

Table 4.2 The results of the sieve analysis belong to the binding materials and wastes

Sieve No	Opening, mm	Fraction of Over Sieving, mm	Particle Size Distribution %			
			Balya W	Emet W	Leonardite BM	Compost BM
5	4	A>4	45.01	12.05	0.97	0.00
10	2	4<B<2	34.92	40.67	11.85	0.09
18	1	2<C<1	11.92	27.00	19.05	36.83
35	0.5	1<D<0.5	4.54	9.25	16.88	31.63
60	0.25	0.5<E<0.25	1.64	5.48	15.08	18.42
-	-	F>0.25	1.98	5.55	36.16	13.04

4.1.2 Metals and Heavy Metal Concentrations of Wastes and Binding Materials

Heavy metal concentrations of waste samples and binding materials were presented in Table 4.3 compared with Earth Crust Average level of metals (Haynes et al., 2016).

It was seen that As, B, Cu, Pb, Tl and Zn concentrations in Balya and Emet wastes were higher than earth crust average level, also, Mn, Sb and Se elements in Balya waste with Ba and Sr elements in Emet waste exceed the earth crust average level. Concentration of As, Mn, Pb and Zn in Balya waste and concentration of As, B and Pb in Emet waste were hundreds of times higher than earth crust average level.

Some metals in compost and leonardite, which were the binding materials, exceeded the average amount in the earth's crust, although not as much as in waste. These metals that were common in both wastes were As, B, and Tl. Additionally, concentrations of Cu and Zn in Compost were higher than the earth crust average level. Ni concentration wasn’t observed above the detection limits in the binding materials. Also, Cu and Pb were not detected in leonardite, nor were Cd and Pb in compost.

Table 4.3 Metals and heavy metal concentrations of wastes and binding materials compared with the earth crust average level

Element	Metal concentrations of waste and binding materials, ppm dm				Earth crust average
	Balya W	Emet W	Leonardite	Compost	ppm
Ag	0.0	16.5	16.4	0.0	0.075
Al	**6050.0**	**26840.0**	**2980.0**	**6830.0**	82300
As	**1051.6**	**1214.6**	**25.8**	**83.0**	1.8
B	**147.09**	**37783.0**	**292.4**	**295.17**	10
Ba	37.5	277.2	27.8	148.5	425
Ca	12664.0	38980.0	151465.0	73791.0	41500
Cd	**67.0**	**3.0**	0.1	0.0	0.15
Co	0.0	2.7	0.0	0.0	25
Cr	27.3	30.6	1.1	56.5	102
Cu	**1070.8**	**158.9**	0.0	**140.1**	60
Fe	**58480**.0	13030.0	5052.8	11954.0	56300
K	4378.0	12224.0	2612.0	6560.9	20900
Mg	15394.0	**28560.0**	**102540.0**	4262.0	23300
Mn	**26160.0**	344.8	128.2	483.45	950
Na	**26360**.0	1942.8	**75640**.0	5994.1	23600
Pb	**13176.0**	**4998.0**	0.0	0.0	14
Sb	**67.0**	0.0	31.5	0.0	0.2
Se	**16.8**	0.0	0.0	0.0	0.05
Sr	80.4	**2514**.0	62.9	270.44	370
Ti	112.5	331.2	0.0	119.3	5650
Tl	**153.8**	**62.3**	**42.2**	**99.7**	0.85
V	40.1	72.1	147.9	32.48	120
Zn	**19866.0**	**722.6**	36.2	**490.33**	70

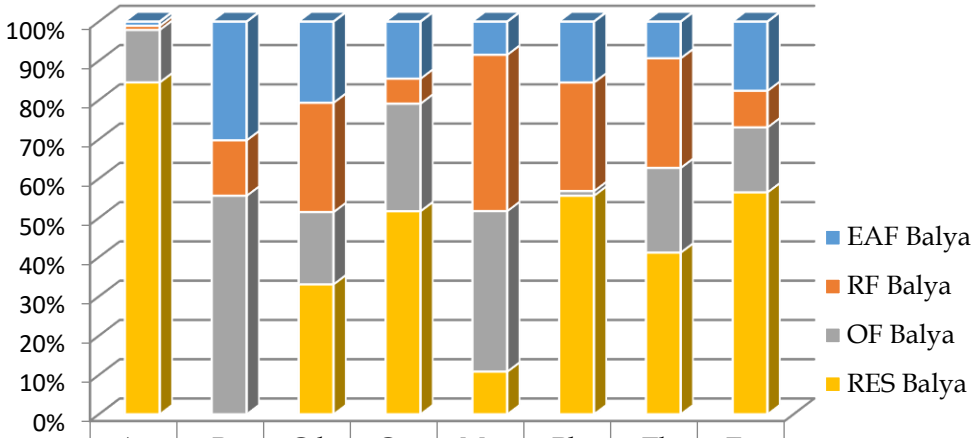
4.1.3 Chemical Speciation of Waste Samples and Binding Materials (BCR)

As, B, Cd, Cu, Mn, Pb, Tl, and Zn were studied because their overall amounts in research materials are considerably higher than the other elements (The bold number in Table 4.3).

4.1.3.1 Chemical Speciation of Balya Waste Sample

In the Balya waste, 84.5% of the As was bonded to the crystal (immobile) matrix (residual fraction - Res Balya), while all of the B was in the mobile forms, especially in the oxidizable fraction (there was no detection in the residual fraction). Mn was

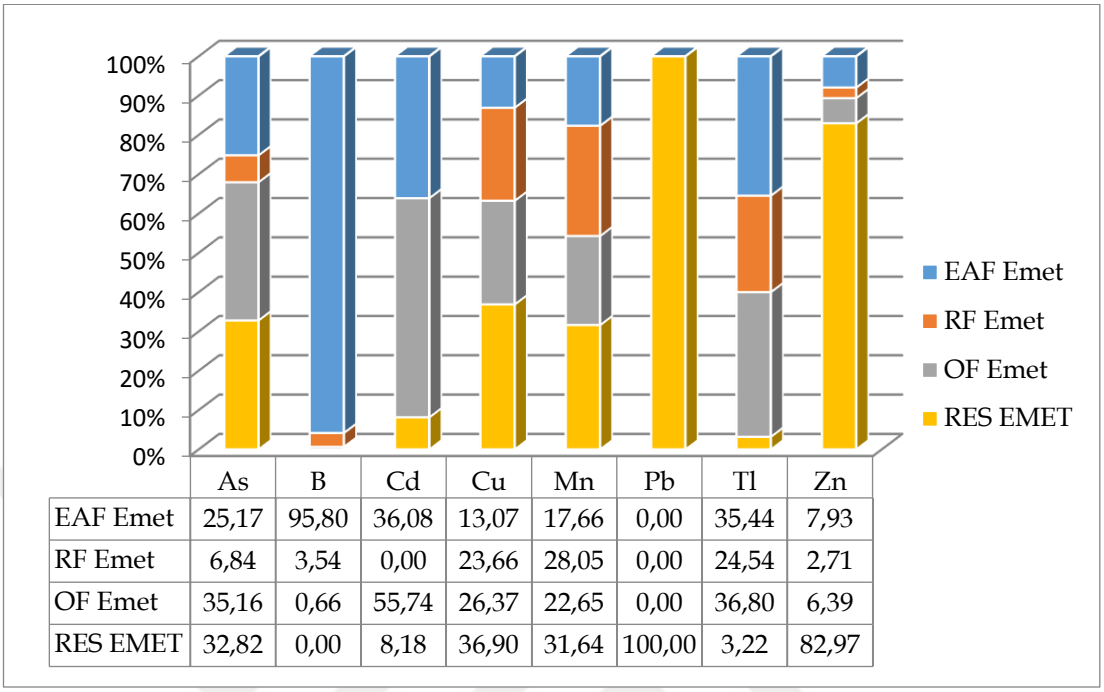
bound up to 10.9% in residual fraction and was usually found in mobile forms. B, Cd and Zn were detected over 15% in the exchangeable and acid soluble fraction (Figure 4.1)



	As	B	Cd	Cu	Mn	Pb	Tl	Zn
EAF Balya	1,04	30,21	20,65	14,53	8,45	15,51	9,33	17,61
RF Balya	1,06	14,14	27,82	6,36	39,79	27,65	27,90	9,33
OF Balya	13,37	55,65	18,42	27,40	40,89	1,16	21,58	16,55
RES Balya	84,53	0,00	33,07	51,71	10,87	55,68	41,19	56,52

Figure 4.1 Chemical binding forms of heavy metals in Balya waste sample

4.1.3.2 Chemical Speciation of Emet Waste Sample

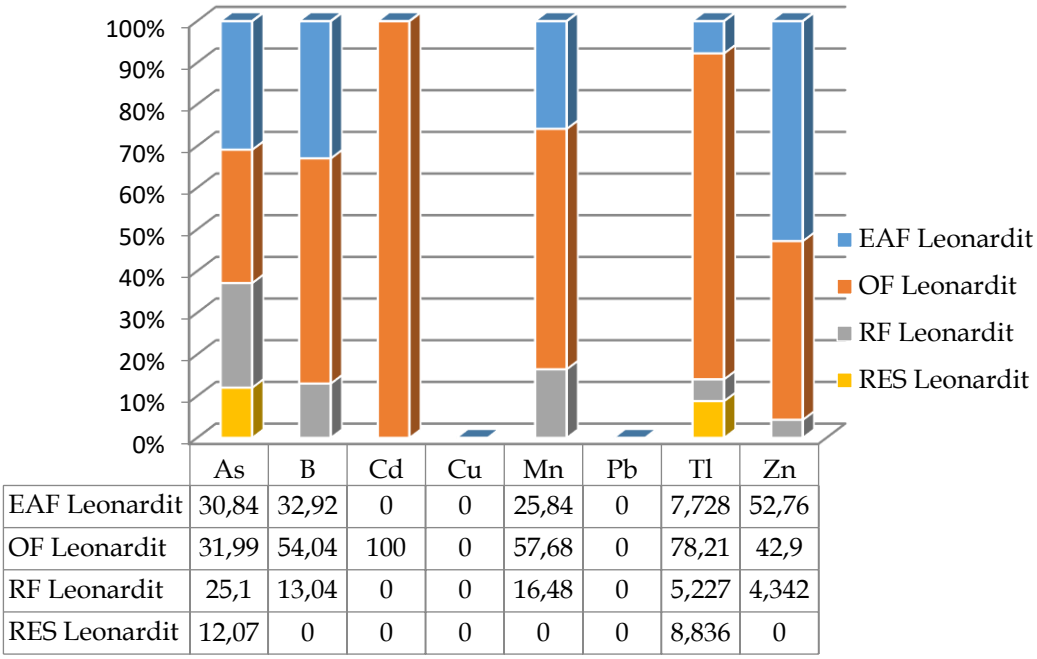


	As	B	Cd	Cu	Mn	Pb	Tl	Zn
EAF Emet	25,17	95,80	36,08	13,07	17,66	0,00	35,44	7,93
RF Emet	6,84	3,54	0,00	23,66	28,05	0,00	24,54	2,71
OF Emet	35,16	0,66	55,74	26,37	22,65	0,00	36,80	6,39
RES EMET	32,82	0,00	8,18	36,90	31,64	100,00	3,22	82,97

Figure 4.2 Chemical binding forms of heavy metals in Emet waste sample

In Emet waste, more than 65% of the As was detected in the mobile forms (Figure 4.2). B was mostly in the form of exchangeable and acid soluble fraction. More than 90% of the Cd was found in mobile forms while Pb was completely in residual fraction. Similarly, up to 80% Zn was in the crystal matrix (immobile). As seen in Balya waste sample, the metals were founded the lowest level in the form of residual fraction, too.

4.1.3.3 Chemical Speciation of Binding Material Leonardite



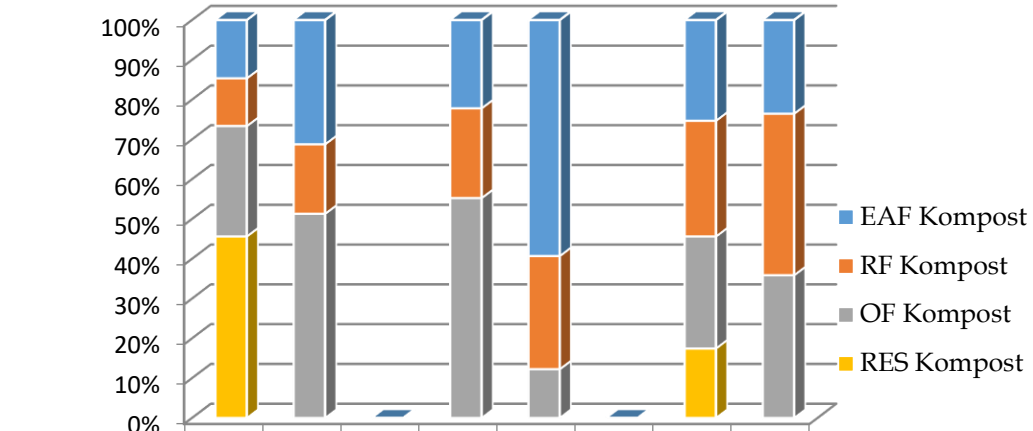
	As	B	Cd	Cu	Mn	Pb	Tl	Zn
EAF Leonardit	30,84	32,92	0	0	25,84	0	7,728	52,76
OF Leonardit	31,99	54,04	100	0	57,68	0	78,21	42,9
RF Leonardit	25,1	13,04	0	0	16,48	0	5,227	4,342
RES Leonardit	12,07	0	0	0	0	0	8,836	0

Figure 4.3 Chemical binding forms of heavy metals in leonardite

Elements found in leonardite are generally found in low concentrations in the residual fraction (for As 12.06% and for Tl 8.8%). The heavy metals in this binding material are frequently found in reducible fraction. Depending on this, metals are releasable form when the environmental conditions become acidic. Also, except Cd, the other elements are found abundantly in the form of exchangeable and acid soluble fraction (Figure 4.3).

4.1.3.4 Chemical Speciation of Binding Material Compost

Only As and Tl were in the form of residual fraction in binding material compost. The metals in the compost were found generally in the form of organic fraction, as expected. Which means, these metals could be released from the material under oxidizing conditions. The fraction that the metals were the lowest level is the residual fraction (Figure 4.4).



	As	B	Cd	Cu	Mn	Pb	Tl	Zn
EAF Kompost	14,63	31,22	0	22,17	59,3	0	25,3	23,54
RF Kompost	11,99	17,47	0	22,57	28,45	0	29,08	40,59
OF Kompost	27,76	51,31	0	55,26	12,26	0	28,16	35,86
RES Kompost	45,61	0	0	0	0	0	17,46	0

Figure 4.4 Chemical binding forms of heavy metals in compost

4.1.4 The results of Acid Production Potential (AP) and Neutralization Potential (NP) / Static Tests

The acid production potential (AP) and neutralization potential (NP) of the waste samples and binding materials were determined by using sulfur and carbonate contents. AP is a function of Sulfur content multiply with 31.25.

NP was considered as the amount of one ton of $CaCO_3$. The neutralization capacity of waste samples and binding materials was determined in acid mine drainage analysis in two ways:

1) NNP = NP - AP (NNP: Net Neutralization Potential)

NNP >20 kg/t $CaCO_3$: : Material does not have acid production potential

<-20 kg/t $CaCO_3$: : Material has acid production potential

Between 20 and -20 kg/t $CaCO_3$: :Acid production potential is uncertain and kinetic tests are applied

2) NPR = NP/AP (NPR: Neutralization Potential Rate)

NPR < 1:1 :Material has acid production potential

NPR > 3:1 : Material does not have acid production potential

NPR Between 1:1 - 3:1 :Acid production potential is uncertain and kinetic tests are applied.

Table 4.4 showed that AP, NP, NNP and NPR values calculated for the studied materials according to the analysis results.

Table 4.4 Metals and heavy metal concentrations of wastes and binding materials compared with the earth crust average level

Waste/Binding material	**AP, kg $CaCO_3$**	**NP, kg $CaCO_3$**	**NNP, kg $CaCO_3$**	**NPR**
Balya waste	231.25	58.9	**-172.35**	**0.25**
Emet waste	1.88	38.4	36.53	20.43
Leonardite	52.19	63.2	11.01	1.21
Compost	30.63	55.6	24.97	1.82

According to both the NNP and NPR parameters, the acid production potential of Balya waste sample was very high while Emet waste had no acid production potential. Leonardite was in the uncertain zone by means of the acid production potential. Similarly, NPR value of compost was in uncertain zone. However, acid production from leonardite and compost was not expected since their heavy metal concentrations were in the low levels.

4.1.5 Standard and Dynamic Leach Tests

The leaching capabilities of metals in Balya and Emet waste samples were examined by EPA 1310 Extraction Procedure (Standard leach test) and EPA 1320 Multiple Extraction Procedure (Dynamic leach test).

The amount of heavy metals (mg) added to the systems by changing the waste and binding material ratios were given in Table 4.5. It was calculated based on the total heavy metal concentrations obtained in section 4.1.2.

Table 4.5 Quantities of elements added to test systems in standard and dynamic tests by waste and binding materials (mg in 10 g of test sample)

	Balya Waste Sample							Emet Waste Sample						
	Cont.	Leonardite			Compost			Cont.	Leonardite			Compost		
W/B	**10/0**	**9.5/0.5**	**9/1**	**8/2**	**9.5/0.5**	**9/1**	**8/2**	**10/0**	**9.5/0.5**	**9/1**	**8/2**	**9.5/0.5**	**9/1**	**8/2**
As	10.5	10.0	9.5	8.5	10.0	11.0	8.6	12.1	11.6	11.0	9.8	11.6	11.0	9.9
B	1.5	1.5	1.6	1.8	1.5	340.3	1.8	377.8	359.1	340.3	302.8	359.1	340.3	302.9
Cd	0.7	0.6	0.6	0.5	0.6	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cu	10.7	10.2	9.6	8.6	10.2	1.6	8.8	1.6	1.5	1.4	1.3	1.6	1.6	1.6
Mn	261.6	248.6	235.6	209.5	248.8	3.6	210.2	3.4	3.3	3.2	3.0	3.5	3.6	3.7
Pb	131.8	125.2	118.6	105.4	125.2	45.0	105.4	50.0	47.5	45.0	40.0	47.5	45.0	40.0
Tl	1.5	1.5	1.4	1.3	1.5	0.7	1.4	0.6	0.6	0.6	0.6	0.6	0.7	0.7
Zn	198.7	188.7	178.8	159.0	189.0	7.0	159.9	7.2	6.9	6.5	5.9	7.1	7.0	6.8

4.1.5.1 The Results of EPA 1310 Extraction Procedure

The EPA 1310 procedure was a 24-hour test to determine the pollutant leaching behavior of a waste at neutral (pH: 5.0) conditions in landfill. Waste/Binding Material and water ratio (solid:liquid ratio) was taken by 1:16 and the test duration was 24 hours.

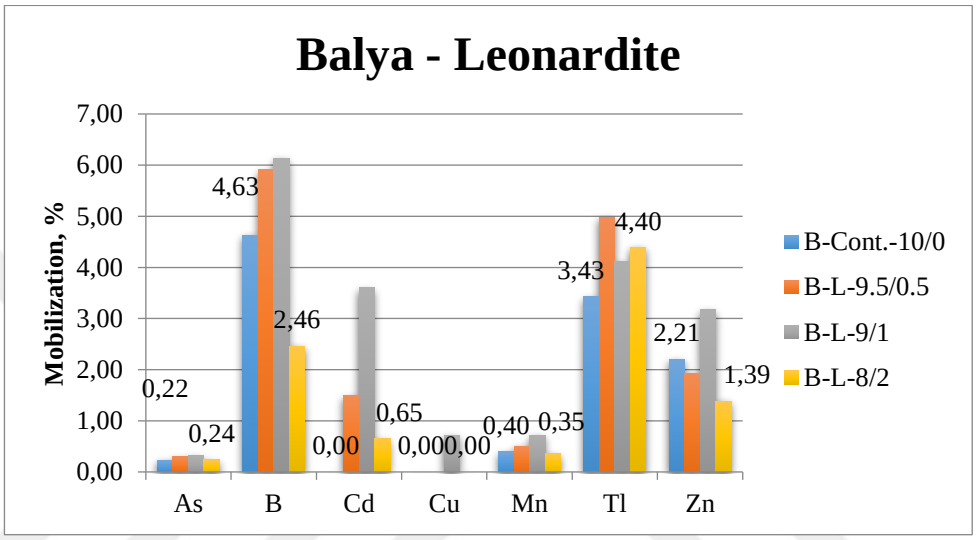
4.1.5.1.1 The Results of EPA 1310 for Balya Waste. According to EPA 1310 extraction procedure test results, Pb was not detected in the Balya waste leaches.

Figure 4.5 and 4.6 showed the metal mobilizations from Balya waste sample according to EPA 1310 B test with binding materials (leonardite and compost).

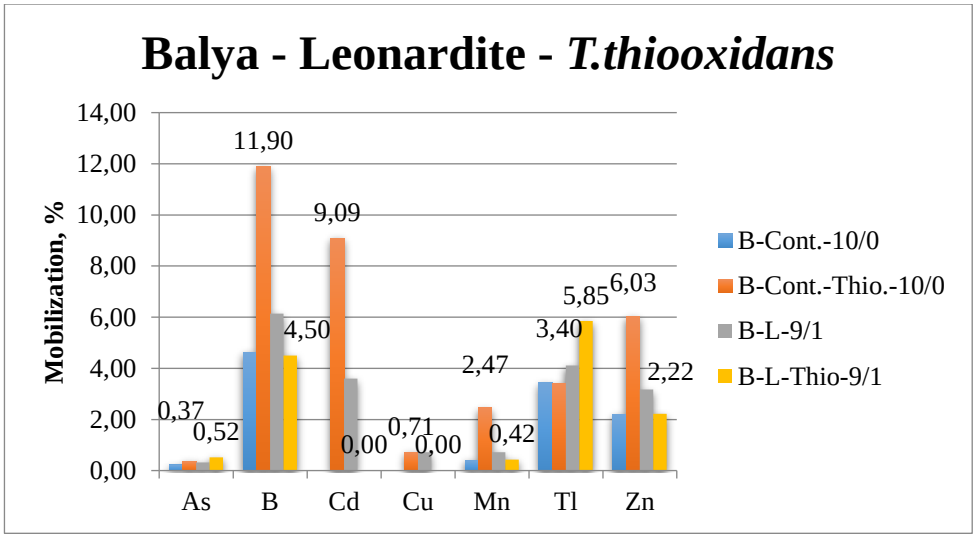
In experimental sets conducted using binding material leonardite, the rate of mobilization was decreased for all of the metals when the waste:binding material ratio (W:B) was used 8:2 (20% binding material). The maximum metal mobilization came out in element B with 6.14% by using W:B ratio 9:1.

The metal mobilization rate increased in the presence of *Thiobacillus thiooxidans* for all of the experimental sets. The maximum metal mobilization was detected in B with 11.9% by adding W:B ratio 10/0.

When compost was used as the binding material, it was seen that W:B ratio had not shown an important effect on the metal mobilization and mobilization values were higher than the binding material leonardite. The maximum metal mobilization rate was in element Zn with 48.44% by using W:B ratio 9/1. The presence of *Thiobacillus thiooxidans* increased the mobility and Mn was the most mobile element with 47.46% by adding W:B ratio 9/1.

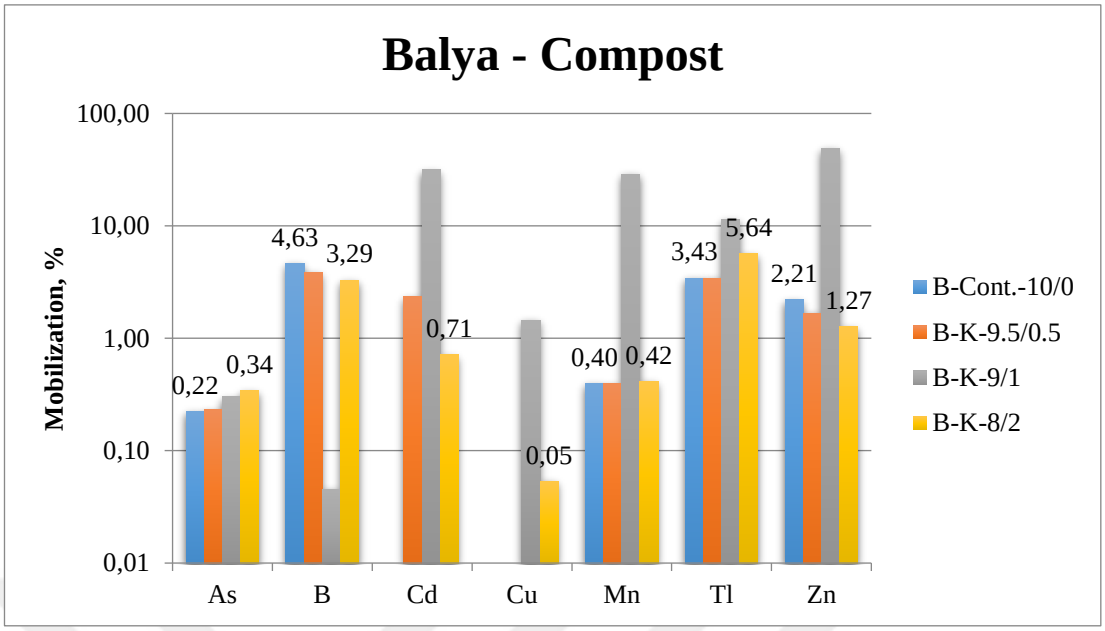


(a)

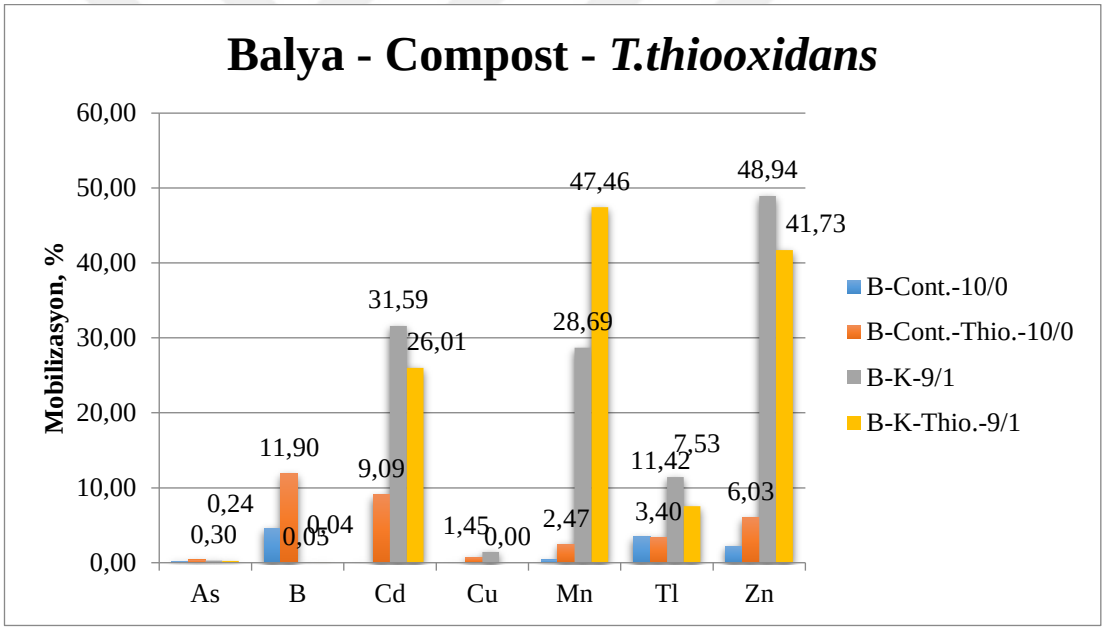


(b)

Figure 4.5 The effect of metal mobilization by using the different ratios of leonardite in Balya waste sample (a) absence of *T. thiooxidans* (b) presence of *T. thiooxidans*



(a)

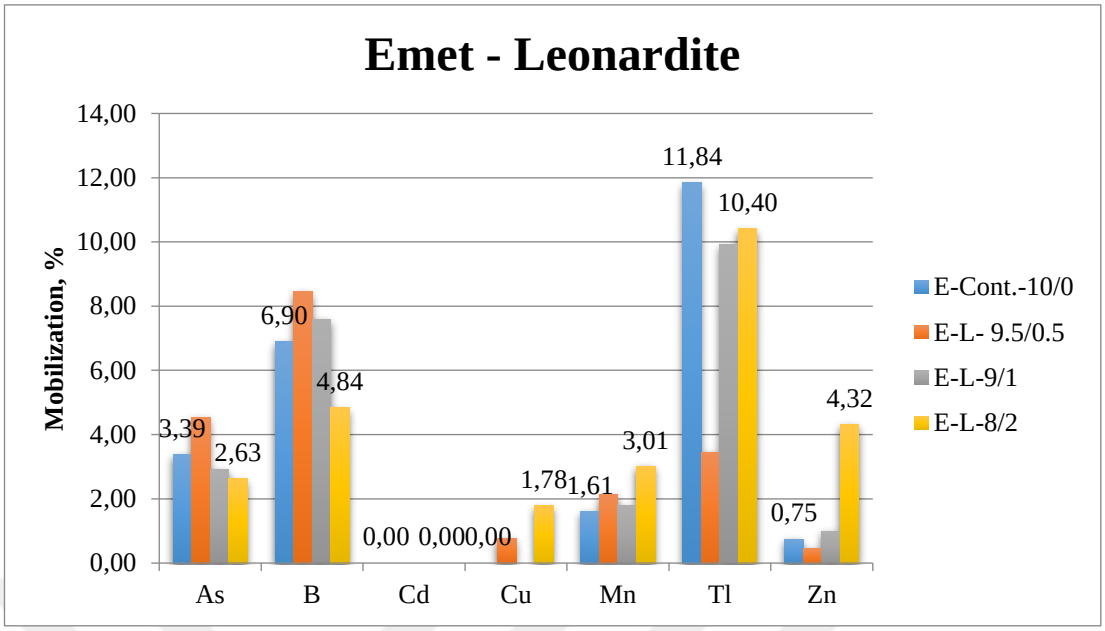


(b)

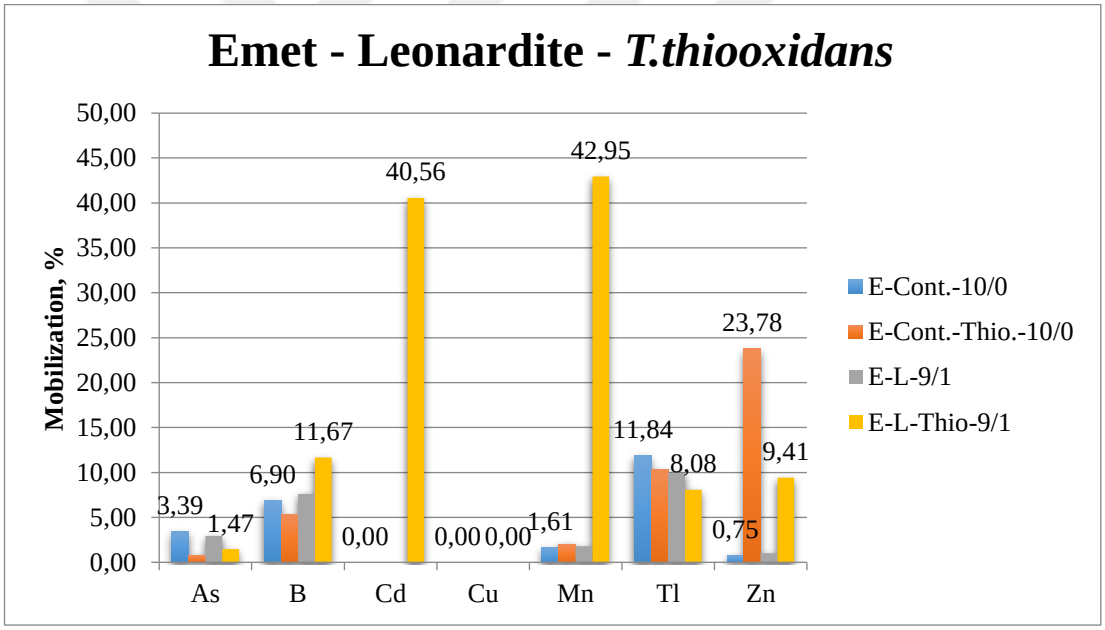
Figure 4.6 The effect of metal mobilization by using the different ratios of compost in Balya waste sample (a) absence of *T. thiooxidans* (b) presence of *T. thiooxidans*

4.1.5.1.2 The Results of EPA 1310 for Emet Waste. As in Balya waste, there was no any leachable Pb in Emet waste.

Figure 4.7 and 4.8 showed the metal mobilizations in Emet waste sample by using the binding materials.



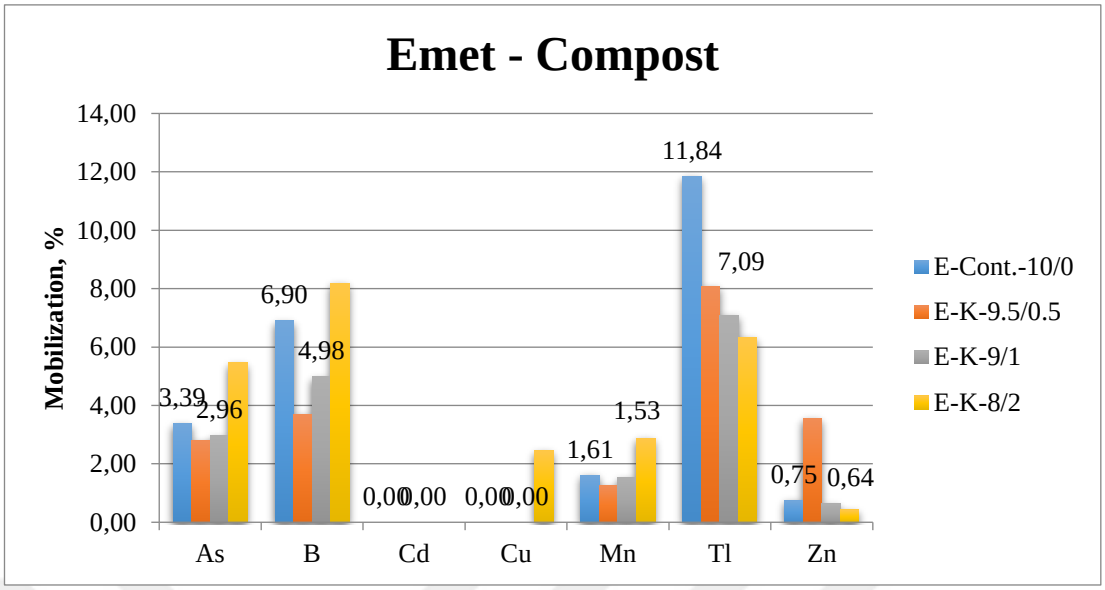
(a)



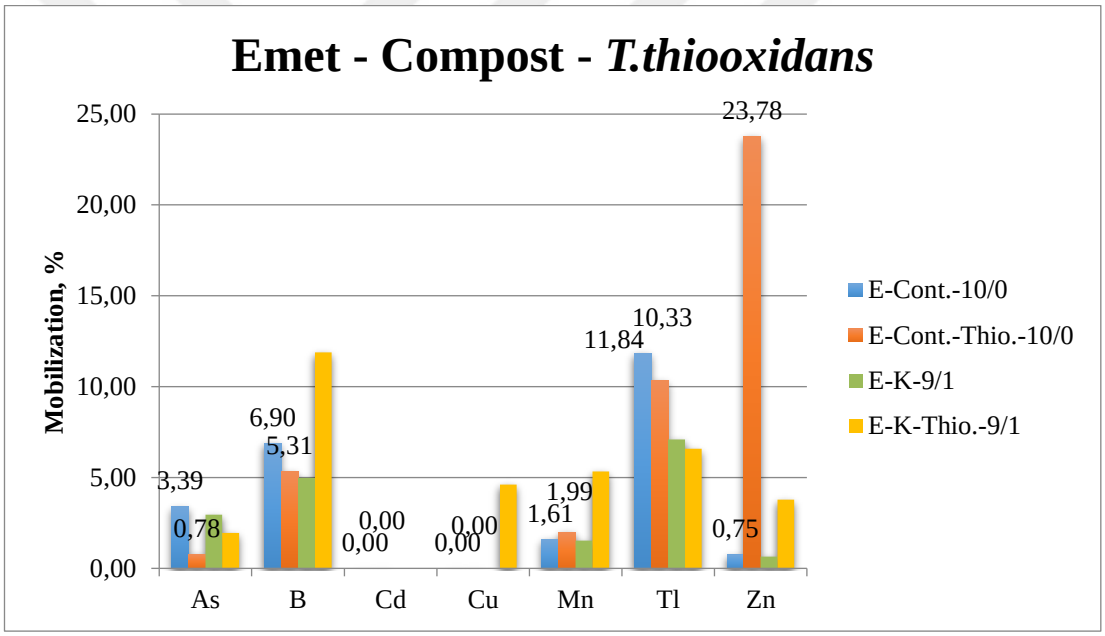
(b)

Figure 4.7 The effect of metal mobilization by using the different ratios of leonardite in Emet waste sample (a) absence of *T. thiooxidans* (b) presence of *T. thiooxidans*

As seen Figure 4.7 (a), the metal mobility increased except As and B as the leonardite ratios increased. Also, metal mobilization was maintained in the presence of *T. thiooxidans* and Cd-Mn mobilized using a W:B ratio of 9/1 with 40.56% and 42.95%, respectively.



(a)



(b)

Figure 4.8 The effect of metal mobilization by using the different ratios of compost in Emet waste sample (a) absence of *T. thiooxidans* (b) presence of *T. thiooxidans*

The use of compost in the Emet waste only showed a decrease in the mobilization of the element Tl. Metal mobilization of Zn increased considerably by using W:B ratio 9,5/0,5 (Figure 4.8).

4.1.5.2 The Results of EPA 1320 Multiple Extraction Procedure

The aim of the EPA 1320 Multiple Extraction Procedure was to determine metal leaching from the waste which occurred in the landfill under acidic conditions. The procedure of EPA 1320 conducted with being filtered liquid part of sample used in the EPA 1310 B extraction procedure. In this method, the filtered liquid part was shaken with water pH 3 (60/40: H_2SO_4/HNO_3) for 24 hours. The water quantity used in this procedure was 20 times of filtered liquid part's weight. After 24 hours, sample was taken for detecting metal mobilization. Then, the same process went on 8 additional times.

In the part of this study, W:B ratio was 9:1 (control group W:B 10/0), presence/absence of *T. thiooxidans.*

4.1.5.2.1 The Results of EPA 1320 for Balya Waste. According to the results of EPA 1320, Cu and Pb were immobilize form in Balya waste.

As seen Figure 4.9, both Tl and B leaked in high rates from the Balya waste sample; it showed that Tl and B were very mobile elements. The leaching of metals was decreased when the leonardite was used as a binding material presence of *T. thiooxidans.*

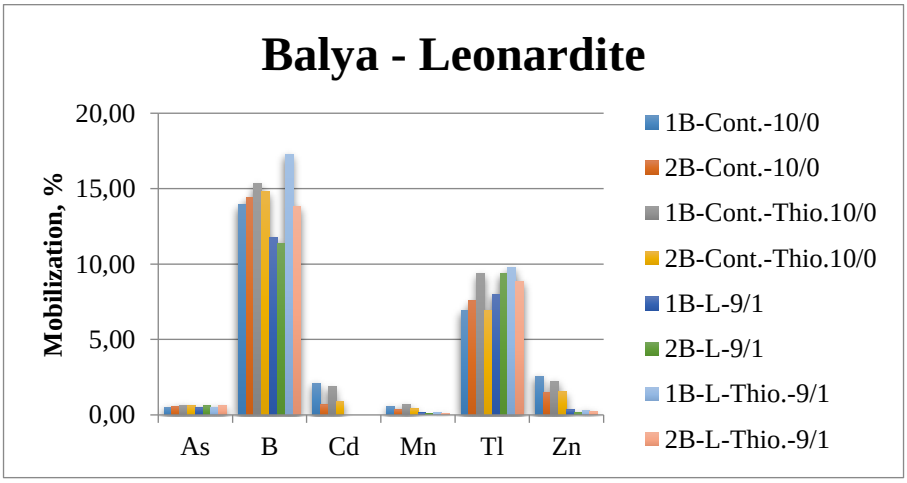


Figure 4.9 The effect of metal mobilization by using the different ratios of leonardite in Balya waste sample (presence/absence of *T. thiooxidans)*

Used compost in the experimental set, mobilization of B continued independently of the binding materials. Also, Mn, Tl, and Zn were very mobile form and the mobility of these elements increased presence of *T. thiooxidans* (Figure 4.10).

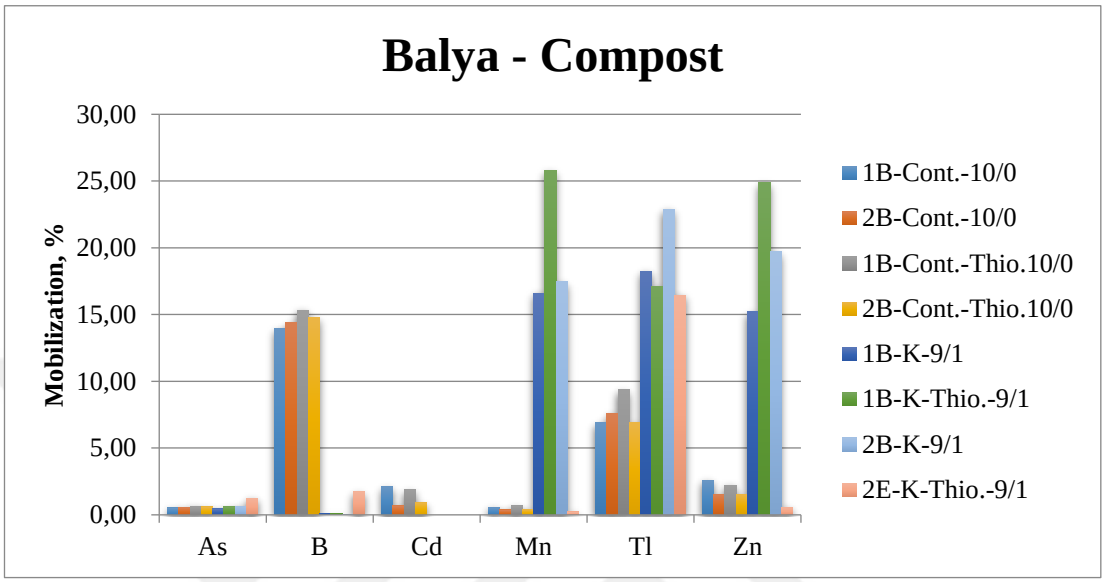


Figure 4.10 The effect of metal mobilization by using the different ratios of compost in Balya waste sample (presence/absence of *T. thiooxidans)*

4.1.5.2.2 The Results of EPA 1320 for Emet Waste. Cu and Pb were no detected an immobilize form as Balya waste both of binding materials.

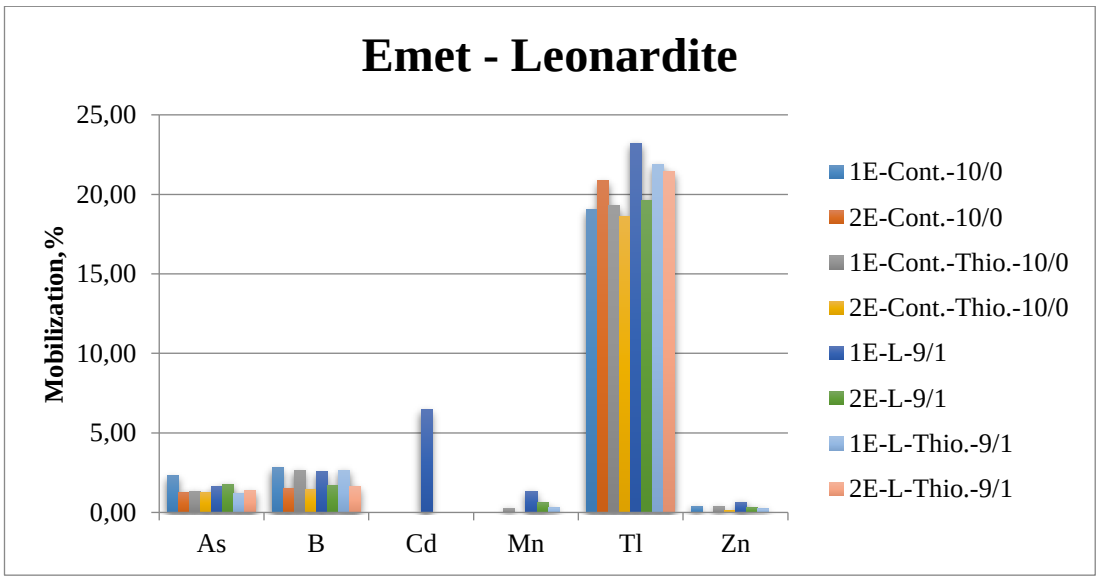


Figure 4.11 The effect of metal mobilization by using the different ratios of leonardite in Emet waste sample (presence/absence of *T. thiooxidans)*

When leonardite was used as a binding material in Emet waste, it was seen that all metals were mobilized at a very low rate except Tl. The effect of *T. thiooxidans* was not noticeable (Figure 4.11).

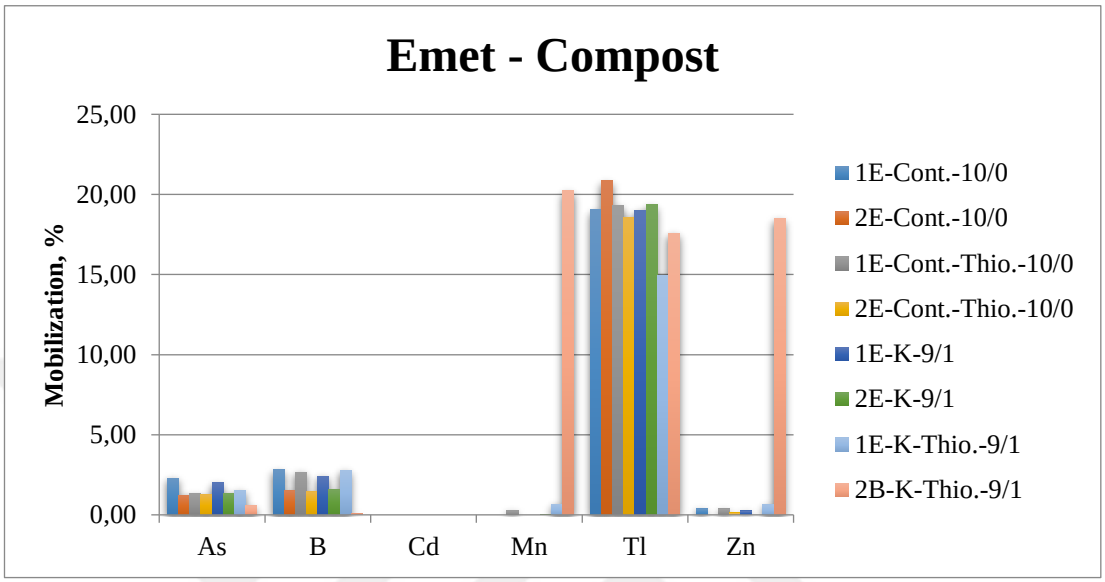


Figure 4.12 The effect of metal mobilization by using the different ratios of compost in Emet waste sample (presence/absence of *T. thiooxidans)*

Mobilization of Tl was very high rate, but the other metals mobilization was low (Figure 4.12).

4.1.6 The Statistical Result of Flask Test

Effecting factors of mobilizations on metals was investigated considering type and rate of both binding material and waste, chemical binding rate of metals via PCA (Principal Component Analysis) and correlation analysis. The total variance which was obtained from correlation matrices and PCA analysis for each experimental set were presented among Appendix 6 - Appendix 19. The main factors affecting the mobilization of metals (principal components) were assessed.

Descriptions of abbreviations in the tables are given below:

Bind.%:	the ratio of binding material
Mobil.%:	mobilization rate of metal, %
S=, kg/t:	The Sulfur content in the waste and binding material mix
CO_3=, kg/t:	The carbonate content in waste and binding material mix
B:	Balya waste
E:	Emet waste
L:	Leonardite
C:	Compost
(B,E, L,K)i, mg:	initial metal amount
(B,E, L,K)-EAF:	Exchangeable and acid soluble fraction
(B,E, L,K)-RF:	Reducible fraction
(B,E, L,K)-OF:	Oxidizable fraction (bound to organics)
(B,E, L,K)-RES:	Residual fraction (bound to crystal matrix)
T.Thioox:	*Thiobacillus thiooxidans*

4.1.6.1 The Statistical Results for Balya Waste

Table 4.6 showed results of relation between using binding material leonardite and absence of *T. thiooxidans*. PCA analysis revealed 95.359% of all factors by determining six factors that affecting the experiment.

Table 4.6 The results of PCA analysis for leonardite used as binding material in Balya wastes

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.886	27.760	27.760	3.886	27.760	27.760	3.199	22.848	22.848
2	3.202	22.869	50.629	3.202	22.869	50.629	2.886	20.614	43.462
3	2.088	14.915	65.544	2.088	14.915	65.544	2.088	14.915	58.377
4	1.675	11.964	77.508	1.675	11.964	77.508	1.934	13.812	72.189
5	1.409	10.064	87.572	1.409	10.064	87.572	1.800	12.858	85.048
6	1.090	7.787	95.359	1.090	7.787	95.359	1.444	10.312	95.359

	1	2	3	4	5	6
Bind.%		0.932				
Mobil.%	**0.502**					0.678
$S^{=}$, kg/t		-0.932				
$CO_3^{=}$, kg/t		0.932				
Bi, mg			0.576	-0.524	0.602	
B-EAF, %	0.769					
B-RF,%	0.504				0.665	
B-OF,%	0.773					
B-RES,%	-0.918					
Li, mg	0.657					
L-EAF,%			0.891			
L-RF,%					0.530	
L-OF,%			0.505	0.704		
L-RES,%	-0.653			0.653		

The first component explained 27.760% of the total variation and in this component metal mobility was found directly related with EAF, RF and OF fractions of metal concentrations in Balya waste (Appendix 6). Mobility was inversely proportional with metals bound to crystal matrix in the Balya waste and leonardite. Also, it was explained that the amount of metal in leonardite was directly proportional to the mobilization.

In the presence of *T. thiooxidans*, the result of the PCA analyses was presented in Table 4.7. According to results, extracted 6 main factors was explained 89.436% of total variance. Metal mobility was directly related with EAF, RF and OF fractions in metal concentrations in Balya waste, too (25.672%, Appendix 7). It was understood that the presence of *T. thiooxidans* in the environment directly increases mobility, as seen in factor 6, which affected the event by 7.844%.

Table 4.7 The results of PCA analysis for leonardite used as binding material in Balya wastes with the presence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.851	25.672	25.672	3.851	25.672	25.672	3.266	21.772	21.772
2	3.293	21.956	47.628	3.293	21.956	47.628	3.025	20.169	41.941
3	2.086	13.905	61.534	2.086	13.905	61.534	2.048	13.654	55.595
4	1.579	10.524	72.058	1.579	10.524	72.058	1.969	13.127	68.722
5	1.430	9.535	81.593	1.430	9.535	81.593	1.800	12.001	80.723
6	1.177	7.844	89.436	1.177	7.844	89.436	1.307	8.714	89.436

	1	**2**	**3**	**4**	**5**	**6**
T.Thioox.						0.698
Bind.%		0.952				
Mobil.%	**0.515**					0.571
$S^{=}$, kg/t		-0.952				
$CO_3^{=}$, kg/t		0.952				
Bi, mg			0.599		0.688	
B-EAF, %	0.791					
B-RF,%	0.513				0.645	
B-OF,%	0.767					
B-RES,%	-0.926					
Li, mg	0.587					
L-EAF,%			0.904			
L-RF,%						
L-OF,%			0.522	0.727		
L-RES,%	-0.699			0.589		

PCA assays for the experiments using Balya waste and compost as a binding material were presented in Tables 4.8 and Table 4.9.

In the absence of *T. thiooxidans*, 5 main factors were detected explaining 90.730% of total variance in the PCA results. Metal mobilization was directly related with EAF fraction in waste where it is explained 19.474% of these variances (90.730%) and it was inversely proportional with RES fraction (bound to crystal matrix) in waste and binding material (Appendix 8).

Table 4.8 The results of PCA analysis for composte used as binding material in Balya wastes with the absence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.985	28.466	28.466	3.985	28.466	28.466	3.433	24.524	24.524
2	3.374	24.101	52.567	3.374	24.101	52.567	2.726	19.474	43.998
3	2.332	16.657	69.224	2.332	16.657	69.224	2.344	16.742	60.739
4	1.888	13.485	82.709	1.888	13.485	82.709	2.329	16.632	77.371
5	1.123	8.020	90.730	1.123	8.020	90.730	1.870	13.358	90.730

	1	2	3	4	5
Bind.%	-0.995				
Mobil.%		0.697			
$S^{=}$, kg/t	0.995				
$CO_3^{=}$, kg/t	0.995				
Bi, mg			0.950		
B-EAF, %		0.961			
B-RF,%					-0.849
B-OF,%				0.842	
B-RES,%		-0.648		-0.692	
Ci, mg	-0.678		0.546		
C-EAF,%				0.859	
C-RF,%			0.878		
C-OF,%					0.942
C-RES,%		-0.768			

Table 4.9 showed that 92.753% of total variance explained by PCA analyses in the presence of *T. thiooxidans* (Appendix 9). The first component explained 27.131% of total variance was revealed that metal mobilization was directly proportional with EAF fraction in binding material and amount of metal attached to OF fraction in waste. At the same time, the rate of binding material and metal mobilization had a positive relation, compost increases mobility of metals. It was seen that metal mobilization increased with the presence of *T. thiooxidans* where the fifth component explained 8.698% of this variance.

Table 4.9 The results of PCA analysis for compost used as binding material in Balya wastes with the presence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	4.070	27.131	27.131	4.070	27.131	27.131	3.598	23.985	23.985
2	3.358	22.385	49.515	3.358	22.385	49.515	2.398	15.984	39.969
3	2.229	14.860	64.375	2.229	14.860	64.375	2.368	15.788	55.757
4	1.910	12.736	77.111	1.910	12.736	77.111	2.289	15.259	71.016
5	1.305	8.698	85.808	1.305	8.698	85.808	1.929	12.860	83.876
6	1.042	6.945	92.753	1.042	6.945	92.753	1.332	8.878	92.753

	1	**2**	**3**	**4**	**5**	**6**
T.Thioox.					0.735	0.566
Bind.%	0.628	-0.733				
Mobil.%	**0.533**				**0.580**	
$S^{=}$, kg/t	-0.628	0.733				
$CO_3^{=}$, kg/t	-0.628	0.733				
Bi, mg			0.785			
B-EAF, %			-0.557			
B-RF,%				-0.740		
B-OF,%	0.556	0.583				
B-RES,%	-0.633	-0.656				
Ci, mg	0.800					
C-EAF,%	0.568					
C-RF,%			0.796			
C-OF,%				0.962		
C-RES,%	-0.586	-0.544				

4.1.6.2 The Statistical Results for Emet Waste

It was seen that the relation between absence of *T. thiooxidans* and used leonardite as a binding material was presented in Table 4.10. PCA analysis explained 88.836% of these factors by determining the five factors affecting the experiment (Appendix 10)

Table 4.10 The results of PCA analysis for leonardite used as binding material in Emet wastes

Total Variance Explained

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.675	26.252	26.252	3.675	26.252	26.252	3.306	23.612	23.612
2	3.022	21.582	47.834	3.022	21.582	47.834	3.216	22.971	46.583
3	2.655	18.961	66.795	2.655	18.961	66.795	2.666	19.043	65.626
4	1.814	12.960	79.755	1.814	12.960	79.755	1.823	13.022	78.648
5	1.271	9.080	88.836	1.271	9.080	88.836	1.426	10.188	88.836

	1	2	3	4	5
Bind.%		0.996			
Mobil.%	0.617				
$S^{=}$, kg/t		0.996			
$CO_3^{=}$, kg/t		0.996			
Ei, mg	0.925				
E-EAF, %	0.951				
E-RF,%					-0.930
E-OF,%			-0.855		
E-RES,%	-0.630		0.731		
Li, mg	0.669				
L-EAF,%			0.827		
L-RF,%			-0.657		
L-OF,%				0.793	
L-RES,%				0.918	

The factors affecting of metal mobilization was found in the first component where explained 23.612% of total variance was. These factors were initial metal concentration in waste and metals attached to EAF fraction. Also, metal mobility was proportional with the initial concentration of leonardite.

In the presence of *T. thiooxidans*, the fifth component which explained 9.272% of total variance was related to mobility and it was showed that in Table 4.11 (Appendix 11).

Table 4.11 The results of PCA analysis for leonardite used as binding material in Emet wastes with the presence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.575	23.833	23.833	3.575	23.833	23.833	3.296	21.975	21.975
2	2.957	19.715	43.547	2.957	19.715	43.547	2.951	19.676	41.652
3	2.561	17.074	60.622	2.561	17.074	60.622	2.656	17.708	59.359
4	1.665	11.103	71.725	1.665	11.103	71.725	1.644	10.961	70.320
5	1.370	9.131	80.856	1.370	9.131	80.856	1.391	9.272	79.592
6	1.184	7.890	88.746	1.184	7.890	88.746	1.373	9.154	88.746

	1	2	3	4	5	6
T.Thioox.					0.610	0.544
Bind.%	0.793	0.581				
Mobil.%					0.646	
$S^{=}$, kg/t	0.793	0.581				
$CO_3^{=}$, kg/t	0.793	0.581				
Ei, mg	0.537	-0.769				
E-EAF, %	0.507	-0.635	0.557			
E-RF,%						0.713
E-OF,%		0.621	0.562			
E-RES,%			-0.929			
Li, mg	0.813					
L-EAF,%			-0.685			
L-RF,%			0.681			
L-OF,%				0.807		
L-RES,%				0.875		

Table 4.12 and 4.13 showed the factors affecting of metal mobilization in Emet waste when compost was used as binding material. The component matrix in Table 4.12 belonged without adding *T. thiooxidans*. The component matrix explained 90.416% of total variance. The mobility was directly proportional to the initial concentration of waste and the amount of metal in EAF fraction in the second component, which explained 20.629 % of the total variance was (Appendix 12).

Table 4.12 The results of PCA analysis for compost used as binding material in Emet wastes

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.707	26.479	26.479	3.707	26.479	26.479	3.465	24.751	24.751
2	3.104	22.171	48.650	3.104	22.171	48.650	2.888	20.629	45.380
3	2.952	21.084	69.735	2.952	21.084	69.735	2.768	19.769	65.148
4	1.675	11.964	81.699	1.675	11.964	81.699	2.066	14.754	79.902
5	1.220	8.718	90.416	1.220	8.718	90.416	1.472	10.515	90.416

	1	2	3	4	5
Bind.%	0.993				
Mobil.%		0.538			0.623
$S^{=}$, kg/t	0.993				
$CO_3^{=}$, kg/t	0.993				
Ei, mg		0.835			
E-EAF, %		0.963			
E-RF,%				0.917	
E-OF,%			-0.939		
E-RES,%		-0.837			
Ci, mg	0.708				
C-EAF,%				0.829	
C-RF,%			0.675	0.515	
C-OF,%			0.786		
C-RES,%					0.878

PCA analysis explained 82.578% of total variance when *T. thiooxidans* was added in the medium (Table 4.13). Metal mobility was clarified by the second (21.270% of total variance) and fifth component (7.955% of total variance). The second component was related to initial metal concentration of waste and amount of metal in the EAF, RF, and OF fraction in compost while the fifth component emphasized the positive relation between mobility and adding *T. thiooxidans* (Appendix 13).

Table 4.13 The results of PCA analysis for compost used as binding material in Emet wastes with the presence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.705	24.703	24.703	3.705	24.703	24.703	3.526	23.509	23.509
2	3.190	21.270	45.972	3.190	21.270	45.972	3.062	20.412	43.921
3	2.839	18.926	64.898	2.839	18.926	64.898	2.599	17.327	61.247
4	1.459	9.725	74.623	1.459	9.725	74.623	1.971	13.138	74.386
5	1.193	7.955	82.578	1.193	7.955	82.578	1.229	8.193	82.578

	1	**2**	**3**	**4**	**5**
T.Thioox.					0.765
Bind.%	0.800	-0.531			
Mobil.%		0.507			0.618
$S^{=}$, kg/t	0.800	-0.531			
$CO_3^{=}$, kg/t	0.800	-0.531			
Ei, mg		0.534	0.824		
E-EAF, %			0.926		
E-RF,%			-0.500	0.759	
E-OF,%	-0.506	-0.799			
E-RES,%			-0.666	-0.625	
Ci, mg	0.875				
C-EAF,%		0.507		0.582	
C-RF,%	0.519	0.562	-0.554		
C-OF,%		0.596			
C-RES,%					

4.1.6.3 The Assessment of As, Mn and Zn Mobility via PCA

The factors affecting of As, Mn and Zn mobility were investigated via PCA analysis in the presence/absence of *T. thiooxidans* by using binding material compost and leonardite in Balya and Emet waste.

4.1.6.3.1 The Assessment of As Mobility. As mobility was directly related with EAF, RF, and OF fractions in the waste (Table 4.14; Appendix –14). The presence of *T. thiooxidans* had no effect on arsenic mobility. The reason of this can be thought that As is a semi metal (Table 4.15; Appendix –15).

Table 4.14 The results of PCA analysis on the As mobility in the absence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7.333	52.380	52.380	7.333	52.380	52.380	7.247	51.762	51.762
2	4.319	30.853	83.233	4.319	30.853	83.233	4.189	29.919	81.681
3	2.112	15.084	98.317	2.112	15.084	98.317	2.329	16.636	98.317

	1	2	3
Bind.%			0.966
Mobil.%	**0.932**		
$S^{=}$, kg/t	-0.987		
$CO_3^{=}$, kg/t	-0.997		
Ai, mg	0.726		-0.666
A-EAF, %	0.995		
A-RF,%	0.995		
A-OF,%	0.995		
A-RES,%	-0.995		
Bğ.i, mg		0.641	0.720
Bğ.-EAF,%		-0.981	
Bğ-L-RF,%		-0.981	
Bğ-OF,%		0.981	
Bğ-RES,%		0.981	

Table 4.15 The results of PCA analysis on the As mobility in the presence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7.137	47.582	47.582	7.137	47.582	47.582	7.104	47.358	47.358
2	4.288	28.589	76.171	4.288	28.589	76.171	4.183	27.886	75.244
3	2.291	15.272	91.444	2.291	15.272	91.444	2.430	16.200	91.444

	1	**2**	**3**
Bind.%			0.954
T.Thio.			
Mobil.%	0.832		
$S^{=}$, kg/t	-0.993		
$CO_3^{=}$, kg/t	-0.991		
Ai, mg	0.686		-0.708
A-EAF, %	0.996		
A-RF,%	0.996		
A-OF,%	0.996		
A-RES,%	-0.996		
Bğ.i, mg			0.836
Bğ.-EAF,%		-0.999	
Bğ-L-RF,%		-0.999	
Bğ-OF,%		0.999	
Bğ-RES,%		0.999	

4.1.6.3.2 The Assessment of Mn Mobility. As seen in Table 4.16, without adding *T. thiooxidans*, there was a positive relationship between Mn mobility with EAF, RF and OF fraction in waste (Appendix - 16).

Table 4.16 The results of PCA analysis on the Mn mobility in the absence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7.478	57.523	57.523	7.478	57.523	57.523	7.473	57.486	57.486
2	3.376	25.970	83.493	3.376	25.970	83.493	3.205	24.652	82.138
3	1.593	12.253	95.746	1.593	12.253	95.746	1.769	13.608	95.746

	1	**2**	**3**
Bind.%			0.972
Mobil.%	-0.730		
$S^{=}$, kg/t	0.995		
$CO_3^{=}$, kg/t	0.989		
Ai, mg	0.993		
A-EAF, %	-0.998		
A-RF,%	0.998		
A-OF,%	0.998		
A-RES,%	-0.998		
Bğ.i, mg			0.841
Bğ.-EAF,%		-0.997	
Bğ-L-RF,%		0.997	
Bğ-OF,%		0.997	

It was understood that the main factor affecting of mobility was addition of *T. thiooxidans* in the medium (Table 4.17) (Appendix -17).

Table 4.17 The results of PCA analysis on the Mn mobility in the presence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	Variance	e %	Total	Variance	e %	Total	Variance	e %
1	6.976	49.832	49.832	6.976	49.832	49.832	6.975	49.823	49.823
2	3.337	23.839	73.671	3.337	23.839	73.671	3.173	22.663	72.486
3	1.713	12.234	85.905	1.713	12.234	85.905	1.822	13.016	85.502
4	1.400	10.001	95.906	1.400	10.001	95.906	1.457	10.404	95.906

	1	**2**	**3**	**4**
Bind.%			0.967	
T.Thio.				0.832
Mobil.%				0.874
$S^{=}$, kg/t	0.998			
$CO_3^{=}$, kg/t	0.995			
Ai, mg	0.996			
A-EAF, %	-0.999			
A-RF,%	0.999			
A-OF,%	0.999			
A-RES,%	-0.999			
Bğ.i, mg			0.856	
Bğ.-EAF,%		-0.996		
Bğ-L-RF,%		0.996		
Bğ-OF,%		0.996		

4.1.6.3.3 The assessment of Zn Mobility. Zinc mobility was independent of the factors that determine the conditions in the environment (Table 4.18; Table 4.19). Because Zn is one of the most common in nature and it disperses equally to chemical binding form in both wastes and binding materials (Appendix – 18; Appendix – 19).

Table 4.18 The results of PCA analysis on the Zn mobility in the absence of *T. thiooxidans*

Component	Initial Eigenvalues			Loadings			Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	7.150	54.999	54.999	7.150	54.999	54.999	7.149	54.993	54.993
2	3.504	26.954	81.953	3.504	26.954	81.953	3.375	25.965	80.958
3	1.364	10.495	92.448	1.364	10.495	92.448	1.494	11.489	92.448

	1	**2**	**3**
Bind.%			0.971
Mobil.%			
$S^{=}$, kg/t	0.994		
$CO_3^{=}$, kg/t	0.993		
Ai, mg	0.980		
A-EAF, %	0.998		
A-RF,%	0.998		
A-OF,%	0.998		
A-RES,%	-0.998		
Bğ.i, mg		-0.600	0.728
Bğ.-EAF,%		0.997	
Bğ-L-RF,%		0.997	
Bğ-OF,%		-0.997	

Table 4.19 The results of PCA analysis on the Zn mobility in the presence of *T. thiooxidans*

	1	**2**	**3**	**4**
Bind.%				0.957
T.Thio.			0.889	
Mobil.%			0.897	
$S^{=}$, kg/t	0.996			
$CO_3^{=}$, kg/t	0.995			
Ai, mg	0.988			
A-EAF, %	1.000			
A-RF,%	1.000			
A-OF,%	1.000			
A-RES,%	-1.000			
Bğ.i, mg		-0.565		0.756
Bğ.-EAF,%		0.995		
Bğ-L-RF,%		0.995		
Bğ-OF,%		-0.995		

4.1.7 The Overall Assessment and Suggestions for the Flask Test

- Total Sulfur concentration of Balya waste was detected by 7.4%. It should be investigated the potential of acid mine drainage as this value is much higher than the limit value (0.1%) specified in the regulation.
- Concentrations of As, B, Cd, Cu, Pb and Zn were at a high level in both Balya waste and Emet waste.
- As, B and Tl concentrations in both leonardite and compost; Sb concentration in Leonardite and Zn concentration in compost were high level than the earth crust level. But their concentration is low according to waste materials.
- The metals except bound to crystal matrix where they were immobile (residual fraction) were found chemical binding forms in both types of waste under normal conditions.
- The rate of metal in crystal form (residual fraction) was very low both leonardite and compost.
- According to static test, Net Neutralization Potential of Balya waste is -172.35 kg $CaCO_3$. So, Balya waste was evaluated as it has an acid production potential. Other waste (Emet) and binding materials (leonardite and compost) had no an acid production potential.
- No statistically significant reduction in metal mobilization was observed with EPA 1310 B procedure in short-term and neutral conditions when Leonardite and compost were mixed the ratios of 9.5/0.5 (5%), 9/1 (10%) and 8/2 (20%).
- Metal mobilization increased generally in the presence of *T. thiooxidans* according to the results of EPA 1310 B and EPA 1320 procedures.
- It is seen that addition of *T. thiooxidans* had no influence only on the As mobilization via PCA analysis applied with the results of EPA 1310 B.
- According to the results of EPA 1310 B, metal mobilization was directly proportional with amount of metal in EAF fraction in waste for investigated all of the other metals except Zn.
- The metals were bounded to OF and RF fractions in waste contribute to metal mobility secondary priority.

- It was understood with EPA 1310 B short term kinetic test that the metals bound to EAF fraction in binding materials are mobile.
- As a result of EPA 1310 B, it is seen that 0.22% of As; 4.63% of B; 0.4% of Mn; 3.43% of Tl and 2.21% of Zn are mobile in the experimental set without binding material in Balya waste.
- As a result of EPA 1310 B, it is seen that 3.39% of As; 6.9% of B; 1.61% of Mn; 11.84 % of Tl and 0.75 % of Zn are mobile form in the experimental set without binding material in Emet waste.
- The metals in Emet waste were much more mobile form than the Balya waste.
- B had the highest mobility both wastes.
- The metals were much more mobile under neutralize condition in the experimental set not used binding material in the experiments performed with EPA 1320 long term and under acidic condition (pH=3).
- B mobility decreased 202 times by using 10% of leonardite in the long-term kinetic test. B mobilized at the rate of 28.32% without binding material while it mobilized at the rate of 0.14% in the presence of leonardite.
- Cd was only mobile in the presence of *T. thiooxidans* in both long-term kinetic test under acidic condition and short-term kinetic test under neutral condition.

4.2 The Factors of Effecting the Metal Mobilization in Column Test

4.2.1 The Properties Waste Sample and Binding Materials

Balya waste sample, which was also utilized in the flask test experimental setup, was used in this section. The characterization study of the Balya waste sample was carried out in the flask test experimental set up. In addition, TSP (Triple Super Phosphate) and marble dust were used as binding material in this experimental set up. Table 4.20 indicated that pH and organic matter belong to the control, waste sample, and binding materials.

Table 4.20 General characterization of waste sample and binding materials

	Balya Waste Sample	Fine Gravel	TSP	Marble Dust
pH	6.04	10.02	3.18	7.60
Organic matter (OM, % dm)	0.60	0.08	19.10	0.13

Balya mine sample was measured a slightly acidic pH level (6.04) while TSP had a strong acidic pH level. Marble dust was a neutral pH (7.6) in spite of high carbonate content and inert structure. Fine gravel used as a control material was considerably an alkaline pH (10.02) Among the binding materials and Balya mine waste, only TSP had a high content of organic matter. The others were detected no significant content of organic matter.

This experimental set up was run based on EPA 1627 Method. According to the method, pH, conductivity, acidity, alkalinity, and dissolved metals were determine and measurements were recorded for 15 weeks.

4.2.2 Metals and Heavy Metal Concentrations of Wastes and Binding Materials

Metal/heavy metal concentrations of Balya waste sample and binding materials were demonstrated in Table 21. Compared the results with earth's crust level (Haynes et al., 2016), As, Ba, Ca, Cu, Fe, Pb, Sb, and Zn concentrations were higher in Balya waste sample. Sb concentration was higher in both marble dust and TSP than in the earth's crust. Also, Cd concentration in TSP was higher than it should be. The other binding material concentrations were detected at lower levels. The higher concentrations than the earth's crust was marked with bold type in Table 4.21.

Table 4.21 Metal/heavy metal concentration in waste sample and binding materials (mg/kg)

Metal/Heavy Metal	Balya Mine Waste	Marble Dust	TSP	*Earth's crust Average, ppm dw
Al	15.669,64	8.45	133	82.300
As	**2.372,66**	-	-	1.8
Ba	**555,91**	9.74	7.46	425
Ca	**46.295,80**	-	-	41.500
Cd	**152,38**	-	**1.89**	0.15
Cr	59,75	0.25	16.02	102
Cu	**2.638,74**	0.58	4.57	60
Fe	**172.891,65**	-	139.5	56.300
K	12.254,55	-	265.8	20.900
Mo	-	0.11	0,5	1.2
Na	3.823,77	455.58	889.4	23.600
Ni	10.39	-	3.33	84
Pb	**28.131,91**	-	-	14
Sb	**47**	**0.62**	**0.75**	0.2
Zn	**68.545,37**	-	63.48	70

*CRC Handbook of Chemistry and Physics, 97th edition

4.2.3 The results of EPA 1310 B Methods

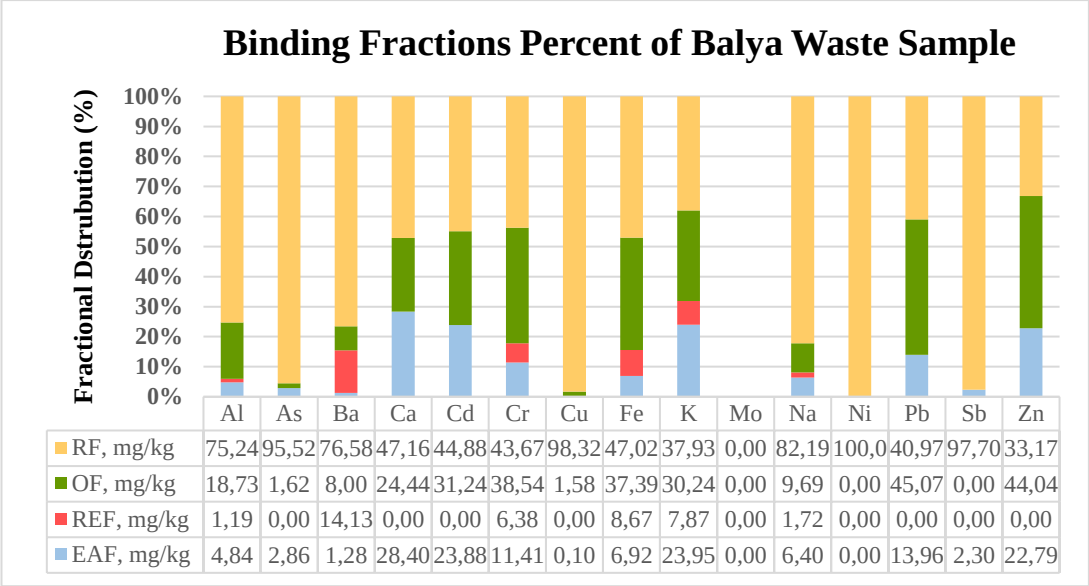
The releasable metal amount from the waste sample and binding materials were given in Table 4.22. When the results are compared with Turkish Regulation of Sanitary Landfilling of Wastes, Cd, Pb, and Zn concentrations were higher than both of regulations. As, Cu, Fe, Mo, Ni, and Sb were not detected. At the same time, the percentage of leaching was calculated based on the total concentrations of these metals. According to the results, Cd, Pb, and Zn, which are above the limit values according to both regulations, had leachable at a rate of 13.18%, 0.20%, and 6.7%, respectively. These releasable heavy metals should be kept under the control.

Table 4.22 Comparing the results of EPA 1310 B extraction procedure with TRSLW[1]

	Turkish Regulation of Sanitary Landfilling of Wastes		
	The criteria of landfilling for non-hazardous waste		
	The limit values for 2. class landfill facilities limit value (mg/l)	**Balya waste sample (mg/l)**	**Balya waste sample (% Leach)**
Al		0.072	0.0046
As	0.2	-	-
Ba	10	0.018	0.03
Ca		143.817	3.11
Cd	0.1	**2.009**	13.18
Cr	1	0.047	0.79
Cu	5	-	-
Fe		-	-
K		27.688	2.26
Mo	1	-	-
Na		50.515	13.21
Ni	1	-	-
Pb	1	**5.522**	0.2
Sb	0.07	-	-
Zn	5	**459.565**	6.7

1: *TRSLW: Turkish Regulation of Sanitary Landfilling of Wastes

4.2.4 Evaluation Chemical Speciation of Balya Waste Sample (BCR)



	Al	As	Ba	Ca	Cd	Cr	Cu	Fe	K	Mo	Na	Ni	Pb	Sb	Zn
RF, mg/kg	75,24	95,52	76,58	47,16	44,88	43,67	98,32	47,02	37,93	0,00	82,19	100,0	40,97	97,70	33,17
OF, mg/kg	18,73	1,62	8,00	24,44	31,24	38,54	1,58	37,39	30,24	0,00	9,69	0,00	45,07	0,00	44,04
REF, mg/kg	1,19	0,00	14,13	0,00	0,00	6,38	0,00	8,67	7,87	0,00	1,72	0,00	0,00	0,00	0,00
EAF, mg/kg	4,84	2,86	1,28	28,40	23,88	11,41	0,10	6,92	23,95	0,00	6,40	0,00	13,96	2,30	22,79

Figure 4.13 Chemical binding forms of heavy metals in Balya waste sample

All of the elements in percentage were bounded to residual fraction at most (Ni is bounded to ratio of 100%). In the second, organic fraction followed which most of the elements were bounded to this fraction (except Mo, Ni, and Sb). Then, except Mo and Ni, the other elements were bounded to exchangeable and acid soluble fraction Ca, Cd, K, Pb, and Zn were mobilized to the soil when compared with the other elements. The elements bounded to reducible fraction were less than the other fractions. Ba was found the highest percent with 14.1% as Al had the least percentage for the reducible fraction.

4.2.5 The Evaluation of the Majored Parameters in Column Tests

4.2.5.1 pH Variation in the Column Test

For 15 weeks, pH levels in all of the columns were observed an increase (Figure 4.14). The highest pH value was in the control column (C1-9,7) with no added binding material at the 14th week. It is reason may be that the fine gravel had the highest pH value initially (10.02). The other maximum pH followed this value was 8,3 in C5 that column was added marble dust. Marble dust had been served as a buffer in column despite it had approximately neutral range (7.6). Marble dust showed much more efficient effect than the other binding material TSP. The lowest pH in columns was detected with added TSP 2% in C4 (4.15). The reason for this could be that the pH values in the added TSP columns have been reduced because TSP had a low pH. At the end of the 14th weeks, pH values in all of the columns were alkaline ranges.

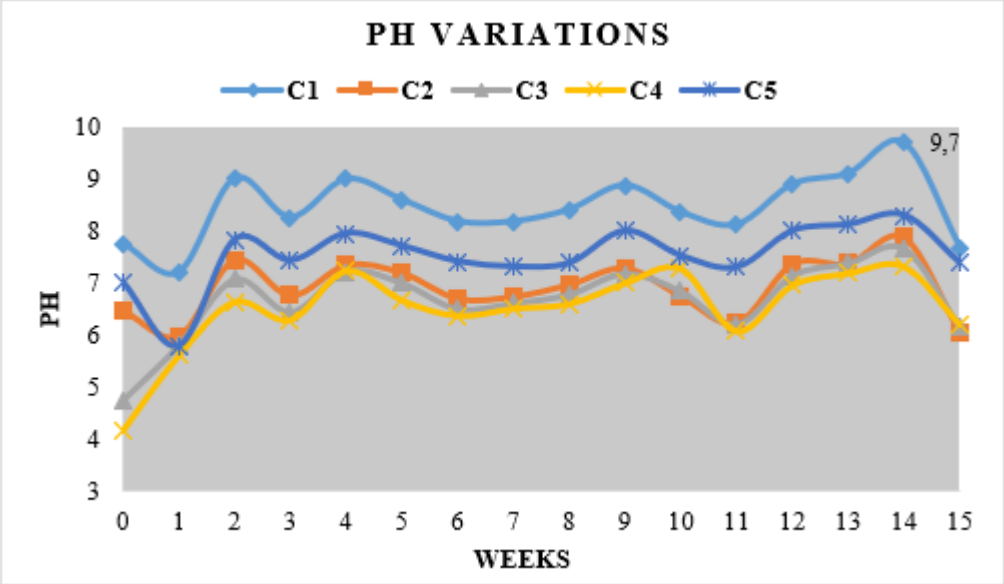


Figure 4.14 Overall pH variations in the columns for 15 weeks

4.2.5.2 EC Variation in the Column Test

For 15 weeks, EC values in all of the columns reached to the maximum point at the end of the 1st week and then they had begun to fall down to 4th and 5th weeks (Figure 4.15). C1 included fine gravel was a control column and was washed with distilled water and 2% HNO_3. On the other hand, the maximum EC value was 3440 µS/cm in C2 in the initial that loaded with only Balya sample (not added binding material). After 1st week, this value had fallen to about 2400 µS/cm. At the 11th week, while the EC value was 2417 µS/cm in C4, it was 231 µS/cm in C5. The highest average EC value was obtained in C5 at the end of the operation period. EC value was high level at the end of the operation period even though using binding materials.

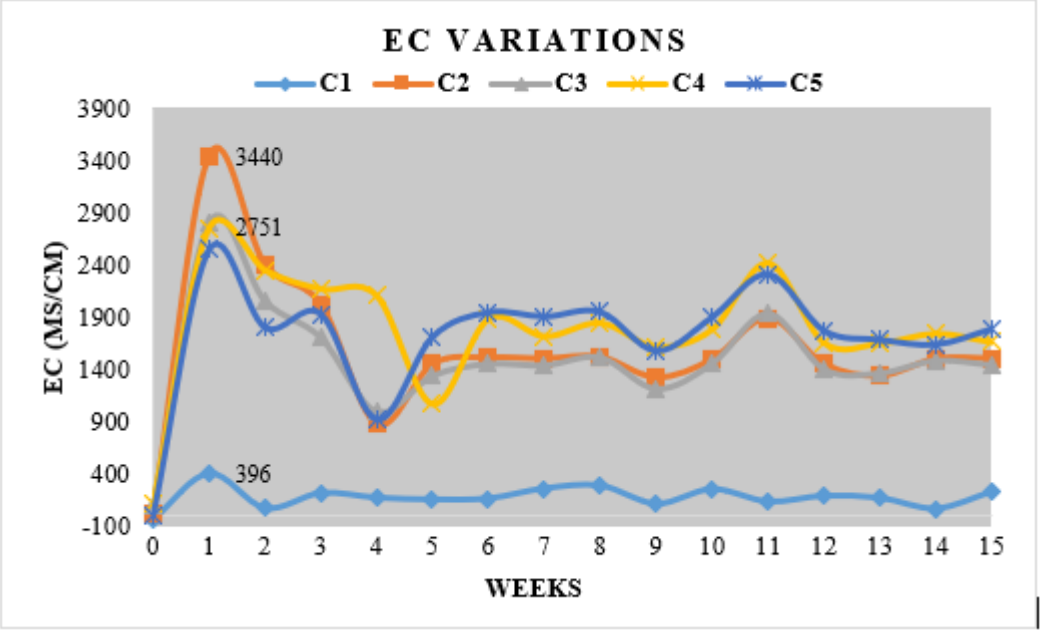


Figure 4.15 Overall EC variations in the columns for 15 weeks

4.2.5.3 Alkalinity Variation in the Column Test

As the seen that Figure 4.16, alkalinity values in the columns raised from 0th to 1st week except C5. The maximum alkalinity was determined by 582 mg/l in C5 at the beginning of the operation period while the minimum alkalinity was measured by 15.6 mg/l in Balya mine sample no added binding material (C2). After two weeks later, fluctuations were similar between C2, C3 and C4 columns, C1 and C5 columns were similar to each other. It is detected marble dust is more effective than TSP used to tampon to acidic ions.

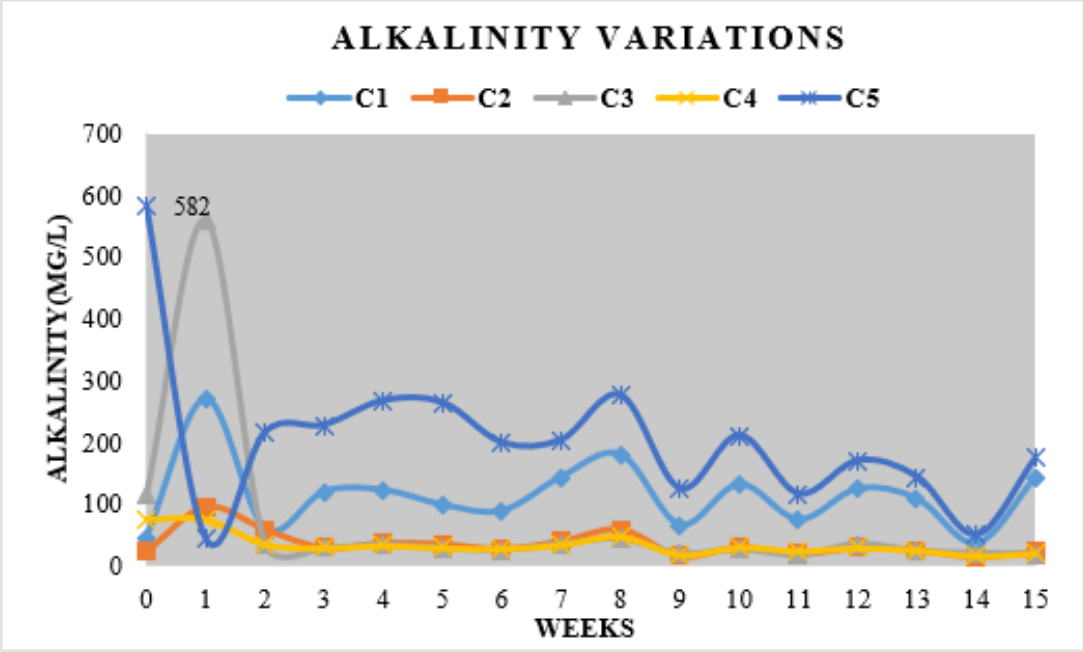


Figure 4.16 Overall alkalinity variations in columns for 15 weeks

4.2.5.4 Acidity Variation in the Column Test

Control column (C1) no added binding material were basic character. Acidity values were measured constantly negative in this column. Similarly, acidity was negative value in added powdered marble (C5) because marble dust had a high tampon capacity. As seen the Figure 4.17, the maximum acidity was detected by 7300 mg/l in adding 2% TSP C4 at the beginning of the operation period.

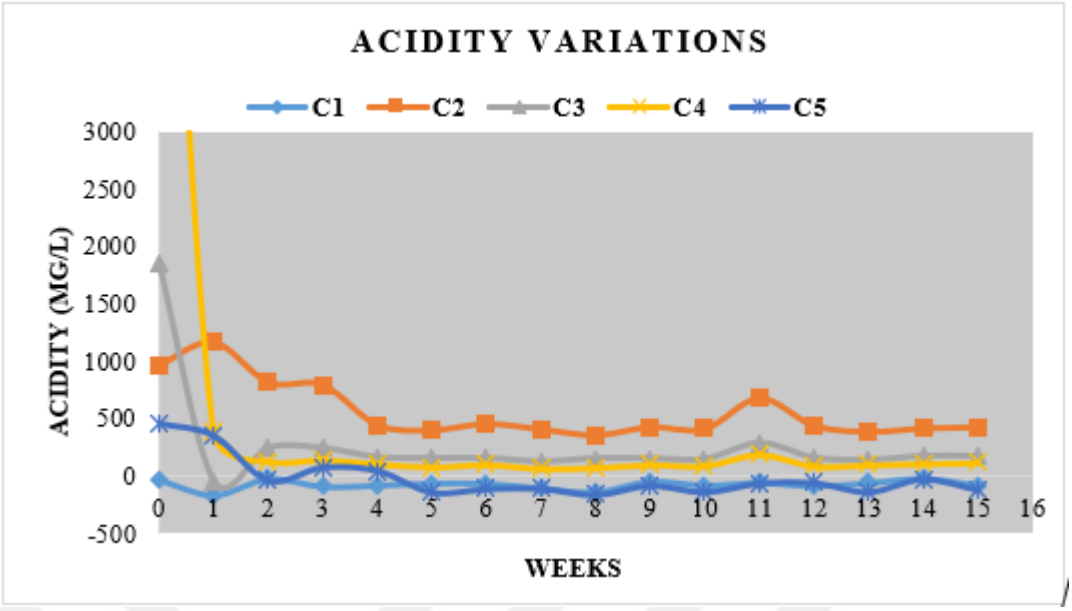


Figure 4.17 Overall acidity variations in columns for 15 weeks

4.2.5.5 Variation of Metal/Heavy Metal Concentrations

Zn Concentration was detected in columns between 10th and 15th week while As, Ba and Cd concentrations was not detected in columns.

4.2.5.5.1 Overall Cadmium (Cd) Variations. As seen the Figure 4.18, Cd concentration decreased gradually until 10th week in C2. The element Cd was not detected in control column (C1). Concentration of Cd in Balya mine sample (C2) was measured 67 ppm that it was higher than 446 times from the average of the earth's crustacean (Cox, 1989). The highest Cd concentration was 2.95 ppm in Balya mine sample (C2) at the end of the first week. It was not determined in any columns between 10th and 15th week throughout operation period. Although Cd concentration in C2 was measured by 0.625 ppm in the 10th week, this value is high enough for Turkish Regulation on Landfill of Waste threshold value of 0.1 mg/l. It is found that immobilization of Cd is inadequate in Balya mine waste when TSP and powdered marble is used for a binding material.

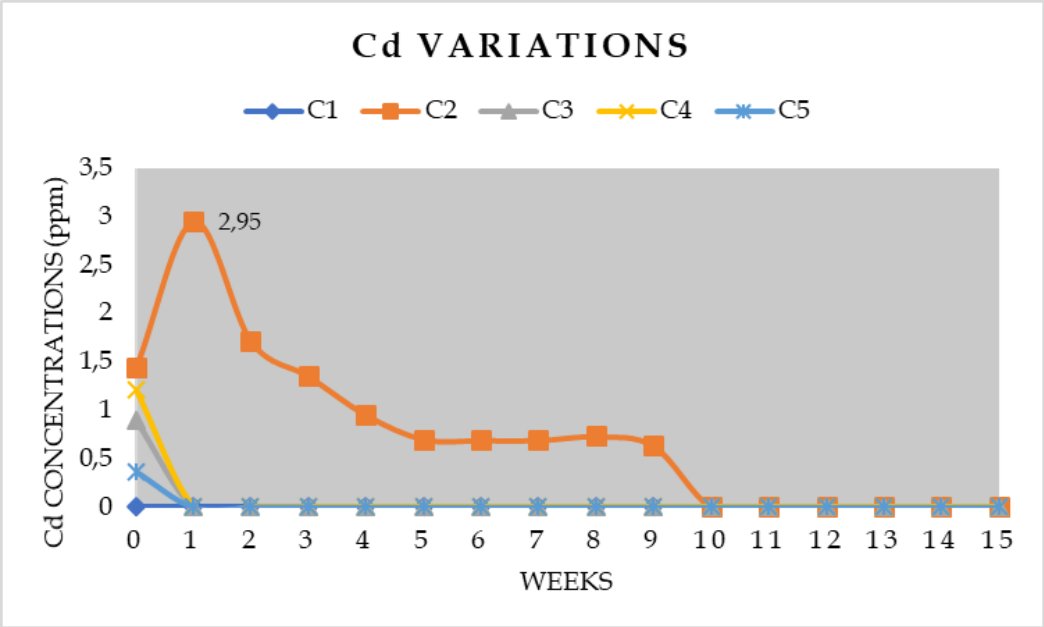


Figure 4.18 Overall Cadmium variations in columns for 15 weeks

4.2.5.5.2 Overall Zinc (Zn) Variations. Zn concentration was detected in almost all columns during the experimental duration. The maximum Zn concentration was 508,2 ppm in C2 (Balya mine sample) at the end of the first week. There was no concentration of Zn in control column (C1) until the half of the experiment period. Then, it was measured 0.0301; 3.123; and 0.3877 ppm, in 8th, 11th, and 13th week, respectively. In the initial, all concentrations were in the range of 200-300 ppm. But, especially after 10th week later, these values fell to 0 in all columns in some weeks. The values of Zn concentration were high level in columns added TSP (C3 and C4) and powdered marble (C5) according to Turkish Regulation on Landfill of Waste threshold value of 5 mg/l. So, it is not appropriate to use for a binding material, due to ineffective on immobilization of element Zn (Figure 4.19).

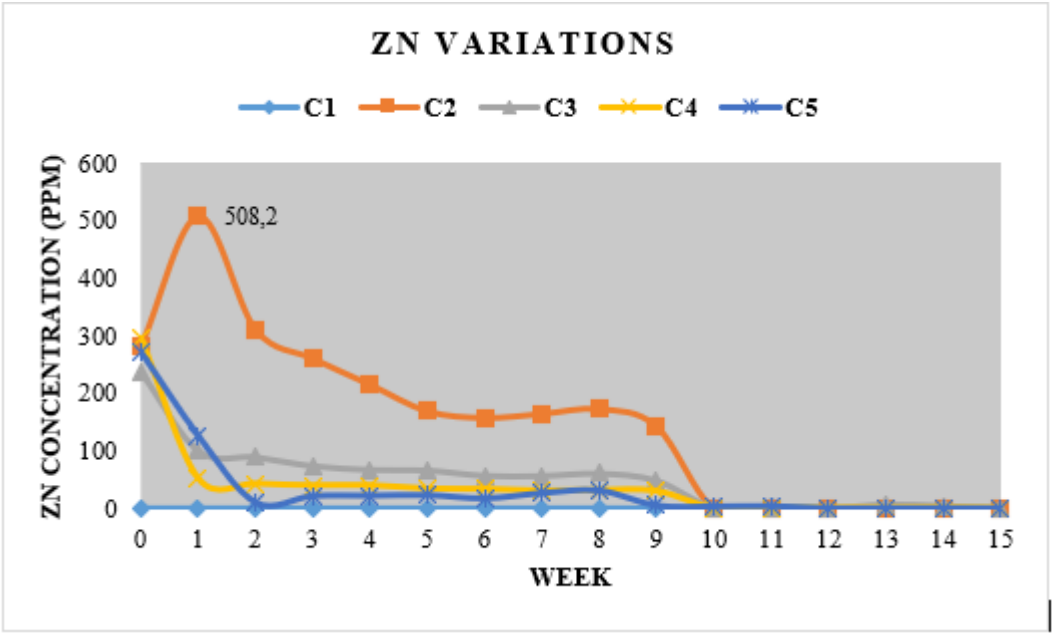


Figure 4.19 Overall Zinc variations in columns for 15 weeks

4.2.5.5.3 Overall Arsenic (As) Variations. Element As was measured only in C3, C4, and C5 throughout operation period (Figure 4.20). In this case, it may be considered that Arsenic originated from binding materials (TSP and powderized marble). But it is known that As is a residual fraction in a ratio 85% in previous analyzes (Figure 4.1). The highest As concentration in columns was determined 18.69, 7.77 and 0.05 ppm, respectively in C4, C3, and C5. TSP can't be used for a binding material to immobile As because as concentrations in columns added TSP is higher than Turkish Regulation on Landfill of Waste threshold value of 0.2 mg/l. The mobilization of As increased as TSP ratio increased. As concentration was detected 0.05 ppm below the threshold value of 0.2 ppm in C5. So, it can be thought that powdered marble is used for a binding material to immobile As.

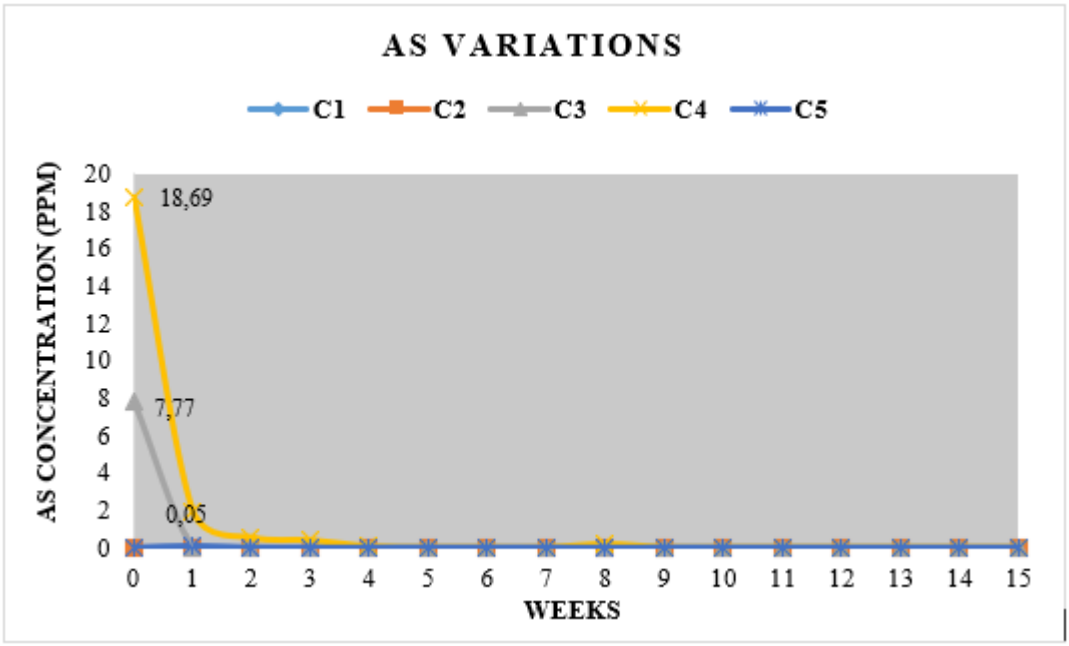


Figure 4.20 Overall Arsenic variations in columns for 15 weeks

4.2.5.5.4 Overall Barium (Ba) Variations. Figure 4.21 showed Barium variations in columns for 15 weeks. Ba concentration was lower than the threshold value 10 ppm throughout the operation period. Ba concentration was 0,12, 0,0829, and 0,022 ppm, in columns C4, C5, C3, respectively. They were quite low levels compared to Turkish Regulation on Landfill of Waste threshold value of 10 mg/l. As a result of these values, TSP and marble dust was used for a binding material to immobilize Ba. Also, Ba was determined 37.5 ppm in Balya mine sample; it is lower than the average of the earth's crustacean (240 ppm) (Cox, 1989).

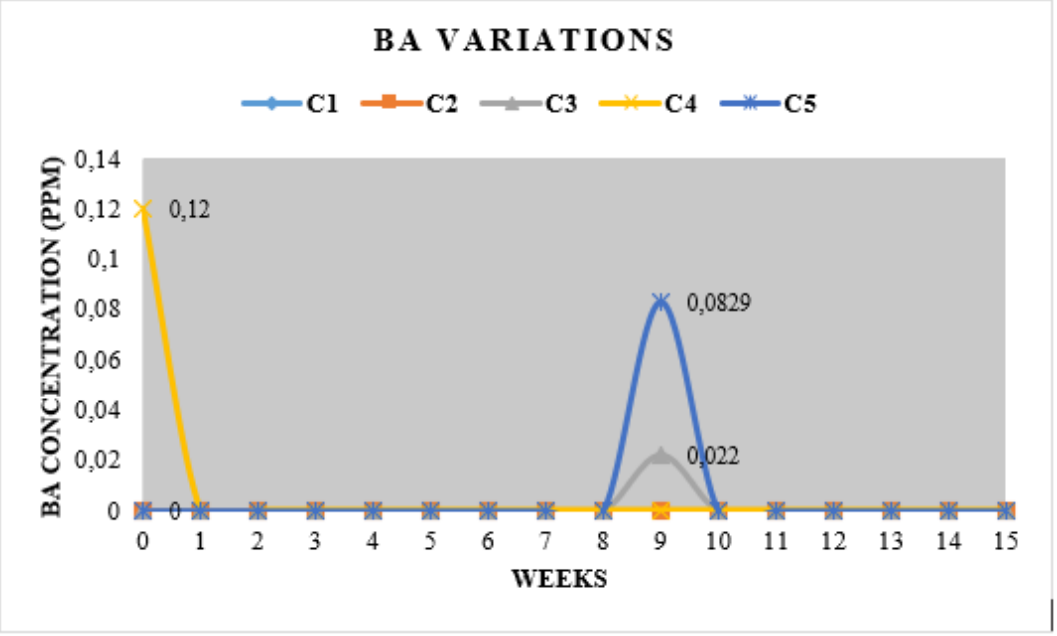


Figure 4.21 Overall Barium variations in columns for 15 weeks

4.2.3 The Overall Evaluation of the Process

The overall evaluation of the process is as follows:

1. The most effective of AMD control in terms of pH level, Acidity and Alkalinity parameters is the columns was in which 1% of marble dust is used as binding material.
2. The columns added 1% TSP for EC and TDS was found to be more efficient to control of AMD.
3. Marble dust was more effective compared with TSP in terms of immobilization of heavy metal.
4. Increase in the TSP ratio caused to more mobile in some elements. So, TSP did not appropriate used by a binding material on immobilization.
5. The level of Cd, As and Zn concentrations in leachate samples was exceeded in terms of the Turkish Regulation on Landfill of Waste, II. Class.
6. It was understood that the use of 1% marble dust as binding material was insufficient for some elements for the AMD control.

7. Ba concentrations showed that both TSP and powdered marble was able to used for a binding material.

4.3 The Factors of Effecting the Metal Mobilization of Paste Test

The experimental set up was designed with Balya waste sample by using different binding materials and their ratios in 50 ml centrifuge tubes.

4.3.1 pH and EC Values in Waste Samples and Binding Materials

Table 4.21 showed pH and EC values of binding materials used in the experimental set up. Binding materials were alkaline character except bentonite. The highest acidic value was measured in bentonite (3.77) and the highest alkaline value was detected in cement binding material (13.6). Cement had the highest EC value because of containing different minerals (5420 µS/cm). Marble dust was the lowest EC value (186.6 µS/cm).

Among the waste samples, the highest and the lowest pH were detected in No4 and No1, respectively while conductivity was the highest in No2 and the lowest in No3 (Table 4.21).

Table 4.23 pH and EC values for waste samples and binding materials

Waste Sample / Binding Material	pH	Conductivity (µS/cm)
No1	3.59	2640
No2	3.93	4425
No3	4.99	2335
No4	5.32	2642
No5	4.45	3011
Marble dust	9.94	186.8
Ash	12.9	1265
Cement	13.6	5420
Bentonite	3.77	519

4.3.2 The Results of Acid Production Potential (AP) and Neutralization Potential (NP) / Static Tests

Waste samples had been prepared considering the total sulfur, pyritic sulfur, total carbonate, neutralization potential, and acid production potential of each sample. The results of the parameters were demonstrated in Table 4.25.

Table 4.24 The results Total S, Pyritic S, inert C (Carbonate C), NP, AP, and NP/AP ratio in the waste samples and binding materials

	Total $S^{=}$ (%)	**Pyritic $S^{=}$ (%)**	**Carbonate C (%)**	**AP, kg $CaCO_3$/ton**	**NP, kg $CaCO_3$/ton**	**NP/AP**	**NNP = NP-AP**
No 1	9.45	0.52	0.12	16.145	9.904	0.613	-6.242
No 2	17.78	3.1	0.28	96.927	23.166	0.239	5.244
No 3	11.36	3.35	1.32	104.815	110.06	1.05	-73.761
No 4	36.54	19.29	1.1	602.784	92.054	0.153	-510.73
No 5	23.81	9.343	0.697	294.347	84.152	0.285	-210.19
Marble dust	0.05	0.05	10.29	1.5	857.16	570.25	855.65
Ash	3.47	0.09	1.82	2.78	151.89	54.54	149.11
Cement	1.27	0.00	1.70	0.04	141.45	4022.92	141.42
Bentonite	0.60	0.03	0.10	0.89	8.09	9.11	7.2

NP/AP results explained that all of the waste samples except No3 had acid production potential since values were lower than 1. NP/AP value of No3 waste sample had the highest NP/AP ratio. It means that it is uncertain zone for the acid production and one of the kinetic tests must be applied. Figure 4.22 and Figure 4.23 were demonstrated the distribution of NP/AP and NP - AP levels of the waste samples used in the experimental set up.

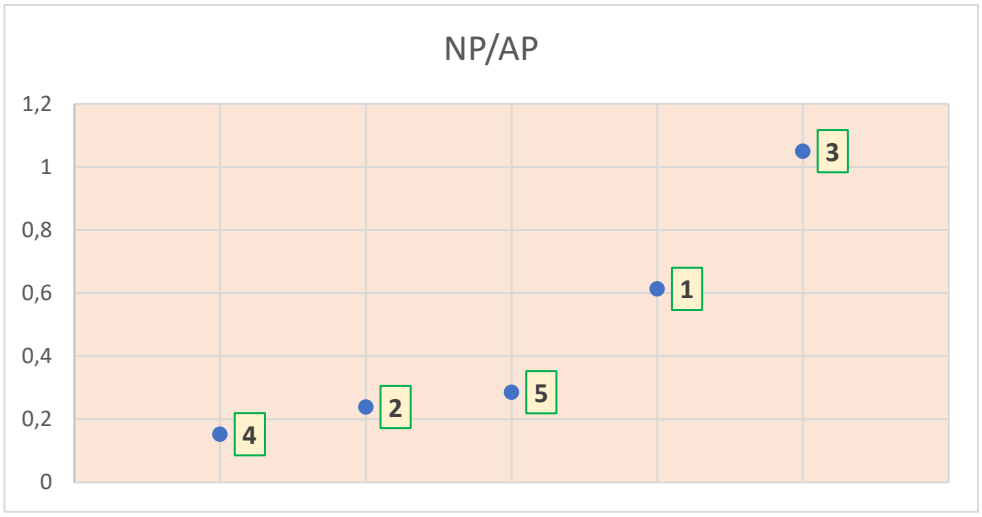


Figure 4.22 Distribution of NP/AP ratio in waste samples

When the NNP values were evaluated, it was seen that except No2 waste sample all of the waste samples were negative. Only, because No1 waste sample result was -6.242, it was difficult to determine acid production potential. So, it must be referred to kinetic tests.

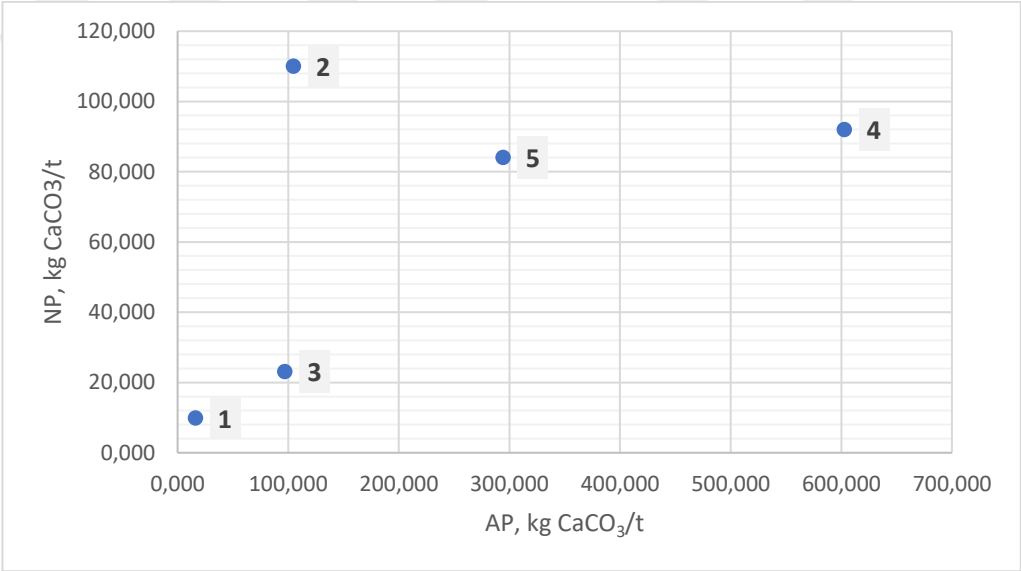


Figure 4.23 Distribution of NP and AP in waste samples

The risk of AMD occurrence is considered in materials having sulfur concentration above 0.3% in mass. In addition, any sample having sulfur above 1% in mass should be evaluated for its AMD production potential according to EPA and EU criteria. Total

sulfur values in the waste samples were measured higher than 3. According to the results. all of the waste samples had potential production of AMD and advanced technics such as kinetic tests should be applied to detect the production potential of AMD.

4.3.3 Metals and Heavy Metal Concentrations of Wastes and Binding Materials

According to the results, As, Ca, Cd, Cu, Fe, Mo (Except No5), Pb, Sb. and Zn concentrations were higher than the earth's crust level (Table 4.26). These concentrations are ordinary because the samples were collected from the Pb-Zn mine area.

Compared the binding materials with earth's crust level. As was only high in fly ash while Mo concentration in Cement and bentonite was higher than the earth's crust level (Table 24).

Table 4.25 The results of metal/heavy metal concentrations in waste samples and compared with earth's level crust

Metal/ Heavy Metal	**No1**	**No2**	**No3**	**No4**	**No5**	***Earth's crust Average. ppm dw**
Al	1.311,06	883.56	2.878,71	370.26	1.150,48	82.300
As	**3.248,45**	**4.772,08**	**2.856,23**	**7.643,35**	**6.349,44**	1.8
Ba	108.49	81.32	37.7	6.21	28.39	425
Ca	**3.488,97**	**55.873,76**	**8.669,49**	**46.042,52**	**57.230,88**	41.500
Cd	**37.5**	**305.45**	**322.71**	**264**	**282.14**	0.15
Cr	5.46	1.54	8.98	1.57	4.56	102
Cu	**829.38**	**1.394,77**	**2.031,70**	**718.14**	**1.184,68**	60
Fe	**3.340,52**	**14.287,47**	**8.268,41**	**10.112,02**	**181.303.06**	56.300
K	2.682,12	2.337,33	915.47	224.68	664.76	20.900
Mo	**2.64**	**3.34**	**2.66**	**1.25**	0.7	1.2
Na	4.180,77	3.751,25	3.480,29	3.293,99	3.557,52	23.600
Ni	-	2.04	14.66	24.83	19.16	84
Pb	**6.698,38**	**99.173,08**	**40.339,66**	**23.323,02**	**42.084,38**	14
Sb	**292.84**	**851.03**	**215.36**	**246.18**	**310.5**	0.2
Zn	**8.829,41**	**45.481,17**	**2.293,12**	**38.996,21**	**43.075,96**	70

Table 4.26 The results of metal/heavy metal concentrations in binding materials and compared with earth's level crust

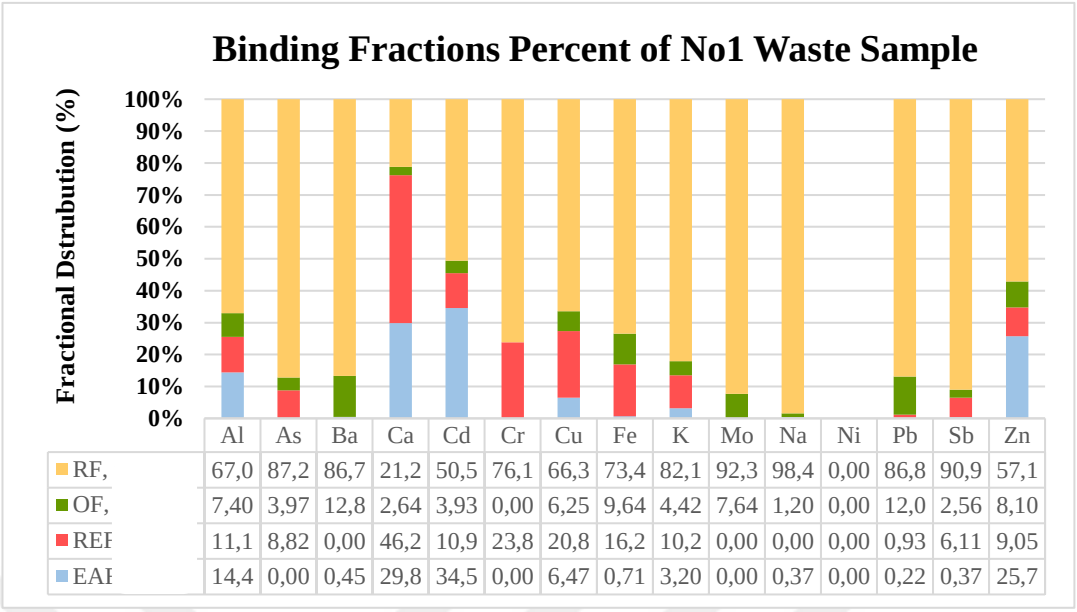
Metal/ Heavy Metal	Marble dust	Fly ash	Cement	Bentonite	*Earth's crust Average, ppm dw
Al	8.45	2.131,46	2.840.38	8.354,44	82.300
As	-	**4.81**	-	-	1.8
Ba	9.74	33.2	29.85	162.95	425
Ca	-	-	-	10.375,42	41.500
Cd	-	-	0.07	-	0.15
Cr	0.25	4.46	20.57	13.28	102
Cu	0.58	0.58	2.71	34.17	60
Fe	-	1.369,77	2.272,44	8.697,08	56.300
K	-	765.45	345.48	1.186,14	20.900
Mo	0.11	0.15	**1.6**	**1.78**	1.2
Na	455.58	463.61	413.24	3.216,95	23.600
Ni	-	2.7	10.18		84
Pb	-	-	-	-	14
Sb	**0.62**	**0.47**	**0.65**	-	0.2
Zn	-	-	-	-	70

4.3.4 Evaluation Chemical Speciation of Waste Samples (BCR)

4.3.4.1 Evaluation of BCR Result for No1 Waste Sample

In the No1 waste sample. the elements in percent were bounded mostly to residual fraction (RF). Especially. Na, Sb, Mo, As, Ba, and K were above the 80%. Although most of the elements were in the residual fraction. some of the elements such as Al (14.4%), Ca (29.8%), Cd (34.5%), Cu (6.47%). and Zn (25.7%) were bounded to exchangeable and acid soluble fraction (EAF) which elements in this fraction can be released easily to the environment. All the elements except Ba, Mo, Na bounded to reducible fraction (REF) and these elements were released after the reduction reaction. Organic fraction (OF) had the least percentage among the other fractions and there was no found in the element of Cr. The elements in oxidizable (organic) fraction are released presence of oxygen (Figure 4.24).

Ba. Mo. and Na Elements were bounded to only two fractions: residual and organic. These elements only can be released presence of oxygen or in strong acidic levels.



	Al	As	Ba	Ca	Cd	Cr	Cu	Fe	K	Mo	Na	Ni	Pb	Sb	Zn
RF,	67,0	87,2	86,7	21,2	50,5	76,1	66,3	73,4	82,1	92,3	98,4	0,00	86,8	90,9	57,1
OF,	7,40	3,97	12,8	2,64	3,93	0,00	6,25	9,64	4,42	7,64	1,20	0,00	12,0	2,56	8,10
REF	11,1	8,82	0,00	46,2	10,9	23,8	20,8	16,2	10,2	0,00	0,00	0,00	0,93	6,11	9,05
EAF	14,4	0,00	0,45	29,8	34,5	0,00	6,47	0,71	3,20	0,00	0,37	0,00	0,22	0,37	25,7

Figure 4.24 Chemical binding forms of heavy metals in No1 Balya waste sample

4.3.4.2 Evaluation of BCR Result for No2 Waste Sample

As in the No1 waste sample. the fraction with the highest percentage was the residual fraction for all of the elements. For that matter. Mo and Ni were only in this fraction. The elements in this fraction can be mobilize only in extreme acidic pH conditions. Al, As, Ca, Cd, Cr, Fe, K, Na, Pb, Sb, and Zn which bounded to reducible fraction can be released in the presence of reduction conditions in the soil Except for the elements less than 1% in the exchangeable and acid soluble fraction. only 5 elements were bound to this fraction (Al-17.58%, Ca-48.83%, Cd-24.97%, Cu-7.47%, and Zn-20.89%). The other elements except Mo and Ni could be mobile only in the presence of oxygen as they were bounded to organic fraction (Figure 4.25)

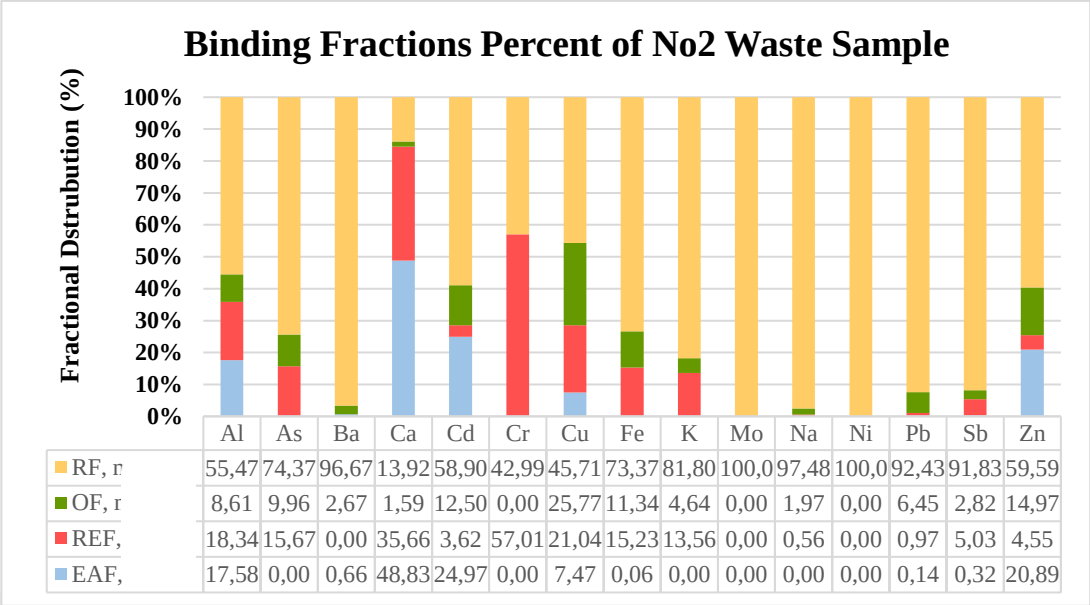
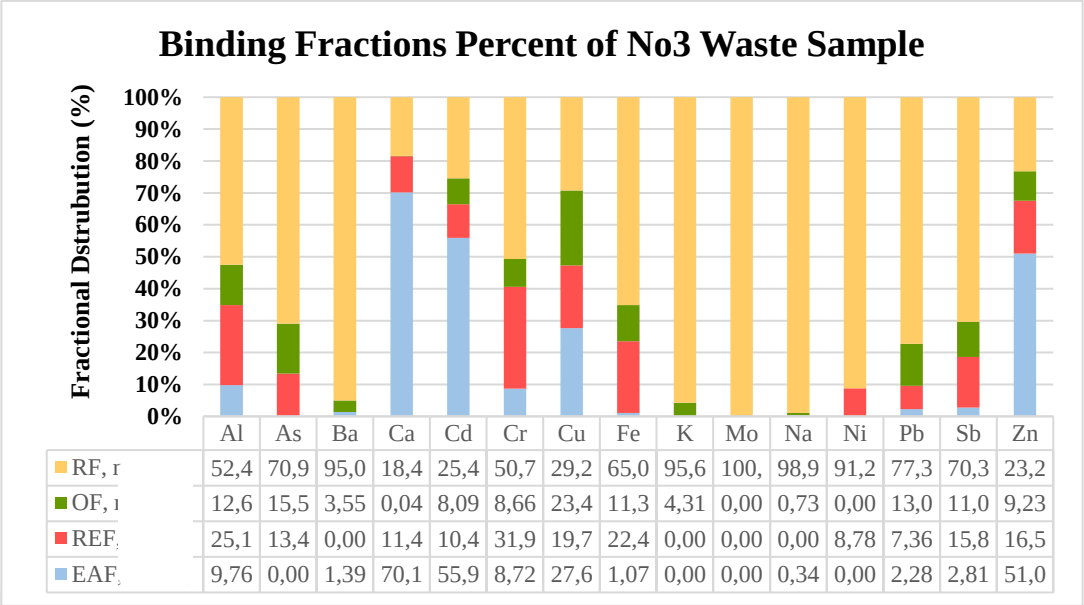


Figure 4.25 Chemical binding forms of heavy metals in No2 Balya waste sample

4.3.4.3 Evaluation of BCR result for No3 waste sample

Residual fraction had the highest ratios of percentage for all elements. Mo was bounded with ratio of 100% in this fraction. Al (9.76%), Ba (1.39%), Ca (70.1%), Cd (55.9%), Cu (27.6%), Fe (1.07%), Na (0.34%), Pb (2.28%), Sb (2.81%), and Zn (51%) were mobilized easily in the soil because they were dissolved even in the leanest acidic conditions. As, K, Mo, and Ni did not mobilize easily in the environment which they had a high ratio of residual fraction. Maybe, Na element can be incorporated into the group as the ratio of exchangeable and acid soluble fraction was under the 1 (0.34%). The elements except Mo and Ni were bounded to organic fraction. Cu was the highest ratio of organic fraction (23.4%) while Ca was the lowest ratio of organic fraction (0.04%). Al, As, Ca, Cd, Cr, Cu, Fe, Ni, Pb, Sb, and Zn were the elements bounded to reducible fraction. Na. Mo. K. and Ba couldn't be determined in this fraction. The elements in this fraction can be leached through reducible reactions (Figure 4.26).

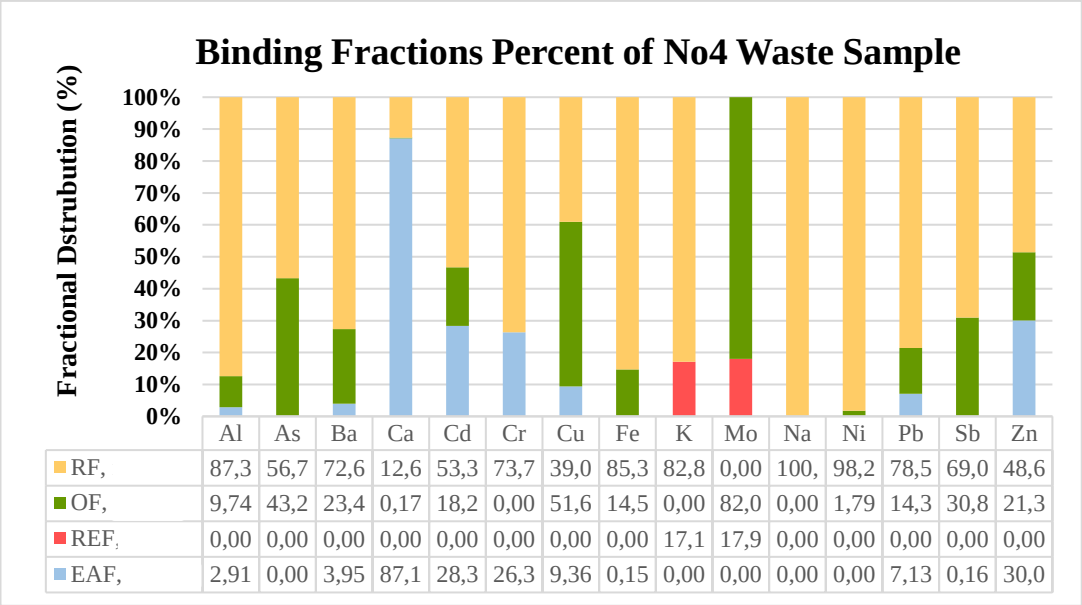


	Al	As	Ba	Ca	Cd	Cr	Cu	Fe	K	Mo	Na	Ni	Pb	Sb	Zn
RF, r	52,4	70,9	95,0	18,4	25,4	50,7	29,2	65,0	95,6	100,	98,9	91,2	77,3	70,3	23,2
OF, r	12,6	15,5	3,55	0,04	8,09	8,66	23,4	11,3	4,31	0,00	0,73	0,00	13,0	11,0	9,23
REF	25,1	13,4	0,00	11,4	10,4	31,9	19,7	22,4	0,00	0,00	0,00	8,78	7,36	15,8	16,5
EAF	9,76	0,00	1,39	70,1	55,9	8,72	27,6	1,07	0,00	0,00	0,34	0,00	2,28	2,81	51,0

Figure 4.26 Chemical binding forms of heavy metals in No3 Balya waste sample

4.3.4.4 Evaluation of BCR Result for No4 Waste Sample

As seen the Figure 4.27, residual fraction was the highest percentages among the other fractions. Na was bounded completely to it (100%) while Mo did not detect in this fraction. Only K (17.1%) and Mo (17.9%) were bounded to reducible fraction. These elements can be mobilized just with reducible reactions. Even if the ratio of exchangeable and acid soluble fraction is the lower than the other fractions. Al, Ba, Ca (with the highest ratio-87.1%), Cd, Cr, Cu, Fe, Pb, Sb, and Zn can be leached easily in the weak acidic conditions. Especially. Ca (87.1%) and Zn (30%) can be mobilized easily in the environment. The elements except Cr. K and Na that can be leached easily in the presence of oxygen were bounded to organic fraction. Mo had the highest ratio of this fraction (82%).

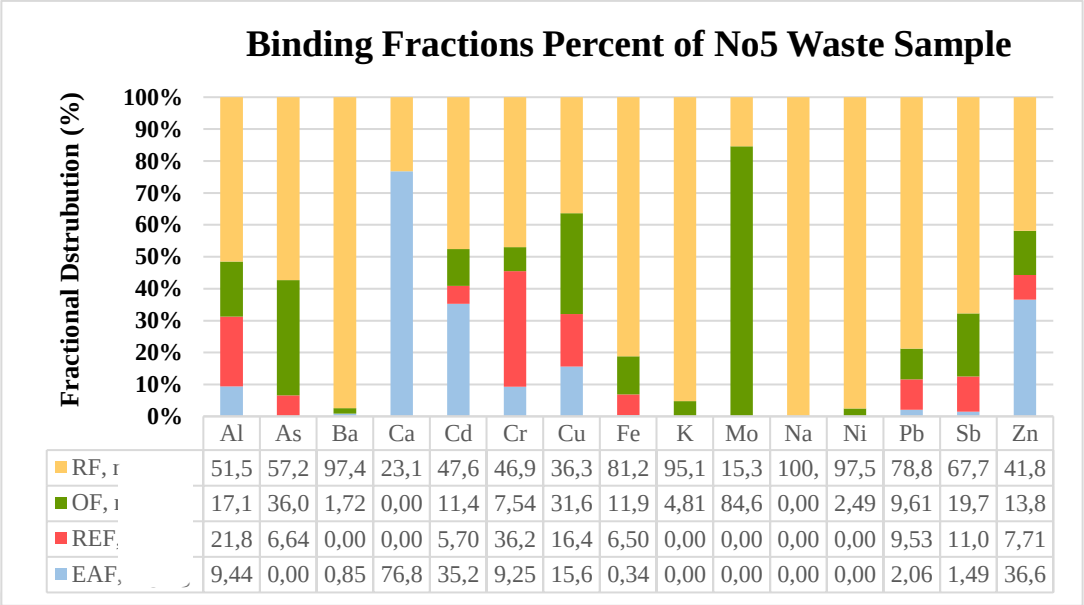


	Al	As	Ba	Ca	Cd	Cr	Cu	Fe	K	Mo	Na	Ni	Pb	Sb	Zn
RF,	87,3	56,7	72,6	12,6	53,3	73,7	39,0	85,3	82,8	0,00	100,	98,2	78,5	69,0	48,6
OF,	9,74	43,2	23,4	0,17	18,2	0,00	51,6	14,5	0,00	82,0	0,00	1,79	14,3	30,8	21,3
REF,	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	17,1	17,9	0,00	0,00	0,00	0,00	0,00
EAF,	2,91	0,00	3,95	87,1	28,3	26,3	9,36	0,15	0,00	0,00	0,00	0,00	7,13	0,16	30,0

Figure 4.27 Chemical binding forms of heavy metals in No4 Balya waste sample

4.3.4.5 Evaluation of BCR Result for No5 Waste Sample

All of the elements were bounded to residual fraction and the percentages were the highest among the others. Na was completely bounded to residual fraction (Figure 4.28). The elements except Ca and Na can be mobilized easily in the presence of oxygen. Especially. Mo was the highest percent in the organic fraction (84.6%). While the highest reducible fraction ratio was determined in Cr with 36.2%; Cd was the lowest ratio with the ratio of 5.7. The elements (Al, Ba, Ca, Cd, Cr, Cu, Fe, Pb, Sb, and Zn) which are dissolved in the weak acidic conditions were bounded to exchangeable and acid soluble fraction. In particular. Ca. Cd. and Zn can be easily mobilized in the soil.



	Al	As	Ba	Ca	Cd	Cr	Cu	Fe	K	Mo	Na	Ni	Pb	Sb	Zn
RF, ı	51,5	57,2	97,4	23,1	47,6	46,9	36,3	81,2	95,1	15,3	100,	97,5	78,8	67,7	41,8
OF, ı	17,1	36,0	1,72	0,00	11,4	7,54	31,6	11,9	4,81	84,6	0,00	2,49	9,61	19,7	13,8
REF,	21,8	6,64	0,00	0,00	5,70	36,2	16,4	6,50	0,00	0,00	0,00	0,00	9,53	11,0	7,71
EAF,	9,44	0,00	0,85	76,8	35,2	9,25	15,6	0,34	0,00	0,00	0,00	0,00	2,06	1,49	36,6

Figure 4.28 Chemical binding forms of heavy metals in No5 Balya waste sample

4.3.5 Evaluation of EPA 1310 B Methods

The releasable metal amount from the waste samples were given in Table 28. According to the results. all of the elements except As were detected in waste samples. When the results are compared with Turkish Regulation of Sanitary Landfilling of Wastes. it was determined that Cd (except in the No1 waste sample). Pb. and. Zn concentrations were higher than the limiting values in all of the waste samples. Also. Cu concentration in No1, No2, No3 waste samples and Ni concentration in No2, No4, and No5 waste samples had high level than the limits. Mo was only high in No1 waste sample.

Table 4.27 Comparing the results of EPA 1310 extraction procedure with TRSLW*

	Turkish Regulation of Sanitary Landfilling of Wastes*					
	The criteria of landfilling for non-hazardous waste	mg/L				
	The limit values for 2. class landfill facilities limit value (mg/l)	**No1**	**No2**	**No3**	**No4**	**No5**
Al		40.257	0.712	0.133	-	-
As	0.2	-	-	-	-	-
Ba	10	-	-	-	0.13	-
Ca		959.32	867.8	1.046,62	1.026,42	1.048,50
Cd	0.1	-	**7.294**	**9.213**	**2.692**	**2.976**
Cr	1	-	-	-	-	-
Cu	5	**18.776**	0.552	1.232	-	0.215
Fe		109.182	-	-	-	-
K		22.062	-	2.736	1.378	-
Mo	1	**1.157**	-	-	-	-
Na		465.821	47.1	44.341	40.797	52.122
Ni	1	-	0.071	0.016	0.106	0.108
Pb	1	**40.515**	**3.85**	**22.454**	**8.522**	**15.95**
Sb	0.07	-	0.029	-	-	0.036
Zn	5	**1.984,04**	**670.6**	**653.243**	**206.448**	**418.417**

Table 4.28 The percentage of leaching in waste samples according to EPA 1310 B extraction procedure

	LEACH %				
	No1	**No2**	**No3**	**No4**	**No5**
Al	30.71	0.81	0.05	-	-
As	-	-	-	-	-
Ba	-	-	-	20.92	0
Ca	10.26	15.53	17.84	22.29	18.32
Cd	-	23.88	28.55	10.2	16.87
Cr	-	-	-	-	-
Cu	22.64	0.4	0.61	-	0.18
Fe	1.31	-	-	-	-
K	8.23	-	-	6.13	-
Mo	437.89	-	-	-	-
Na	111.42	12.56	12.74	12.39	14.65
Ni	0	34.79	1.1	4.29	5.65
Pb	0.71	0.04	0.56	0.37	0.38
Sb	0	0.03	-	-	0.12
Zn	224.71	14.74	12.49	5.29	9.71

Releasable metal amount in percent was shown in Table 4.29. These percentages were calculated on the total amount (TAD results) and generally the potential of leaching was under the 50%. Even if some percentages are low or absent in the table. the leaching can be occurred in a long time. Contact time in EPA 1310 B Extraction Procedure was 24 hours under the neutral conditions.

4.3.6 Evaluation of Paste pH Results Between Continuous and Intermittent Set Up

4.3.6.1 Evaluation of Paste pH of No1 Mine Waste Sample

Overall pH evaluation for No1 sample in the continuous set up: pH values in control group increased firstly for 13 weeks and arrived to 6.81; then it began to decrease a little (at the end of the 15 weeks. pH value was 6.62). Although the No1 control pH showed increase. all of the pH results in this continuous set up were always acidic through the experimental period. The highest pH value in No1 was measured by used 10% of binding materials (the pH of mine samples added marble dust, ash, and cement was 9.14, 11.18, and 12.7. respectively) except the mine sample added bentonite. The highest pH with bentonite added at 1% was 6.78. At the end of the 15 weeks. the highest pH was 12.7 in added 10% cement.

Overall pH evaluation for No1 sample in the intermittent set up: The pH value both in control group and in the added binding materials of No1 mine sample was showed an increase for 15 weeks except the flask with added cement. The reason can be that because it was measured by collecting the liquid fraction of mine sample every week in a single container. At the end of the 15 weeks. the highest control pH was 5.64 while the pH of the mine sample No1 with added different ratio marble dust, ash, cement, and bentonite were detected 10.05, 10.13, 11.63, and 5.86. respectively. The pH of No1 mine sample with added cement at 10% had the highest value after 3 weeks (11.63). The sample with added bentonite had been acidic pH through the experimental period.

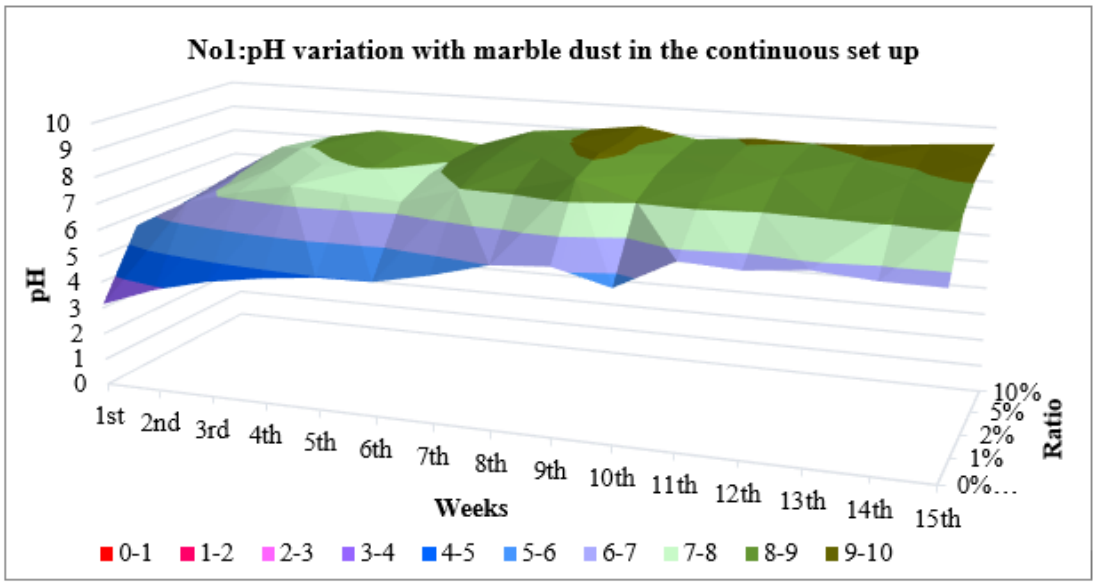


Figure 4.29 pH variation of No1 mine sample added marble dust in the continuous set up

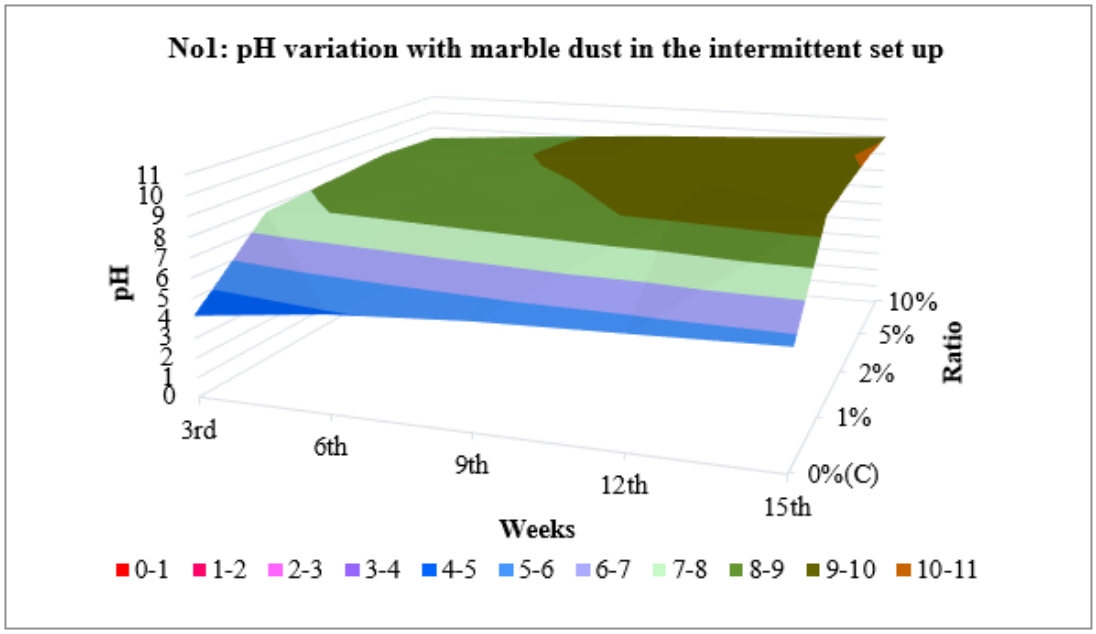


Figure 4.30 pH variation of No1 mine sample added marble dust in the intermittent set up

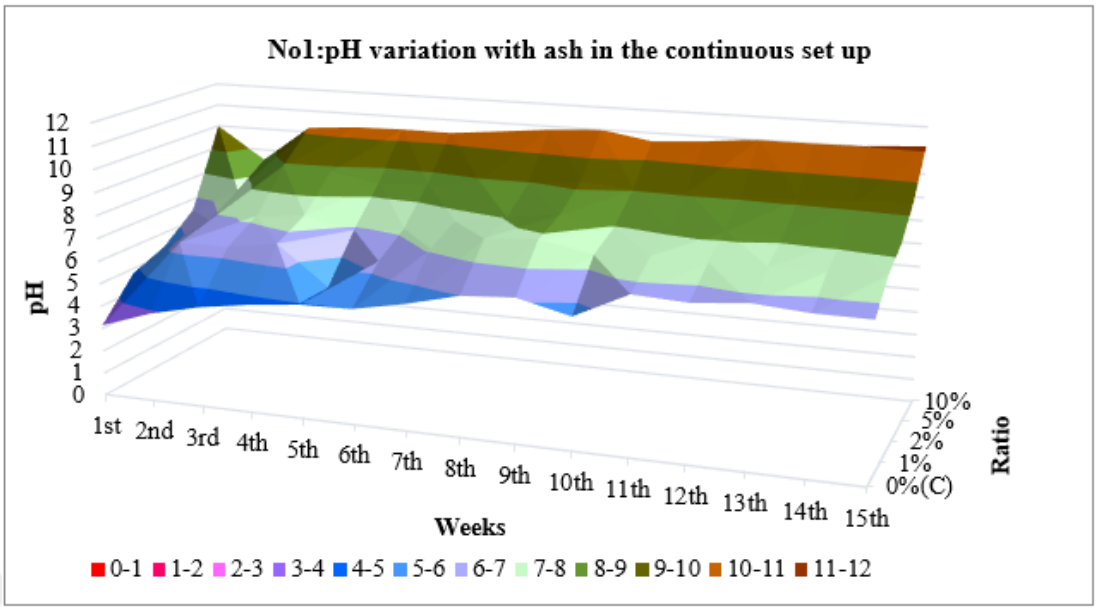


Figure 4.31 pH variation of No1 mine sample added ash in the continuous set up

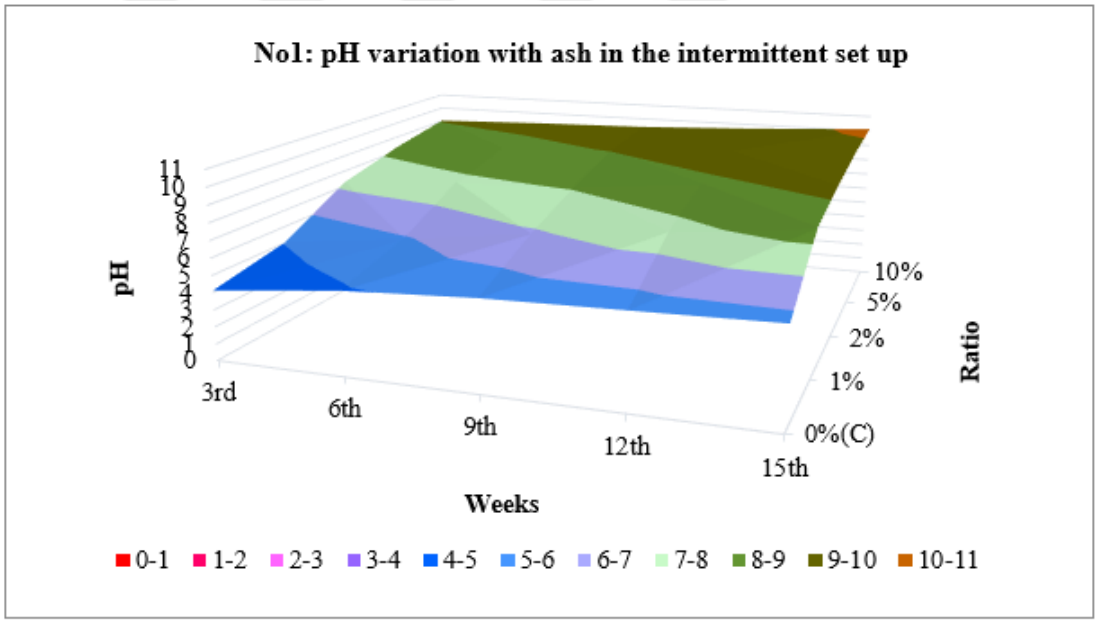


Figure 4.32 pH variation of No1 mine sample added ash in the intermittent set up

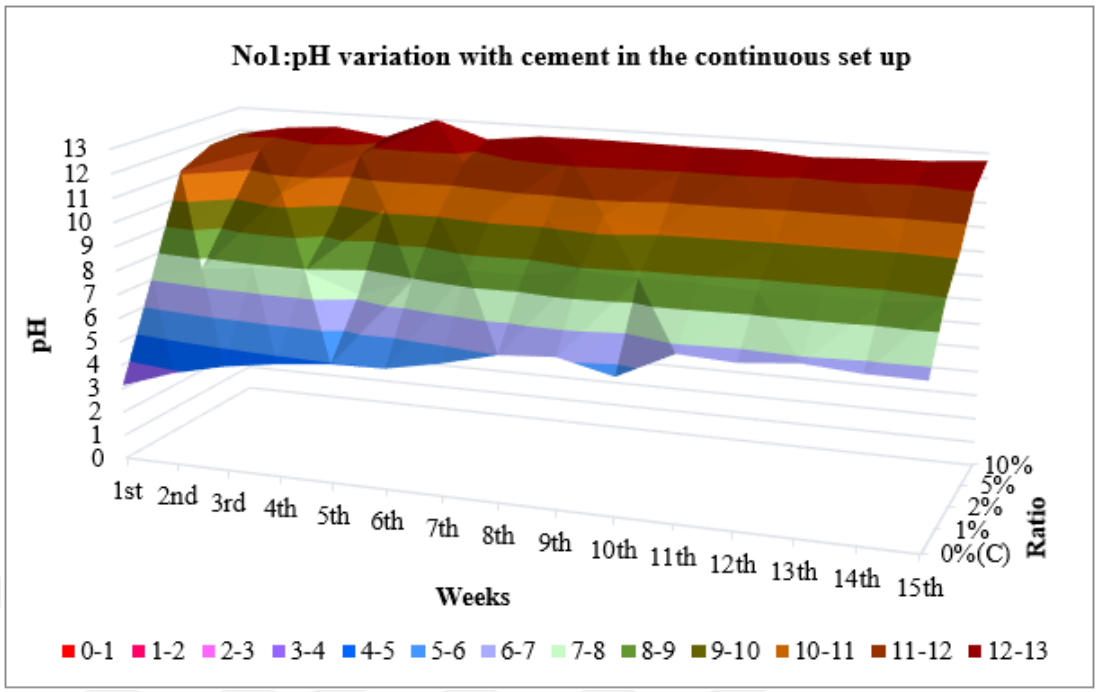


Figure 4.33 pH variation of No1 mine sample added cement in the continuous set up

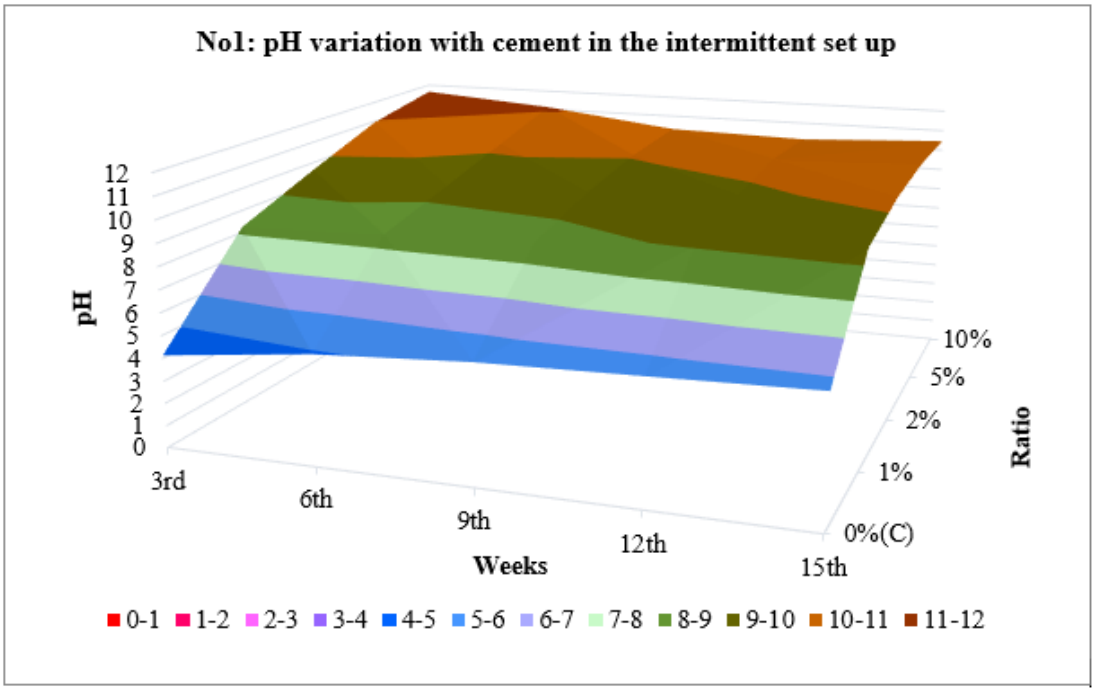


Figure 4.34 pH variation of No1 mine sample added cement in the intermittent set up

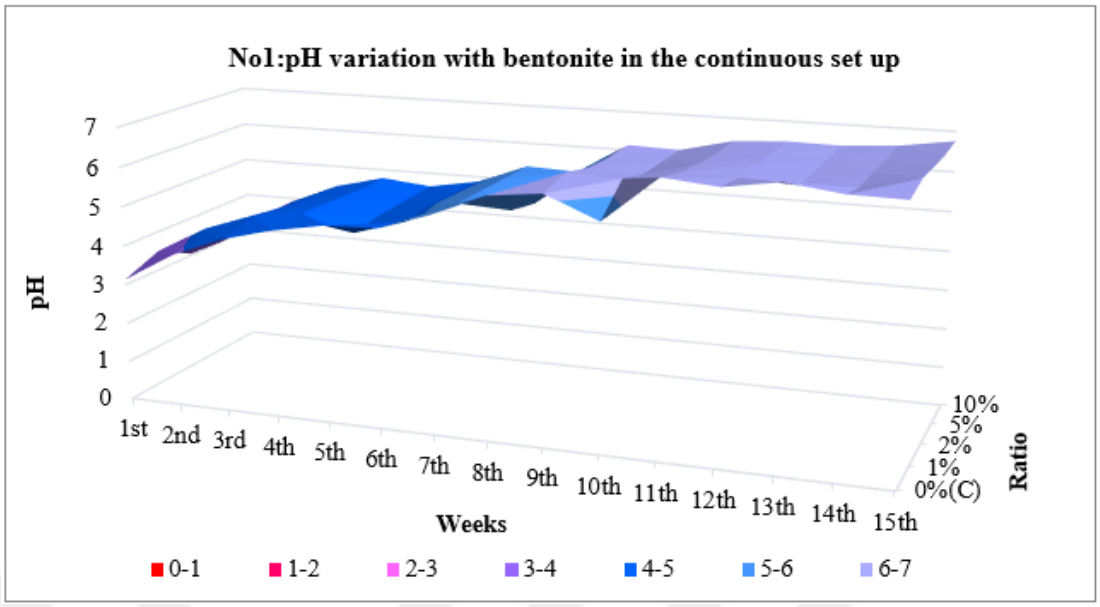


Figure 4.35 pH variation of No1 mine sample added bentonite in the continuous set up

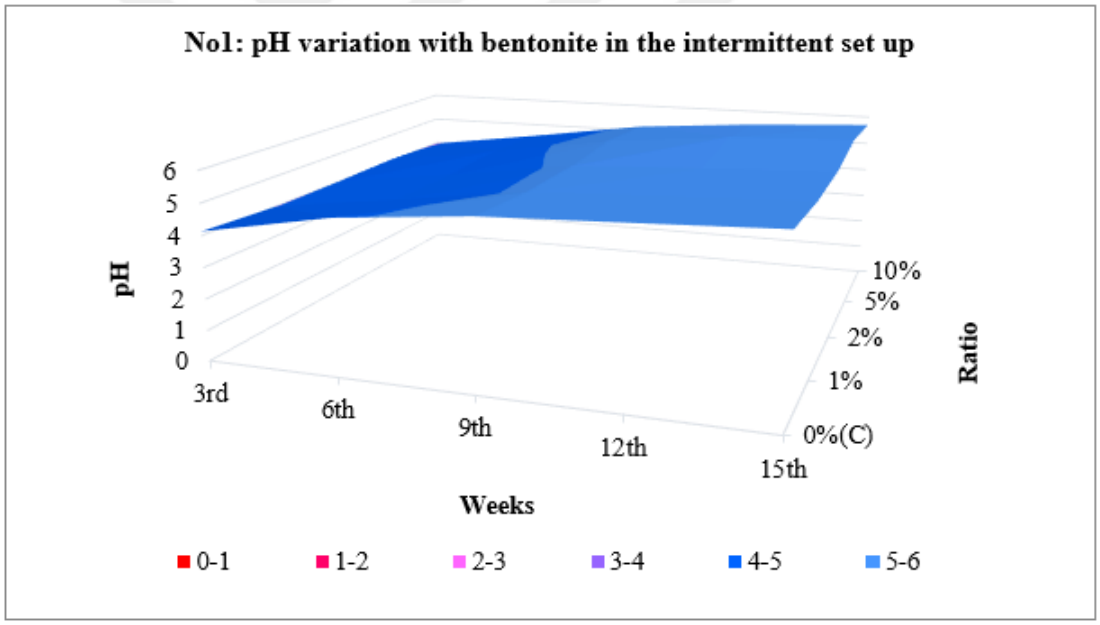


Figure 4.36 pH variation of No1 mine sample added bentonite in the intermittent set up

4.2.6.2 Evaluation of Paste pH of No2 Mine Waste Sample

Overall pH evaluation for No2 sample in the continuous set up: The results of No2 mine sample was nearly the same with No1 mine sample. No2 control pH values increased firstly for 13 weeks and then began to decrease a little. The highest No2 control pH was measured 8.28 after 13 weeks. As the pH of No1 mine sample. The

highest pH value in No2 was detected by used 10% of binding materials (the pH of mine samples added marble dust, ash, and cement was 9.13, 9.06, and 12.85, respectively) except the mine sample with added bentonite. The highest pH detected when 1% bentonite was added was 8.8. At the end of the 15 weeks, the highest pH in this set up was 12.85 with added cement at 10%

Overall pH evaluation for No2 sample in the intermittent set up: No2 mine sample showed similarly with No 1 mine sample in the intermittent set up. The pH value both in control group and in the added binding materials of No2 mine sample was showed an increase for 15 weeks except the flask with added cement. At the beginning of the No2 mine samples pH were almost neutral except the sample added cement at 10%. After 15 weeks. all of the pH values were alkaline. The highest control pH was 8.63 while the pH of No2 mine sample with added different ratio marble dust, ash, cement, and bentonite were detected 10.05, 10.13, 11.63, and 5.86, respectively. The pH of No2 mine sample added cement at 10% had the highest value after 3 weeks (12.77).

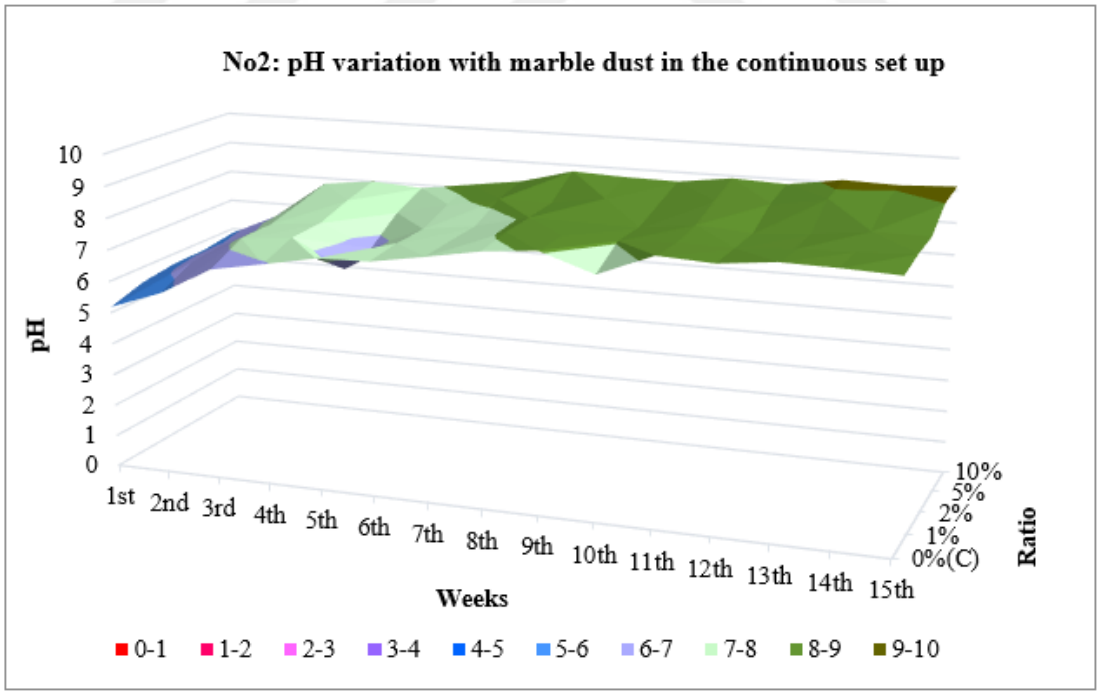


Figure 4.37 pH variation of No2 mine sample added marble dust in the continuous set up

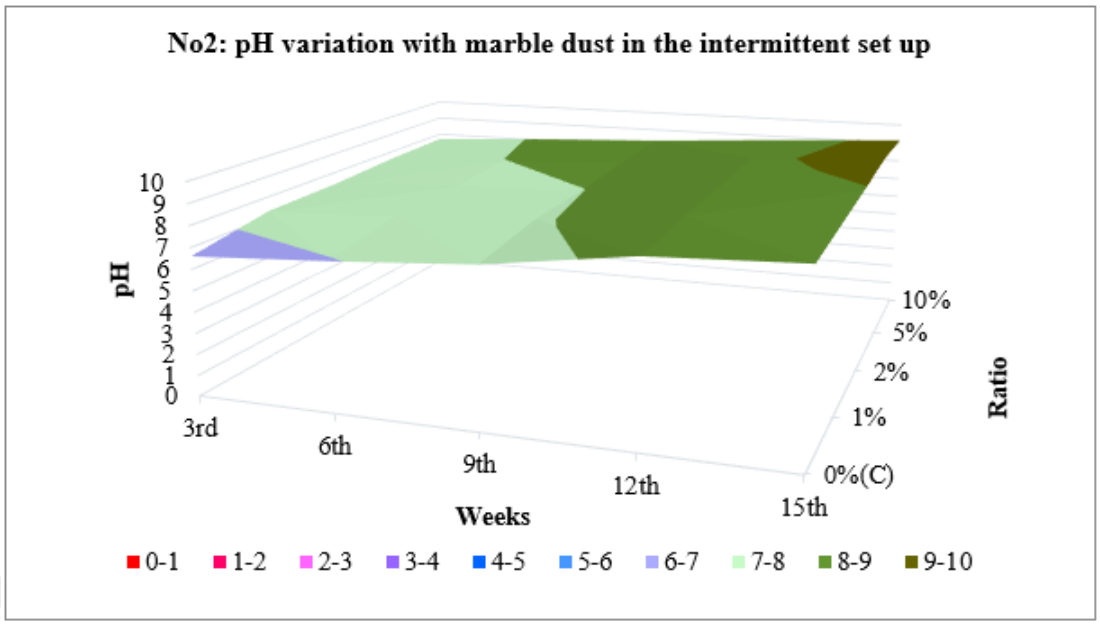


Figure 4.38 pH variation of No2 mine sample added marble dust in the intermittent set up

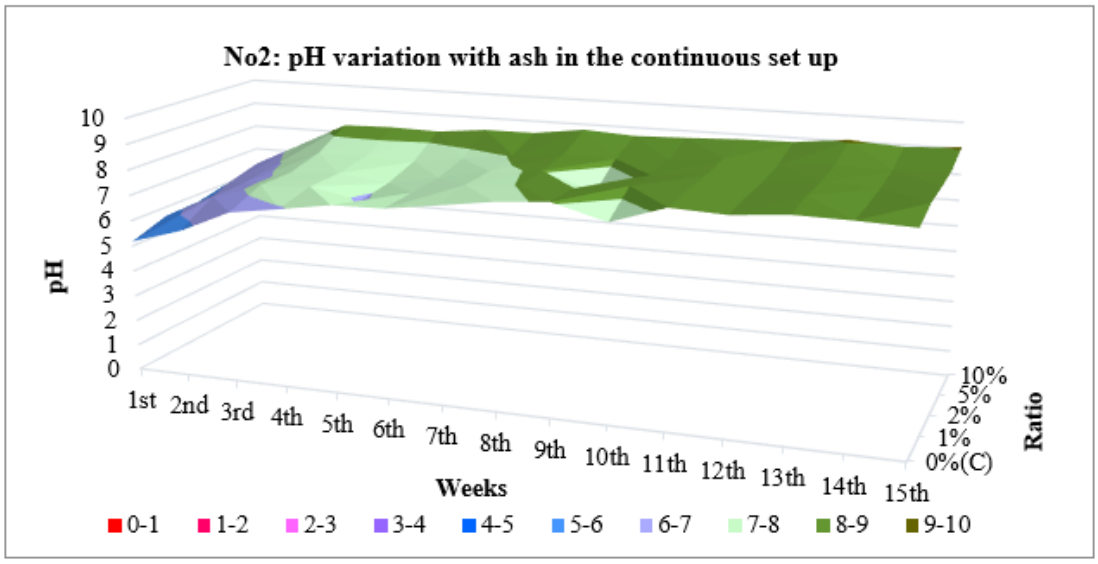


Figure 4.39 pH variation of No2 mine sample added ash in the continuous set up

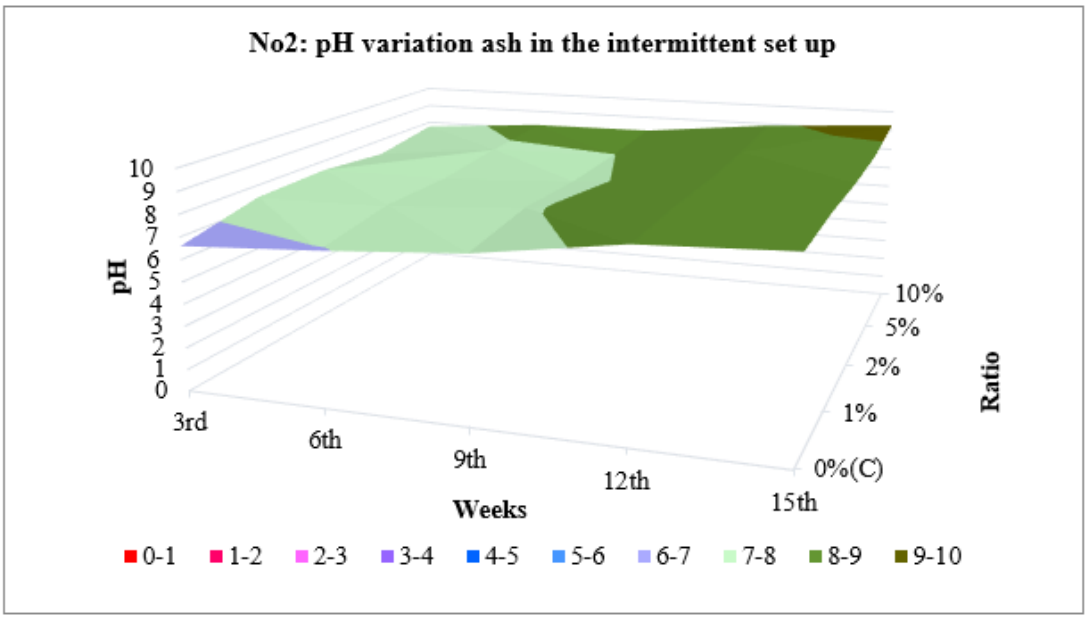


Figure 4.40 pH variation of No2 mine sample added ash in the intermittent set up

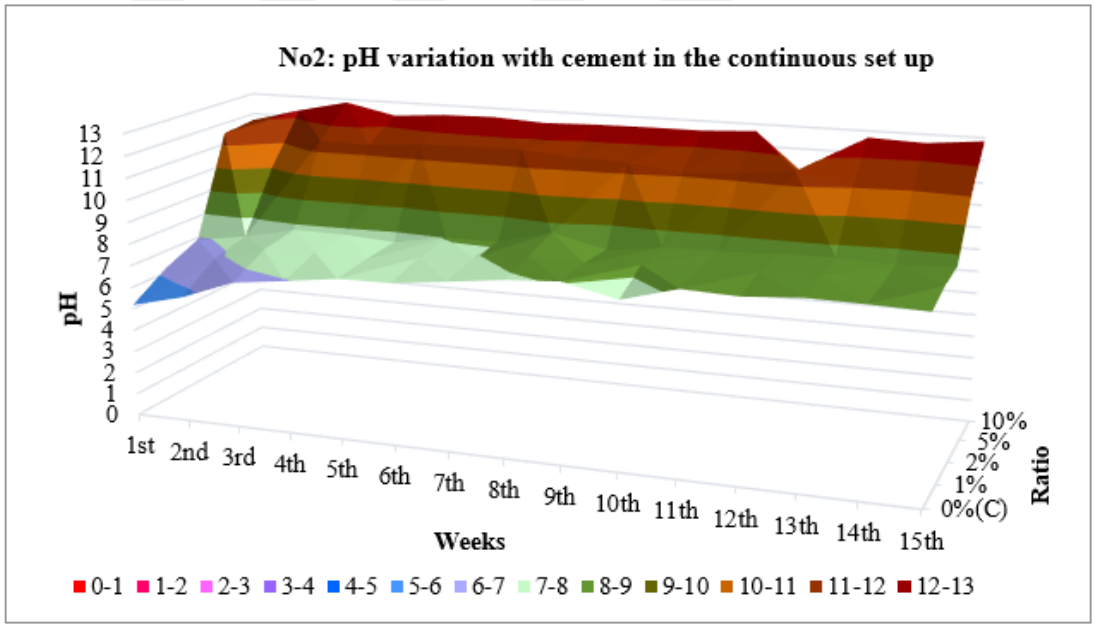


Figure 4.41 pH variation of No2 mine sample added cement in the continuous set up

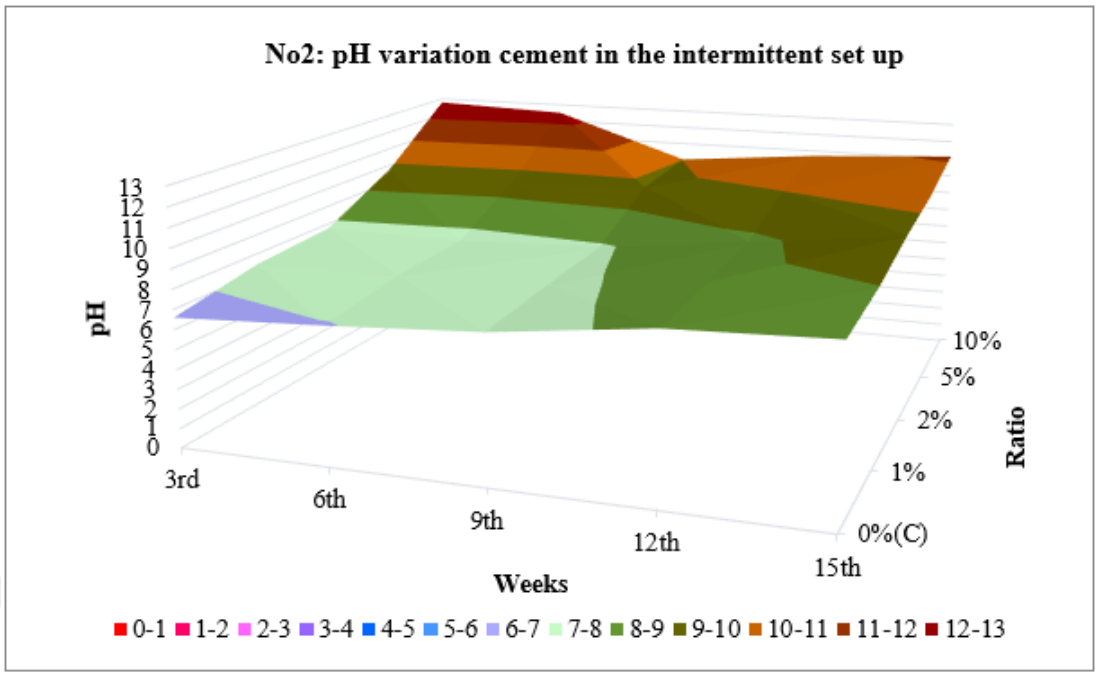


Figure 4.42 pH variation of No2 mine sample added cement in the intermittent set up

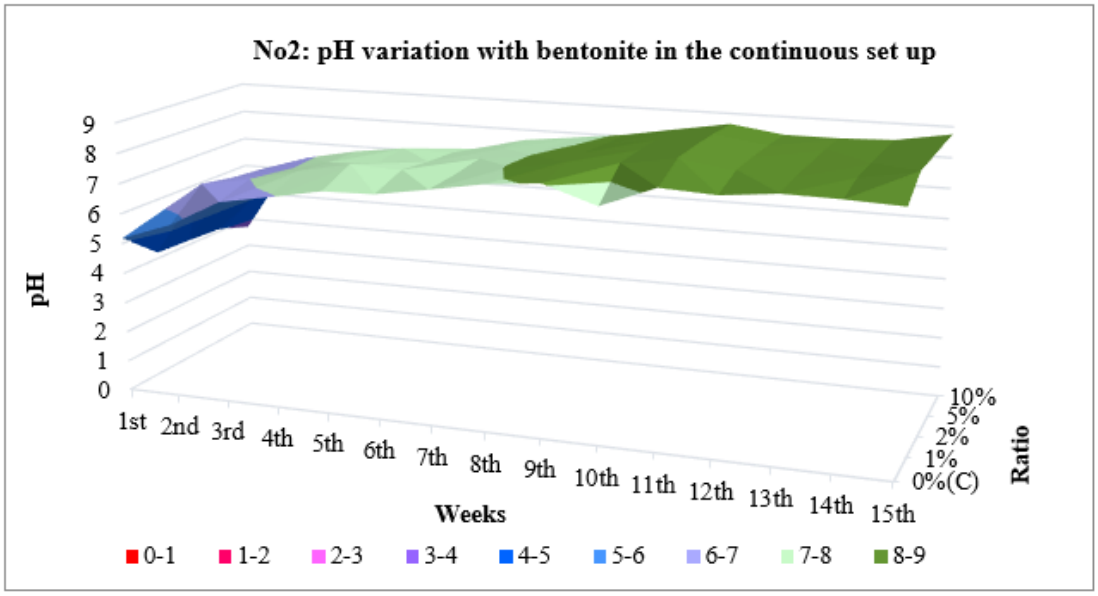


Figure 4.43 pH variation of No2 mine sample added bentonite in the continuous set up

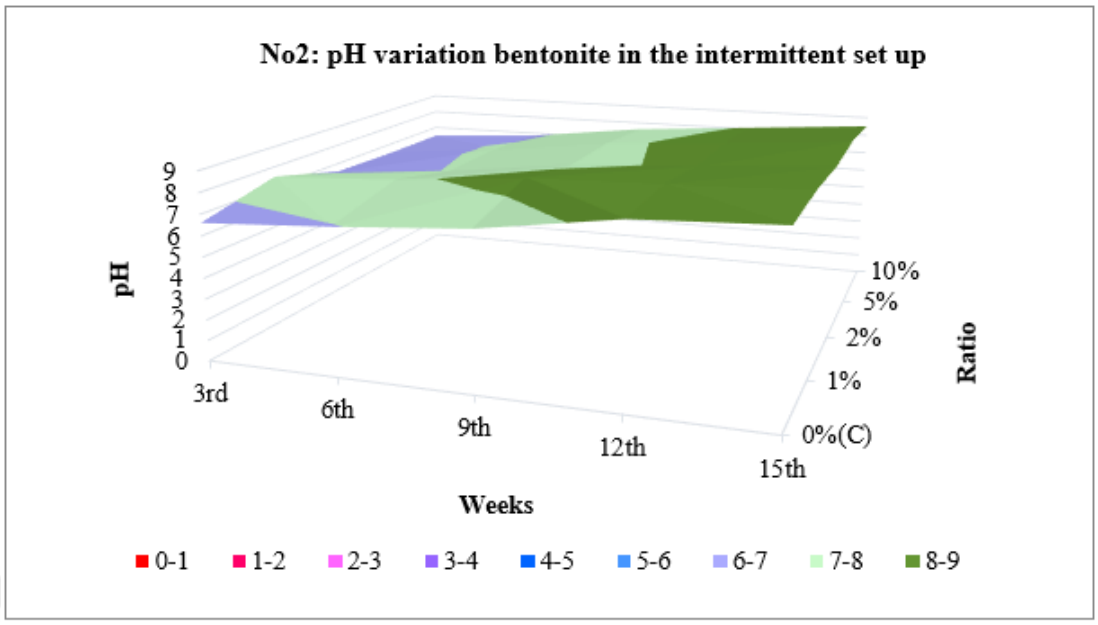


Figure 4.44 pH variation of No2 mine sample added bentonite in the intermittent set up

4.3.6.3 Evaluation of Paste pH of No3 Mine Waste Sample

Overall pH evaluation for No3 sample in the continuous set up: No3 control pH was increased for 15 weeks. and the highest pH value was measured 9.1. The highest pH of mine sample with added bentonite at 1% was 9.67 after 11 weeks when the other highest pH values were detected by used with 10% of binding materials. The pH of mine samples with added marble dust, ash, and cement was 9.46, 10.46, and 13.25, respectively. 13.25 was the highest pH in No3 mine sample added 10% cement after 8 weeks.

Overall pH evaluation for No3 sample in the intermittent set up: As seen the intermittent set up of the other mine samples, increase of pH in the No3 mine sample continued through experimental period. The highest pH value in control group was detected 9.87 while the others which is added marble dust (2%), ash (5%), cement (5%), and bentonite (1%) were measured 9.75, 10.01, 9.95, and 10.2, respectively. The pH of mine sample added cement at 5% was the highest value after 15 weeks (10.2).

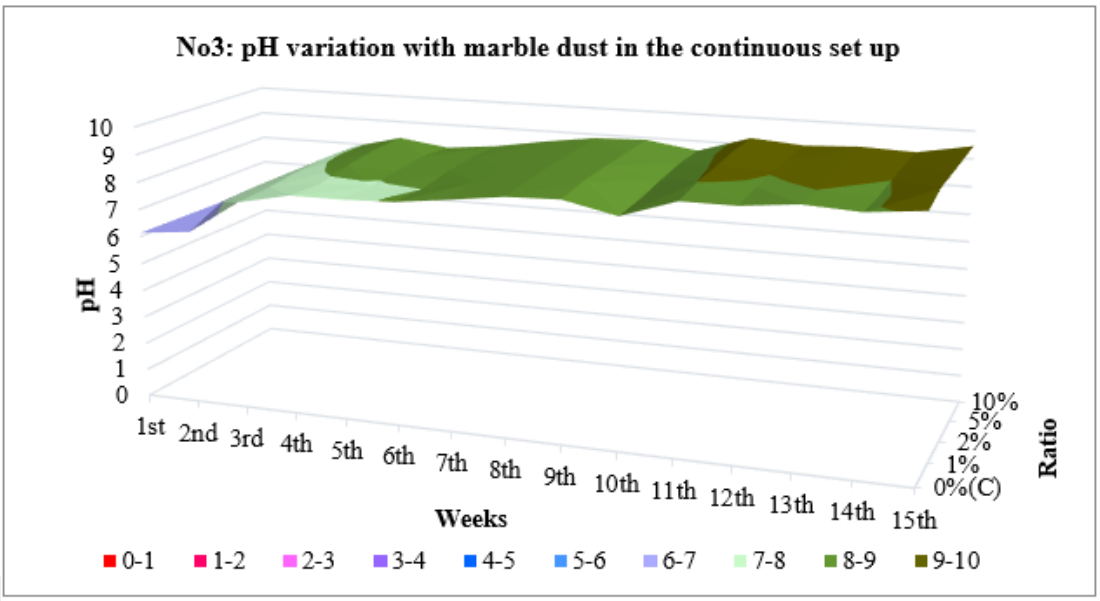


Figure 4.45 pH variation of No3 mine sample added marble dust in the continuous set up

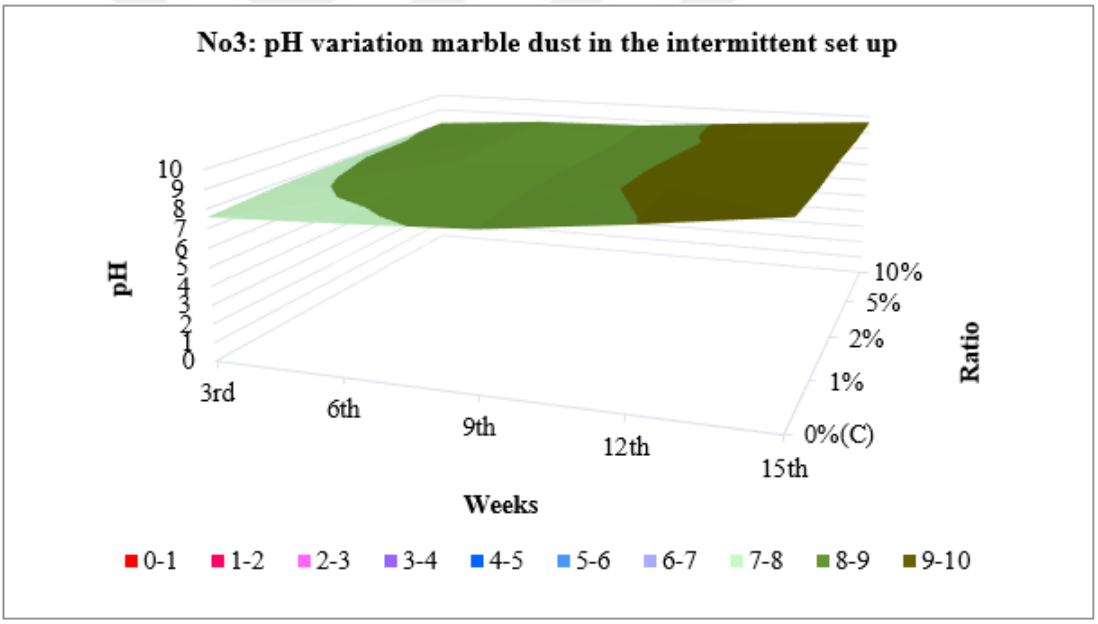


Figure 4.46 pH variation of No3 mine sample added marble dust in the intermittent set up

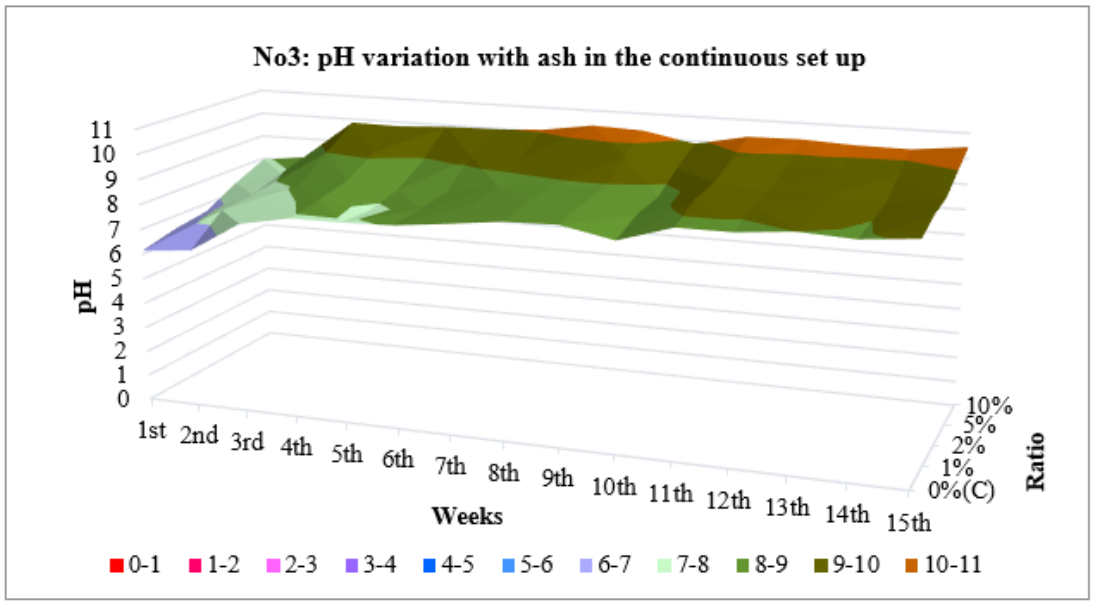


Figure 4.47 pH variation of No3 mine sample added ash in the continuous set up

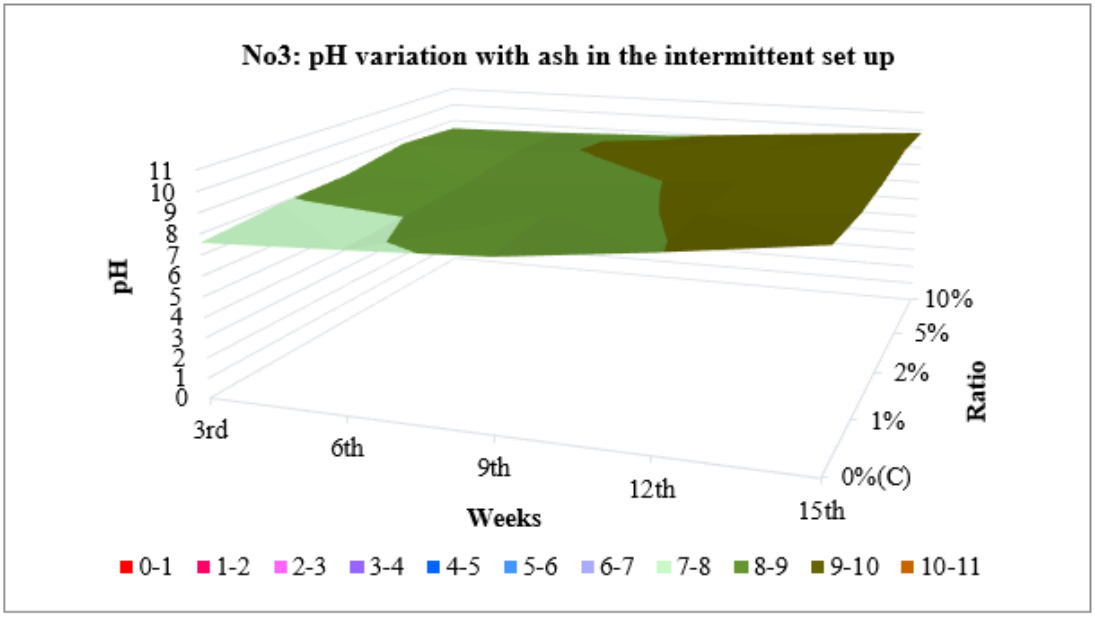


Figure 4.48 pH variation of No3 mine sample added ash in the intermittent set up

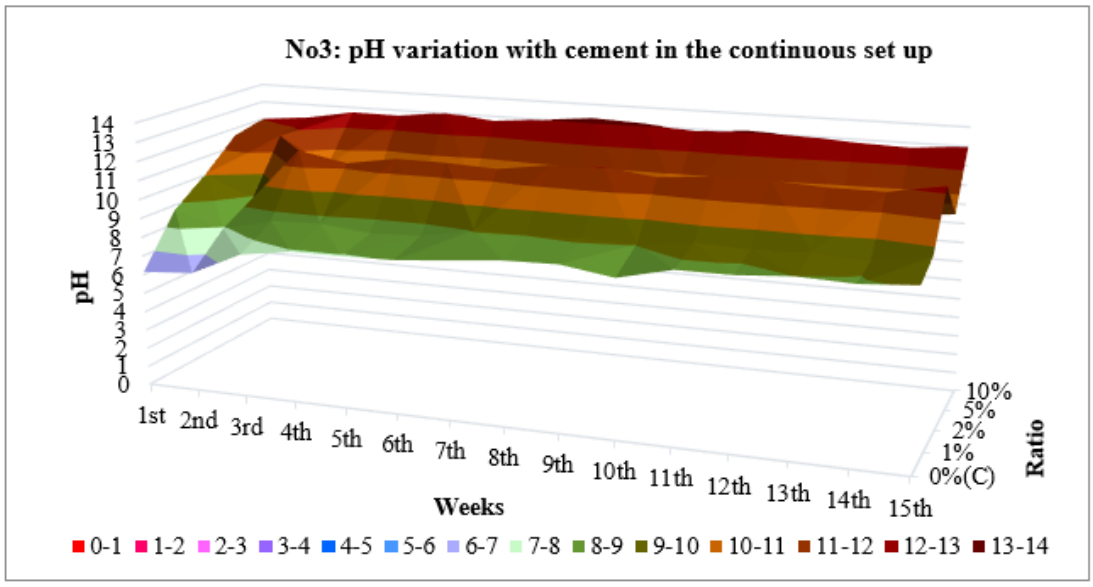


Figure 4.49 pH variation of No3 mine sample added cement in the continuous set up

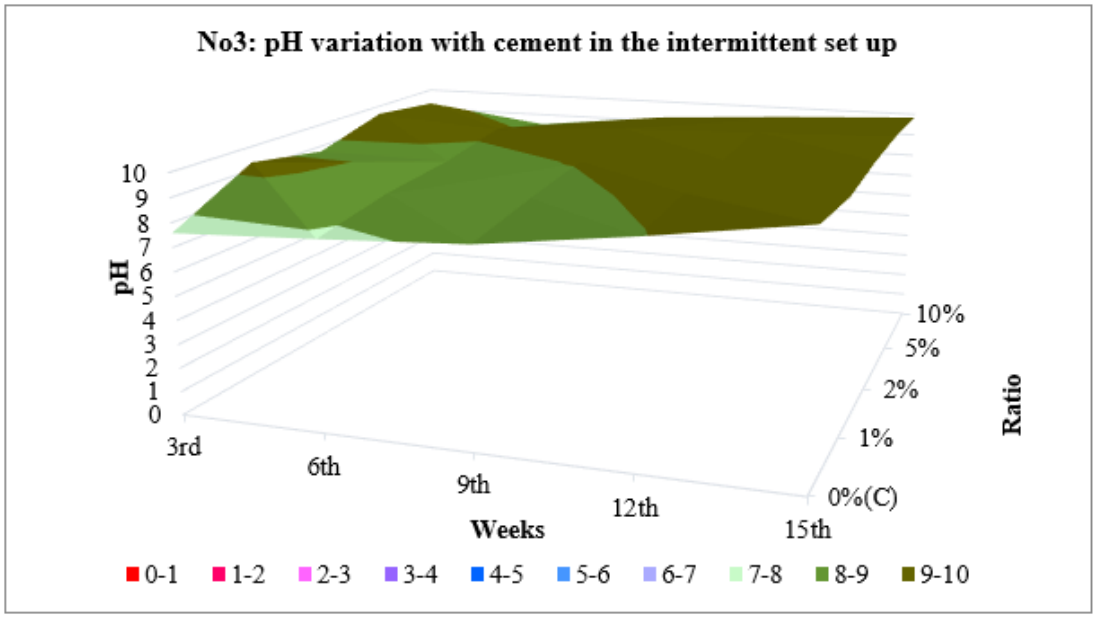


Figure 4.50 pH variation of No3 mine sample added cement in the intermittent set up

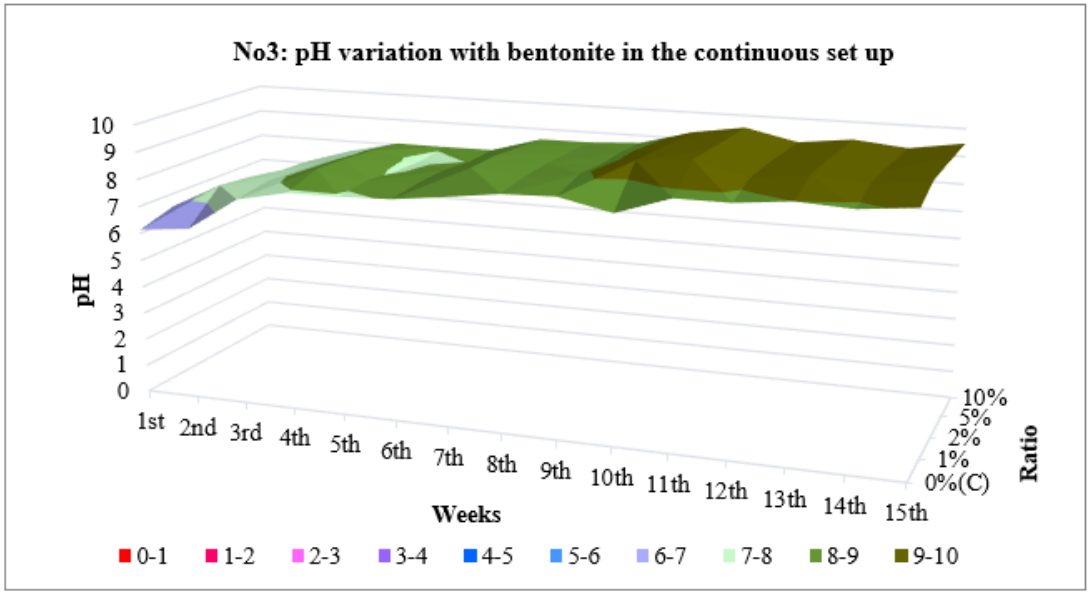


Figure 4.51 pH variation of No3 mine sample added bentonite in the continuous set up

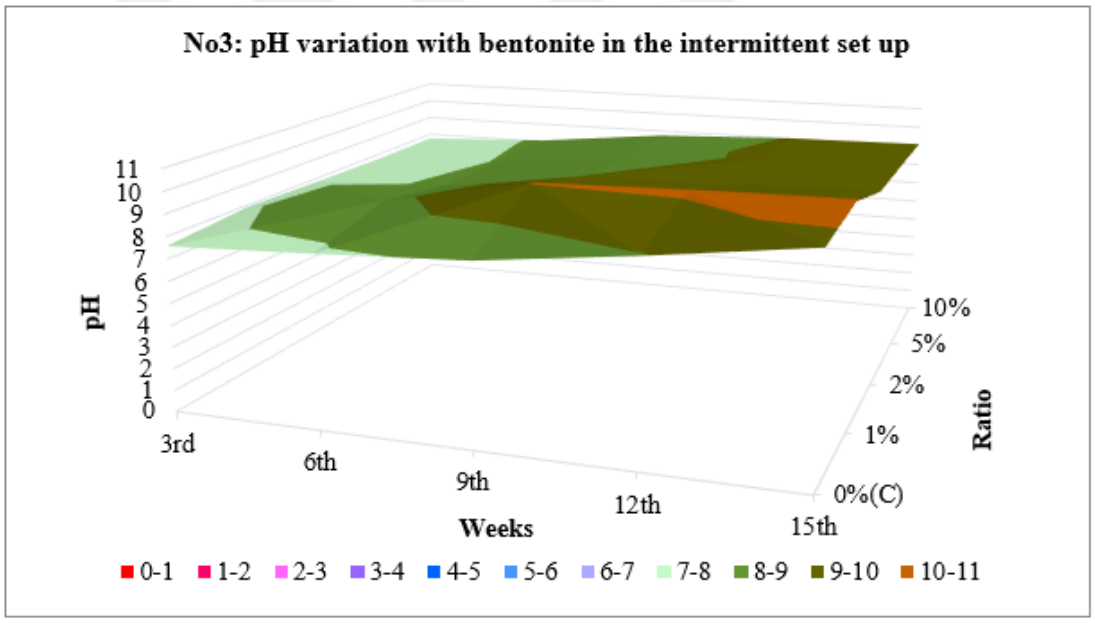


Figure 4.52 pH variation of No3 mine sample added bentonite in the intermittent set up

4.3.6.4 Evaluation of Paste pH of No4 Mine Waste Sample

Overall pH evaluation for No4 sample in the continuous set up: No4 control pH value increased during the experimental set up and it was measured 9.4 at the end of the 15 weeks. The highest initial control pH value was in this mine sample (6.63). As seen the pH value of No1 mine sample. the highest pH values in No4 were detected by

used 10% of binding materials (the pH of mine samples added marble dust, ash, and cement was 9.71, 11.4, and 13.29, respectively) except the mine sample with added bentonite. The highest pH added bentonite at 1% was 9.61 at the end of the 11 weeks. The highest pH was measured 13.29 in sample with added cement at 10% after 9 weeks.

Overall pH evaluation for No4 sample in the intermittent set up: The pH value both in control group and in the added binding materials of No4 mine sample was showed an increase for 15 weeks except mine sample with added bentonite. While the highest control pH was 9.35; the pH of No4 mine sample added marble dust (10%), ash (10%), cement (10%) and bentonite (1%) were detected 9.98, 10.3, 13.9, and 9.69. respectively. The pH of No4 mine sample added cement at 10% had the highest value after 9 weeks (13.9).

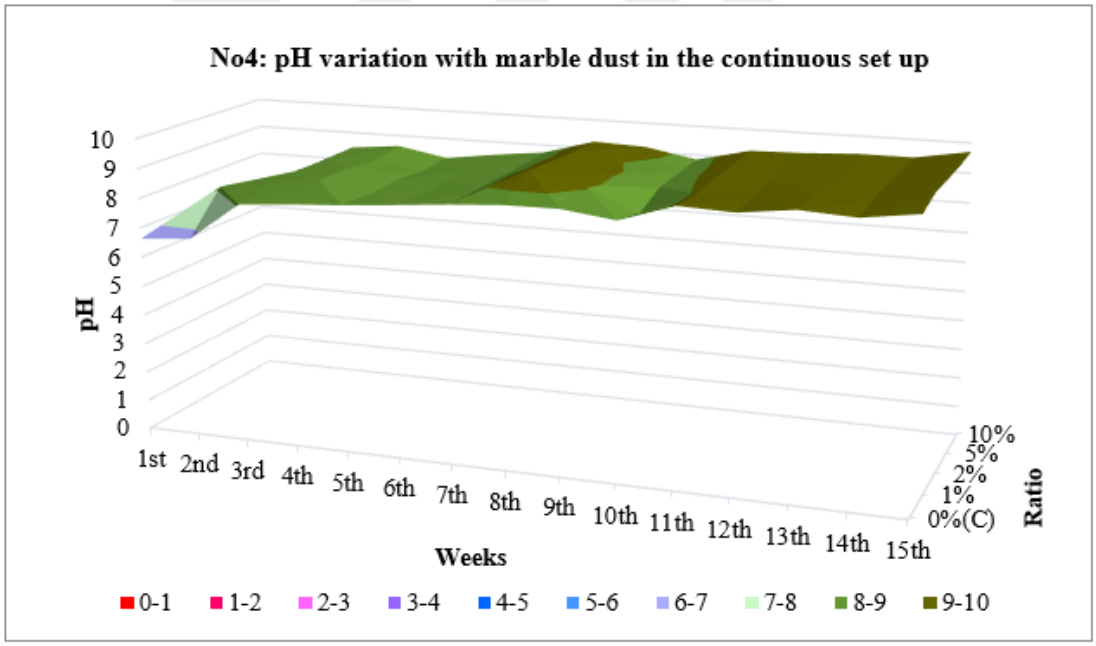


Figure 4.53 pH variation of No4 mine sample added marble dust in the continuous set up

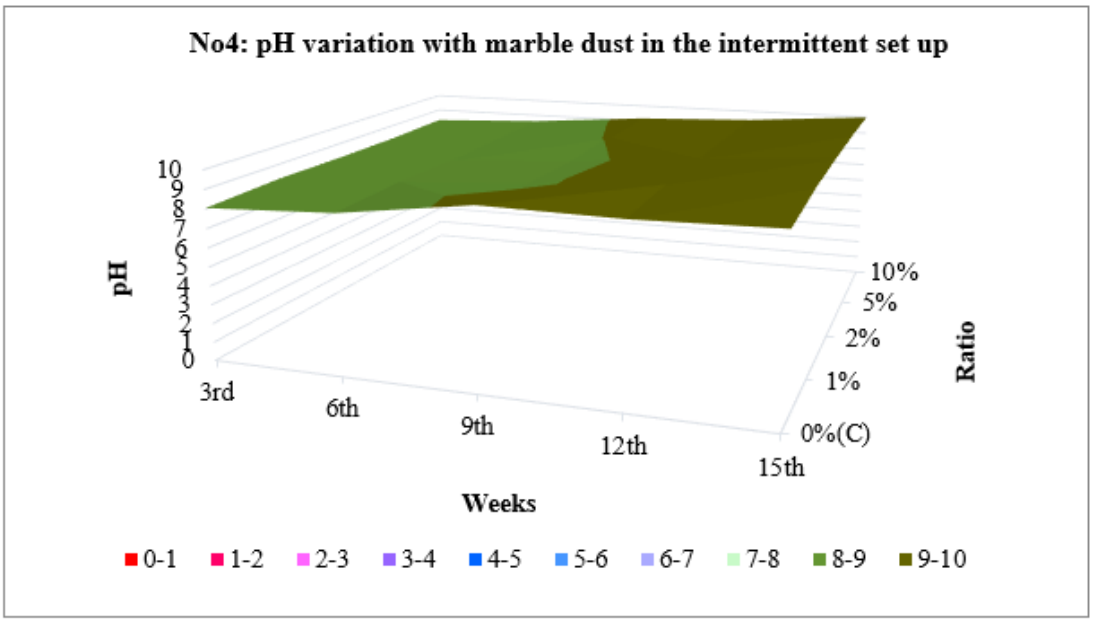


Figure 4.54 pH variation of No4 mine sample added marble dust in the intermittent set up

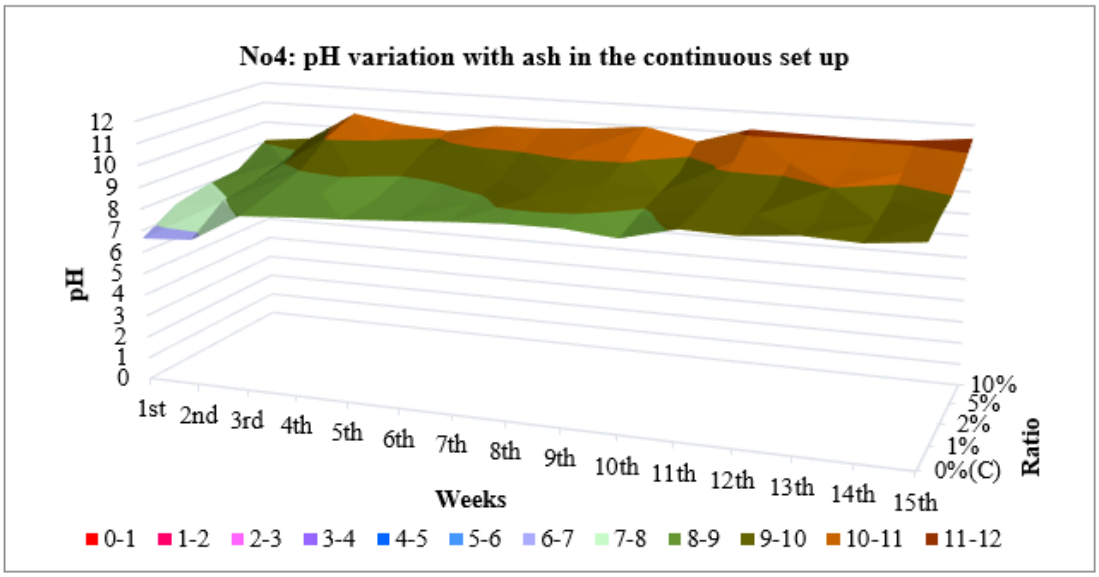


Figure 4.55 pH variation of No4 mine sample added ash in the continuous set up

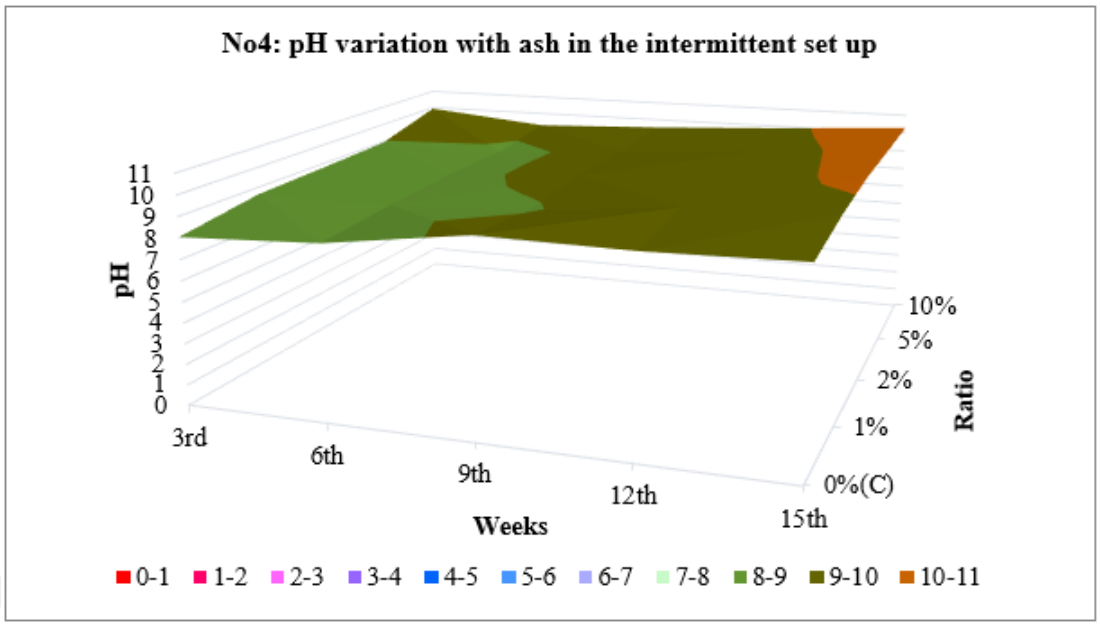


Figure 4.56 pH variation of No4 mine sample added ash in the intermittent set up

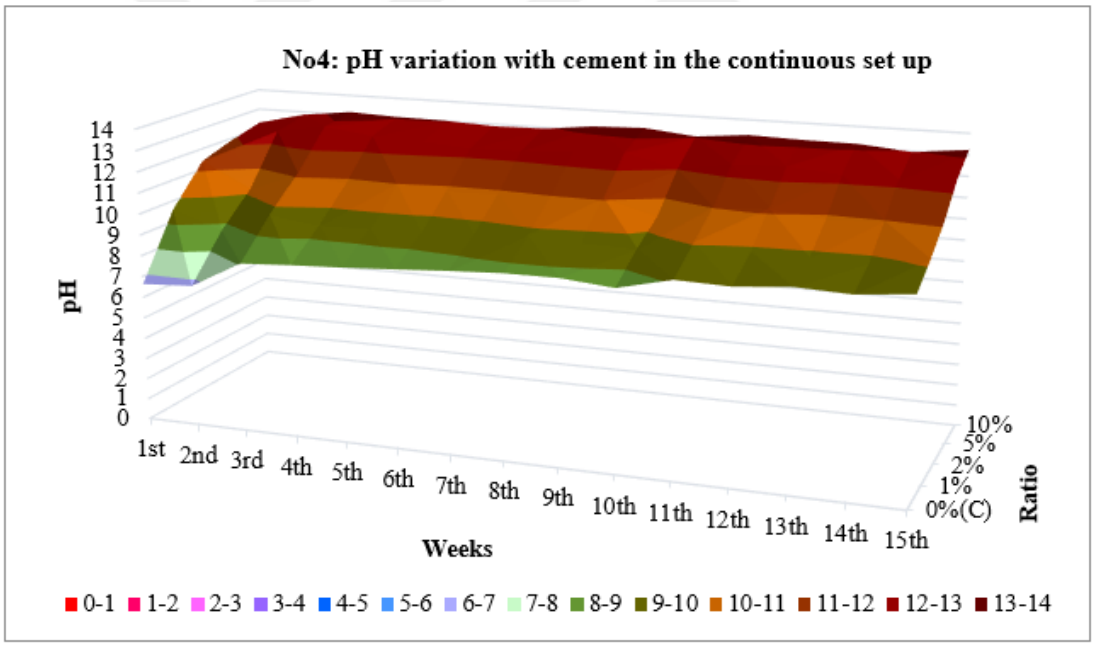


Figure 4.57 pH variation of No4 mine sample added cement in the continuous set up

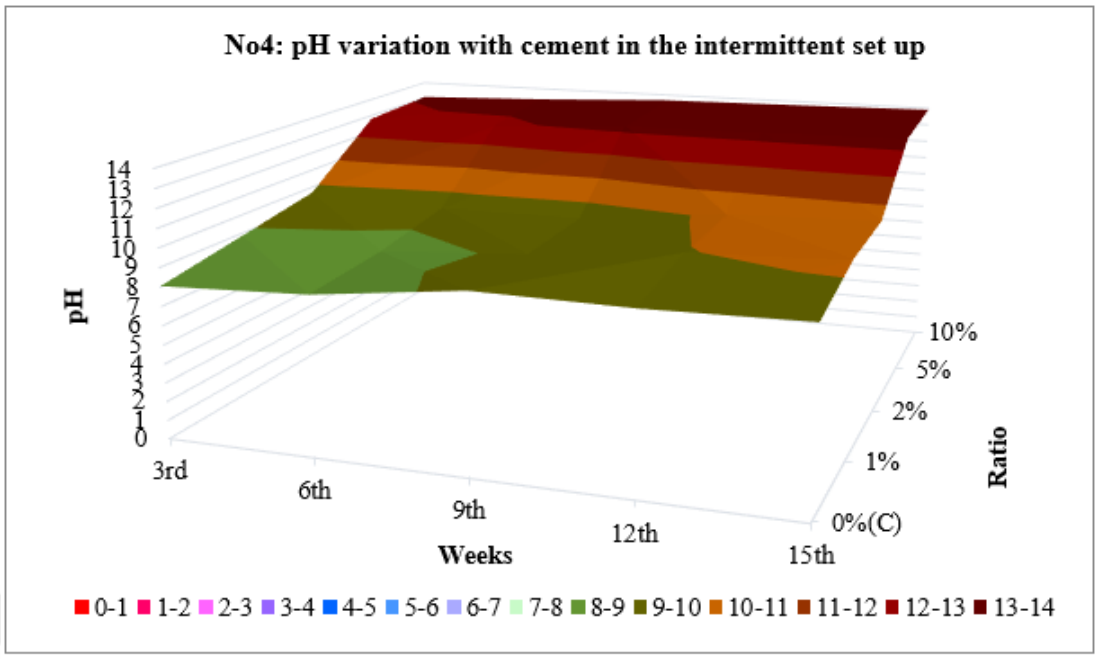


Figure 4.58 pH variation of No4 mine sample added cement in the intermittent set up

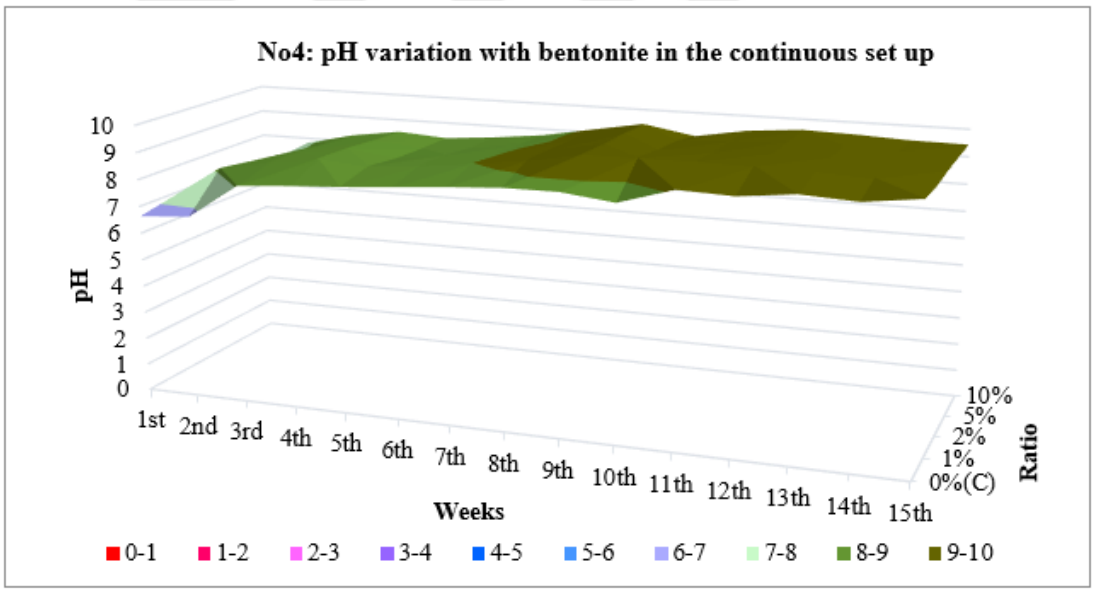


Figure 4.59 pH variation of No4 mine sample added bentonite in the continuous set up

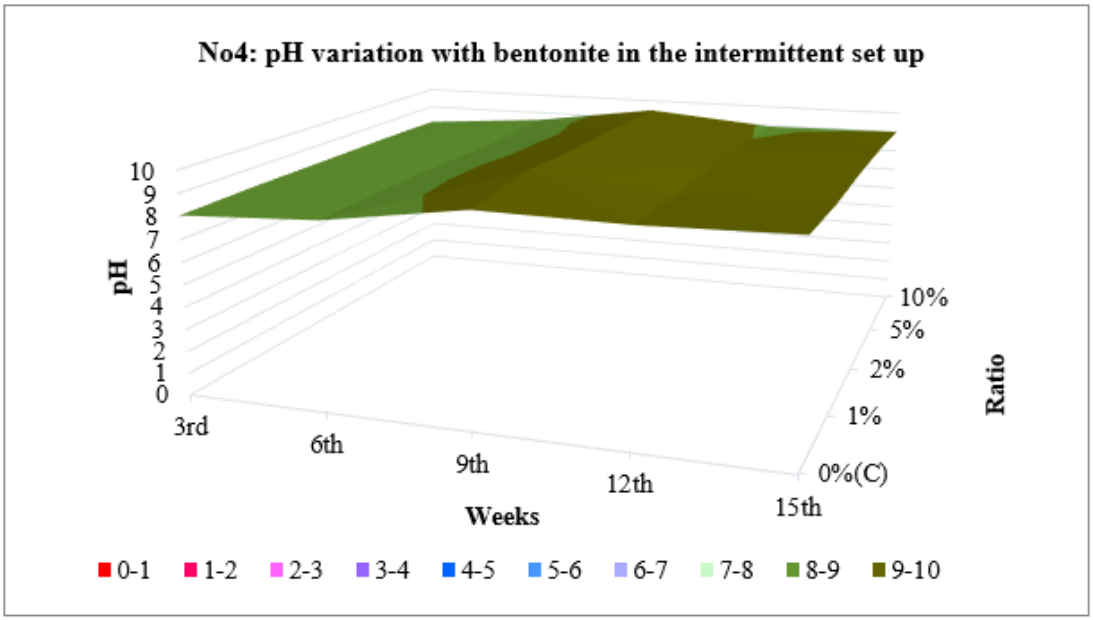


Figure 4.60 pH variation of No. 4 mine sample added bentonite in the intermittent set up

4.3.6.5 Evaluation of Paste pH of No5 Mine Waste Sample

Overall pH evaluation for No5 sample in the continuous set up: The control pH showed an increase from 6.23 to 9.18 during the experimental period. The highest pH was measured 13.36 in the mine sample No5 which was added cement at 10% after 6 weeks. The highest pH in the other mine samples added marble dust at 10%. ash at 10% and bentonite at 5% were detected 9.44 (15. Week), 10.62 (11. Week), and 9.54 (15. week), respectively.

Overall pH evaluation for No5 sample in the intermittent set up: As the other mine samples in the intermittent set up showed up. the similar pH increase continued for this control group. At the end of the 15 weeks. the control pH was 9.39. The highest pH value was measured at the final experimental period except the mine sample No5 with added cement at 10% that it was a highest pH value (9. week-13.17). While the pH of the mine sample with added bentonite at 1% was 9.61; the pH of the mine samples added marble dust at 10% and ash at 10% were 9.45 and 10.13, respectively.

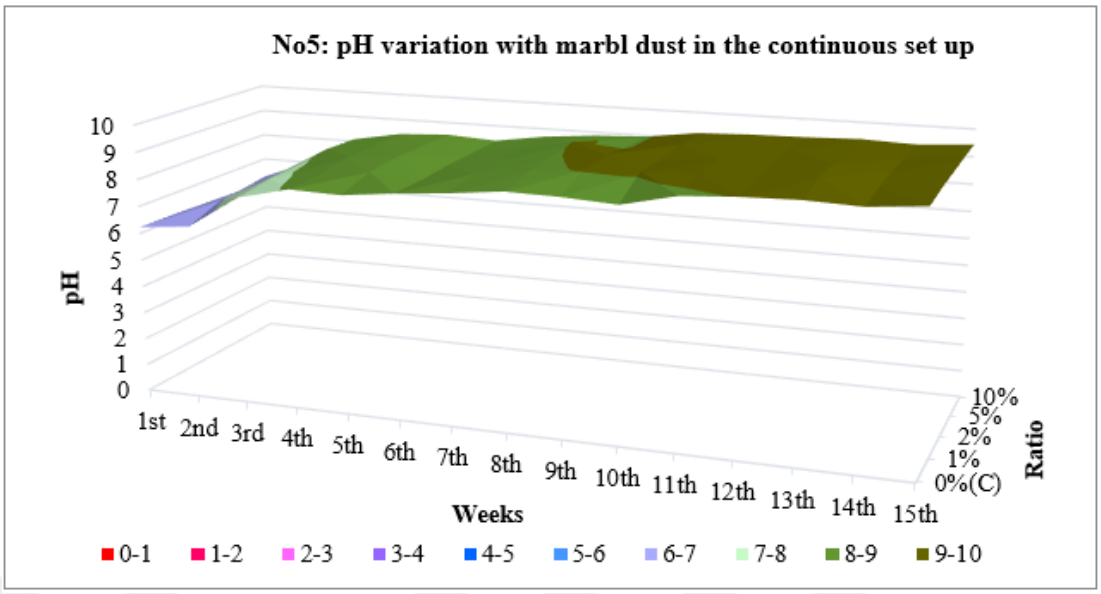


Figure 4.61 pH variation of No5 mine sample added marble dust in the continuous set up

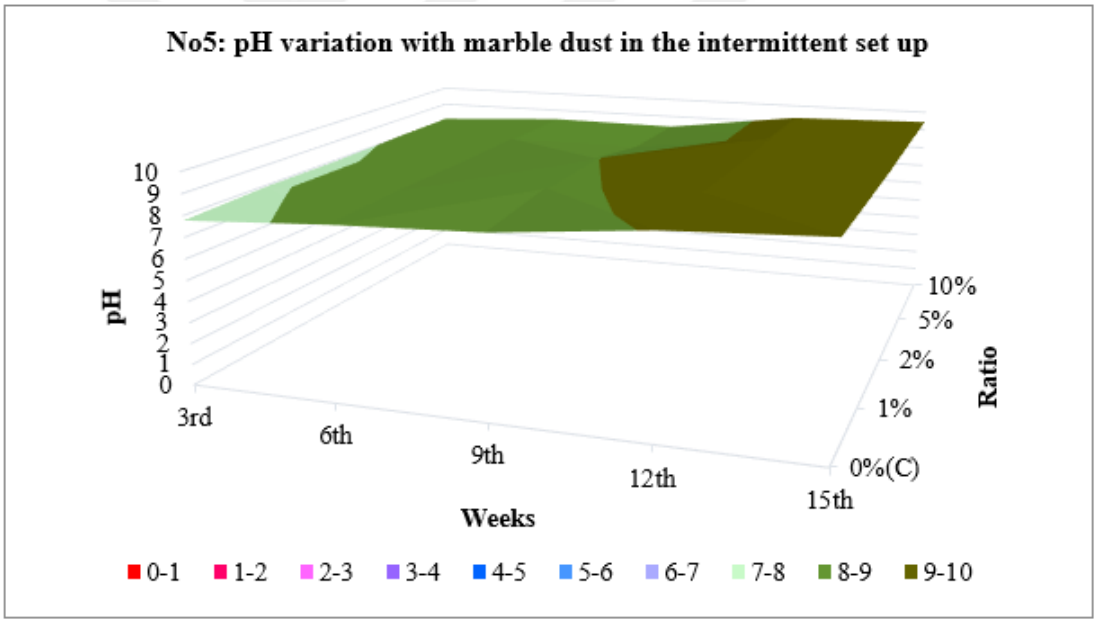


Figure 4.62 pH variation of No5 mine sample added marble dust in the intermittent set up

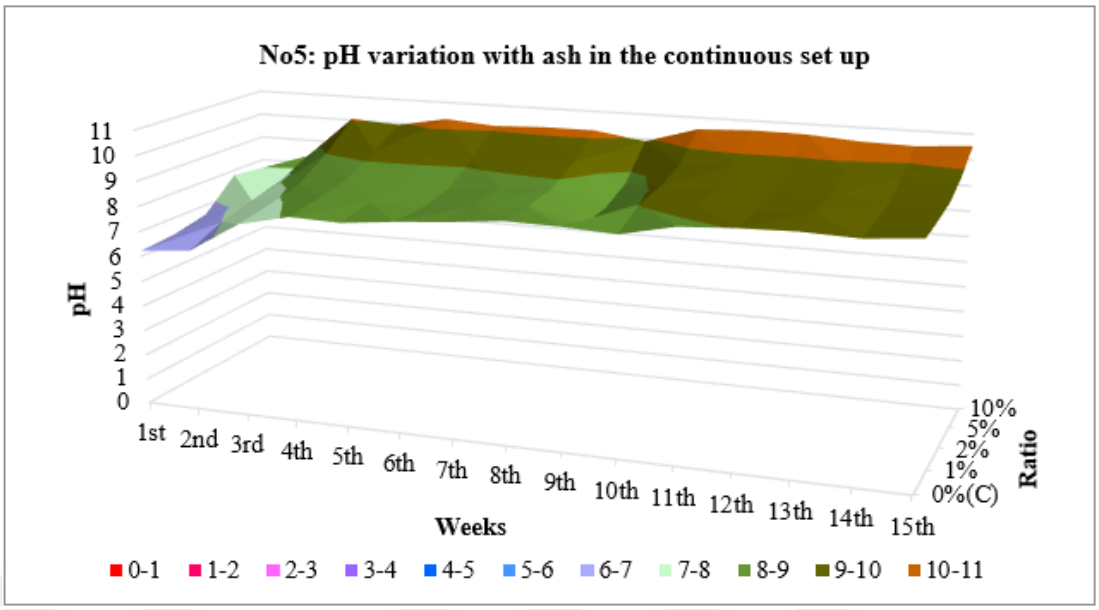


Figure 4.63 pH variation of No5 mine sample added ash in the continuous set up

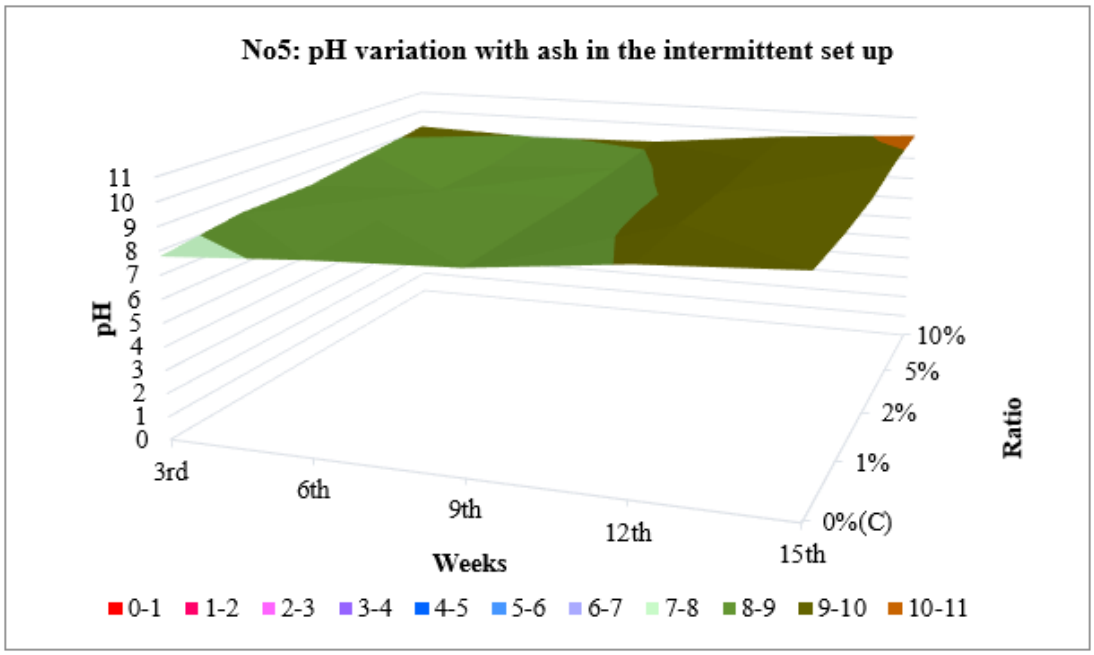


Figure 4.64 pH variation of No5 mine sample added ash in the intermittent set up

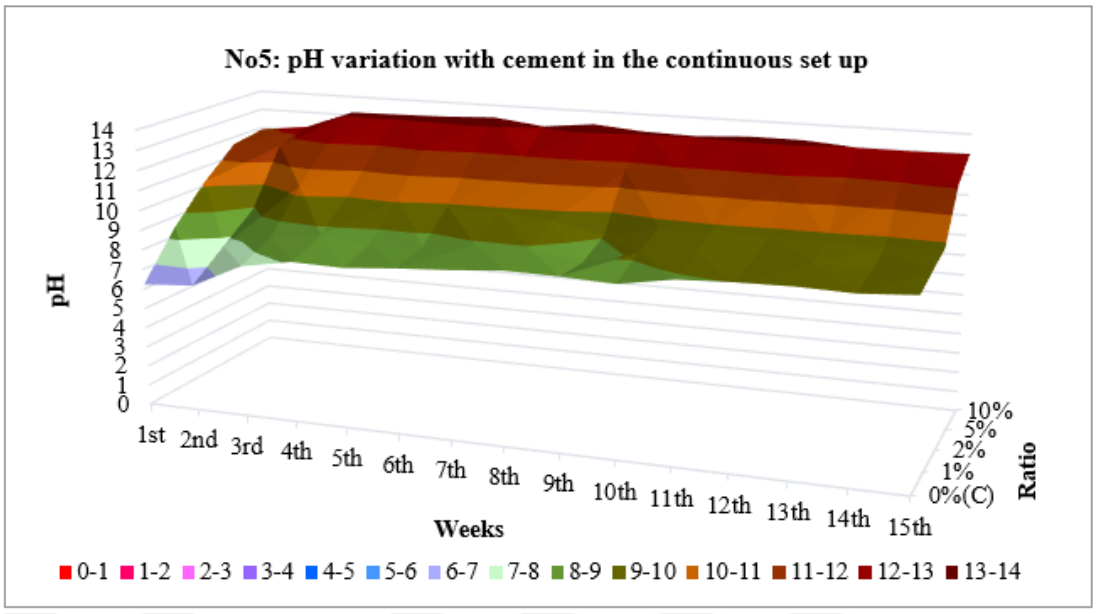


Figure 4.65 pH variation of No5 mine sample added cement in the continuous set up

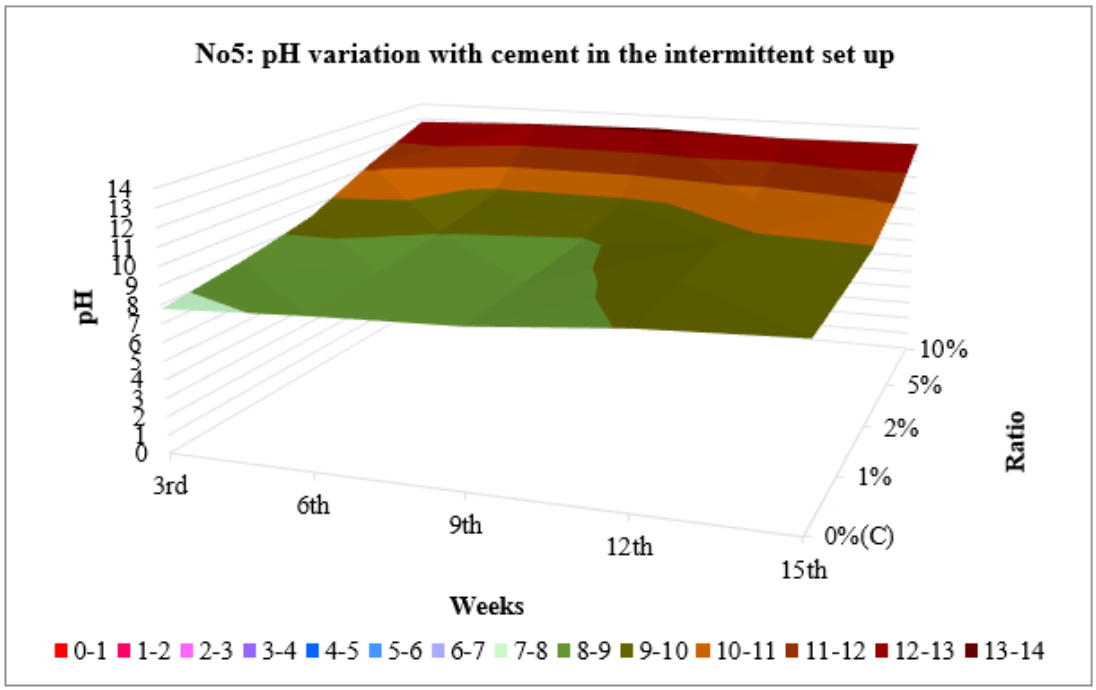


Figure 4.66 pH variation of No5 mine sample added cement in the intermittent set up

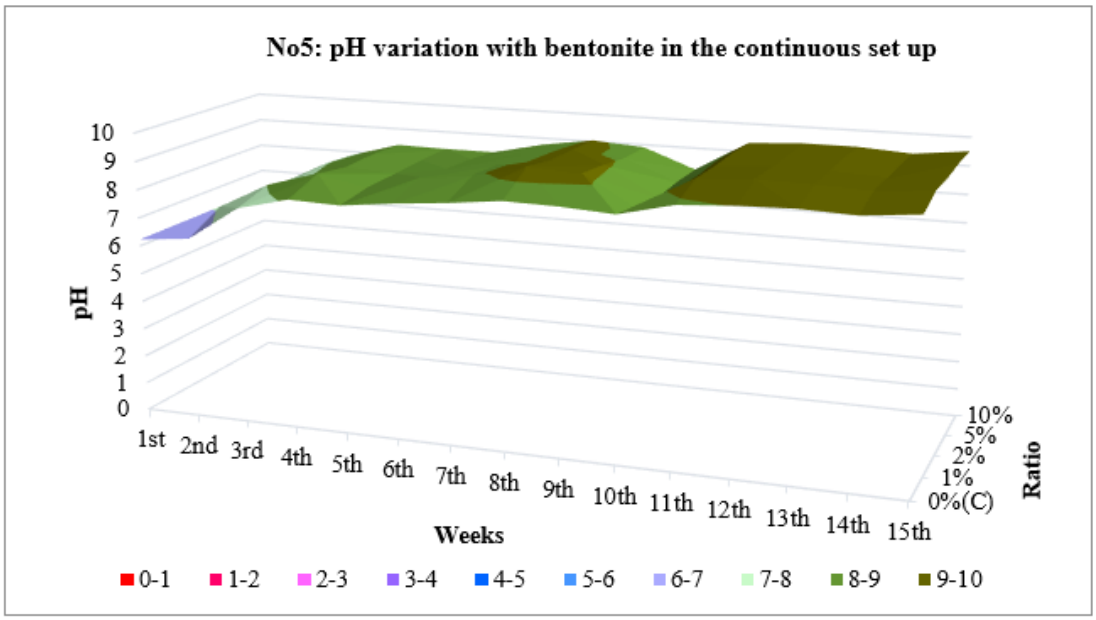


Figure 4.67 pH variation of No5 mine sample added bentonite in the continuous set up

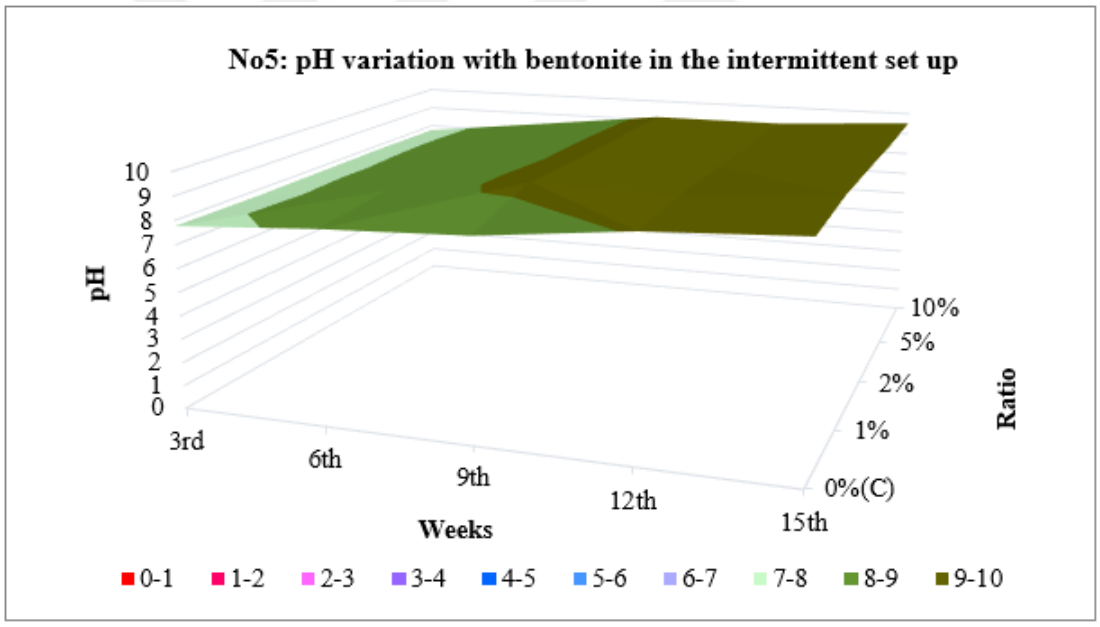


Figure 4.68 pH variation of No5 mine sample added bentonite in the intermittent set up

4.3.6.6. Overall Assessment for the Paste pH

Table 4.29 Minimum and maximum pH values for the paste taste

		min pH values					Max pH values				
	pH	CONT	MD	A	C	B	CONT	MD	A	C	B
No 1	3.6	3.14	5.6	4.8	7.15	3	6.81	9.4	11.18	12.7	6.78
Week		1	1	1	1	1	13	15	15	15	15
Ratio			1%	1%	1%	5%		10%	10%	10%	1%
No 2	3.93	5.18	5.52	5.65	6.21	3.7	8.28	9.13	9.06	12.85	8.8
Week		1	1	1	1	1	13	15	13	15	15
Ratio			1%	1%	1%	10%		10%	10%	10%	1%
No 3	4.99	6.14	5.99	6.47	8.75	6.01	9.1	9.46	10.46	13.25	9.67
Week		1	1	1	1	1	15	15	15	8	11
Ratio			2%	1%	1%	10%		10%	10%	10%	1%
No 4	5.32	6.63	6.62	7.6	9.57	6.5	9.4	9.71	11.4	13.29	9.61
Week		1	1	1	1	1	15	15	15	9	11
Ratio			1%	1%	1%	10%		10%	10%	10%	1%
No 5	4.45	6.23	6.09	6.33	8.48	6.07	9.18	9.44	10.62	13.36	9.54
Week		1	1	1	1	1	15	15	11	6	15
Ratio			5%	1%	1%	10%		10%	10%	10%	5%

The addition of binding materials led to increase of pH in all of the flasks. The addition of bentonite in different ratio was not made a big difference. But the decreases of pH were observed with increasing bentonite ratio in some of the samples in flasks. Except the samples that was added bentonite at 1%, the highest pH value was measured when the other binding materials were added at a ratio 10%. The highest pH value was detected by using cement at 10% in No5 mine sample at the end of the 6 weeks (13.36). Also, the other values were obtained with adding cement at 10% were the highest in throughout the continuous set up. The lowest pH values were detected when different ratio of bentonite was added at the end of the first week (Table 4.29).

4.3.7 Evaluation of EC Results Between Continuous and Intermittent Set Up

4.3.7.1 Evaluation of EC of No1 Mine Waste Sample

Overall EC evaluation for No1 sample in the continuous set up: While initial EC value in control group 1970 µS/cm. final EC was measured 1094 µS/cm. The highest EC values were detected 2118. 2220. and 2216 µS/cm added marble dust (%10). ash (10%) and cement (2%). respectively. The mine sample with added bentonite at 10% was the highest in the 8. Weeks (2043 µS/cm). The samples with added marble dust. bentonite and ash (only at %1-%2) were lower than the initial values. On the contrary. the other mine samples with added cement and ash (only at %10 and %5) binding material were higher than the initial. The lowest EC value was detected 1034 µS/cm with added marble dust at 5% in the sample after 2 weeks.

Overall EC evaluation for No1 sample in the intermittent set up: The initial control EC value was measured 2611 µS/cm that it was the highest EC value in the intermittent set up for this mine sample. At the end of the experimental period. EC values in all of the mine samples with added binding materials were higher than the initial values. The lowest EC value was detected 1004 µS/cm in the sample with added ash at 2% at the end of the 9 weeks.

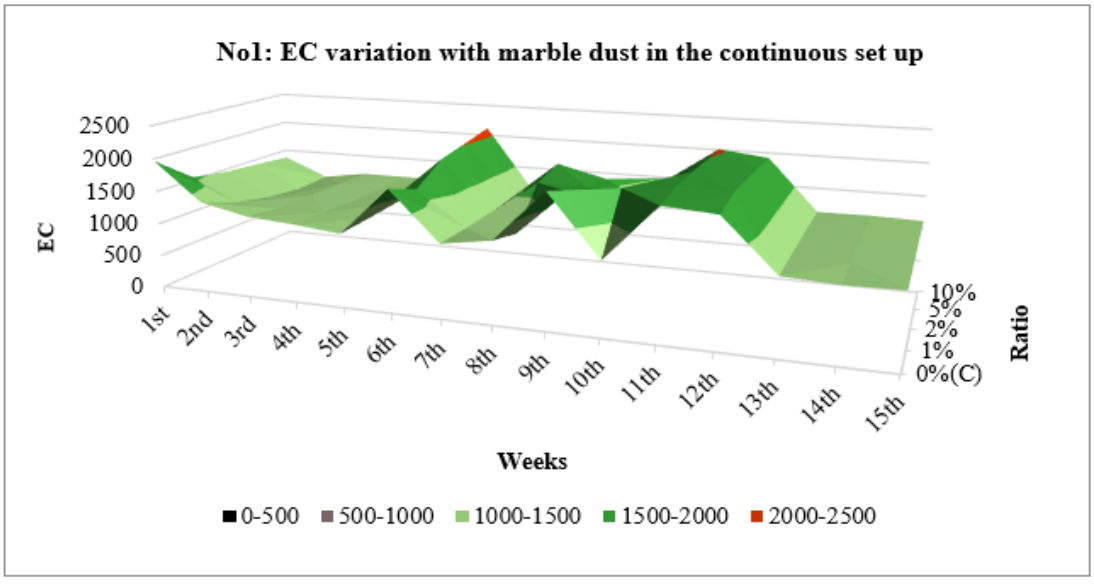


Figure 4.69 EC variation of No1 mine sample added marble dust in the continuous set up

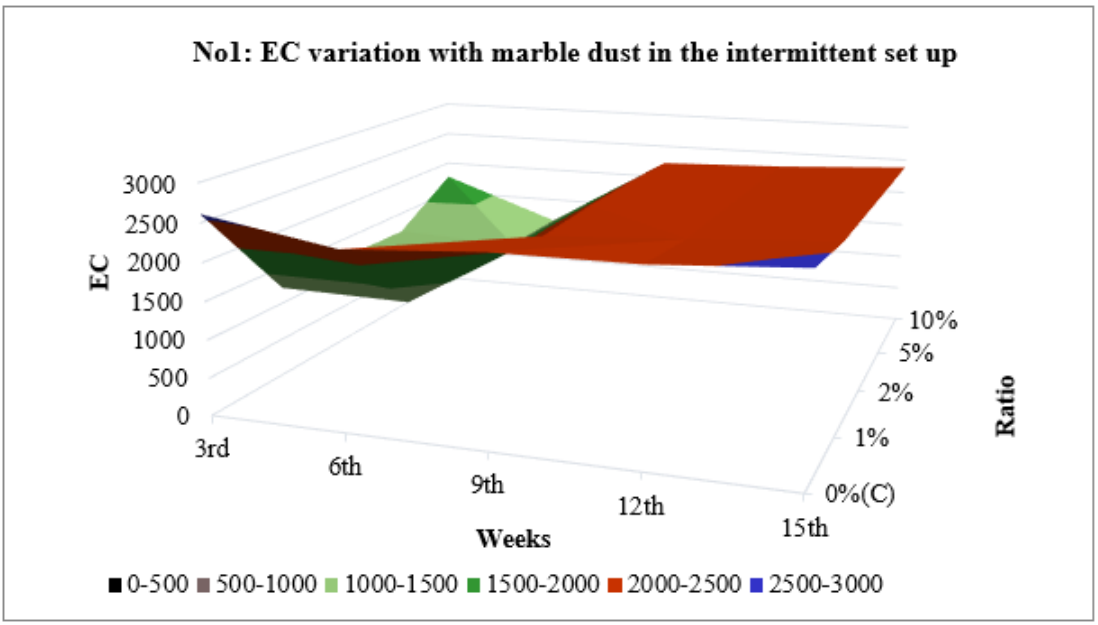


Figure 4.70 EC variation of No1 mine sample added marble dust in the intermittent set up

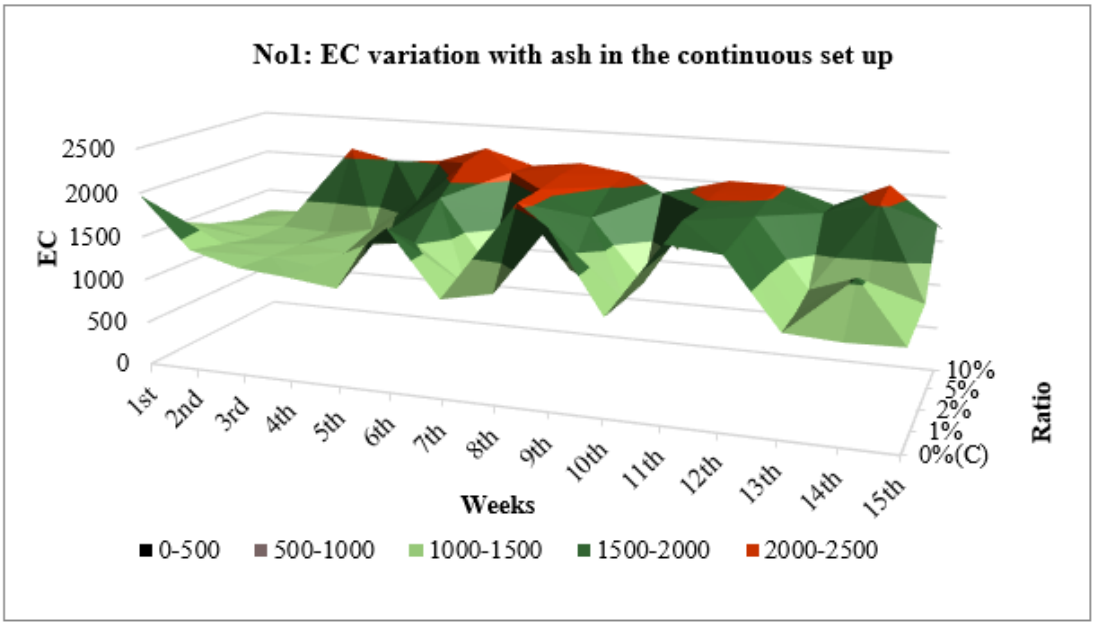


Figure 4.71 EC variation of No1 mine sample added ash in the continuous set up

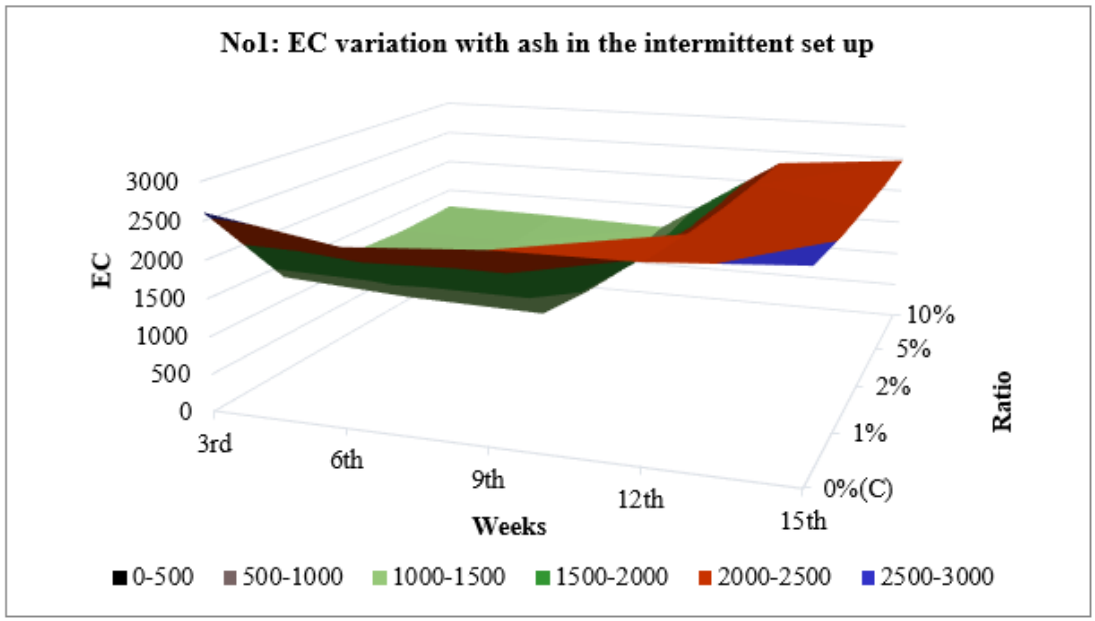


Figure 4.72 EC variation of No1 mine sample added ash in the intermittent set up

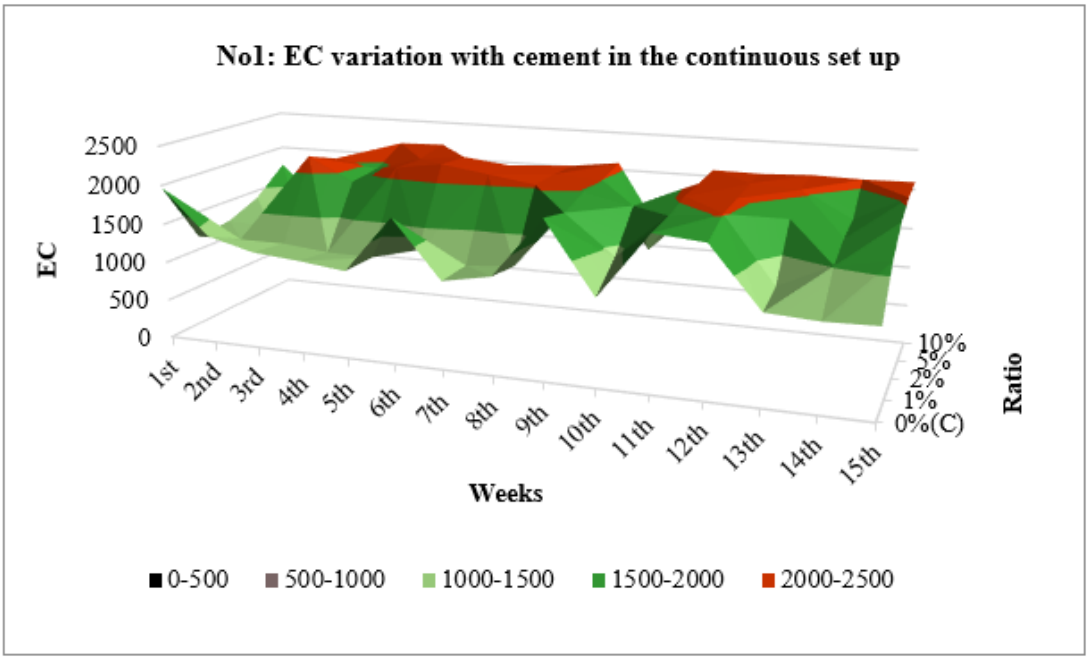


Figure 4.73 EC variation of No1 mine sample added cement in the continuous set up

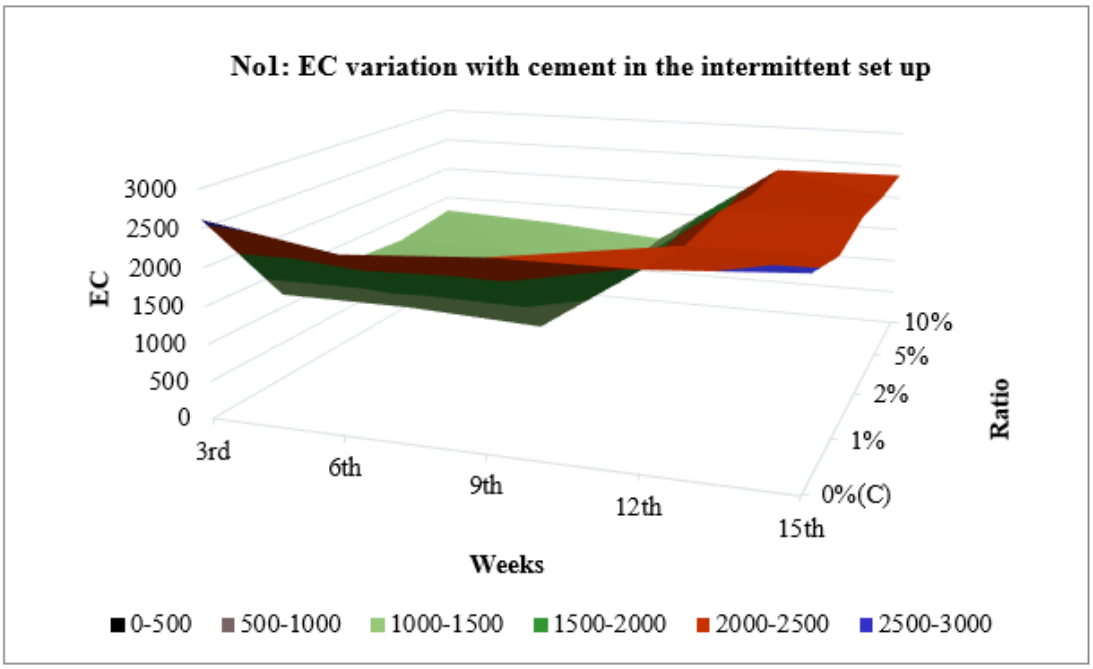


Figure 4.74 EC variation of No1 mine sample added cement in the intermittent set up

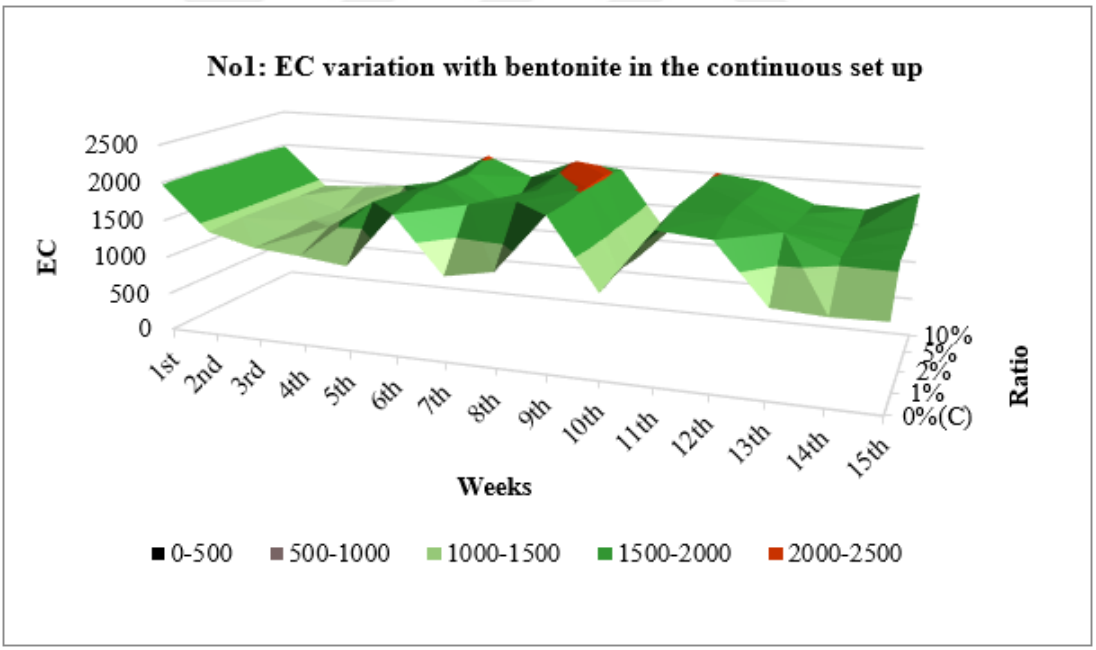


Figure 4.75 EC variation of No1 mine sample added bentonite in the continuous set up

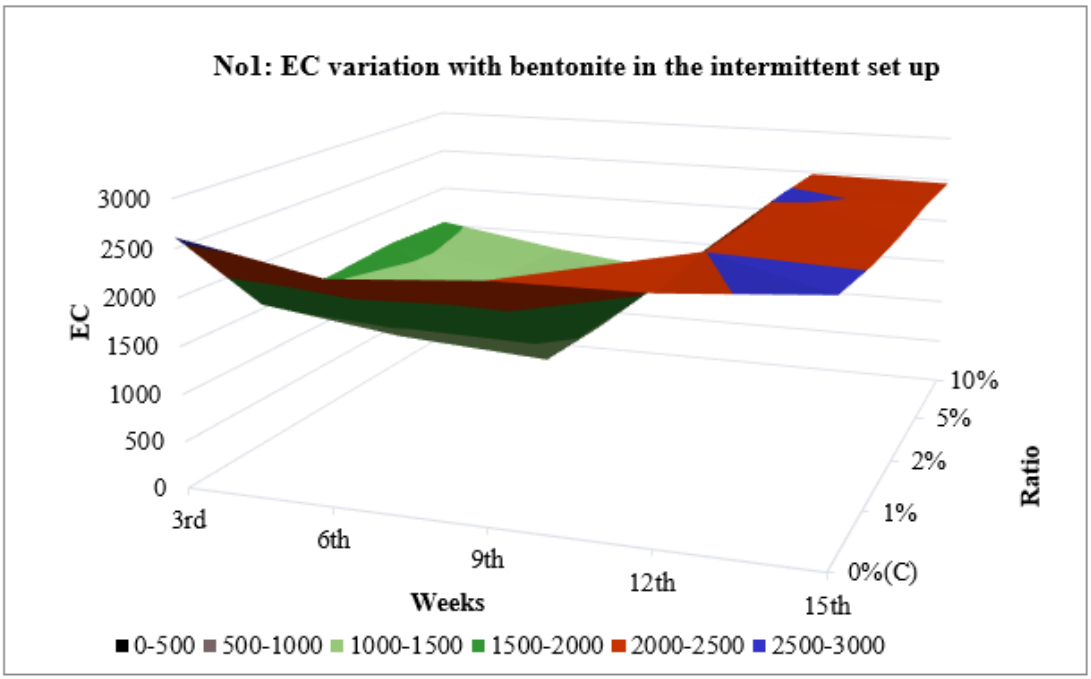


Figure 4.76 EC variation of No1 mine sample added bentonite in the intermittent set up

4.3.7.2 Evaluation of EC of No2 Mine Waste Sample

Overall EC evaluation for No2 sample in the continuous set up: Final EC value in control group was decreased from 3440 µS/cm to 1380 µS/cm. The highest EC values was measured in the first week except the sample with added cement. Final EC values were lower than the initial values that they were 1083. 927. 1073 and 1141 µS/cm added marble dust (%10). ash (1%). cement (1%). and bentonite (1%). respectively. The mine sample with added bentonite at 10% was the highest in the 8. Weeks (2043 µS/cm). The lowest EC value was detected 927 µS/cm in the sample with added ash at 1% in the 10. Weeks while the highest EC value was 3510 µS/cm in the sample with added bentonite at 5% at the end of the first week.

Overall EC evaluation for No2 sample in the intermittent set up: The control EC value showed an increase to final period (The final EC was 2795 µS/cm while the initial value was 2070 µS/cm). Likewise. except the sample with added bentonite. all of the samples with added binding material were higher than the initial. The sample with added bentonite decreased a little according to beginning. The lowest EC value

was detected 1048 µS/cm in the sample with added ash at 10% at the end of the 9 weeks.

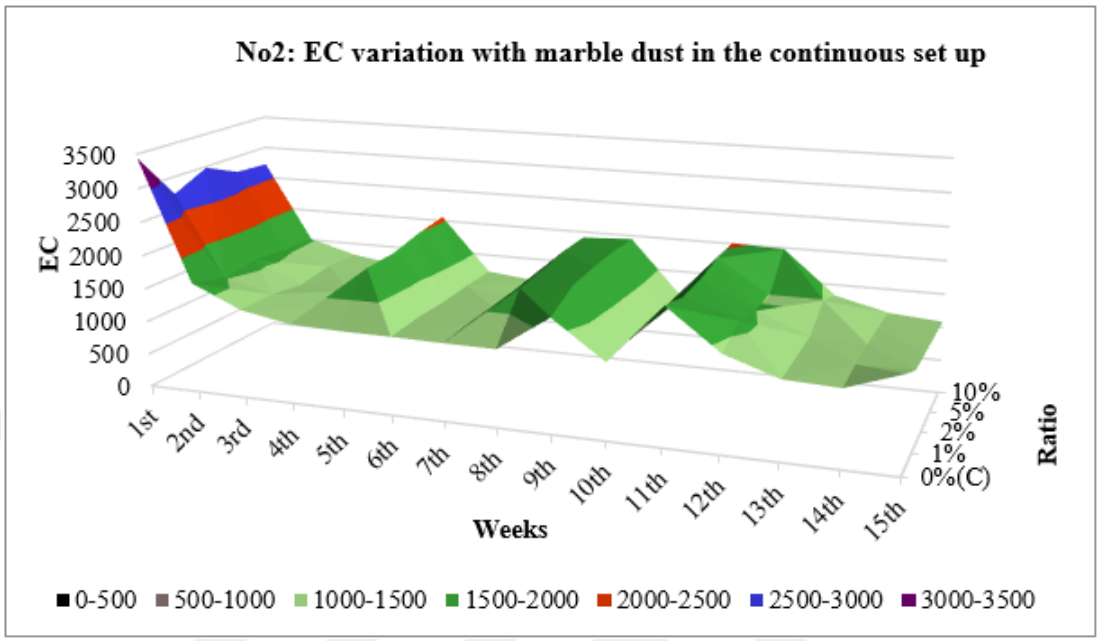


Figure 4.77 EC variation of No2 mine sample added marble dust in the continuous set up

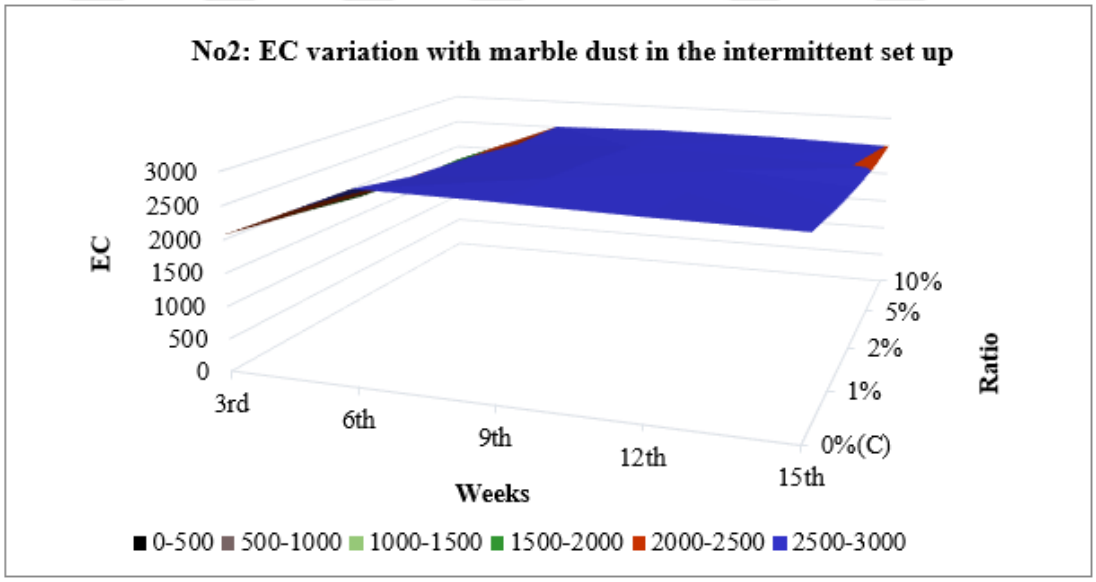


Figure 4.78 EC variation of No2 mine sample added marble dust in the intermittent set up

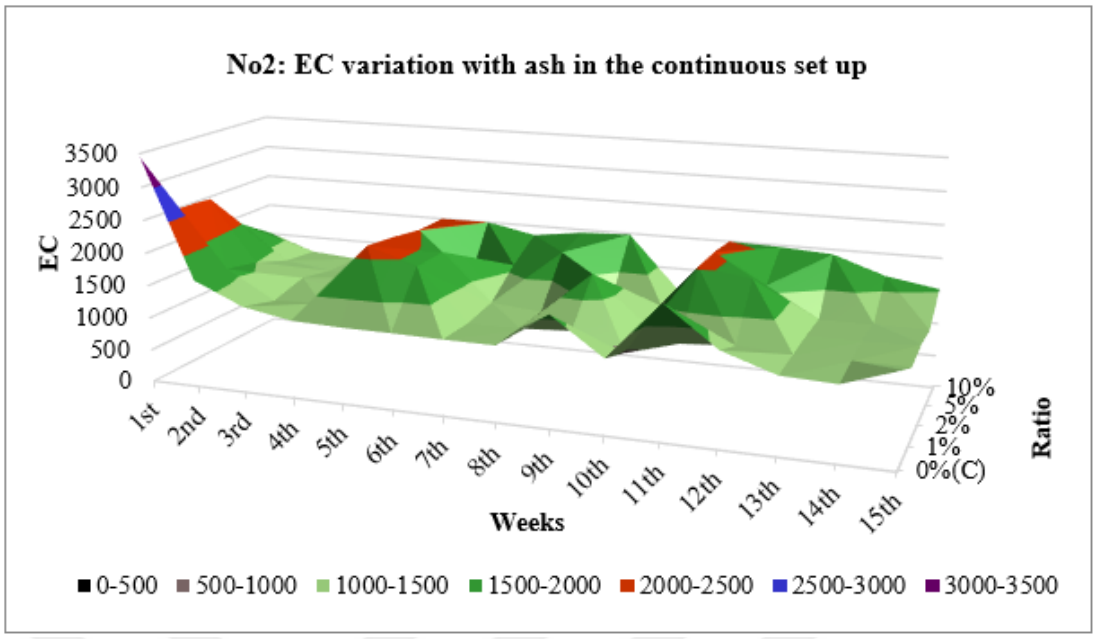


Figure 4.79 EC variation of No2 mine sample added ash in the continuous set up

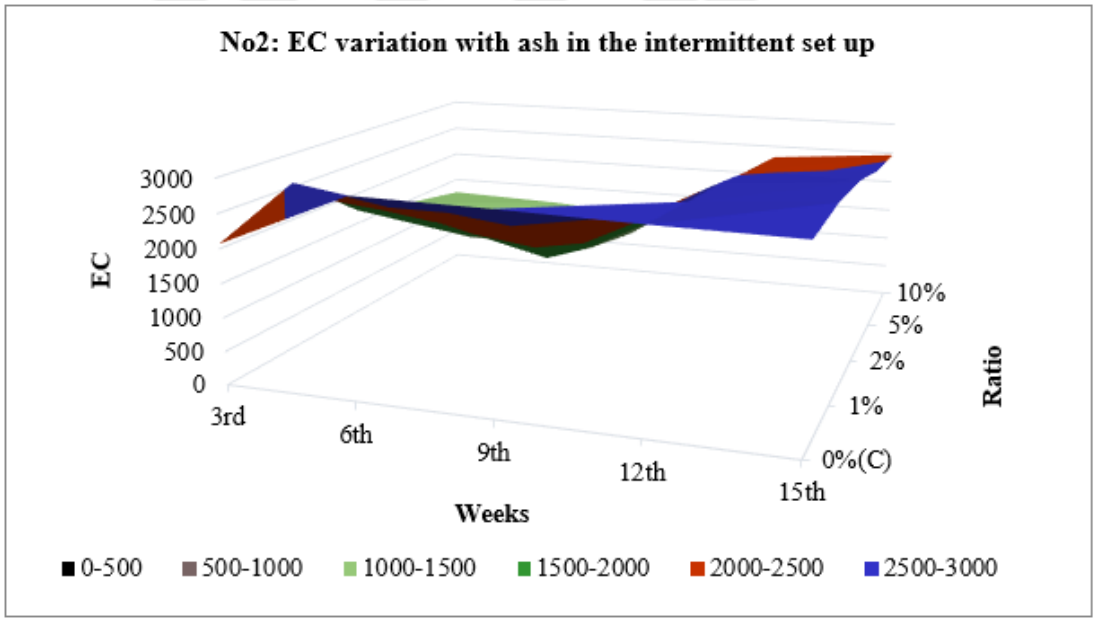


Figure 4.80 EC variation of No2 mine sample added ash in the intermittent set up

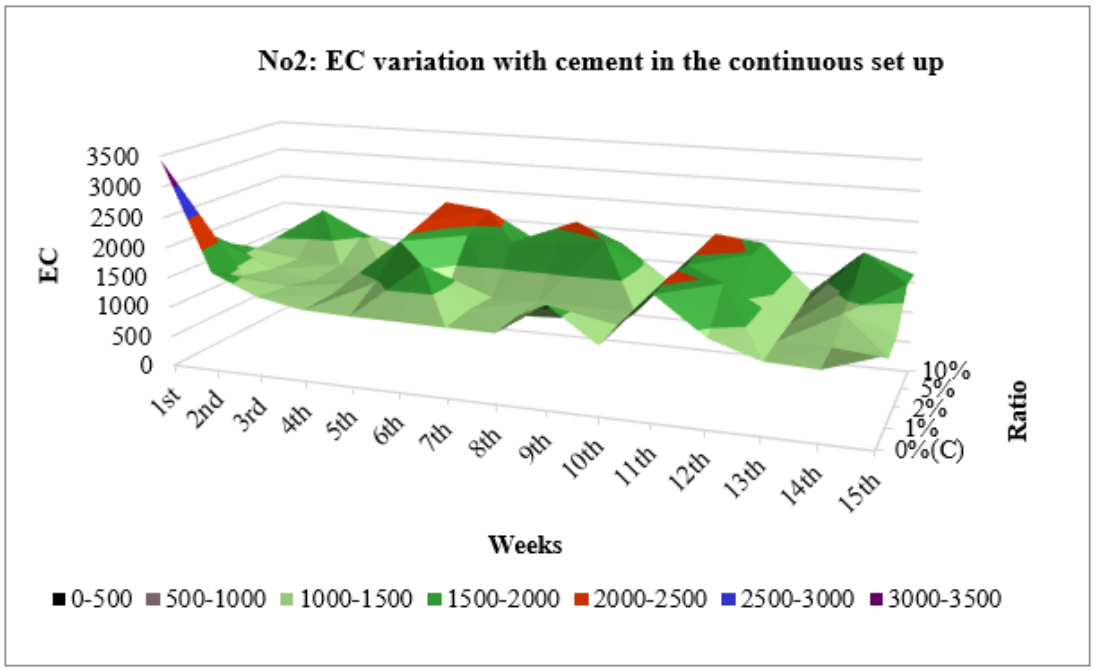


Figure 4.81 EC variation of No2 mine sample added cement in the continuous set up

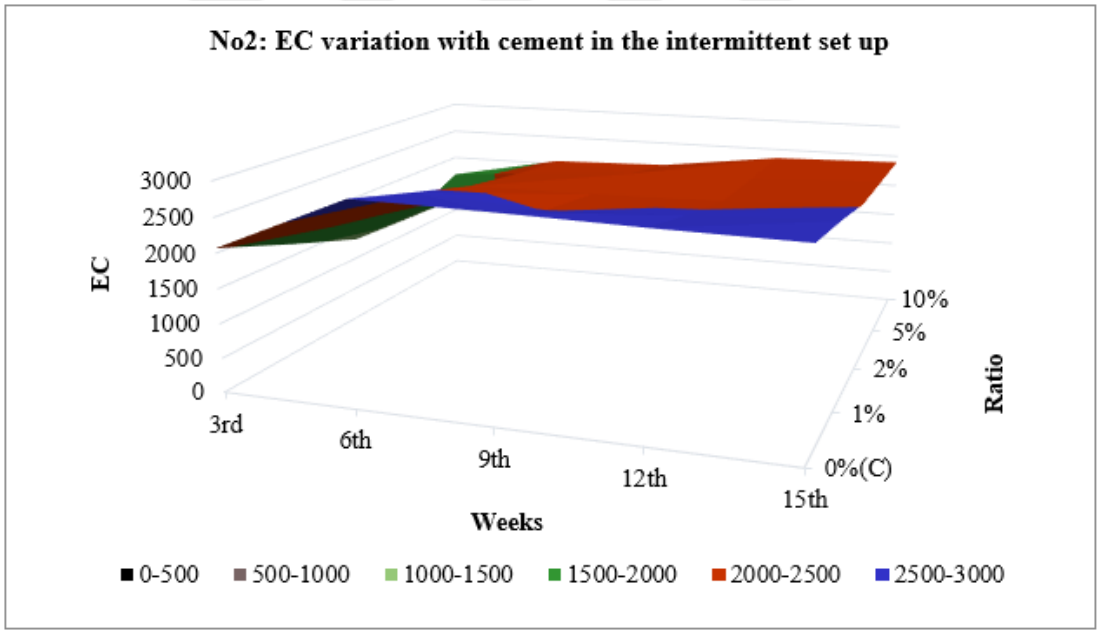


Figure 4.82 EC variation of No2 mine sample added cement in the intermittent set up

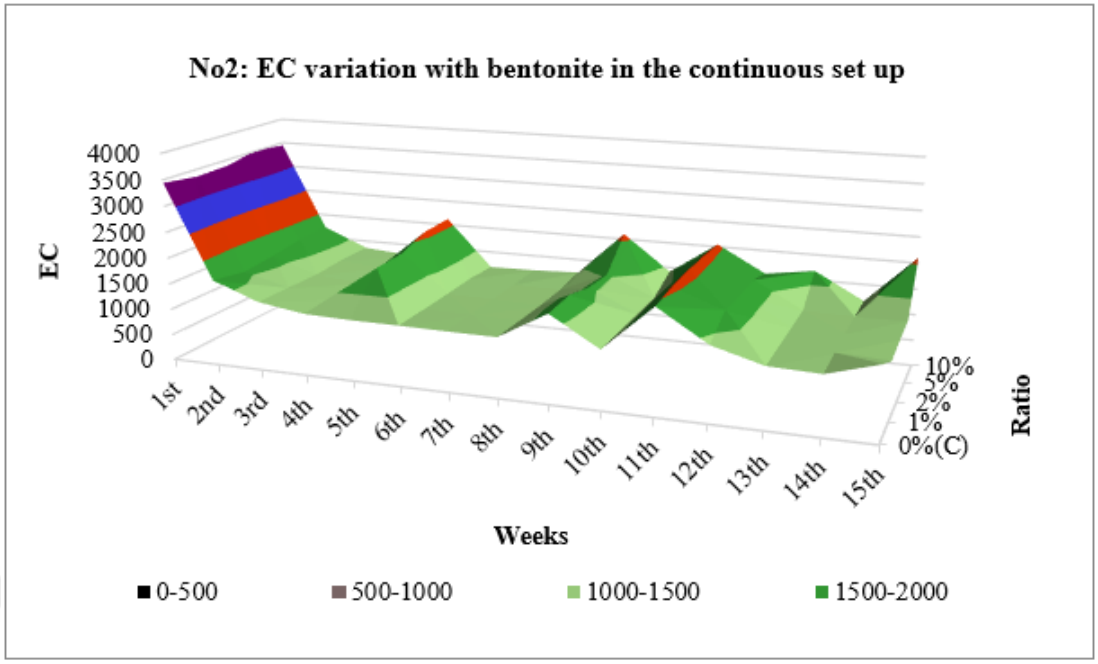


Figure 4.83 EC variation of No2 mine sample added bentonite in the continuous set up

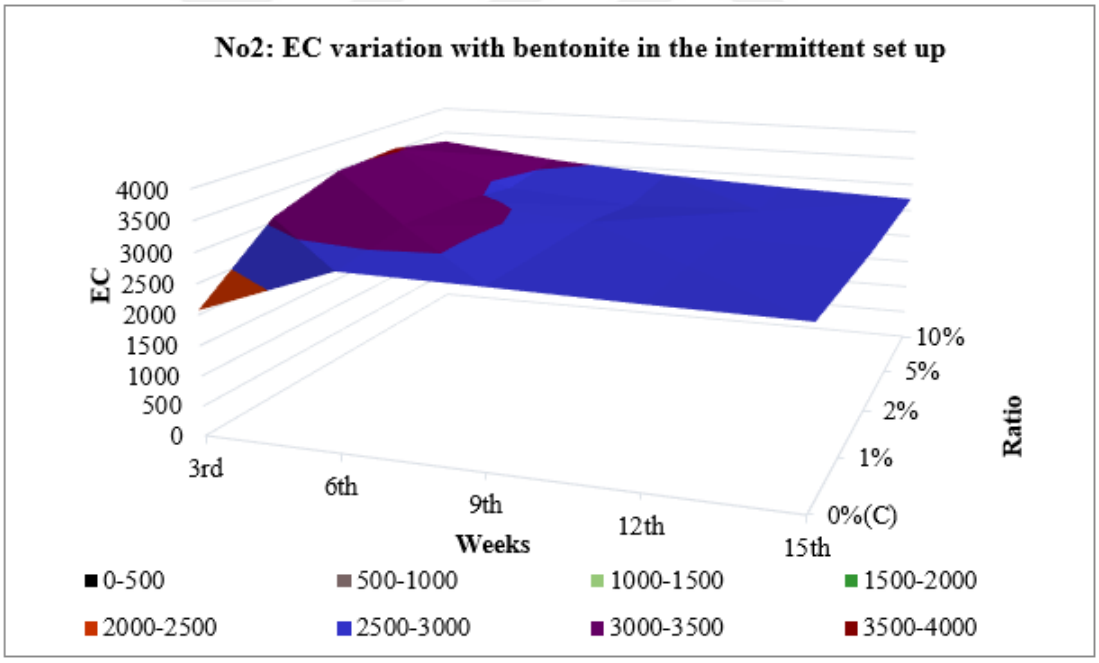


Figure 4.84 EC variation of No2 mine sample added bentonite in the intermittent set up

4.3.7.3 Evaluation of EC of No3 Mine Waste Sample

Overall EC evaluation for No3 sample in the continuous set up: As seen the control group of No2 mine sample. EC value decreased a little at the end of the experimental

period to the initial measurement. The final EC was measured 1415 µS/cm in the control group. While the final EC values in the samples with added marble dust and bentonite were lower than the initial measurement. EC values in the other samples (with added cement and ash) were detected higher than the first week measurement. Generally. the lowest EC values were observed in the samples with added binding material at 1%. According to this. the lowest EC value was detected 1052 µS/cm in where the sample with added marble dust at 1% at the end of the 13. Weeks.

Overall EC evaluation for No3 sample in the intermittent set up: The final control EC value was measured 2648 µS/cm that it was higher than the initial. The highest EC values of the samples with added binding materials had showed as the similar with the control group. All of the EC values were higher than the initial in the samples with added binding material. The lowest EC value was detected 1004 µS/cm in the sample with added cement at 5% after 9 weeks.

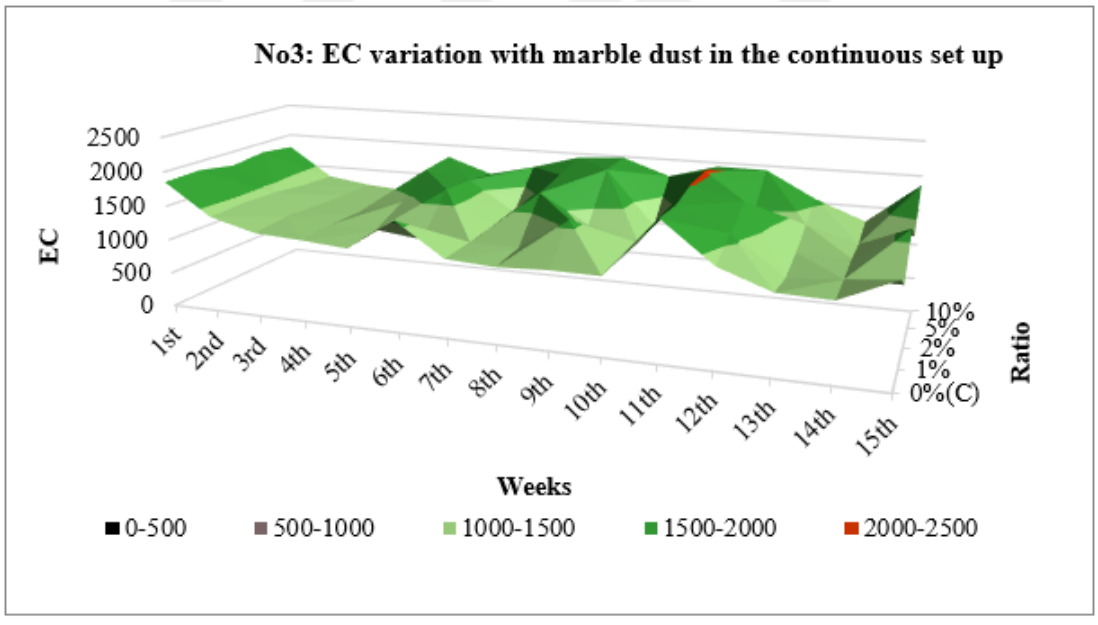


Figure 4.85 EC variation of No3 mine sample added marble dust in the continuous set up

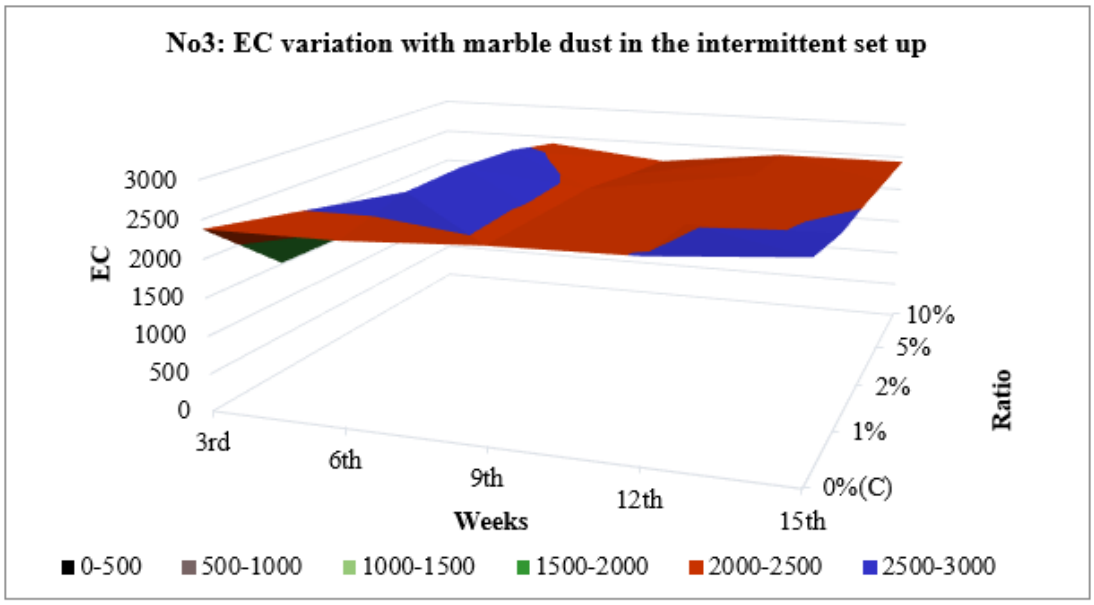


Figure 4.86 EC variation of No3 mine sample added marble dust in the intermittent set up

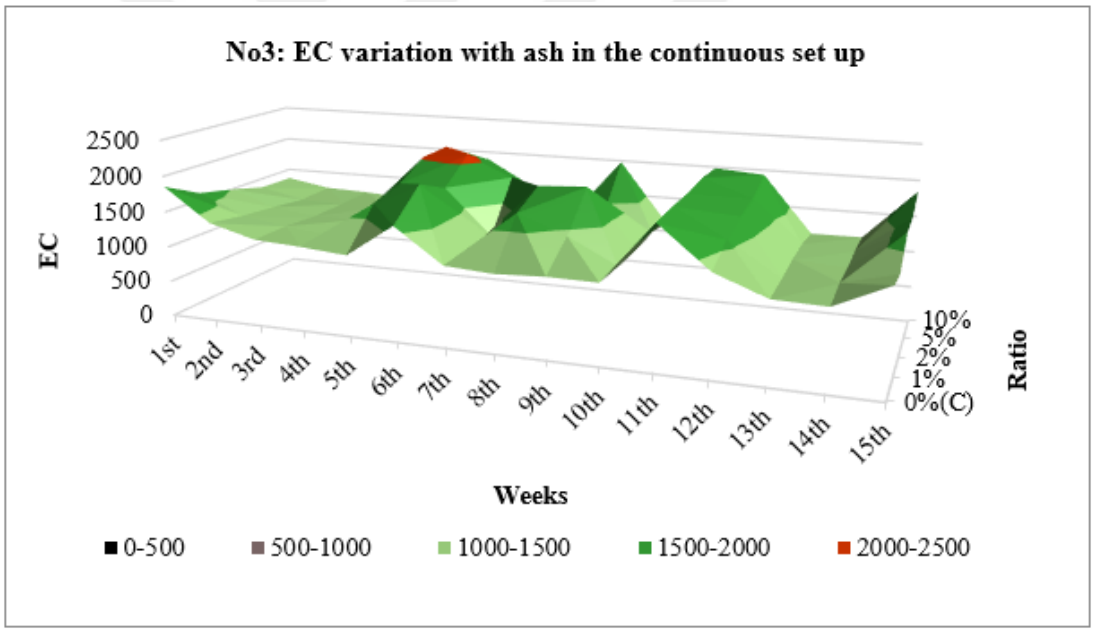


Figure 4.87 EC variation of No3 mine sample added ash in the continuous set up

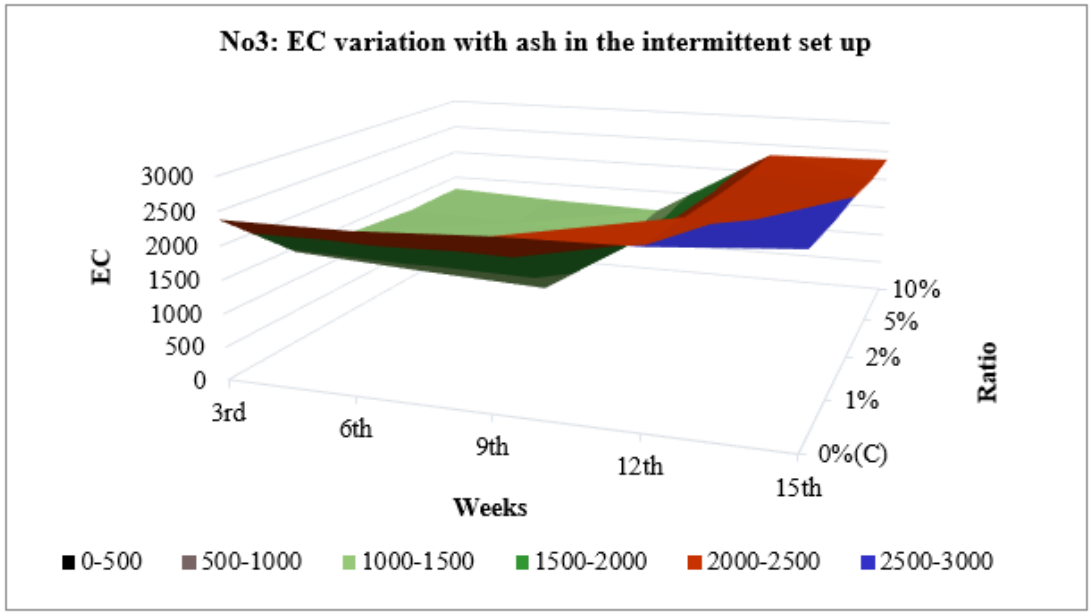


Figure 4.88 EC variation of No3 mine sample added ash in the intermittent set up

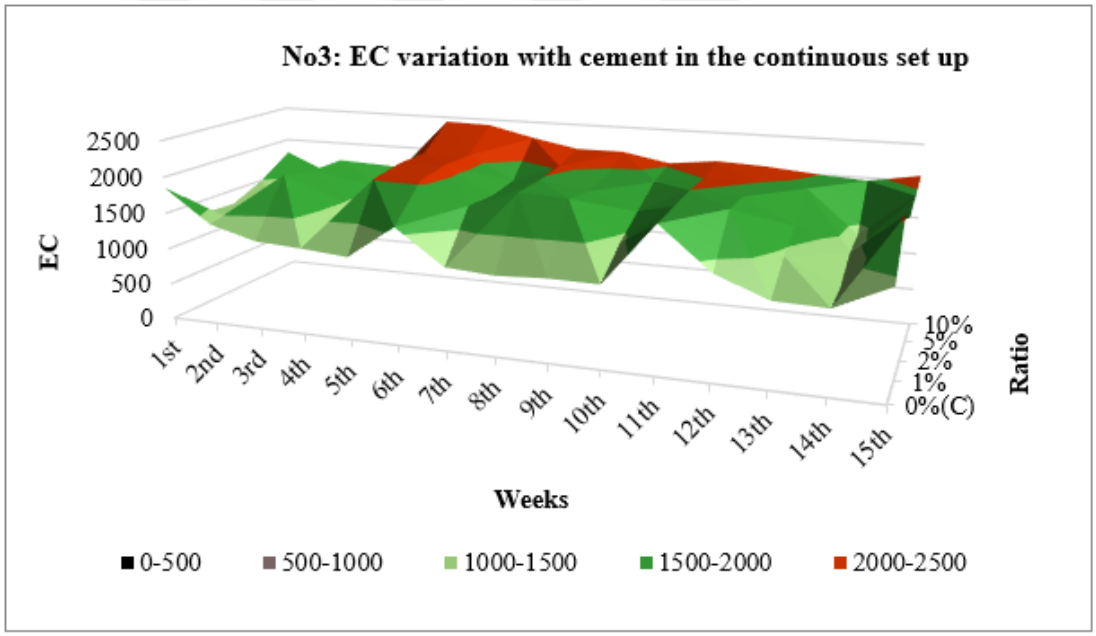


Figure 4.89 EC variation of No3 mine sample added cement in the continuous set up

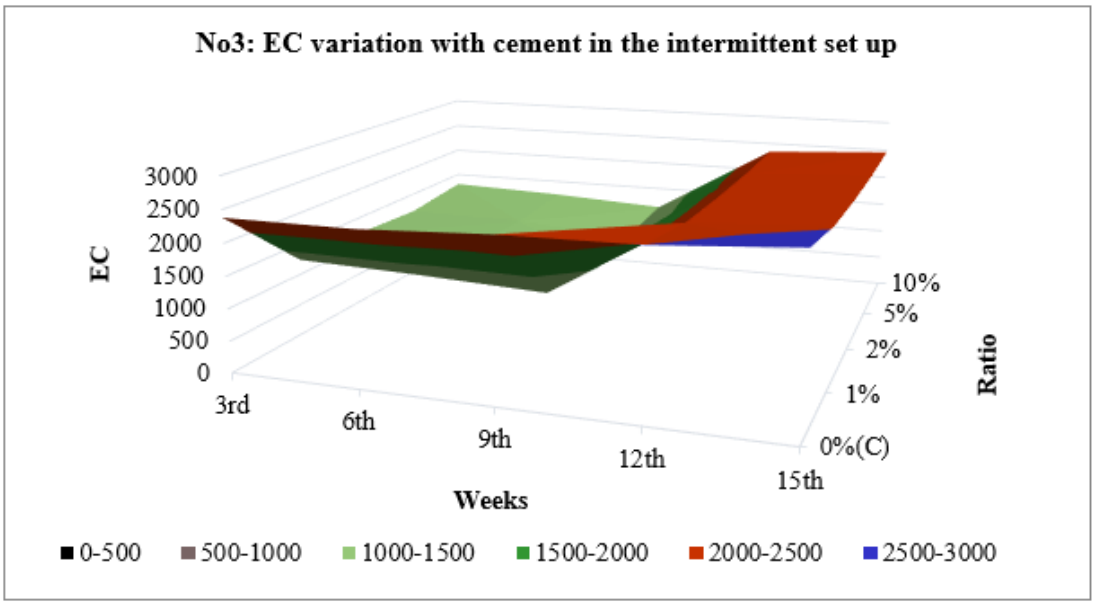


Figure 4.90 EC variation of No3 mine sample added cement in the intermittent set up

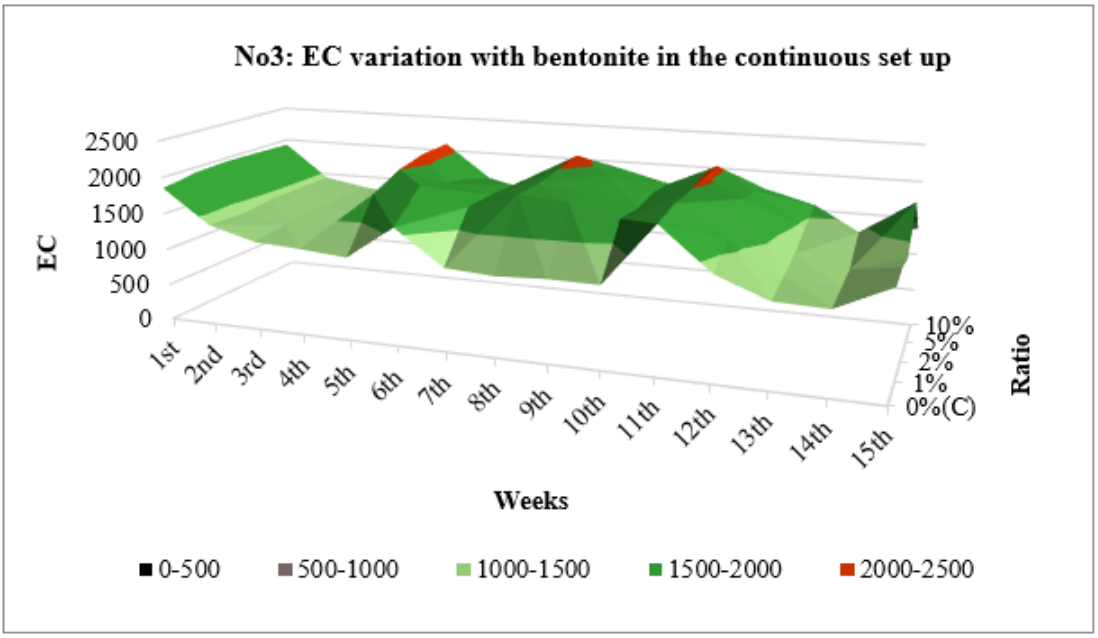


Figure 4.91 EC variation of No3 mine sample added bentonite in the continuous set up

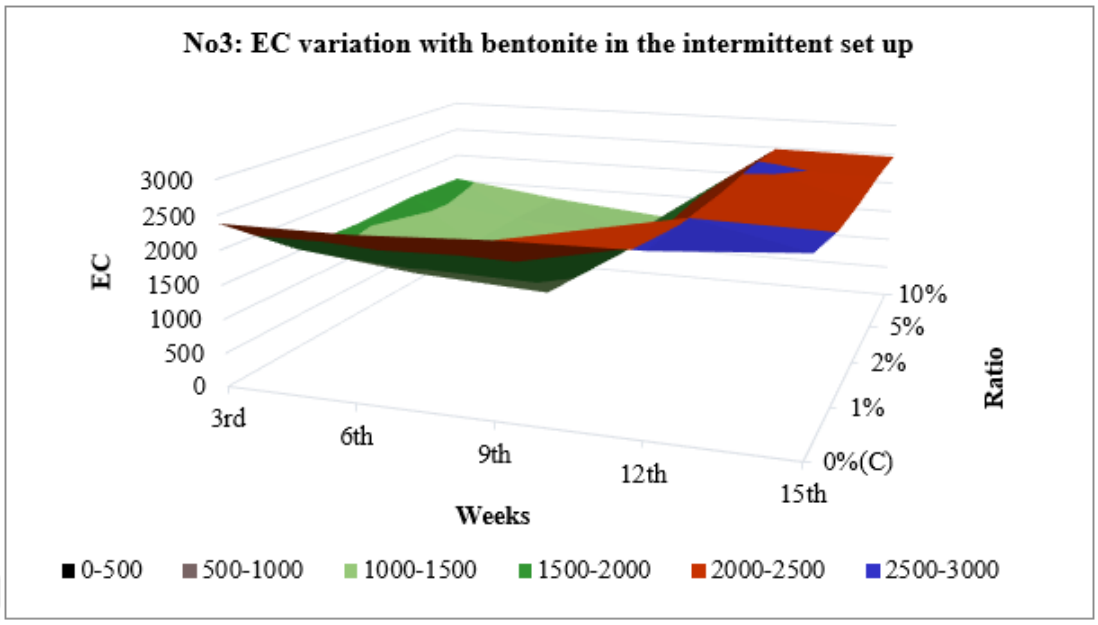


Figure 4.92 EC variation of No3 mine sample added bentonite in the intermittent set up

4.3.7.4 Evaluation of EC of No4 Mine Waste Sample

Overall EC evaluation for No4 sample in the continuous set up: Final EC value in control group was decreased from 3148 µS/cm to 781 µS/cm. All of the EC values in the samples with added binding materials had showed a decrease than the initial EC values. The lowest EC value was 654 µS/cm in the sample with added ash at 1% in the 13. Weeks while the highest EC value was 3110 µS/cm in the sample with added cement at 10% at the end of the first week. It was observed that the lowest EC values were in this mine sample in the continuous set up.

Overall EC evaluation for No4 sample in the intermittent set up: The control EC value in this sample decreased a little to initial period (The final EC was 2095 µS/cm while the initial value was 2120 µS/cm). As in the continuous set up. all of the EC values in the samples with binding materials decreased at the end of the 15. Weeks according to the initial EC values. The lowest EC value was detected 985 µS/cm in the sample with added cement at 1% after 15 weeks. The other EC values were almost the similar that the results of samples with added marble dust. ash. and bentonite were 990 (5%). 993 (1%). and 998 (5%) µS/cm. respectively.

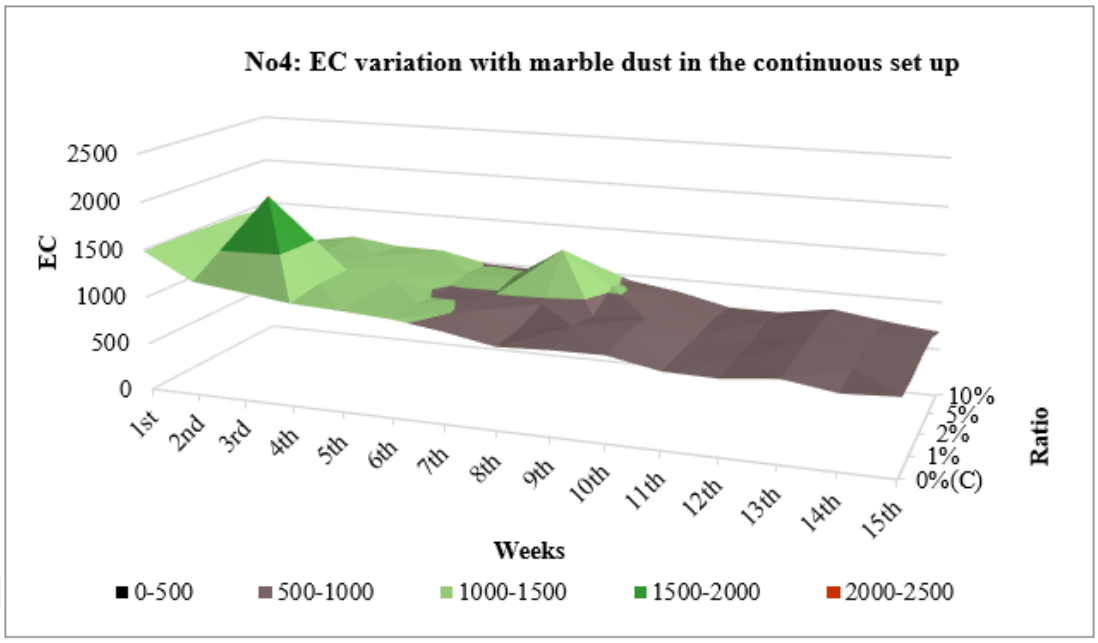


Figure 4.93 EC variation of No4 mine sample added marble dust in the continuous set up

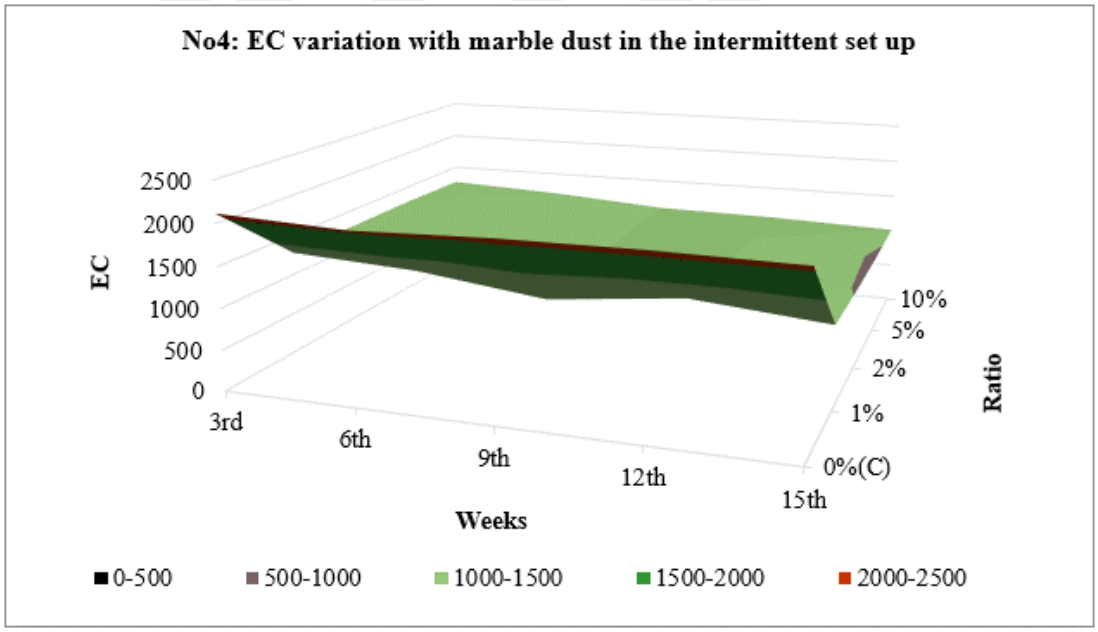


Figure 4.94 EC variation of No4 mine sample added marble dust in the intermittent set up

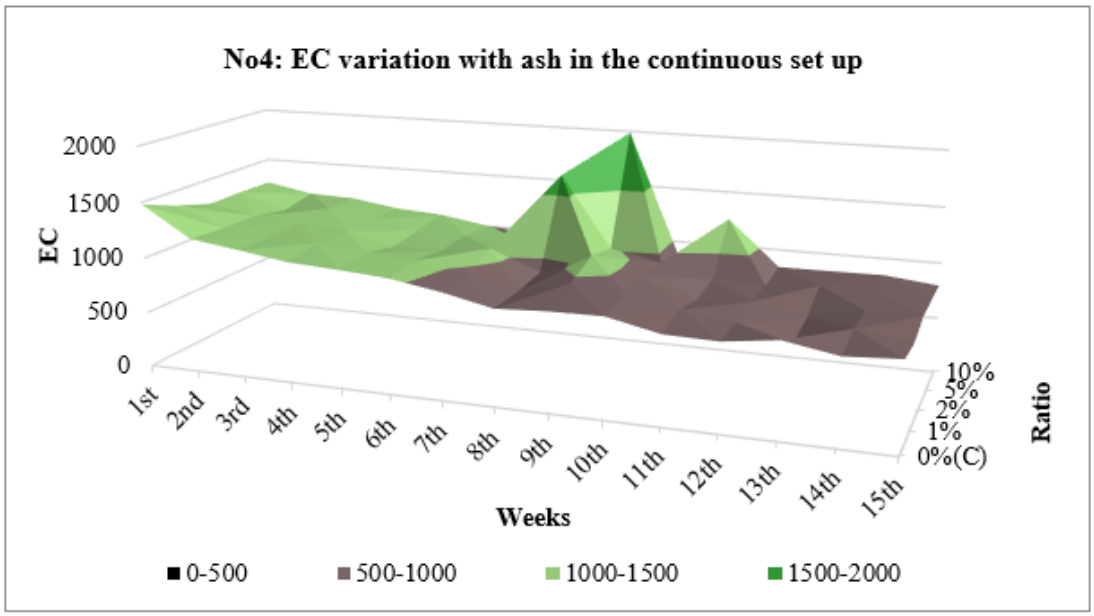


Figure 4.95 EC variation of No4 mine sample added ash in the continuous set up

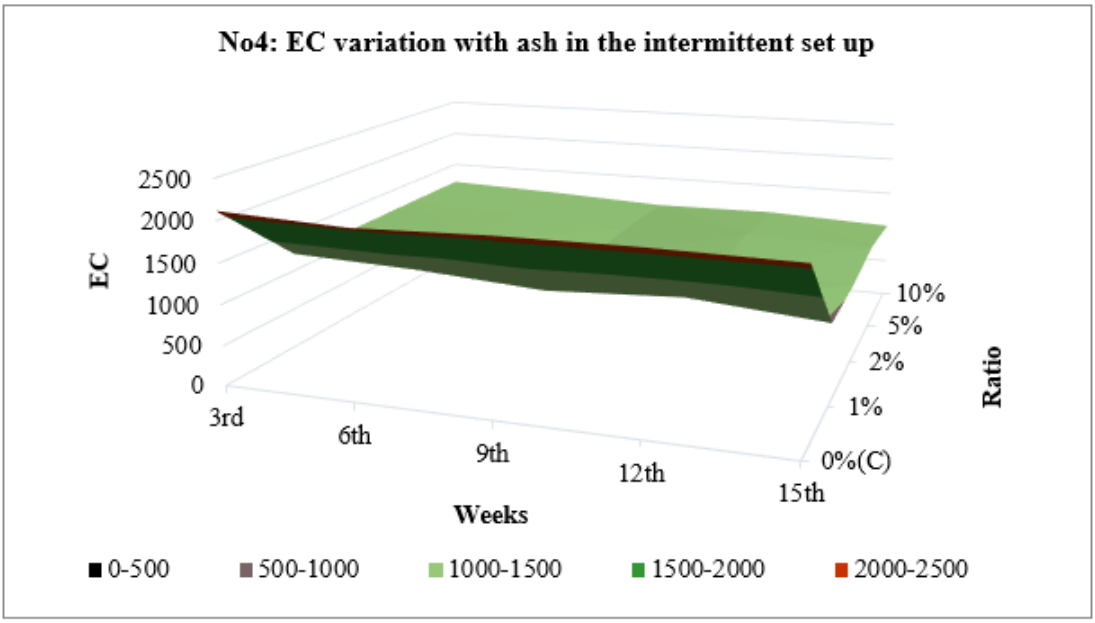


Figure 4.96 EC variation of No4 mine sample added ash in the intermittent set up

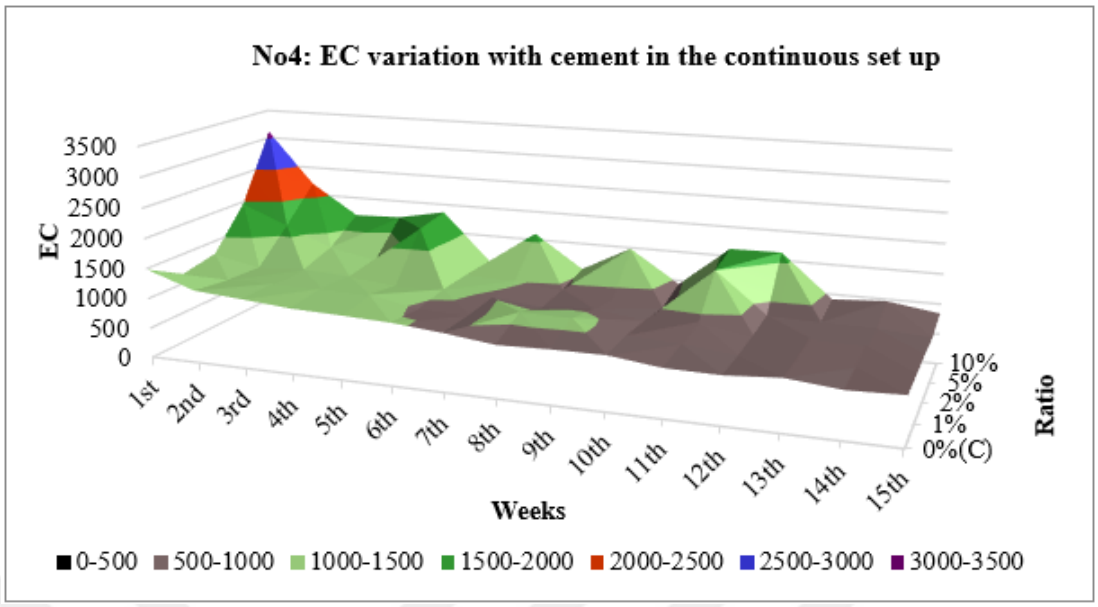


Figure 4.97 EC variation of No4 mine sample added cement in the continuous set up

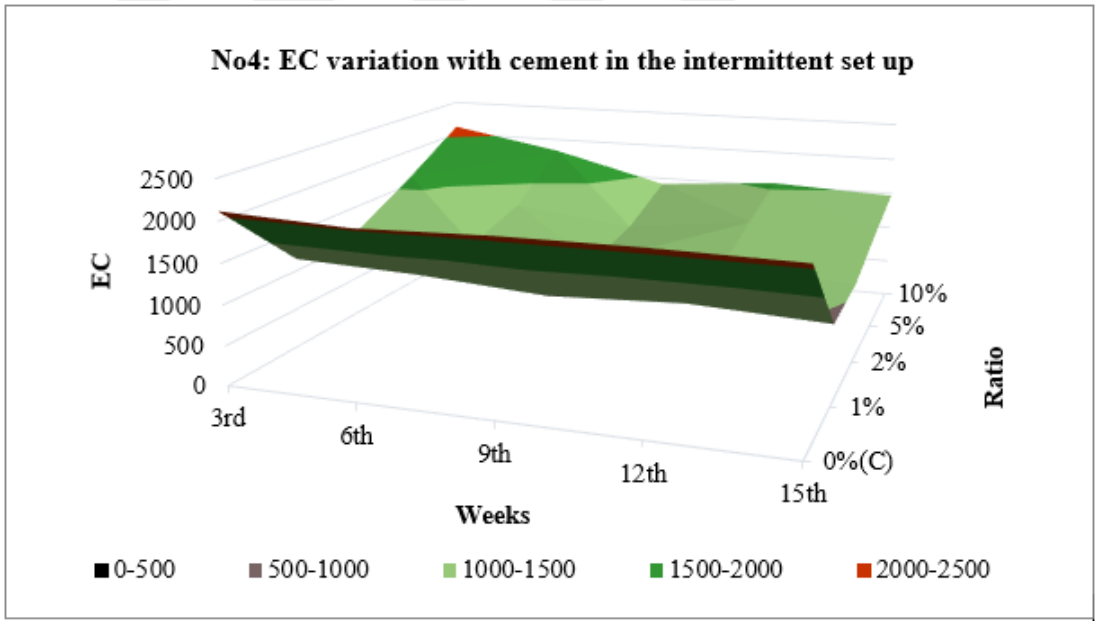


Figure 4.98 EC variation of No4 mine sample added cement in the intermittent set up

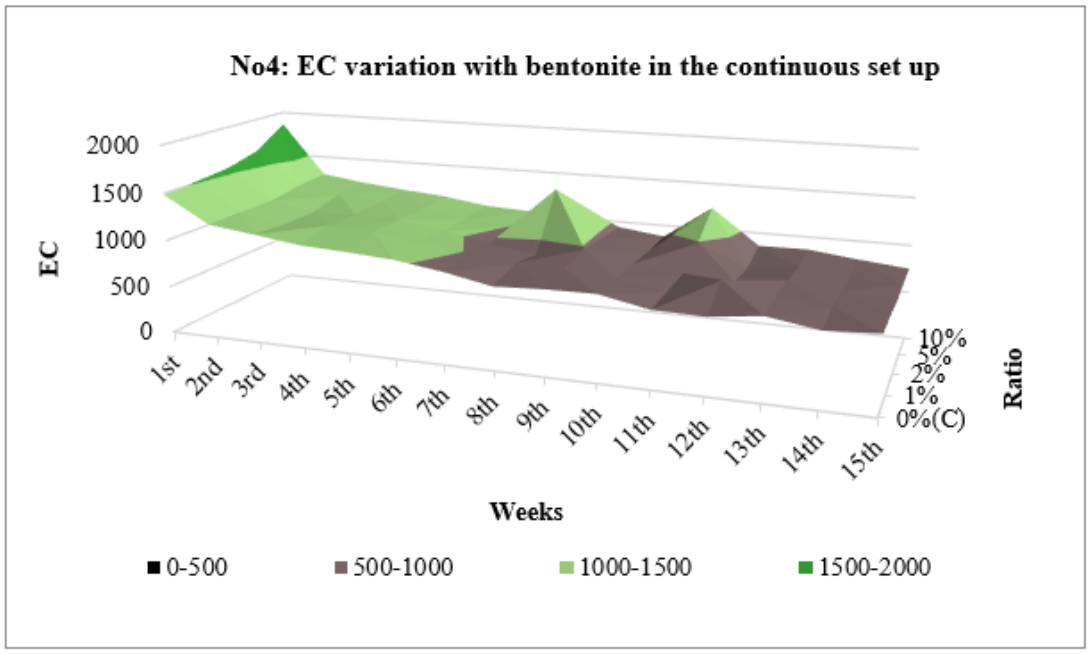


Figure 4.99 EC variation of No4 mine sample added bentonite in the continuous set up

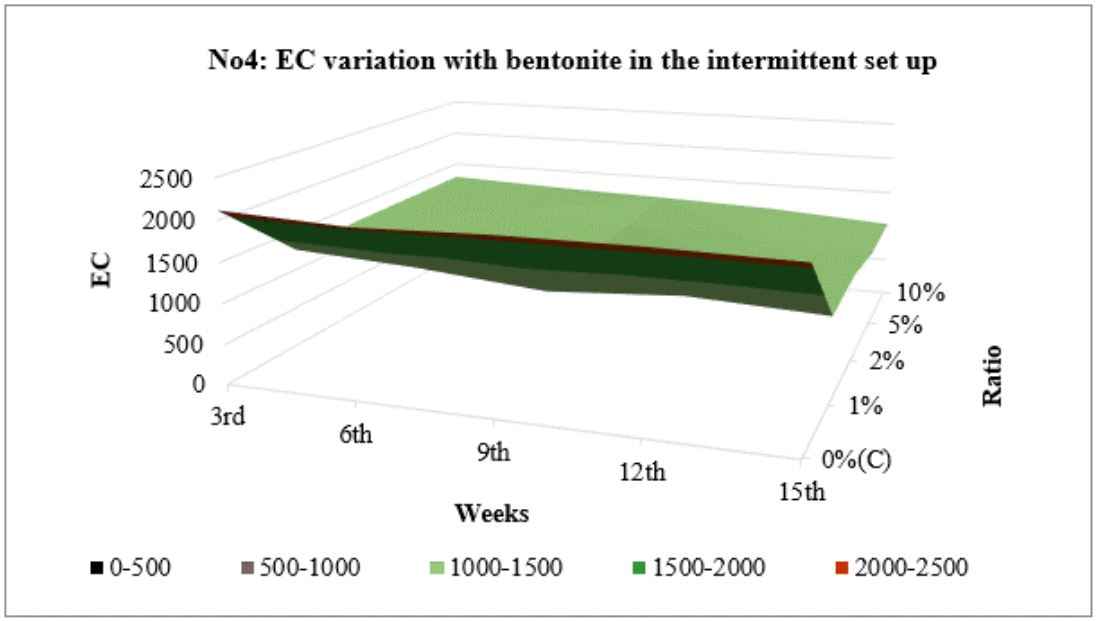


Figure 4.100 EC variation of No4 mine sample added bentonite in the intermittent set up

4.3.7.5 Evaluation of EC of No5 Mine Waste Sample

Overall EC evaluation for No5 sample in the continuous set up: At the end of the experimental period. the control EC value was detected 1606 µS/cm that it was higher than the initial EC value. All of the EC values in the samples with added binding

material were lower than the initial. The lowest EC values were detected in samples where used binding material at 1% except the sample with added ash (ash ratio was 2% in there). The lowest EC value was detected 1035 µS/cm in where the sample with added marble dust at 1% at the end of the 13. Weeks.

Overall EC evaluation for No5 sample in the intermittent set up: The final control EC value was measured 2441 µS/cm that it was higher than the initial. In 9. Weeks. lower EC values were detected in all of the samples with adding binding material. The lowest EC value was 1111 µS/cm in the sample with added ash at 2%. All of the EC values in the samples with added binding materials had showed a decrease than the initial EC values except the sample added cement.

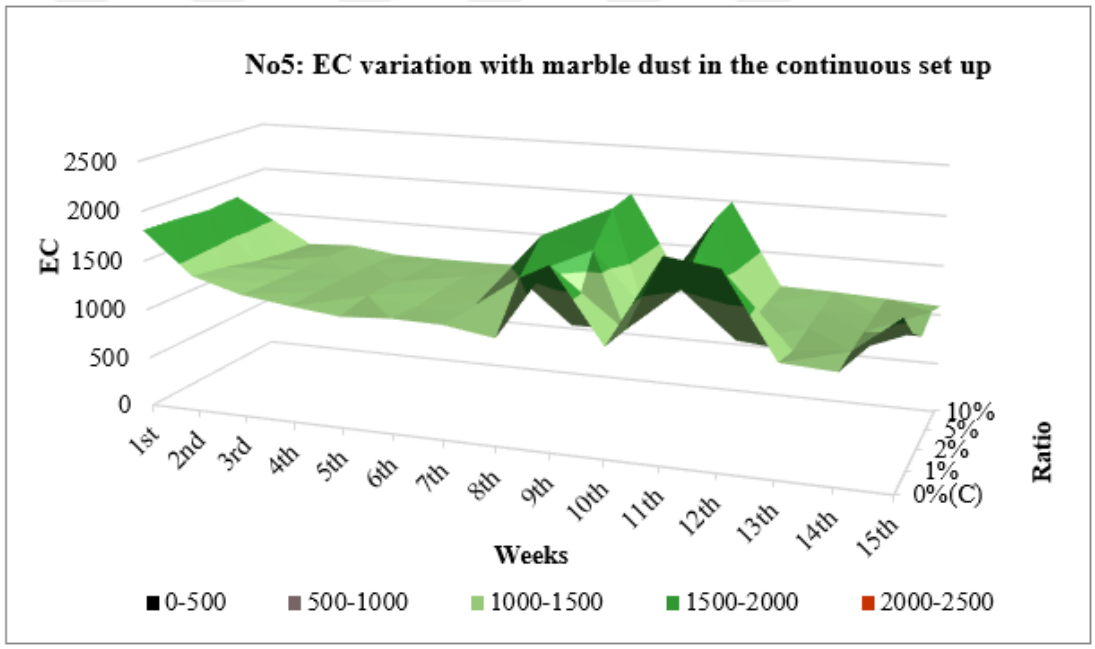


Figure 4.101 EC variation of No5 mine sample added marble dust in the continuous set up

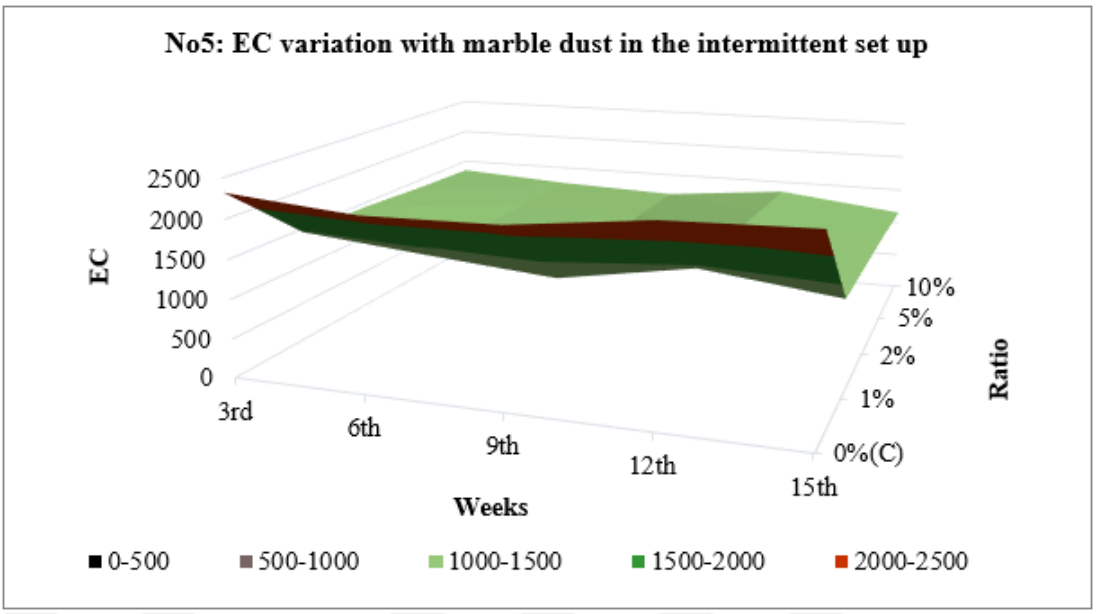


Figure 4.102 EC variation of No5 mine sample added marble dust in the intermittent set up

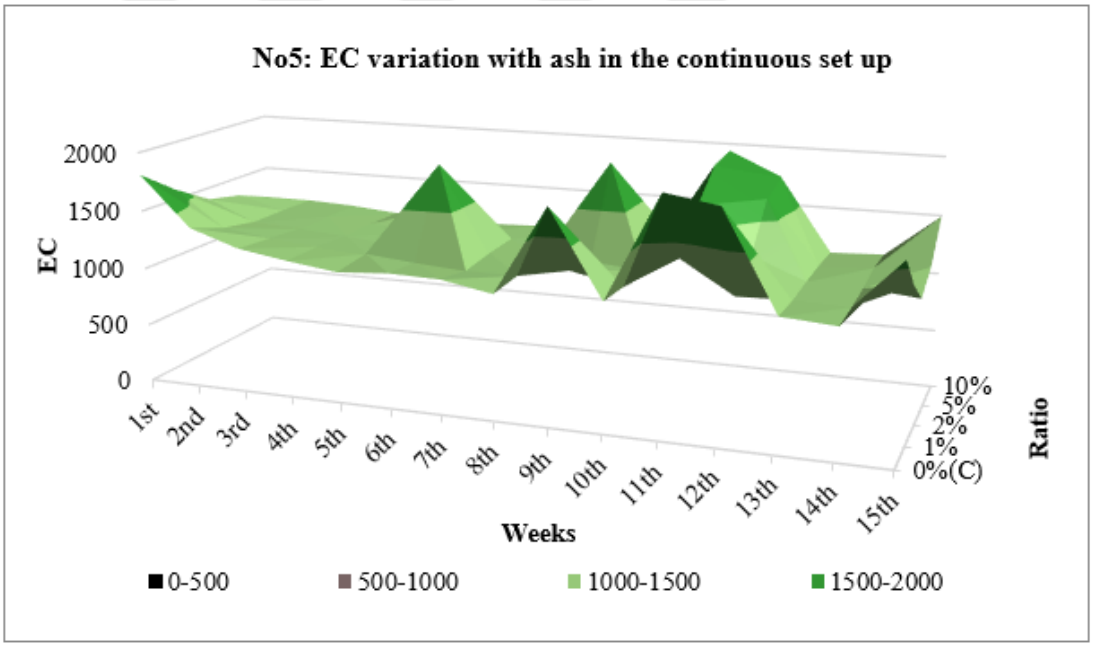


Figure 4.103 EC variation of No5 mine sample added ash in the continuous set up

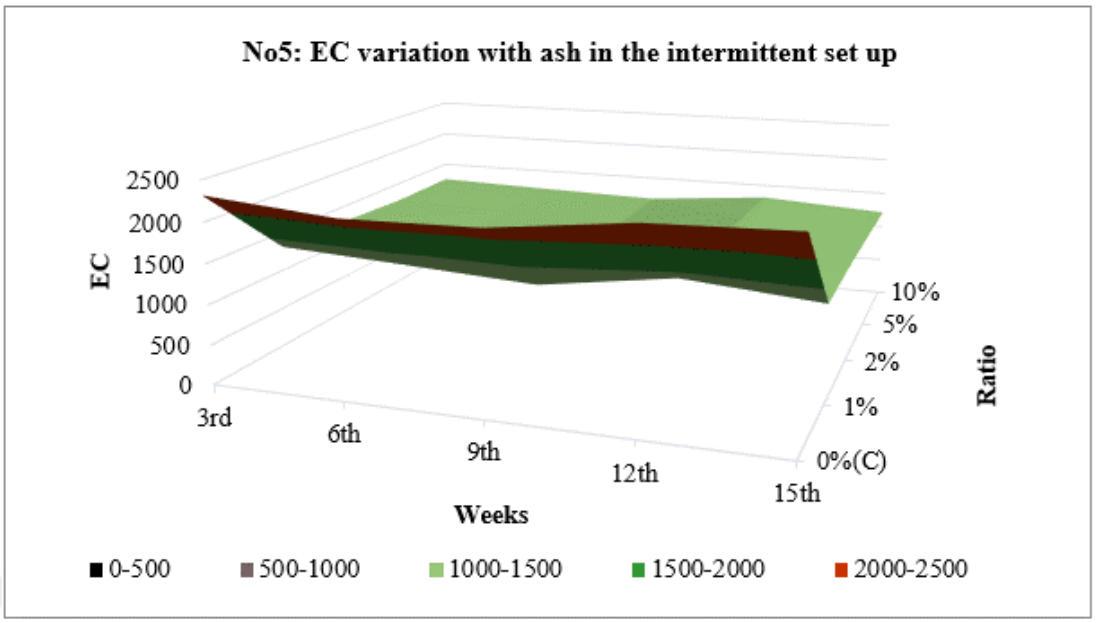


Figure 4.104 EC Variation of No5 mine sample added ash in the intermittent set up

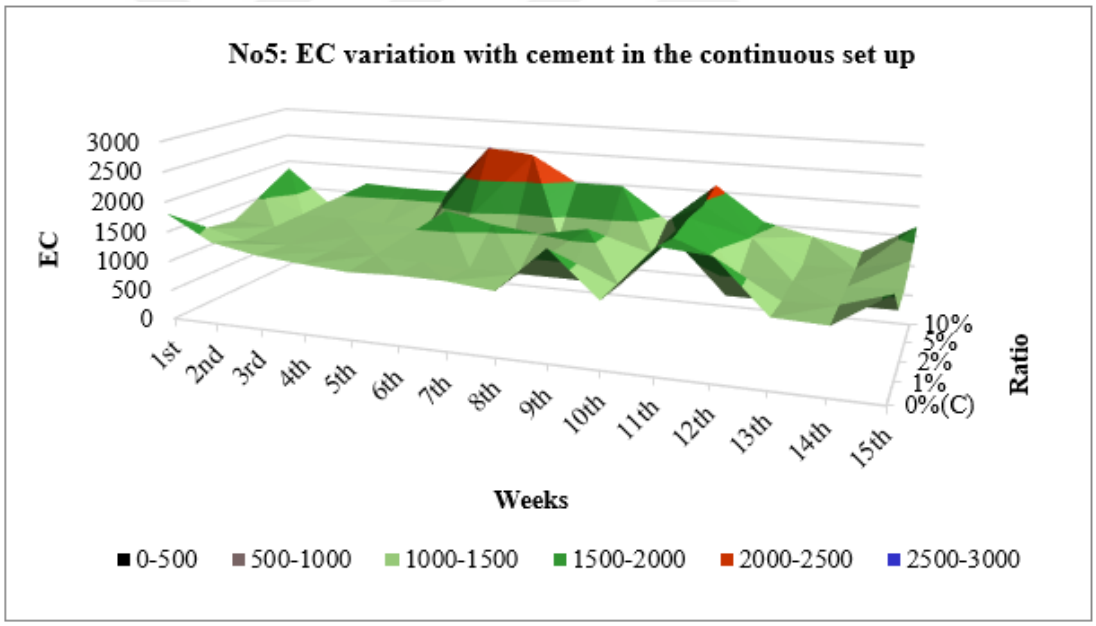


Figure 4.105 EC variation of No5 mine sample added cement in the continuous set up

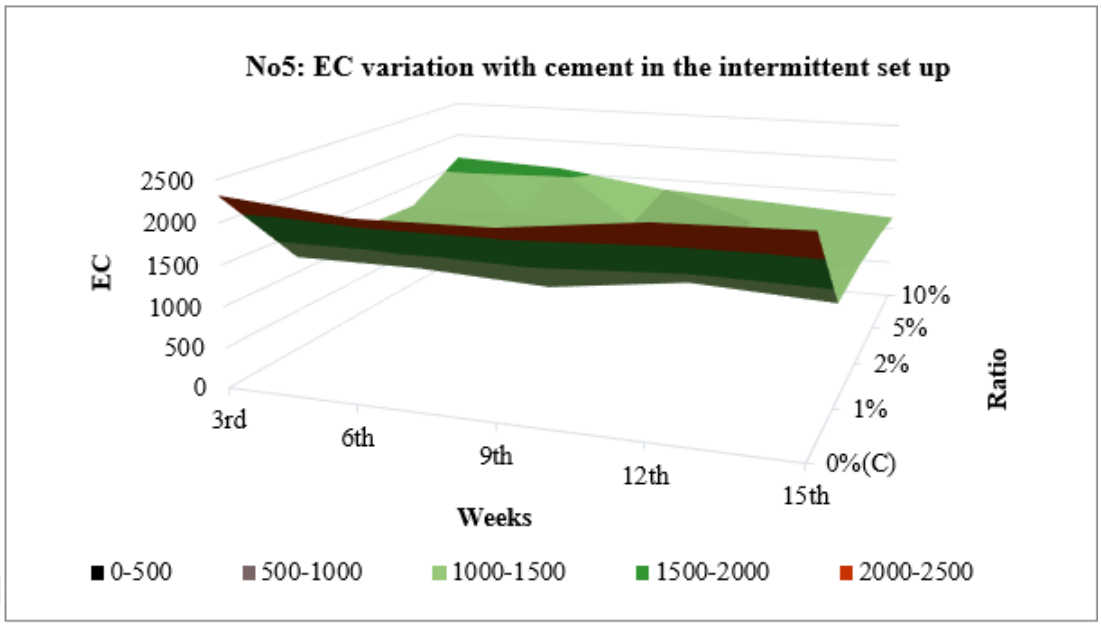


Figure 4.106 EC variation of No5 mine sample added cement in the intermittent set up

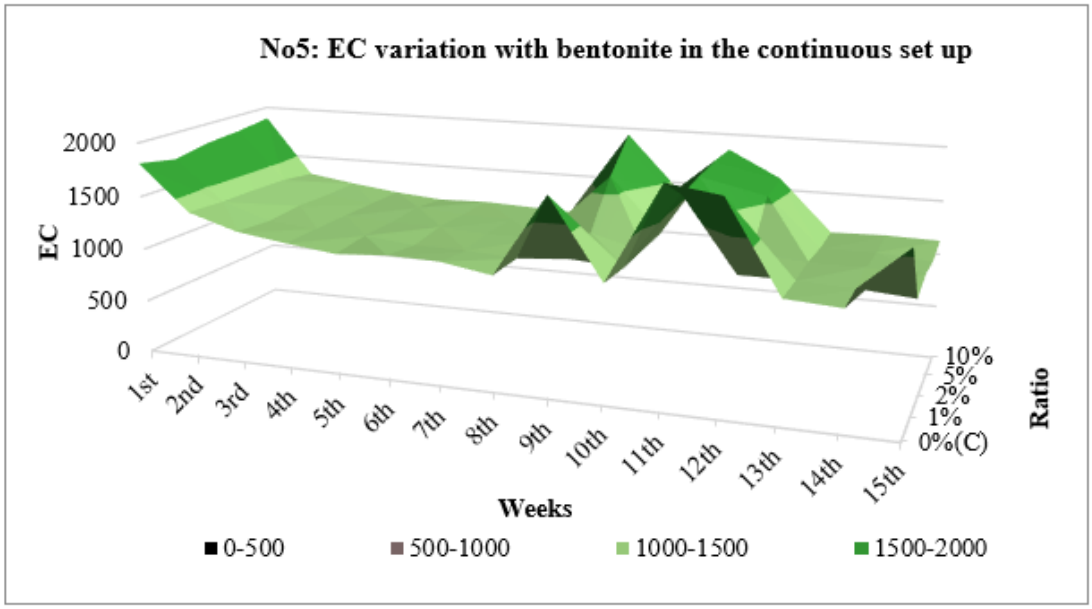


Figure 4.107 EC variation of No5 mine sample added bentonite in the continuous set up

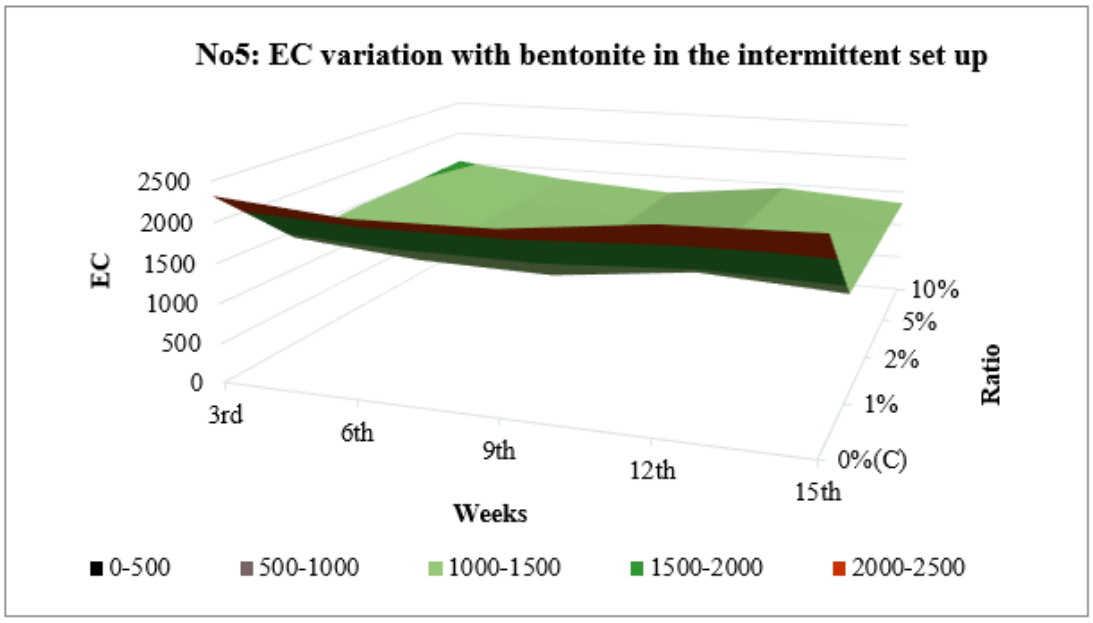


Figure 4.108 EC variation of No5 mine sample added bentonite in the intermittent set up

4.3.7.6 Overall Assessment for the EC

Table 4.30 Minimum and maximum EC values for the EC

		min EC values					Max EC values				
	EC	CONT	MD	A	C	B	CONT	MD	A	C	B
No 1	2640	1078	1034	1090	1110	1121	1978	2118	2220	2216	2040
Week		14	2	10	5	10	9	6	6	6	8
Ratio			5%	1%	1%	10%		10%	10%	2%	10%
No 2	4425	1104	1083	927	1073	1094	3440	2982	2510	2243	3510
Week		14	15	10	15	15	1	1	1	5	1
Ratio			10%	1%	1%	1%		2%	1%	10%	5%
No 3	2335	1077	1052	1095	1116	1109	1916	2030	2094	2434	2098
Week		8	13	8	14	14	11	11	6	5	5
Ratio			1%	5%	1%	1%		5%	5%	10%	10%
No 4	2642	751	739	654	730	738	1483	2020	1987	3110	1860
Week		14	12	13	15	15	1	3	9	1	1
Ratio			10%	1%	5%	2%		1%	10%	10%	10%
No 5	2697	1062	1035	1050	1051	1038	1975	2003	1870	2520	1939
Week		8	13	15	10	15	11	9	9	6	6
Ratio			1%	2%	1%	1%		10%	5%	10%	10%

EC values began to show up a decrease in all of the mine samples towards the last weeks. It was observed that the addition of binding material was not very effective when compared to the control values. On the contrary, the additions led to a little increase in EC values of the mine samples. The highest EC values were detected with using binding materials at a ratio of 10% except No2 mine sample was added bentonite at 5%. The highest EC values in No1, No3, and No5 mine samples were measured by adding cement and ash at a ratio of 10% at the end of the 5 And 6 weeks, respectively. The other the highest EC values were determined by using cement at 10% and bentonite at 5% at the end of the first week in No2 and No4 mine samples, respectively. Except No1 mine sample in which added bentonite at 5%, the lowest EC values were detected when the ratios of binding material were 1%. The lowest EC value was 654 µS/cm in where by using ash at a ratio 5% in No4 mine sample at the end of the 13. Weeks (Table 4.30).

4.3.7.8 Overall Assessment for the Waste Samples. For the No2 sample, the highest pH (9.13) and the lowest EC (1083 µS/cm) values were measured when marble dust at a ratio 10% was used at the end of the 15. weeks. The lowest pH (5.65) and the highest EC (2510 µS/cm) values was obtained with ash at the same ratio (1%) in the first week. Addition of bentonite at a ratio 1% caused to been measured the highest pH (8.8) and the lowest EC (1094 µS/cm) values at the final week. At the end of the first week. the lowest pH and the highest EC were determined by using at the different ratios of marble dust and ash. The highest pH (12.85) and the lowest EC (1073 µS/cm) value were detected with addition at different ratios of cement after 15. weeks.

For the No4 sample, at the end of the first week addition of bentonite at the same ratio (10%) allowed measuring the highest EC (1860 µS/cm) and the lowest pH (6.5) values.

For the No5 sample, it was obtained the highest pH and the lowest EC values with using at the different ratios of bentonite at the end of the 15. weeks. The addition of cement at the same ratio (10%) allowed to be obtained the highest values of both pH (13.36) and EC (2520 µS/cm) at the end of the 6. weeks.

4.3.8 Evaluation of Paste Sulfate Results

Table 4.31 Options and calibration curve

Parameters	Option & Results
Measure Mode	Single wavelength
Curve Evaluate	None
Principle	Conc = f(Abs)
Order of Curve	1st
Equation	Conc = NO1*(Abs) + K0
Calibration Method	Concentrator
K0	-16.01983
NO1	164.90435
R	**0.9999**
Repetition	None
AutoChange Cell	No
Quality	[]
Zero Intercept	No
Blank	Yes
NaturalLogarithm	No

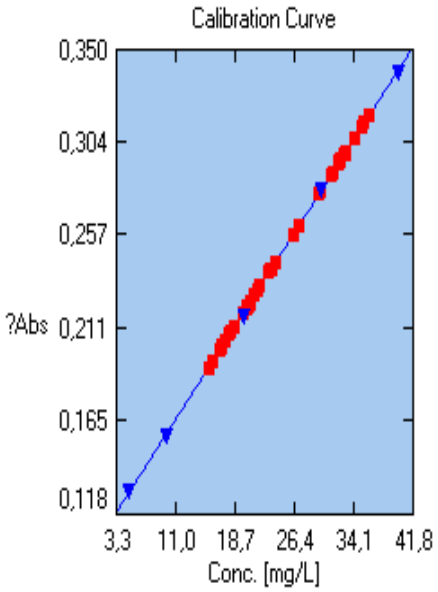


Table 4.31 shows measurement parameters and calibration curve (R^2=0.99). Sulfate values in No1, No2, and No3 (except added with bentonite for No3 sample) samples added with binding material in different ratios had lower than the original samples (not added binding material) (4.32). On the contrary, No4 and No5 samples added with binding material was high compared the original sample (Table 4.33).

Table 4.32 Concentrations of sulfate in control samples (no added binding material)

Sample	Concentration (mg/l)
No1	1415
No2	1350
No3	1415
No4	870
No5	1075

Table 4.33 The Concentration of sulfate in waste samples added binding material

with Marble Dust	Conc. (mg/l)	with Cement	Conc. (mg/l)	with Ash	Conc. (mg/l)	with Bentonite	Conc. (mg/l)
MD5.10	1240	**C5.10**	1665	**A5.10**	1145	**B5.10**	1880
MD5.5	1125	**C5.5**	1625	**A5.5**	1140	**B5.5**	1780
MD5.2	1120	**C5.2**	1590	**A5.2**	1115	**B5.2**	1795
MD5.1	1100	**C5.1**	1540	**A5.1**	1090	**B5.1**	1695
MD4.10	1450	**C4.10**	1680	**A4.10**	1410	**B4.10**	1500
MD4.5	1465	**C4.5**	1415	**A4.5**	1430	**B4.5**	1360
MD4.2	1490	**C4.2**	1375	**A4.2**	1490	**B4.2**	1205
MD4.1	1555	**C4.1**	1310	**A4.1**	1510	**B4.1**	1120
MD3.10	1180	**C3.10**	1010	**A3.10**	830	**B3.10**	2710
MD3.5	880	**C3.5**	1055	**A3.5**	840	**B3.5**	1780
MD3.2	855	**C3.2**	1090	**A3.2**	855	**B3.2**	1735
MD3.1	790	**C3.1**	1120	**A3.1**	905	**B3.1**	1715
MD2.10	915	**C2.10**	645	**A2.10**	865	**B2.10**	1170
MD2.5	1030	**C2.5**	775	**A2.5**	995	**B2.5**	1070
MD2.2	1205	**C2.2**	855	**A2.2**	1005	**B2.2**	1060
MD2.1	1240	**C2.1**	940	**A2.1**	1040	**B2.1**	1095
MD1.10	1655	**C1.10**	1625	**A1.10**	1430	**B1.10**	1970
MD1.5	1575	**C1.5**	1665	**A1.5**	1490	**B1.5**	1815
MD1.2	1625	**C1.2**	1720	**A1.2**	1565	**B1.2**	1780
MD1.1	1575	**C1.1**	1785	**A1.1**	1650	**B1.1**	1630

4.3.9 The Metals Concentration Obtained by Using Binding Material in Waste Samples

4.3.9.1 The Evaluation of Results Obtained by Marble Dust in Waste Samples

According to the Appendix-20 which it is shown the concentrations used as binding material of marble dust,

- Because Na, Ca, Mo, and K values didn't detect in these criteria (EPA and TRWPC), they had not been evaluated. These elements that found the most abundant in the earth crust and their levels were detected in high concentrations in this study, too.
- As, Fe, and Ni weren't detected in this section.

- Al concentration detected in MD2.1 and No4 waste sample (including all of the ratios) were in the 1. Class Water Quality according to TRWPC (Turkish Regulation of Water Pollution Control).
- Ba concentration was under the limit values in all of the samples and their ratios both EPA and TRWPC. According to TRWPC, it was accepted in the 1. Class Water Quality.
- Cd concentration was in the 4. Class Water Quality because it was above both EPA and TRWPC limit values.
- Cr was detected in only MD1.10 and it was under the limit values. According to TRWPC, it was in the 1. Class Water Quality.
- Cu concentration was found only two samples: MD1.10 and MD2.1. Both of them were under the limits. MD1.10 was in the threshold for the 1. Class Water Quality and it can be acceptable.
- Pb concentration was found only in sample No2. These results were quite higher than both EPA and TRWPC. It can be acceptable in the 4. Class Water Quality.
- Sb was detected in all of the samples and their different ratios except No1 Sample. When these results were compared with EPA Standards, only MD2.1 was under the limit value (0.005 mg/l). The others were above the limit value (>0.006 mg/l).
- Zn concentration was only not determined in the MD1.5. All of the samples except MD1.10 had high concentrations and they were in the 4. Class Water Quality. MD1.10 was relatively lower than the other samples. So, it was acceptable in the 2. Class Water Quality.

4.3.9.2 The Evaluation of Results Obtained by Ash in Waste Samples

According to the Appendix-21 which it is shown the concentrations used as binding material of ash:

- In this section where ash was used as a binding material, As, Cr, Fe, and Ni concentration weren't detected in any samples.
- Al concentration was detected in A2.5 and A2.10. They are in the 1. Class Water Quality because these concentrations are under the limits according to TRWPC.

- Ba concentration in all of the samples Except A1.5 was under the limit values both EPA (<2 mg/l) and TRWPC. While A1.5 (3.63 mg/l) is acceptable in the 4. Class Water Quality, all the remaining concentrations are in the 1. Class Water Class Quality.
- Cd concentration aren't run across in A1.5 and A1.10. The values detected in other samples had higher than both EPA and TRWPC Standards. Only A4.10 is acceptable in the 3. Class Water Quality, all the remaining concentrations are in the 4. Class Water Quality.
- Cu concentration in both A1.1 (0.017 mg/l) and A2.1 (0.003 mg/l) were detected under the limit values. According to TRWPC, both of them are in the 1. Class Water Quality.
- Pb concentration was determined only in No1 and No2 sample. All of the concentrations were above the limit values. According to TRWPC, they were acceptable in the 4. Class Water Quality.
- All of the Sb concentrations (it was not detected in No5 sample) had high value for EPA Standards.
- According to TRWPC, Zn concentrations were very much above the limit values.

4.3.9.3 The Evaluation of Results Obtained by Cement in Waste Samples

According to the Appendix-22 which it is shown the concentrations used as binding material of cement,

- In this section where cement was used as a binding material, Fe and Ni concentrations weren't detected in any samples.
- Al concentration was detected in C2.1 (0.05 mg/l), C2.2 (0.019 mg/l), and C5.10 (0.032 mg/l). These concentrations are under the limit values of 1. Class Water Quality.
- As concentration was observed in only C1.2 (0.084 mg/l). While it is acceptable in the 3. Class Water Quality, according to EPA Standards, it was higher than the limit value (0.01 mg/l).

- As Ba concentration in all of the detected samples (it was not determined in No3 sample and C2.10) were under the limit value (2 mg/l) for EPA Standards, they are in 1. Class Water Quality for the TRWPC.
- Cd concentration was generally high values than the limits. According to EPA Standards, only C5.5 concentration was in the threshold, the other values were high than the 0.005 mg/l. All the remaining samples were in the 4. Class Water Quality for the TRWPC.
- Cr was detected only in C1.10 (0.027mg/l). This value was under the limits both EPA Standards (0.1 mg/l) and TRWPC. According to the TRWPC, it was in the 2. Class Water Quality.
- Cu concentration was found in only C1.2 (0.01mg/l), C1.5 (0.003 mg/l), and C1.10 (0.029 mg/l). When compared with EPA Standards, they are under the limit value (1.3 mg/l). C1.10 was in the 2. Class Water Quality while C1.2 and C1.5 were acceptable in the 1. Class Water Quality.
- Pb concentration was detected only in C1.2 (3.241 mg/l), C2.1 (1.631 mg/l), and C2.2 (1.856 mg/l). These concentrations were above the limit values for both EPA Standards (0.015mg/l) and TRWPC (for 4. Class >0.05 mg/l).
- Zn concentrations in C1.1, C2.1, C2.2, C3.1, C3.2, C3.10, and C5.1 were much higher than the limits of TRWPC. C2.5 (0.05 mg/l), C4.1 (1.031 mg/l), and C5.2 (1.332 mg/l) were acceptable in the 2. Class Water Quality.

4.3.9.4 The Evaluation of Results Obtained by Bentonite in Waste Samples

According to the Appendix-23 which it is shown the concentrations used as binding material of bentonite,

- In this section where bentonite was used as a binding material, As, Cr, Fe, and Ni concentrations weren't detected in any samples.
- Al concentration was detected in No1 and No2 Samples. According to the TRWPC, while No1 sample values are in the 4. Class Water Quality, No2 sample values were in the 1. Class Water Quality.

- Ba concentration in detected all of the sample were below the limit values both EPA Standards (2 mg/l) and TRWPC (for 1. Class <1 mg/l).
- Cd concentration was higher than both EPA Standards (0.005 mg/l) and TRWPC (for 4. Class >0.01 mg/l).
- Cu concentration was determined in No1 and No2 samples. According to EPA Standards, all of the results are under the limit value (1.3 mg/l). While the concentrations belonging to B2.2 (0.007 mg/l), B2.5 (0.005 mg/l), and B2.10 (0.004 mg/l) are in the 1. Class Water Quality, the concentrations in No1 sample was in the 4. Class Water Quality (>0.2 mg/l).
- Pb concentration was detected only two samples: No1 and No2. According to both EPA Standards (0.015 mg/l))and TRWPC (>0.05 mg/l), all of the concentrations were higher than the limits.
- According to TRWPC, Zn concentrations were very much above the limit values.

4.3.10 Statistical Results of Paste Test

The results of the study were evaluated by using SPSS 24.0 (IBM Inc. Chicago, Ill. USA). Each of binding materials was evaluated separately via PCA (Principal Component Analysis) and correlation analysis. The total variances which was obtained from correlation matrices and PCA analysis were set for the each experimental.

The parameters used in this study:

'additive rate, time, total $S^{=}$, pyritic $S^{=}$, inert C, AP, NP, NP/AP, additive total $S^{=}$, additive pyritic $S^{=}$, additive inert C, additive AP, additive NP, additive NP/AP, mixed total $S^{=}$, mixed pyritic $S^{=}$, mixed inert C, mixed AP, mixed NP, mixed NP/AP, %Volume leached, pH, EC, and $SO_4^{=}$.'

4.3.10.1 The Statistical Results for Binding Material: Marble Dust

Table 4.35 showed results of relation between using binding material marble dust and the other factors. PCA analysis revealed 89.405% of all factors by determining

five factors that affecting the experiment (Table 4.34). The first component explained 31.911% of the total variation and in this component additive/marble dust was found directly related with Add Tot. S, Add Pyr. $S^{=}$, Add Inert C, Add NP, Add AP, Additive rate, % in all of the samples (Appendix - 24).

Table 4.34 Total variance for marble dust

Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.085	33.689	33.689	8.085	33.689	33.689	7.659	**31.911**	31.911
2	7.477	31.153	64.842	7.477	31.153	64.842	7.048	**29.367**	61.278
3	2.695	11.229	76.07	2.695	11.229	76.07	3.222	**13.424**	74.702
4	2.155	8.981	85.051	2.155	8.981	85.051	2.319	**9.662**	84.364
5	1.045	4.354	89.405	1.045	4.354	89.405	1.21	**5.041**	**89.405**

Table 4.35 Component matrix for marble dust

	Component				
	1 (31.91)	**2 (29.367)**	**3 (13.424)**	**4 (9.662)**	**5 (5.041)**
Add Tot. S, %	**0.995**				
Add Pyr. $S^{=}$	**0.995**				
Add Inert C	**0.995**				
Add NP	**0.995**				
Add AP	**0.995**				
Additive rate,. %	**0.995**				
Mixed inert C	0.747		0.615		
Mixed NP	0.74		0.61		
Add NP/AP	0.548				
Tot. S. %		**0.993**			
Mixed tot. $S^{=}$		**0.991**			
AP, kg/ton		**0.966**			
Pyr. $S^{=}$ %		**0.966**			
Mixed AP		**0.965**			
Mixed pyr. S=		**0.965**			
NP/AP		-0.757	0.604		
Inert C, %			**0.921**		
NP, kg/ton			**0.892**		
Time, d				**0.889**	
pH				**0.851**	
% Vol Leached				**0.816**	
SO_4, mg/l					**0.767**
Mixed NP/AP					**0.521**
EC					

4.3.10.2 The Statistical Results for Binding Material: Ash

Table 4.37 showed that results of relation between using binding material ash and the other factors. PCA analysis revealed 85.521% of all factors by determining four factors that affecting the experiment (Table 4.36). The first component explained 31.103% of the total variation. In this component, both samples and mixed (sample+binding material) was found directly related with Tot. S, Mixed tot. $S^{=}$, AP kg/ton, Pyr. $S^{=}$, Mixed AP, Mixed Pyr. $S^{=}$ in all of the samples (Appendix - 25).

Table 4.36 Total variance for ash

Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.344	34.765	34.765	8.344	34.765	34.765	7.465	**31.103**	31.103
2	7.275	30.313	65.078	7.275	30.313	65.078	6.97	**29.042**	60.145
3	3.201	13.339	78.417	3.201	13.339	78.417	4.304	**17.933**	78.078
4	1.705	7.105	85.521	1.705	7.105	85.521	1.786	**7.443**	**85.521**

Table 4.37 Component matrix for ash

	Component			
	1 (31.103)	2 (29.042)	3 (17.933)	4 (7.443)
Tot. S=, %	**0.991**			
Mixed tot. $S^{=}$	**0.99**			
AP, kg/ton	**0.963**			
Pyr. $S^{=}$, %	**0.963**			
Mixed AP	**0.962**			
Mixed pyr. S=	**0.962**			
NP/AP	-0.763		0.565	
Mixed NP/AP	-0.631			
EC	-0.546			
Add Pyr. S=		**0.991**		
Add Tot. S, %		**0.991**		
Add AP		**0.991**		
Add Inert C		**0.991**		
Add NP		**0.991**		
Additive rate, %		**0.991**		
pH		0.592		0.577
Add NP/AP		0.558		
Inert C, %			**0.935**	
NP, kg/ton			**0.915**	
Mixed inert C			**0.901**	
Mixed NP			0.888	
SO_4, mg/l				
Time, d				0.875
% Vol Leached				0.807

4.3.10.3 The Statistical Results for Binding Material: Cement

Table 4.38 showed that results of relation between using binding material ash and the other factors. PCA analysis revealed 87.865% of all factors by determining four factors that affecting the experiment (Table 4.39). The first component explained 30.992% of the total variation and in this component additive/cement was found directly related with Add Tot. S, Add Pyr. S=, Add Inert C, Add NP, Add AP, Additive rate, % and pH in all of the samples (Appendix - 26).

Table 4.38 Total variance for cement

Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	**% of Variance**	**Cumulative %**	**Total**	**% of Variance**	**Cumulative %**	**Total**	**% of Variance**	**Cumulative %**
1	8.068	33.616	33.616	8.068	33.616	33.616	7.438	**30.992**	30.992
2	7.708	32.116	65.732	7.708	32.116	65.732	7.066	**29.44**	60.432
3	3.101	12.921	78.653	3.101	12.921	78.653	4.354	**18.143**	78.575
4	1.157	4.819	83.472	1.157	4.819	83.472	1.142	**4.759**	83.333
5	1.054	4.394	87.865	1.054	4.394	87.865	1.088	**4.532**	**87.865**

Table 4.39 Component matrix for cement

	Component				
	1 (30.992)	**2 (29.440)**	**3 (18.143)**	**4 (4.759)**	**5 (4.532)**
Add Tot. S.%	**0.991**				
Add Pyr. S=	**0.991**				
Add Inert C	**0.991**				
Add NP	**0.991**				
Add AP	**0.991**				
Additive rate. %	**0.991**				
pH	0.864				
Add NP/AP	0.57				
Tot. S, %		**0.983**			
Mixed tot. S=		**0.983**			
Mixed AP		**0.932**			
AP, kg/ton		**0.932**			
Mixed pyr. S=		**0.932**			
Pyr. S=. %		**0.932**			
NP/AP		-0.825	0.516		
Mixed NP/AP		-0.652		0.577	
EC		-0.554			
Inert C, %			**0.966**		
NP, kg/ton			**0.942**		
Mixed inert C			**0.928**		
Mixed NP			**0.91**		
Time, d				0.797	
% Vol Leached				0.678	
SO_4 , mg/l					0.957

4.3.10.4 The Statistical Results for Binding Material: Bentonite

4.41 showed that results of relation between using binding material bentonite and the other factors. PCA analysis revealed 87.865% of all factors by determining four factors that affecting the experiment. The first component explained 31.288% of the total variation (Table 4.40). In this component, both samples and mixed (sample+binding material) was found directly related with Tot. S, Mixed tot. S=, AP, kg/ton, Pyr. S=, Mixed AP, Mixed Pyr. S= in all of the samples (Appendix - 27).

Table 4.40 Total variance for bentonite

Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.808	36.699	36.699	8.808	36.699	36.699	7.509	**31.288**	31.288
2	6.511	27.13	63.83	6.511	27.13	63.83	6.546	**27.275**	58.563
3	4.183	17.427	81.257	4.183	17.427	81.257	5.313	**22.137**	80.701
4	1.457	6.071	87.328	1.457	6.071	87.328	1.591	**6.627**	**87.328**

Table 4.41 Component matrix for bentonite

	Component			
	1 (31.288)	2 (27.275)	3 (22.137)	4 (6.627)
Tot. S, %	**0.971**			
Mixed tot. S=	**0.969**			
AP, kg/ton	**0.907**			
Pyr. S=. %	**0.906**			
Mixed AP	**0.906**			
Mixed pyr. S=	**0.906**			
Mixed NP/AP	-0.87			
NP/AP	-0.862			
SO_4 mg/l	-0.565	0.506		
EC	-0.507			
Add Tot. S, %		**0.995**		
Add Inert C		**0.995**		
Add NP		**0.995**		
Additive rate, %		**0.995**		
Add AP		**0.995**		
Add Pyr. S=		**0.995**		
Add NP/AP		0.573		
Inert C, %			**0.978**	
Mixed inert C			**0.977**	
NP, kg/ton			**0.963**	
Mixed NP			**0.962**	
Time, d				**0.907**
pH			0.558	0.657

4.4 Evaluation of Pollution Indices

4.4.1 The Evaluation of Pollution Indices in Waste Samples

4.4.1.1 Comparison of the Total Acid Digestion (TAD) Results of the Waste Samples and Binding Materials with SQuiRTs Chart and Earth's Crust Level

When the total concentrations in waste samples were compared with earth's crust level, it was shown that the concentrations of As, Ca, Cd, Cu, Fe, Pb, Sb, and Zn elements were higher than the limits in all of the waste samples. Mo concentration was higher than the earth crust in No1, No2, No3, and No4 waste samples. It was under the limit in the No5 waste sample. On the contrary, Al, Cr, K, Na, and Ni concentrations were lower than the earth crust in all of the waste samples. Ba concentration except in No6 waste sample were quietly lower than the earth crust (Appendix-28).

While Al and Cr concentrations were lower than the background values (mean). As, Cu, Fe, Pb, Sb, and Zn concentrations were higher than the background values in all of the waste samples. As, Ba, and Cr concentrations in No6 waste sample had high level compared the limit values. They had under the limits in other waste samples. Mo concentration except No5 waste sample was higher than the limits in all remaining waste samples. Cr concentrations except No6 waste sample had quite low values according to the SQuiRTs Chart. Ni concentration had high level in No2 and No6 waste samples when the compared with the limit values.

When the element concentrations compared with Dutch Standards (intervention), it was detected that As, Cd, Cu, Pb, Sb, and Zn concentrations were higher than the limit values and Ba, Cr, Mo, and Ni concentrations had low values in all of the waste samples.

According to ECO-SSL, As, Cd, Cu, Pb, and Zn results were higher than avian, inverts, mammals, plants, and microbes for all of the waste samples. Al concentration in plants had high value in all of the waste samples. But waste samples except No4

were higher when compared with mammals' values. The concentrations of Ba were high for mammals in all of the waste samples. While Cr concentration was lower in No1, No2, No3, No4, and No5 waste samples according to mammals' value, it was only higher in No6 waste sample. The concentrations of Cr in all of the waste samples were higher according to ECO-SSL (59.75 ppm). Fe concentration in microbes was quietly high while Mo concentration in microbes had low values for all of the waste samples. Ni concentrations in all of waste samples were lower than the values of avian, inverts, plants, and microbes; when the compared with mammals, it was detected higher value in No3, No4, and No5 waste samples. Sb concentration for mammals and plants was higher than limiting value.

There were no Pb and Zn in any binding materials. As and Sb concentrations in cement and Ca and Mo concentrations in bentonite were higher than the earth crust level. Both Mo and Sb had high values in ash. Also, Sb concentration was only high in marble dust when compared with the earth crust. Al, Ba, Cr, Cu, Fe, K, Na, and Ni concentrations in binding materials were either below detection limit or couldn't be detected according to the earth crust level (Appendix-29).

According to background values, both Cu and Mo concentrations and Mo and Sb were high in bentonite and ash, respectively. Sb concentration was had high value in only marble dust. As in the comparing earth crust, Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Na, and Ni concentrations in binding materials were either below detection limit or couldn't be detected according to the earth crust level.

When concentrations compared with Dutch Standards (intervention), it was determined that all of the elements were below the limit values.

According to ECO-SSL, As, Ni, and Sb results in all of the binding materials were below for all of the groups. Al concentrations in binding materials except marble dust were higher than limits for plant and microbes. Ba concentration had high value for mammals than the limits; but it was under limit values for other ECO-SSL groups. While Cd concentration in ash was higher (0.07 ppm) than the limit value (0.00222

ppm) for mammals, it was below in the other groups. Cr and Cu concentration (except bentonite for Cu) was under the limit value for mammals. Fe concentration in all binding materials was high for microbes while Mo concentration was lower than the limit value for microbes and plants. Sb couldn't be detected in bentonite. But it was higher for the mammals in marble dust, ash, and cement while it was lower than the limit value for inverts and plants.

4.4.1.2 Pollution Index (PI)

Pollution index is classified as either low (PI $\leqslant$ 1), middle (1 < PI $\leqslant$ 3) or high (PI > 3) (Chen et al., 2005; Darko et al., 2017).

All of the PI results were much more than 3 (Table 4.42). It is said that the potential of heavy metal pollution was considerably very high and all of the waste samples were highly polluted with these elements. The higher value shows lower retention time of the metals in the soil and higher risk to the environment. (Nemati et al., 2011).

Table 4.42 Results of pollution index (PI) values

Waste Sample	Pollution Index (PI)
No1	145.82
No2	313.26
No3	202.96
No4	164.27
No5	203.1
No6	229.56

PI values above 3 (high pollution index) indicate that the soils might be polluted by anthropogenic inputs

4.4.1.3 Enrichment Factor (EF)

Table 4.43 demonstrates the five categories used to evaluate the enrichment factor (Sutherland, 2000).

Table 4.43 EF categories

EF CATEGORIES	
Value	**Quality**
EF<2	Deficiency to minimal enrichment
2< EF <5	Moderate enrichment
5< EF <20	Significant enrichment
20< EF <40	Very high enrichment
EF>40	Extremely high enrichment

According to the EF results, As, Cd, Cu, Pb, Sb, and Zn elements were had extremely high enrichment all of the waste samples (EF>40). Cr was the lower categories in all of the waste samples. Except No2 Cr value in other waste samples was in moderate enrichment category. Cr level in No2, K level in No3, Ni and Pb level in No6 waste samples were minimal enrichment category as their values were under 2 (Table 4.44).

Table 4.44 Results of enrichment factors (EF) values

	WASTE SAMPLES					
ELEMENTS	**No1**	**No2**	**No3**	**No4**	**No5**	**No6**
Al[1]	1	1	1	1	1	1
As	113287.6	246943.2	45365.2	943853.7	252338.6	6923.1
Ba	16	17.8	2.5	3.2	4.8	6.9
Ca	141.4	125.4	40.4	246.6	98.7	5.9
Cd	15693.3	189675.5	61507.4	391202.6	134551.4	5335.5
Cr	3.4	1.4	2.5	3.4	3.2	3.1
Cu	867.7	2165.3	968.1	2660.4	1412.4	231
Fe	92.9	189.1	49.9	829.5	230.4	16.1
K	8.1	10.4	1.3	2.4	2.3	3.1
Mo	138.2	258.9	63.3	231.2	41.5	0
Na	11.1	14.8	4.2	31	10.8	0.9
Ni	0	2.3	5	65.7	16.3	0.6
Pb	254226.7	659823.1	82377	370297.1	215037.4	10553.9
Sb	91914.1	396348	30785.4	273596.3	111060.3	1234.4
Zn	7917.9	60519.5	21357.4	123827.7	44020.8	5143.1

1: Reference element

4.4.1.4 Geoaccumulation Index (Igeo)

Contamination levels used to evaluate Igeo are shown in Table 4.45. The results showed that the half of waste samples were contaminated with heavy metals. Especially, As, Cd, Pb, Sb, and Zn were classified as extremely contaminated (Class 6) for all of the waste samples. It had heavily to extremely contaminated (Class 5) in No3 and No6 waste samples while Igeo index for Cu were heavily contaminated level (Class 4) in No1, No2, and No5 waste samples. Also, Cu element in No4 waste sample had only Class 3 (moderately to heavily contaminated) level.

Table 4.45 Classes of geoaccumulation index (Igeo)

Index of geoaccumulation(Igeo) and contamination level		
Igeo	class	Contamination level
≤0	0	practically uncontaminated
0-1	1	Uncontaminated to moderately contaminated
1-2	2	Moderately contaminated
2-3	3	Moderately to heavily contaminated
3-4	4	Heavily contaminated
4-5	5	Heavily to extremely contaminated
5≥	6	Extremely contaminated

It was found that the environmentally most toxic metals such as As, Cd, Pb, Sb, and Zn were significantly accumulated in this waste sample. It was very normal as waste samples were taken from abandoned Pb-Zn mining area. In contrast, the Igeo value of negative Al, Ba, Cr, K, Na, and Ni are less than zero suggesting that the area was not polluted by these metals (Table 4.46).

Table 4.46 Results of geoaccumulation index (Igeo) values*

	No1	PC	No2	PC	No3	PC	No4	PC	No5	PC	No6	PC
Al	-6.557	0	-7.126	**0**	5.422	**0**	8.381	0	-6.746	0	-2.978	0
As	**10.233**	6	**10.787**	6	**10.047**	6	**11.467**	6	**11.199**	6	**9.779**	6
Ba	-2.555	0	-2.971	**0**	-4.08	**0**	-6.682	0	-4.489	0	-0.198	0
Ca	0.587	1	-0.156	**0**	-0.085	**0**	-0.435	0	-0.121	0	-0.427	0
Cd	**7.381**	6	**10.407**	6	**10.487**	6	**10.196**	6	**10.292**	6	**9.403**	6
Cr	-4.809	0	-6.63	**0**	-4.091	**0**	-6.609	0	-5.069	0	-1.357	0
Cu	3.204	4	3.954	**4**	4.497	**5**	2.996	3	3.718	4	4.874	5
Fe	-0.019	0	0.436	**1**	0.219	**1**	1.315	2	1.102	2	1.034	2
K	-3.547	0	-3.746	**0**	-5.098	**0**	-7.124	0	-5.559	0	-1.355	0
Mo	0.553	1	0.89	**1**	0.562	**1**	-0.528	0	-1.37	0	0	0
Na	-3.082	0	-3.2389	**0**	-3.346	**0**	-3.426	0	-3.315	0	-3.211	0
Ni	0	0	-5.952	**0**	-3.103	**0**	-2.343	0	-2.717	0	-3.6	0
Pb	**11.399**	6	**12.205**	6	**10.908**	6	**10.117**	6	**10.969**	6	**10.388**	6
Sb	**9.939**	6	**11.47**	6	**9.488**	6	**9.681**	6	**10.015**	6	**7.292**	6
Zn	**6.394**	6	**8.759**	6	**8.96**	6	**8.537**	6	**8.68**	6	**9.351**	6

*PC: Pollution Class

4.4.1.5 Contamination Factor (Cf)

Contamination factor results (Table 4.48) was assessed according to Table 4.47.

Table 4.47 Classes of contamination (CF) values (Hakanson, 1980)

The Range of Contamination Factor (CF)	Contamination Classes
1<CF	low contamination
1<CF≤3	moderate contamination
3<CF≤6	considerable contamination
CF>6	very high contamination

In all the samples, As, Cd, Cu, Pb, Sb, and Zn were detected in the highest contamination class while Al, Cr, K, Na, and Ni were found in the lowest contamination class. While the CF value of Fe in samples No1, No2, No3 is in the moderate contamination class, it is in the considerable contamination class in samples No4, No5, and No6.

Table 4.48 The evaluation of contamination (CF) values with contamination factor classes

	No1	No2	No3	No4	No5	No6
Al	0.0159	0.0107	0.035	0.0045	0.014	0.1904
As	1804.6949	2651.1558	1586.7939	4246.3047	3527.4641	1318.1422
Ba	0.2553	0.1913	0.0887	0.0146	0.0668	1.308
Ca	2.2527	1.3464	1.4137	1.1095	1.3791	1.1156
Cd	249.9973	2036.336	2151.4193	1759.982	1880.9053	1015.8667
Cr	0.0535	0.0151	0.088	0.0154	0.0447	0.5858
Cu	13.823	23.2461	33.8616	11.969	19.7447	43.9791
Fe	1.4803	2.03	1.7454	3.732	3.2203	3.0709
K	0.1283	0.1118	0.0438	0.0108	0.0318	0.5863
Mo	2.2012	2.7793	2.2144	1.0401	0.5803	-
Na	0.1772	0.159	0.1475	0.1396	0.1507	0.162
Ni	-	0.0242	0.1746	0.2956	0.2281	0.1237
Pb	4049.8843	7083.7911	2881.4046	1665.9303	3006.0273	2009.4221
Sb	1464.211	4255.1505	1076.819	1230.883	1552.5215	235.0165
Zn	126.1344	649.7309	747.0446	557.0887	615.3709	979.2195

4.4.1.6 Pollution Load Index (PLI)

According to Tomlinson et al. (1980), PLI is evaluated in three categories: PLI = 0 there is no pollution in the area, PLI = 1 offers there is a tolerable pollution in the area (basic level), and PLI > 1 describes that there is extremely pollution in the area.

Table 4.49 Results of pollution load index values

Waste Sample	Pollution Load Index (PI)
No1	6.34
No2	5.753
No3	5.983
No4	3.573
No5	5.125
No6	10.341

PI values showed that the mine waste samples had in an extremely pollution because all of them were >1 (Table 4.49).

4.4.2 The Evaluation of Pollution Indices in Leach Samples

4.4.2.1 Heavy Metal Pollution Index (HPI)

A HPI level below 100 indicates low HM contamination. Whereas 100 is the threshold value at which adverse health effects become likely. A HPI level of over 100 indicates that the water is unsafe for consumption (Kumar et al., 2019).

Table 4.50 Results of heavy metal pollution index (HPI) values

w/Marble Dust	**HPI**	w/Ash	**HPI**	w/Cement	**HPI**	w/Bentonite	**HPI**
MD1.1	11408.75	**A1.1**	18337.8	**C1.1**	4467.3	**B1.1**	26934.52
MD1.2	6162.58	**A1.2**	11564.04	**C1.2**	11676.34	**B1.2**	25980.72
MD1.5	1854.71	**A1.5**	4075	**C1.5**	**63.12**	**B1.5**	34263.01
MD1.10	2670.55	**A1.10**	**79.13**	**C1.10**	**74.44**	**B1.10**	24132.73
MD2.1	138817.58	**A2.1**	105008.61	**C2.1**	96980.73	**B2.1**	125306.8
MD2.2	87066.85	**A2.2**	89001.13	**C2.2**	67416.42	**B2.2**	109315.12
MD2.5	58296.33	**A2.5**	54963.54	**C2.5**	443.46	**B2.5**	113167.24
MD2.10	58902.97	**A2.10**	9268.71	**C2.10**	130.66	**B2.10**	114974.75
MD3.1	63500.19	**A3.1**	52218.83	**C3.1**	20919.29	**B3.1**	6056.24
MD3.2	75421.83	**A3.2**	21028.3	**C3.2**	10750.47	**B3.2**	90446.73
MD3.5	49440.04	**A3.5**	621.2	**C3.5**	969.6	**B3.5**	99818.62
MD3.10	59406.62	**A3.10**	5467.55	**C3.10**	16225.76	**B3.10**	87197.32
MD4.1	16549.8	**A4.1**	7362.18	**C4.1**	2216.38	**B4.1**	14103.31
MD4.2	13867.95	**A4.2**	2355.91	**C4.2**	2216.38	**B4.2**	15433.2
MD4.5	12301.5	**A4.5**	635.01	**C4.5**	**65.16**	**B4.5**	13819.74
MD4.10	8163.87	**A4.10**	239.41	**C4.10**	**65.06**	**B4.10**	14197.27
MD5.1	32368.29	**A5.1**	28896.92	**C5.1**	13882.81	**B5.1**	33899.82
MD5.2	40298.21	**A5.2**	19667.12	**C5.2**	1564.26	**B5.2**	36377.08
MD5.5	26913.41	**A5.5**	2645.92	**C5.5**	172.03	**B5.5**	32965.91
MD5.10	19931.33	**A5.10**	400.09	**C5.10**	**70.87**	**B5.10**	36834.59

According to Table 4.50, most of the results were higher than 100. Especially, the samples with adding bentonite had very high values. In general, samples with 5% and 10% cement were below 100 (marked with bold red in Table 4.50). These results indicated low contamination. The other results may have adverse effects on the living.

4.4.2.2 Heavy Metal Evaluation Index (HEI)

The HEI index is classified as below:

HEI<10 : Low

HEI=10-20 : Moderate

HEI>20 : High

Table 4.51 Results of HEI Index

w/Marble Dust	**HEI**	w/Ash	**HEI**	w/Cement	**HEI**	w/Bentonite	**HEI**
MD1.1	91.72	**A1.1**	1057.55	**C1.1**	52.8	**B1.1**	1719.76
MD1.2	44.38	**A1.2**	394.76	**C1.2**	2182.79	**B1.2**	1630.18
MD1.5	**14.46**	**A1.5**	756.08	**C1.5**	**5.33**	**B1.5**	1536.71
MD1.10	20.91	**A1.10**	**10.93**	**C1.10**	**9.26**	**B1.10**	1672.21
MD2.1	2935.32	**A2.1**	2210.39	**C2.1**	2152.38	**B2.1**	3801.84
MD2.2	2320.08	**A2.2**	2001.81	**C2.2**	1931.44	**B2.2**	2381.58
MD2.5	2828.07	**A2.5**	1252.73	**C2.5**	**5.32**	**B2.5**	2309.48
MD2.10	2780.7	**A2.10**	274.9	**C2.10**	38.83	**B2.10**	2453.58
MD3.1	731.66	**A3.1**	607.74	**C3.1**	256.3	**B3.1**	79.14
MD3.2	867.08	**A3.2**	250.15	**C3.2**	137.95	**B3.2**	1053.2
MD3.5	685.48	**A3.5**	21.53	**C3.5**	22.48	**B3.5**	1166.79
MD3.10	574.31	**A3.10**	79.02	**C3.10**	193.01	**B3.10**	1021.82
MD4.1	199.48	**A4.1**	83.34	**C4.1**	27.04	**B4.1**	167.9
MD4.2	168.65	**A4.2**	31.81	**C4.2**	**7.22**	**B4.2**	186.34
MD4.5	146.87	**A4.5**	**12.05**	**C4.5**	**5.69**	**B4.5**	169.51
MD4.10	100.08	**A4.10**	**2.74**	**C4.10**	**6.03**	**B4.10**	169.32
MD5.1	377.83	**A5.1**	331.67	**C5.1**	157.51	**B5.1**	402.84
MD5.2	478.6	**A5.2**	224.4	**C5.2**	**17.81**	**B5.2**	435.81
MD5.5	311.58	**A5.5**	29.86	**C5.5**	**9.48**	**B5.5**	397.55
MD5.10	234.57	**A5.10**	**4.53**	**C5.10**	**7.89**	**B5.10**	441.3

The results were obtained similarly to the HPI values. Consequently, the risk of contamination was low in samples containing 5% and 10% cement, and the fourth and fifth samples added 10% ash (marked with bold red). Some samples (marked with bold blue) yielded moderate results, but others yielded results with a high level of contamination risk (Table 4.51).

4.4.2.3 The Degree of Contamination (Cd)

This index is evaluated : <1 for low, 1-3 for moderate, and >3 for high pollution of heavy metals as proposed by Backman (Backman et al., 1998).

The similar results were obtained with HEI results. According to Table 4.52, low levels of heavy metal contamination were observed in some samples with adding 5% and 10% binding material. Other results showed that heavy metal pollution was high.

Table 4.52 Results of Cd values

w/Marble Dust	**Cd**	w/Ash	**Cd**	w/Cement	**Cd**	w/Bentonite	**Cd**
MD1.1	81.72	**A1.1**	1047.55	**C1.1**	42.8	**B1.1**	1709.76
MD1.2	34.38	**A1.2**	384.76	**C1.2**	2172.79	**B1.2**	1620.18
MD1.5	4.46	**A1.5**	746.08	**C1.5**	**-4.67**	**B1.5**	1526.71
MD1.10	10.91	**A1.10**	**0.93**	**C1.10**	**-0.74**	**B1.10**	1662.21
MD2.1	2925.32	**A2.1**	2200.39	**C2.1**	2142.38	**B2.1**	3791.84
MD2.2	2310.08	**A2.2**	1991.81	**C2.2**	1921.44	**B2.2**	2371.58
MD2.5	2818.07	**A2.5**	1242.73	**C2.5**	**-4.68**	**B2.5**	2299.48
MD2.10	2770.7	**A2.10**	264.9	**C2.10**	28.83	**B2.10**	2443.58
MD3.1	721.66	**A3.1**	597.74	**C3.1**	246.3	**B3.1**	69.14
MD3.2	857.08	**A3.2**	240.15	**C3.2**	127.95	**B3.2**	1043.2
MD3.5	675.48	**A3.5**	11.53	**C3.5**	12.48	**B3.5**	1156.79
MD3.10	564.31	**A3.10**	69.02	**C3.10**	183.01	**B3.10**	1011.82
MD4.1	189.48	**A4.1**	73.34	**C4.1**	17.04	**B4.1**	157.9
MD4.2	158.65	**A4.2**	21.81	**C4.2**	**-2.78**	**B4.2**	176.34
MD4.5	136.87	**A4.5**	**2.05**	**C4.5**	**-4.31**	**B4.5**	159.51
MD4.10	90.08	**A4.10**	**-7.26**	**C4.10**	**-3.97**	**B4.10**	159.32
MD5.1	367.83	**A5.1**	321.67	**C5.1**	147.51	**B5.1**	392.84
MD5.2	468.6	**A5.2**	214.4	**C5.2**	7.81	**B5.2**	425.81
MD5.5	301.58	**A5.5**	19.86	**C5.5**	**-0.52**	**B5.5**	387.55
MD5.10	224.57	**A5.10**	**-5.47**	**C5.10**	**-2.11**	**B5.10**	431.3

4.4.2.4 Water Pollution Index (WPIi)

The WPIi index is classified as below:

WPIi>1: Water polluted n times. Should be diluted with water of best quality in the acceptable range

WPIi 0-1: Acceptable for specific purpose

WPIi <0: Water deficient in factor

As seen the Table 4.53, As, Fe, and Ni concentrations were not detected in any of the samples. While Al in sample No6 was at an acceptable level. Al in sample No1 was at a high level of pollution. Ba concentration was determined in No1, No3, No4, and No6 samples and was found to be within the acceptable range in all of them. Ca concentration was determined just above the pollution limit in all samples except No6. The Cd concentration was significantly above the permissible threshold in all of the waste samples. Cr was observed in No3 and No6 samples and the values were not in the unacceptable range. K (in No3 sample), Mo (in No4 sample), and Na (all of the samples) values are acceptable limits for the WPI. Pb and Zn were obtained in high levels of contamination.

Table 4.53 Results of water pollution index

	WPI-No1	WPI-No2	WPI-No3	WPI-No4	WPI-No5	WPI-No6
Al	6.09731	0	0	0	0	-1.81943
As	0	0	0	0	0	0
Ba	-0.35856	0	-0.34252	-0.35126	0	-0.36238
Ca	1.15086	1.1067	1.21416	1.06624	1.19268	-0.1279
Cd	11.81506	78.518	47.6679	9.76718	23.7008	25.56224
Cr	0	0	-0.08688	0	0	-0.04459
Cu	-0.41195	-0.672	0	0	0	0
Fe	0	0	0	0	0	0
K	0	0	-0.19242	0	0	0.15061
Mo	0	0	0	-0.33857	0	0
Na	-0.55195	-0.58	-0.58329	-0.58952	-0.574	-0.56143
Ni	0	0	0	0	0	0
Pb	22.73908	21.914	0	0	0	36.22316
Sb	0.23932	0.2033	0	0	-0.03906	0
Zn	7.64341	33.177	11.38023	0.65125	5.80148	20.15916

CHAPTER FIVE
CONCLUSION

In this research, the determinant factors on the formation and control Acid Mine Drainage (AMD) were investigated in order to prevent metals' mobilization from mine waste. The use of binding materials to immobilize heavy metals is focused in the content of the thesis. Considering the research completed, the most important outcomes of the thesis are listed below:

- The metals' chemical speciation forms in waste, and NP and AP of waste mix are the parameters dominantly affecting the metals' mobilization in waste (between 31-43% of the total impacts)
- If the metal in waste is dominantly in mobile forms, it leaches either in acidic, neutral or alkaline conditions
- Initial concentration of metals in waste is an important factor on their mobility, since the amount of metals in labile chemical fractions (especially the extractable (EAF) and reducible (REF) fractions) is also increasing with increasing initial concentration.
- The presence of *Thiobacillus thiooxidans* in waste medium increases metals' mobilization between 8-10%, compared to the control.
- The presence of *Thiobacillus thiooxidans* in waste has no impact on metalloids' (As) mobility.
- When the mobility of a single element is assessed, it is seen that:
    i. About 51-57% of metals mobility is directly linked with the NP, AP and elements chemical speciation forms in waste.
    ii. 24-30% of metals' mobility is linked with binding material metals' chemical speciation.
    iii. 11-16% of the metal mobility is related with the presence of *Thiobacillus thiooxidans* in the medium.
- TSP is binding metalloids (As and Ba) sufficiently, but not all the metals.

- The leach elemental levels are lower with marble dust, which has higher pH value than TSP, which can be explained with its higher carbonate content and therefore neutralization/buffering capacity.
- Not only the difference between NP and AP (NNP) but also the ratio of NP and AP (NP/AP) are influencing AMD.
- The major factors influencing the metals mobility are determined as follows (according to importance):
    1. HMs' chemical speciation in waste
    2. Initial Concentration of HM
    3. NP/AP or NNP of binding material
    4. NP/AP or NNP of waste
    5. Impurities (HMs) in binding materials
    6. Presence of Thiobacillus sp. in the medium
- According to the leach pollution indices, the most successful binding material is determined as cement (5% and 10%). However, discharge water pH values will be above 9 with cement.

The findings show that different binding materials can give different results on metal mobility. In particular, binding materials with higher buffering capacity (with high carbonate C and low sulfur content) are more effective in metal mobilization. In addition, it is important that to select binding materials which are low in cost or free, abundant in nature, and readily available.

Here marble dust and cement were selected as the most appropriate binding materials among others investigated in the content of the research. Marble dust is a waste product and it comes out as tons of waste after the processing of marble. The high efficiency of marble dust in metal immobilization has been one of the important findings of this study.

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APPENDICES

APPENDIX-1: Preparation of Waste Sample No1

No 1	**Inert C < 0.5%**										
450 g taken from each waste.	**Sample No**	**Sampling type / Depths (cm)**	**Water Content (%)**	**Conductivity (µS/cm)**	**pH**	**Total $S^{=}$ (%)**	**Pyritic $S^{=}$ (%)**	**Carbonate C (%)**	**AP (kg $CaCO_3$/ton)**	**NP (kg $CaCO_3$/ton)**	**NP/AP**
	ATK.01.B2-1-a	0-60	17.92	2580	3.28	11.25	1.470	0.076	45.952	6.338	0.138
	ATK.01.B2-3-a	0-40	19.32	2360	3.73	8.74	0.648	0.101	20.264	8.375	0.413
	ATK.01.B2-10-a	0-50	15.10	2750	3.21	9.48	0.862	0.102	26.944	8.488	0.315
	ATK.01.B2-11-a	0-65	15.07	3000	2.9	11.83	1.558	0.101	48.684	8.421	0.173
	ATK.01.B2-12-a	0-30	13.17	4170	2.61	13.16	1.250	0.102	39.051	8.538	0.219
	ATK.01.B2-14-a	0-60	8.80	3050	3.03	14.61	0.243	0.105	7.579	8.722	1.151
	ATK-01.B3-2	Profile composite	16.23	2740	4.8	4.71	0.029	0.150	0.915	12.492	13.660
	ATK.01.B7-1	Collection by hand	0.34	211	4.38	6.81	0.037	0.226	1.144	18.868	16.494
	ATK.01.B9-3	Profile composite	14.11	2750	3.11	7.11	0.002	0.099	0.069	8.230	119.280
	ATK.01.B9-4	Profile composite	10.58	3270	4.79	7.04	0.002	0.219	0.069	18.277	264.880
	ATK.01.B9-5-a	0-110	11.99	2430	3.76	9.45	0.041	0.083	1.287	6.923	5.381
	ATK.01.B9-5-b	110-220	15.28	2360	3.51	9.25	0.057	0.062	1.789	5.171	2.891
Total		-	**13.16**	**2640**	**3.59**	**9.45**	**0.52**	**0.12**	**16.145**	**9.904**	**0.613**

APPENDIX-2: Preparation of Waste Sample No2

No 2	**Inert C < 1.25%**										
650 g taken from each waste.	**Sample No**	**Sampling type / Depths (cm)**	**Water Content (%)**	**Conductivity (µS/cm)**	**pH**	**Total $S^{=}$ (%)**	**Pyritic $S^{=}$ (%)**	**Carbonate C (%)**	**AP (kg $CaCO_3$/ton)**	**NP (kg $CaCO_3$/ton)**	**NP/AP**
	ATK.01.B2-5-a	0-100	9.08	4350	4.22	30.97	17.835	0.123	557.330	10.244	0.018
	ATK-01.B3-3	Profile composite	11.36	3270	4.49	15.62	3.419	0.650	106.855	54.131	0.507
	ATK.01.B4-1	Profile composite	9.84	8560	1.81	16.59	0.002	0.126	0.069	10.460	151.500
	ATK.01.B4-2	Surface composite	13.68	5470	4.3	15.32	0.002	0.164	0.069	13.666	198.060
	ATK.01.B9-2	Profile composite	12.09	4610	5.21	15.31	0.542	0.272	16.927	22.670	1.339
	ATK.01.B9-5-c	220-270	18.47	2360	4.41	17.71	0.221	0.172	6.919	14.366	2.076
	ATK.01.B9-7	Profile composite	9.14	2670	4.57	15.63	0.739	0.627	23.094	52.243	2.262
	ATK.01.B2-13-a	0-45	9.71	4110	2.42	15.12	2.053	0.091	64.152	7.546	0.118
Total		-	**11.67**	**4425**	**3.93**	**17.78**	**3.10**	**0.28**	**96.927**	**23.166**	**0.239**

APPENDIX-3: Preparation of Waste Sample No3

No 3	**Inert C< 1.8%**										
600 g taken from each waste	**Sample No**	**Sampling type / Depths (cm)**	**Water Content (%)**	**Conductivity (µS/cm)**	**pH**	**Total $S^{=}$ (%)**	**Pyritic $S^{=}$ (%)**	**Carbonate C (%)**	**AP (kg $CaCO_3$/ton)**	**NP (kg $CaCO^3$/ton)**	**NP/AP**
	ATK.01.B2-4-a	0-35	10.29	2260	5.71	12.66	4.090	1.790	127.798	149.167	1.167
	ATK.01.B2-10-b	50-180	20.09	2650	4.97	13.39	3.428	1.611	107.119	134.266	1.253
	ATK.01.B2-11-b	65-140	14.12	2410	2.92	14.83	3.309	1.480	103.422	123.296	1.192
	ATK-01.B3-1	Profile composite	22.06	2510	5.04	7.74	2.526	1.670	78.924	139.171	1.763
	ATK.01.B5-2	Surface composite	10.44	3510	5.09	8.85	2.981	0.262	93.163	21.831	0.234
	ATK.01.B6-2	Composite-General	3.20	2320	5.25	13.32	2.949	1.005	92.168	83.777	0.909
	ATK.01.B6-3-a	0-30	10.62	863	4.97	13.14	4.952	0.769	154.740	64.119	0.414
	ATK.01.B6-3-b	30-90	12.72	2120	5.68	10.73	3.310	1.667	103.430	138.884	1.343
	ATK.01.B6-3-c	90-130	29.02	2370	5.28	7.58	2.642	1.632	82.575	136.024	1.647
Total		-	**14.73**	**2335**	**4.99**	**11.36**	**3.35**	**1.32**	**104.815**	**110.060**	**1.05**

APPENDIX-4: Preparation of Waste Sample No4

No 4	**Inert C < %1.25**										
600 g taken from each waste	**Sample No**	**Sampling type / Depths (cm)**	**Water Content (%)**	**Conductivity (µS/cm)**	**pH**	**Total $S^{=}$ (%)**	**Pyritic $S^{=}$ (%)**	**Carbonate C (%)**	**AP (kg $CaCO_3$/ton)**	**NP (kg $CaCO_3$/ton)**	**NP/AP**
	ATK.01.B2-5-b	100-130	8.33	3240	4.79	23.45	10.357	1.174	323.654	97.798	0.302
	ATK.01.B2-11-c	140-340	7.49	2220	5.37	43.34	20.020	0.943	625.625	78.554	0.126
	ATK.01.B2-11-d	340-430	7.00	2270	5.55	38.85	21.557	1.078	673.660	89.859	0.133
	ATK.01.B2-12-b	30-70	7.41	2500	5.3	31.99	13.035	1.153	407.354	96.100	0.236
	ATK.01.B2-12-c	70-270	4.73	2370	5.41	38.97	25.648	1.225	801.493	102.058	0.127
	ATK.01.B2-12-d	270-440	4.59	4160	5.54	33.26	10.832	1.168	338.511	97.320	0.287
	ATK.01.B2-13-c	80-230	3.91	2470	5.38	41.31	26.560	1.029	829.989	85.730	0.103
	ATK.01.B2-13-d	230-400	4.41	2340	5.36	40.02	24.609	1.047	769.022	87.218	0.113
	ATK.01.B2-14-c	120-280	4.89	2210	5.14	37.64	20.984	1.126	655.745	93.849	0.143
Total		-	**5.86**	**2642**	**5.32**	**36.54**	**19.29**	**1.10**	**602.784**	**92.054**	**0.15**

APPENDIX-5: Preparation of Waste Sample No5

No 5										
Sample No	**The Mixed Quantity (g)**	**Water Content (%)**	**Conductivity (µS/cm)**	**pH**	**Total $S^{=}$ (%)**	**Pyritic $S^{=}$ (%)**	**Carbonate C (%)**	**AP (kg $CaCO_3$ /ton)**	**NP (kg $CaCO_3$ /ton)**	**NP/AP**
1	200	13.160	2640.00	3.590	9.45	0.52	0.12	16.145	9.904	35.416
2	200	11.67	4425.00	3.93	11.36	3.35	1.32	96.92694	23.16567	1.10
3	800	14.73	2335.00	4.99	17.78	3.10	0.28	104.8154	110.0595	44.49
4	800	5.86	2642.00	5.32	36.54	19.29	1.10	602.7837	92.05404	0.17
No 5 Total		**11.355**	**3011**	**4.45**	**23.810**	**9.343**	**0.697**	**294.347**	**84.152**	**0.285**

APPENDIX-6: The Correlation and Total Variance of Balya Waste Sample and Leonardite Binding Material in Flask Test in the Absence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Bi, mg	B-EAF, %	B-RF,%	B-OF,%	B-RES,%	Li, mg	L-EAF,%	L-RF,%	L-OF,%	L-RES,%
Correlation	Bağ.%	**1.000**	-0.054	-1.000	1.000	0.015	0.000	0.000	0.000	0.000	0.445	0.000	0.000	0.000	0.000
	Mobil.%	-0.054	**1.000**	0.054	-0.054	-0.162	**0.516**	0.124	0.378	**-0.435**	0.247	0.142	0.385	-0.131	0.002
	S=, kg/t	-1.000	0.054	**1.000**	-1.000	-0.015	0.000	0.000	0.000	0.000	-0.445	0.000	0.000	0.000	0.000
	CO3=, kg/t	1.000	-0.054	-1.000	**1.000**	0.015	0.000	0.000	0.000	0.000	0.445	0.000	0.000	0.000	0.000
	Bi, mg	0.015	-0.162	-0.015	0.015	**1.000**	-0.048	0.084	-0.107	0.032	-0.040	0.704	-0.117	-0.010	-0.358
	B-EAF, %	0.000	0.516	0.000	0.000	-0.048	**1.000**	0.022	0.565	-0.646	0.382	0.056	0.217	-0.466	-0.709
	B-RF,%	0.000	0.124	0.000	0.000	0.084	0.022	**1.000**	0.287	-0.653	0.101	-0.287	0.690	-0.134	-0.271
	B-OF,%	0.000	0.378	0.000	0.000	-0.107	0.565	0.287	**1.000**	-0.865	0.625	0.102	-0.024	0.165	-0.476
	B-RES,%	0.000	-0.435	0.000	0.000	0.032	-0.646	-0.653	-0.865	**1.000**	-0.512	0.068	-0.399	0.132	0.624
	Li, mg	0.445	0.247	-0.445	0.445	-0.040	0.382	0.101	0.625	-0.512	**1.000**	0.259	0.051	0.247	-0.185
	L-EAF,%	0.000	0.142	0.000	0.000	0.704	0.056	-0.287	0.102	0.068	0.259	**1.000**	-0.184	0.471	-0.013
	L-RF,%	0.000	0.385	0.000	0.000	-0.117	0.217	0.690	-0.024	-0.399	0.051	-0.184	**1.000**	-0.161	-0.012
	L-OF,%	0.000	-0.131	0.000	0.000	-0.010	-0.466	-0.134	0.165	0.132	0.247	0.471	-0.161	**1.000**	0.539
	L-RES,%	0.000	0.002	0.000	0.000	-0.358	-0.709	-0.271	-0.476	0.624	-0.185	-0.013	-0.012	0.539	**1.000**

a. This matrix is not positive definite.

APPENDIX-7: The Correlation and Total Variance of Balya Waste Sample and Leonardite Binding Material in Flask Test with the Presence of *T. thiooxidans*

Correlation Matrix[a]

		T.Thioox.	Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Bi, mg	B-EAF, %	B-RF,%	B-OF,%	B-RES,%	Li, mg	L-EAF,%	L-RF,%	L-OF,%	L-RES,%
Correlation	T.Thioox.	**1.000**	0.000	0.216	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Bağ.%	0.000	**1.000**	-0.152	-1.000	1.000	-0.036	0.000	0.000	0.000	0.000	0.478	0.000	0.000	0.000	0.000
	Mobil.%	0.216	-0.152	**1.000**	0.152	-0.152	-0.086	**0.571**	0.102	0.358	**-0.432**	0.155	0.157	0.362	-0.145	-0.163
	S=, kg/t	0.000	-1.000	0.152	**1.000**	-1.000	0.036	0.000	0.000	0.000	0.000	-0.478	0.000	0.000	0.000	0.000
	CO3=, kg/t	0.000	1.000	-0.152	-1.000	**1.000**	-0.036	0.000	0.000	0.000	0.000	0.478	0.000	0.000	0.000	0.000
	Bi, mg	0.000	-0.036	-0.086	0.036	-0.036	**1.000**	-0.069	0.124	-0.081	0.006	-0.038	0.697	-0.115	0.015	-0.366
	B-EAF, %	0.000	0.000	0.571	0.000	0.000	-0.069	**1.000**	0.022	0.565	-0.646	0.347	0.056	0.217	-0.466	-0.709
	B-RF,%	0.000	0.000	0.102	0.000	0.000	0.124	0.022	**1.000**	0.287	-0.653	0.091	-0.287	0.690	-0.134	-0.271
	B-OF,%	0.000	0.000	0.358	0.000	0.000	-0.081	0.565	0.287	**1.000**	-0.865	0.568	0.102	-0.024	0.165	-0.476
	B-RES,%	0.000	0.000	-0.432	0.000	0.000	0.006	-0.646	-0.653	-0.865	**1.000**	-0.465	0.068	-0.399	0.132	0.624
	Li, mg	0.000	0.478	0.155	-0.478	0.478	-0.038	0.347	0.091	0.568	-0.465	**1.000**	0.236	0.047	0.224	-0.168
	L-EAF,%	0.000	0.000	0.157	0.000	0.000	0.697	0.056	-0.287	0.102	0.068	0.236	**1.000**	-0.184	0.471	-0.013
	L-RF,%	0.000	0.000	0.362	0.000	0.000	-0.115	0.217	0.690	-0.024	-0.399	0.047	-0.184	**1.000**	-0.161	-0.012
	L-OF,%	0.000	0.000	-0.145	0.000	0.000	0.015	-0.466	-0.134	0.165	0.132	0.224	0.471	-0.161	**1.000**	0.539
	L-RES,%	0.000	0.000	-0.163	0.000	0.000	-0.366	-0.709	-0.271	-0.476	0.624	-0.168	-0.013	-0.012	0.539	**1.000**

APPENDIX-8: The Correlation and Total Variance of Balya Waste Sample and Compost Binding Material in Flask Test with the Absence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Bi, mg	B-EAF, %	B-RF,%	B-OF,%	B-RES,%	Ki, mg	K-EAF,%	K-RF,%	K-OF,%	K-RES,%
Correlation	Bağ.%	**1.000**	0.009	-1.000	-1.000	0.015	0.000	0.000	0.000	0.000	0.625	0.000	0.000	0.000	0.000
	Mobil.%	0.009	**1.000**	-0.009	-0.009	-0.076	**0.571**	0.102	**0.358**	-0.432	0.021	-0.042	0.025	0.134	-0.253
	S=, kg/t	-1.000	-0.009	**1.000**	1.000	-0.015	0.000	0.000	0.000	0.000	-0.625	0.000	0.000	0.000	0.000
	CO3=, kg/t	-1.000	-0.009	1.000	**1.000**	-0.015	0.000	0.000	0.000	0.000	-0.625	0.000	0.000	0.000	0.000
	Bi, mg	0.015	-0.076	-0.015	-0.015	**1.000**	-0.048	0.084	-0.107	0.032	0.528	0.412	0.723	-0.076	-0.313
	B-EAF, %	0.000	0.571	0.000	0.000	-0.048	**1.000**	0.022	0.565	-0.646	0.081	-0.127	-0.120	0.281	-0.715
	B-RF,%	0.000	0.102	0.000	0.000	0.084	0.022	**1.000**	0.287	-0.653	0.107	0.462	0.013	-0.653	-0.412
	B-OF,%	0.000	0.358	0.000	0.000	-0.107	0.565	0.287	**1.000**	-0.865	0.240	0.616	0.046	0.336	-0.475
	B-RES,%	0.000	-0.432	0.000	0.000	0.032	-0.646	-0.653	-0.865	**1.000**	-0.208	-0.515	0.009	0.048	0.695
	Ki, mg	0.625	0.021	-0.625	-0.625	0.528	0.081	0.107	0.240	-0.208	**1.000**	0.450	0.447	0.092	-0.254
	K-EAF,%	0.000	-0.042	0.000	0.000	0.412	-0.127	0.462	0.616	-0.515	0.450	**1.000**	0.575	0.101	-0.254
	K-RF,%	0.000	0.025	0.000	0.000	0.723	-0.120	0.013	0.046	0.009	0.447	0.575	**1.000**	0.372	-0.217
	K-OF,%	0.000	0.134	0.000	0.000	-0.076	0.281	-0.653	0.336	0.048	0.092	0.101	0.372	**1.000**	-0.068
	K-RES,%	0.000	-0.253	0.000	0.000	-0.313	-0.715	-0.412	-0.475	0.695	-0.254	-0.254	-0.217	-0.068	**1.000**

APPENDIX-9: The Correlation and Total Variance of Balya Waste Sample and Compost Binding Material in Flask Test with the Presence of *T. thiooxidans*

Correlation Matrix[a]

		T.Thioox.	Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Bi, mg	B-EAF, %	B-RF,%	B-OF,%	B-RES,%	Ki, mg	K-EAF,%	K-RF,%	K-OF,%	K-RES,%
Correlation	T.Thioox.	**1.000**	0.000	**0.386**	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Bağ.%	0.000	**1.000**	0.294	-1.000	-1.000	-0.036	0.000	0.000	0.000	0.000	0.659	0.000	0.000	0.000	0.000
	Mobil.%	0.386	0.294	**1.000**	-0.294	-0.294	0.293	0.115	0.252	0.049	-0.188	**0.479**	0.146	0.146	-0.213	-0.246
	S=, kg/t	0.000	-1.000	-0.294	**1.000**	1.000	0.036	0.000	0.000	0.000	0.000	-0.659	0.000	0.000	0.000	0.000
	CO3=, kg/t	0.000	-1.000	-0.294	1.000	**1.000**	0.036	0.000	0.000	0.000	0.000	-0.659	0.000	0.000	0.000	0.000
	Bi, mg	0.000	-0.036	0.293	0.036	0.036	**1.000**	-0.069	0.124	-0.081	0.006	0.413	0.459	0.725	-0.099	-0.319
	B-EAF, %	0.000	0.000	0.115	0.000	0.000	-0.069	**1.000**	0.022	0.565	-0.646	0.072	-0.127	-0.120	0.281	-0.715
	B-RF,%	0.000	0.000	0.252	0.000	0.000	0.124	0.022	**1.000**	0.287	-0.653	0.096	0.462	0.013	-0.653	-0.412
	B-OF,%	0.000	0.000	0.049	0.000	0.000	-0.081	0.565	0.287	**1.000**	-0.865	0.214	0.616	0.046	0.336	-0.475
	B-RES,%	0.000	0.000	-0.188	0.000	0.000	0.006	-0.646	-0.653	-0.865	**1.000**	-0.186	-0.515	0.009	0.048	0.695
	Ki, mg	0.000	0.659	0.479	-0.659	-0.659	0.413	0.072	0.096	0.214	-0.186	**1.000**	0.401	0.398	0.082	-0.227
	K-EAF,%	0.000	0.000	0.146	0.000	0.000	0.459	-0.127	0.462	0.616	-0.515	0.401	**1.000**	0.575	0.101	-0.254
	K-RF,%	0.000	0.000	0.146	0.000	0.000	0.725	-0.120	0.013	0.046	0.009	0.398	0.575	**1.000**	0.372	-0.217
	K-OF,%	0.000	0.000	-0.213	0.000	0.000	-0.099	0.281	-0.653	0.336	0.048	0.082	0.101	0.372	**1.000**	-0.068
	K-RES,%	0.000	0.000	-0.246	0.000	0.000	-0.319	-0.715	-0.412	-0.475	0.695	-0.227	-0.254	-0.217	-0.068	**1.000**

a. This matrix is not positive definite.

APPENDIX-10: The Correlation and Total Variance of Emet Waste Sample and Leonardite Binding Material in Flask Test with the Absence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Ei, mg	E-EAF, %	E-RF,%	E-OF,%	E-RES,%	Li, mg	L-EAF,%	L-RF,%	L-OF,%	L-RES,%
Correlation	Bağ.%	**1.000**	0.062	1.000	1.000	-0.036	0.000	0.000	0.000	0.000	0.445	0.000	0.000	0.000	0.000
	Mobil.%	0.062	**1.000**	0.062	0.062	**0.430**	**0.521**	0.163	-0.224	-0.462	0.269	0.082	0.197	0.226	0.422
	S=, kg/t	1.000	0.062	**1.000**	1.000	-0.036	0.000	0.000	0.000	0.000	0.445	0.000	0.000	0.000	0.000
	CO3=, kg/t	1.000	0.062	1.000	**1.000**	-0.036	0.000	0.000	0.000	0.000	0.445	0.000	0.000	0.000	0.000
	Ei, mg	-0.036	0.430	-0.036	-0.036	**1.000**	0.925	-0.346	-0.607	-0.414	0.563	0.277	0.013	0.204	-0.238
	E-EAF, %	0.000	0.521	0.000	0.000	0.925	**1.000**	-0.346	-0.301	-0.692	0.562	0.035	0.292	0.163	-0.080
	E-RF,%	0.000	0.163	0.000	0.000	-0.346	-0.346	**1.000**	0.056	-0.101	-0.068	-0.372	-0.254	0.001	0.087
	E-OF,%	0.000	-0.224	0.000	0.000	-0.607	-0.301	0.056	**1.000**	-0.368	-0.460	-0.732	0.445	-0.189	0.343
	E-RES,%	0.000	-0.462	0.000	0.000	-0.414	-0.692	-0.101	-0.368	**1.000**	-0.251	0.601	-0.487	-0.045	-0.179
	Li, mg	0.445	0.269	0.445	0.445	0.563	0.562	-0.068	-0.460	-0.251	**1.000**	0.259	0.051	0.247	-0.185
	L-EAF,%	0.000	0.082	0.000	0.000	0.277	0.035	-0.372	-0.732	0.601	0.259	**1.000**	-0.184	0.471	-0.013
	L-RF,%	0.000	0.197	0.000	0.000	0.013	0.292	-0.254	0.445	-0.487	0.051	-0.184	**1.000**	-0.161	-0.012
	L-OF,%	0.000	0.226	0.000	0.000	0.204	0.163	0.001	-0.189	-0.045	0.247	0.471	-0.161	**1.000**	0.539
	L-RES,%	0.000	0.422	0.000	0.000	-0.238	-0.080	0.087	0.343	-0.179	-0.185	-0.013	-0.012	0.539	**1.000**

a. This matrix is not positive definite.

APPENDIX-11: The Correlation and Total Variance of Emet Waste Sample and Leonardite Binding Material in Flask Test with the Presence of *T. thiooxidans*

Correlation Matrix[a]

		T.Thioox.	Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Ei, mg	E-EAF, %	E-RF,%	E-OF,%	E-RES,%	Li, mg	L-EAF,%	L-RF,%	L-OF,%	L-RES,%
Correlation	T.Thioox.	**1.000**	0.000	0.349	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Bağ.%	0.000	**1.000**	0.249	1.000	1.000	-0.023	0.000	0.000	0.000	0.000	0.478	0.000	0.000	0.000	0.000
	Mobil.%	0.349	0.249	**1.000**	0.249	0.249	-0.007	0.028	0.004	-0.004	-0.028	0.183	0.072	0.296	-0.047	-0.124
	S=, kg/t	0.000	1.000	0.249	**1.000**	1.000	-0.023	0.000	0.000	0.000	0.000	0.478	0.000	0.000	0.000	0.000
	CO3=, kg/t	0.000	1.000	0.249	1.000	**1.000**	-0.023	0.000	0.000	0.000	0.000	0.478	0.000	0.000	0.000	0.000
	Ei, mg	0.000	-0.023	-0.007	-0.023	-0.023	**1.000**	0.927	-0.346	-0.608	-0.415	0.525	0.278	0.014	0.204	-0.239
	E-EAF, %	0.000	0.000	0.028	0.000	0.000	0.927	**1.000**	-0.346	-0.301	-0.692	0.510	0.035	0.292	0.163	-0.080
	E-RF,%	0.000	0.000	0.004	0.000	0.000	-0.346	-0.346	**1.000**	0.056	-0.101	-0.062	-0.372	-0.254	0.001	0.087
	E-OF,%	0.000	0.000	-0.004	0.000	0.000	-0.608	-0.301	0.056	**1.000**	-0.368	-0.418	-0.732	0.445	-0.189	0.343
	E-RES,%	0.000	0.000	-0.028	0.000	0.000	-0.415	-0.692	-0.101	-0.368	**1.000**	-0.228	0.601	-0.487	-0.045	-0.179
	Li, mg	0.000	0.478	0.183	0.478	0.478	0.525	0.510	-0.062	-0.418	-0.228	**1.000**	0.236	0.047	0.224	-0.168
	L-EAF,%	0.000	0.000	0.072	0.000	0.000	0.278	0.035	-0.372	-0.732	0.601	0.236	**1.000**	-0.184	0.471	-0.013
	L-RF,%	0.000	0.000	0.296	0.000	0.000	0.014	0.292	-0.254	0.445	-0.487	0.047	-0.184	**1.000**	-0.161	-0.012
	L-OF,%	0.000	0.000	-0.047	0.000	0.000	0.204	0.163	0.001	-0.189	-0.045	0.224	0.471	-0.161	**1.000**	0.539
	L-RES,%	0.000	0.000	-0.124	0.000	0.000	-0.239	-0.080	0.087	0.343	-0.179	-0.168	-0.013	-0.012	0.539	**1.000**

a. This matrix is not positive definite.

APPENDIX-12: The Correlation and Total Variance of Emet Waste Sample and Compost Binding Material in Flask Test with the Absence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Ei, mg	E-EAF, %	E-RF,%	E-OF,%	E-RES,%	Ki, mg	K-EAF,%	K-RF,%	K-OF,%	K-RES,%
Correlation	Bağ.%	**1.000**	0.037	1.000	1.000	-0.036	0.000	0.000	0.000	0.000	0.625	0.000	0.000	0.000	0.000
	Mobil.%	0.037	**1.000**	0.037	0.037	0.362	**0.485**	0.175	-0.170	**-0.463**	-0.028	0.155	0.167	0.231	0.331
	S=, kg/t	1.000	0.037	**1.000**	1.000	-0.036	0.000	0.000	0.000	0.000	0.625	0.000	0.000	0.000	0.000
	CO3=, kg/t	1.000	0.037	1.000	**1.000**	-0.036	0.000	0.000	0.000	0.000	0.625	0.000	0.000	0.000	0.000
	Ei, mg	-0.036	0.362	-0.036	-0.036	**1.000**	0.925	-0.346	-0.607	-0.414	0.065	0.147	-0.129	0.476	-0.207
	E-EAF, %	0.000	0.485	0.000	0.000	0.925	**1.000**	-0.346	-0.301	-0.692	-0.074	-0.012	-0.355	0.250	-0.102
	E-RF,%	0.000	0.175	0.000	0.000	-0.346	-0.346	**1.000**	0.056	-0.101	0.081	0.638	0.401	0.086	-0.051
	E-OF,%	0.000	-0.170	0.000	0.000	-0.607	-0.301	0.056	**1.000**	-0.368	-0.459	-0.530	-0.632	-0.680	0.301
	E-RES,%	0.000	-0.463	0.000	0.000	-0.414	-0.692	-0.101	-0.368	**1.000**	0.344	0.091	0.614	0.152	-0.070
	Ki, mg	0.625	-0.028	0.625	0.625	0.065	-0.074	0.081	-0.459	0.344	**1.000**	0.450	0.447	0.092	-0.254
	K-EAF,%	0.000	0.155	0.000	0.000	0.147	-0.012	0.638	-0.530	0.091	0.450	**1.000**	0.575	0.101	-0.254
	K-RF,%	0.000	0.167	0.000	0.000	-0.129	-0.355	0.401	-0.632	0.614	0.447	0.575	**1.000**	0.372	-0.217
	K-OF,%	0.000	0.231	0.000	0.000	0.476	0.250	0.086	-0.680	0.152	0.092	0.101	0.372	**1.000**	**-0.068**
	K-RES,%	0.000	0.331	0.000	0.000	-0.207	-0.102	-0.051	0.301	-0.070	-0.254	-0.254	-0.217	-0.068	**1.000**

a. This matrix is not positive definite.

APPENDIX-13: The Correlation and Total Variance of Emet Waste Sample and Compost Binding Material in Flask Test with the Presence of *T. thiooxidans*

Correlation Matrix[a]

		T.Thioox.	Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Ei, mg	E-EAF, %	E-RF,%	E-OF,%	E-RES,%	Ki, mg	K-EAF,%	K-RF,%	K-OF,%	K-RES,%
Correlation	T.Thioox.	**1.000**	0.000	**0.239**	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Bağ.%	0.000	**1.000**	-0.106	1.000	1.000	-0.023	0.000	0.000	0.000	0.000	0.659	0.000	0.000	0.000	0.000
	Mobil.%	0.239	-0.106	**1.000**	-0.106	-0.106	0.237	0.217	0.012	**-0.356**	0.004	-0.021	0.158	**0.399**	0.235	-0.010
	S=, kg/t	0.000	1.000	-0.106	**1.000**	1.000	-0.023	0.000	0.000	0.000	0.000	0.659	0.000	0.000	0.000	0.000
	CO3=, kg/t	0.000	1.000	-0.106	1.000	**1.000**	-0.023	0.000	0.000	0.000	0.000	0.659	0.000	0.000	0.000	0.000
	Ei, mg	0.000	-0.023	0.237	-0.023	-0.023	**1.000**	0.927	-0.346	-0.608	-0.415	0.064	0.147	-0.130	0.477	-0.207
	E-EAF, %	0.000	0.000	0.217	0.000	0.000	0.927	**1.000**	-0.346	-0.301	-0.692	-0.066	-0.012	-0.355	0.250	-0.102
	E-RF,%	0.000	0.000	0.012	0.000	0.000	-0.346	-0.346	**1.000**	0.056	-0.101	0.072	0.638	0.401	0.086	-0.051
	E-OF,%	0.000	0.000	-0.356	0.000	0.000	-0.608	-0.301	0.056	**1.000**	-0.368	-0.410	-0.530	-0.632	-0.680	0.301
	E-RES,%	0.000	0.000	0.004	0.000	0.000	-0.415	-0.692	-0.101	-0.368	**1.000**	0.307	0.091	0.614	0.152	-0.070
	Ki, mg	0.000	0.659	-0.021	0.659	0.659	0.064	-0.066	0.072	-0.410	0.307	**1.000**	0.401	0.398	0.082	-0.227
	K-EAF,%	0.000	0.000	0.158	0.000	0.000	0.147	-0.012	0.638	-0.530	0.091	0.401	**1.000**	0.575	0.101	-0.254
	K-RF,%	0.000	0.000	0.399	0.000	0.000	-0.130	-0.355	0.401	-0.632	0.614	0.398	0.575	**1.000**	0.372	-0.217
	K-OF,%	0.000	0.000	0.235	0.000	0.000	0.477	0.250	0.086	-0.680	0.152	0.082	0.101	0.372	**1.000**	-0.068
	K-RES,%	0.000	0.000	-0.010	0.000	0.000	-0.207	-0.102	-0.051	0.301	-0.070	-0.227	-0.254	-0.217	-0.068	**1.000**

a. This matrix is not positive definite.

APPENDIX-14: The Correlation and Total Variance of As Mobility in Flask Test with the Absence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Ai, mg	A-EAF, %	A-RF,%	A-OF,%	A-RES,%	Bğ.i, mg	Bğ.-EAF,%	Bğ-L-RF,%	Bğ-OF,%	Bğ-RES,%
Correlation	Bağ.%	**1.000**	0.061	-0.053	0.084	-0.747	0.000	0.000	0.000	0.000	0.775	0.000	0.000	0.000	0.000
	Mobil.%	0.061	**1.000**	-0.921	-0.916	**0.564**	**0.925**	**0.925**	**0.925**	**-0.925**	0.152	-0.053	-0.053	0.053	0.053
	S=, kg/t	-0.053	-0.921	**1.000**	0.990	-0.625	-0.995	-0.995	-0.995	0.995	-0.048	0.009	0.009	-0.009	-0.009
	CO3=, kg/t	0.084	-0.916	0.990	**1.000**	-0.725	-0.992	-0.992	-0.992	0.992	0.036	0.035	0.035	-0.035	-0.035
	Ai, mg	-0.747	0.564	-0.625	-0.725	**1.000**	0.663	0.663	0.663	-0.663	-0.579	0.000	0.000	0.000	0.000
	A-EAF, %	0.000	0.925	-0.995	-0.992	0.663	**1.000**	1.000	1.000	-1.000	0.000	0.000	0.000	0.000	0.000
	A-RF,%	0.000	0.925	-0.995	-0.992	0.663	1.000	**1.000**	1.000	-1.000	0.000	0.000	0.000	0.000	0.000
	A-OF,%	0.000	0.925	-0.995	-0.992	0.663	1.000	1.000	**1.000**	-1.000	0.000	0.000	0.000	0.000	0.000
	A-RES,%	0.000	-0.925	0.995	0.992	-0.663	-1.000	-1.000	-1.000	**1.000**	0.000	0.000	0.000	0.000	0.000
	Bğ.i, mg	0.775	0.152	-0.048	0.036	-0.579	0.000	0.000	0.000	0.000	**1.000**	-0.482	-0.482	0.482	0.482
	Bğ.-EAF,%	0.000	-0.053	0.009	0.035	0.000	0.000	0.000	0.000	0.000	-0.482	**1.000**	1.000	-1.000	-1.000
	Bğ-L-RF,%	0.000	-0.053	0.009	0.035	0.000	0.000	0.000	0.000	0.000	-0.482	1.000	**1.000**	-1.000	-1.000
	Bğ-OF,%	0.000	0.053	-0.009	-0.035	0.000	0.000	0.000	0.000	0.000	0.482	-1.000	-1.000	**1.000**	1.000
	Bğ-RES,%	0.000	0.053	-0.009	-0.035	0.000	0.000	0.000	0.000	0.000	0.482	-1.000	-1.000	1.000	**1.000**

a. This matrix is not positive definite.

APPENDIX-15: The Correlation and Total Variance of As Mobility in Flask Test with the Presence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	T.Thio.	Mobil.%	S=, kg/t	CO3=, kg/t	Ai, mg	A-EAF, %	A-RF,%	A-OF,%	A-RES,%	Bğ.i, mg	Bğ.-EAF,%	Bğ-L-RF,%	Bğ-OF,%	Bğ-RES,%
Correlation	Bağ.%	**1.000**	-0.255	0.172	-0.049	0.078	-0.720	0.000	0.000	0.000	0.000	0.790	0.000	0.000	0.000	0.000
	T.Thio.	-0.255	**1.000**	-0.338	0.012	-0.020	0.184	0.000	0.000	0.000	0.000	-0.202	0.000	0.000	0.000	0.000
	Mobil.%	0.172	-0.338	**1.000**	**-0.781**	**-0.761**	**0.411**	**0.787**	**0.787**	**0.787**	**-0.787**	**0.225**	-0.045	-0.045	0.045	0.045
	S=, kg/t	-0.049	0.012	-0.781	**1.000**	0.991	-0.658	-0.996	-0.996	-0.996	0.996	-0.045	0.008	0.008	-0.008	-0.008
	CO3=, kg/t	0.078	-0.020	-0.761	0.991	**1.000**	-0.747	-0.993	-0.993	-0.993	0.993	0.037	0.030	0.030	-0.030	-0.030
	Ai, mg	-0.720	0.184	0.411	-0.658	-0.747	**1.000**	0.692	0.692	0.692	-0.692	-0.569	0.000	0.000	0.000	0.000
	A-EAF, %	0.000	0.000	0.787	-0.996	-0.993	0.692	**1.000**	1.000	1.000	-1.000	0.000	0.000	0.000	0.000	0.000
	A-RF,%	0.000	0.000	0.787	-0.996	-0.993	0.692	1.000	**1.000**	1.000	-1.000	0.000	0.000	0.000	0.000	0.000
	A-OF,%	0.000	0.000	0.787	-0.996	-0.993	0.692	1.000	1.000	**1.000**	-1.000	0.000	0.000	0.000	0.000	0.000
	A-RES,%	0.000	0.000	-0.787	0.996	0.993	-0.692	-1.000	-1.000	-1.000	**1.000**	0.000	0.000	0.000	0.000	0.000
	Bğ.i, mg	0.790	-0.202	0.225	-0.045	0.037	-0.569	0.000	0.000	0.000	0.000	**1.000**	-0.450	-0.450	0.450	0.450
	Bğ.-EAF,%	0.000	0.000	-0.045	0.008	0.030	0.000	0.000	0.000	0.000	0.000	-0.450	**1.000**	1.000	-1.000	-1.000
	Bğ-L-RF,%	0.000	0.000	-0.045	0.008	0.030	0.000	0.000	0.000	0.000	0.000	-0.450	1.000	**1.000**	-1.000	-1.000
	Bğ-OF,%	0.000	0.000	0.045	-0.008	-0.030	0.000	0.000	0.000	0.000	0.000	0.450	-1.000	-1.000	**1.000**	1.000
	Bğ-RES,%	0.000	0.000	0.045	-0.008	-0.030	0.000	0.000	0.000	0.000	0.000	0.450	-1.000	-1.000	1.000	**1.000**

a. This matrix is not positive definite.

APPENDIX-16: The Correlation and Total Variance of Mn Mobility in Flask Test with the Absence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Ai, mg	A-EAF, %	A-RF,%	A-OF,%	A-RES,%	Bğ.i, mg	Bğ.-EAF,%	Bğ-L-RF,%	Bğ-OF,%
Correlation	Bağ.%	**1.000**	**0.239**	-0.053	0.084	-0.085	0.000	0.000	0.000	0.000	0.743	0.000	0.000	0.000
	Mobil.%	0.239	**1.000**	-0.677	-0.643	-0.683	**0.694**	-0.694	-0.694	**0.694**	0.197	0.055	-0.055	-0.055
	S=, kg/t	-0.053	-0.677	**1.000**	0.990	0.999	-0.995	0.995	0.995	-0.995	-0.047	-0.009	0.009	0.009
	CO3=, kg/t	0.084	-0.643	0.990	**1.000**	0.985	-0.992	0.992	0.992	-0.992	0.032	-0.035	0.035	0.035
	Ai, mg	-0.085	-0.683	0.999	0.985	**1.000**	-0.993	0.993	0.993	-0.993	-0.063	0.000	0.000	0.000
	A-EAF, %	0.000	0.694	-0.995	-0.992	-0.993	**1.000**	-1.000	-1.000	1.000	0.000	0.000	0.000	0.000
	A-RF,%	0.000	-0.694	0.995	0.992	0.993	-1.000	**1.000**	1.000	-1.000	0.000	0.000	0.000	0.000
	A-OF,%	0.000	-0.694	0.995	0.992	0.993	-1.000	1.000	**1.000**	-1.000	0.000	0.000	0.000	0.000
	A-RES,%	0.000	0.694	-0.995	-0.992	-0.993	1.000	-1.000	-1.000	**1.000**	0.000	0.000	0.000	0.000
	Bğ.i, mg	0.743	0.197	-0.047	0.032	-0.063	0.000	0.000	0.000	0.000	**1.000**	0.511	-0.511	-0.511
	Bğ.-EAF,%	0.000	0.055	-0.009	-0.035	0.000	0.000	0.000	0.000	0.000	0.511	**1.000**	-1.000	-1.000
	Bğ-L-RF,%	0.000	-0.055	0.009	0.035	0.000	0.000	0.000	0.000	0.000	-0.511	-1.000	**1.000**	1.000
	Bğ-OF,%	0.000	-0.055	0.009	0.035	0.000	0.000	0.000	0.000	0.000	-0.511	-1.000	1.000	**1.000**

a. This matrix is not positive definite.

APPENDIX-17: The Correlation and Total Variance of Mn Mobility in Flask Test with the Presence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	T.Thio.	Mobil.%	S=, kg/t	CO3=, kg/t	Ai, mg	A-EAF, %	A-RF,%	A-OF,%	A-RES,%	Bğ.i, mg	Bğ.-EAF,%	Bğ-L-RF,%	Bğ-OF,%
Correlation	Bağ.%	**1.000**	-0.255	0.112	-0.049	0.078	-0.078	0.000	0.000	0.000	0.000	0.760	0.000	0.000	0.000
	T.Thio.	-0.255	**1.000**	0.459	0.012	-0.020	0.020	0.000	0.000	0.000	0.000	-0.194	0.000	0.000	0.000
	Mobil.%	0.112	0.459	**1.000**	-0.036	-0.022	-0.038	0.032	-0.032	-0.032	0.032	0.107	0.035	-0.035	-0.035
	S=, kg/t	-0.049	0.012	-0.036	**1.000**	0.991	1.000	-0.996	0.996	0.996	-0.996	-0.044	-0.008	0.008	0.008
	CO3=, kg/t	0.078	-0.020	-0.022	0.991	**1.000**	0.987	-0.993	0.993	0.993	-0.993	0.033	-0.030	0.030	0.030
	Ai, mg	-0.078	0.020	-0.038	1.000	0.987	**1.000**	-0.994	0.994	0.994	-0.994	-0.060	0.000	0.000	0.000
	A-EAF, %	0.000	0.000	0.032	-0.996	-0.993	-0.994	**1.000**	-1.000	-1.000	1.000	0.000	0.000	0.000	0.000
	A-RF,%	0.000	0.000	-0.032	0.996	0.993	0.994	-1.000	**1.000**	1.000	-1.000	0.000	0.000	0.000	0.000
	A-OF,%	0.000	0.000	-0.032	0.996	0.993	0.994	-1.000	1.000	**1.000**	-1.000	0.000	0.000	0.000	0.000
	A-RES,%	0.000	0.000	0.032	-0.996	-0.993	-0.994	1.000	-1.000	-1.000	**1.000**	0.000	0.000	0.000	0.000
	Bğ.i, mg	0.760	-0.194	0.107	-0.044	0.033	-0.060	0.000	0.000	0.000	0.000	**1.000**	0.478	-0.478	-0.478
	Bğ.-EAF,%	0.000	0.000	0.035	-0.008	-0.030	0.000	0.000	0.000	0.000	0.000	0.478	**1.000**	-1.000	-1.000
	Bğ-L-RF,%	0.000	0.000	-0.035	0.008	0.030	0.000	0.000	0.000	0.000	0.000	-0.478	-1.000	**1.000**	1.000
	Bğ-OF,%	0.000	0.000	-0.035	0.008	0.030	0.000	0.000	0.000	0.000	0.000	-0.478	-1.000	1.000	**1.000**

a. This matrix is not positive definite.

APPENDIX-18: The Correlation and Total Variance of Zn Mobility in Flask Test with the Absence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	Mobil.%	S=, kg/t	CO3=, kg/t	Ai, mg	A-EAF, %	A-RF,%	A-OF,%	A-RES,%	Bğ.i, mg	Bğ.-EAF,%	Bğ-L-RF,%	Bğ-OF,%
Correlation	Bağ.%	**1.000**	0.092	-0.053	0.084	0.094	0.000	0.000	0.000	0.000	0.599	0.000	0.000	0.000
	Mobil.%	0.092	**1.000**	**0.434**	**0.448**	**0.387**	**0.424**	**0.424**	**0.424**	**-0.424**	0.000	-0.153	-0.153	0.153
	S=, kg/t	-0.053	0.434	**1.000**	0.990	0.964	0.995	0.995	0.995	-0.995	-0.041	0.009	0.009	-0.009
	CO3=, kg/t	0.084	0.448	0.990	**1.000**	0.974	0.992	0.992	0.992	-0.992	0.014	0.035	0.035	-0.035
	Ai, mg	0.094	0.387	0.964	0.974	**1.000**	0.982	0.982	0.982	-0.982	0.056	0.000	0.000	0.000
	A-EAF, %	0.000	0.424	0.995	0.992	0.982	**1.000**	1.000	1.000	-1.000	0.000	0.000	0.000	0.000
	A-RF,%	0.000	0.424	0.995	0.992	0.982	1.000	**1.000**	1.000	-1.000	0.000	0.000	0.000	0.000
	A-OF,%	0.000	0.424	0.995	0.992	0.982	1.000	1.000	**1.000**	-1.000	0.000	0.000	0.000	0.000
	A-RES,%	0.000	-0.424	-0.995	-0.992	-0.982	-1.000	-1.000	-1.000	**1.000**	0.000	0.000	0.000	0.000
	Bğ.i, mg	0.599	0.000	-0.041	0.014	0.056	0.000	0.000	0.000	0.000	**1.000**	-0.611	-0.611	0.611
	Bğ.-EAF,%	0.000	-0.153	0.009	0.035	0.000	0.000	0.000	0.000	0.000	-0.611	**1.000**	1.000	-1.000
	Bğ-L-RF,%	0.000	-0.153	0.009	0.035	0.000	0.000	0.000	0.000	0.000	-0.611	1.000	**1.000**	-1.000
	Bğ-OF,%	0.000	0.153	-0.009	-0.035	0.000	0.000	0.000	0.000	0.000	0.611	-1.000	-1.000	**1.000**

a. This matrix is not positive definite.

APPENDIX-19: The Correlation and Total Variance of Zn Mobility in Flask Test with the Presence of *T. thiooxidans*

Correlation Matrix[a]

		Bağ.%	T.Thio.	Mobil.%	S=, kg/t	CO3=, kg/t	Ai, mg	A-EAF, %	A-RF,%	A-OF,%	A-RES,%	Bğ.i, mg	Bğ.-EAF,%	Bğ-L-RF,%	Bğ-OF,%
Correlation	Bağ.%	**1.000**	-0.255	-0.153	-0.049	0.078	0.065	0.000	0.000	0.000	0.000	0.618	0.000	0.000	0.000
	T.Thio.	-0.255	**1.000**	0.611	0.012	-0.020	-0.035	0.000	0.000	0.000	0.000	-0.158	0.000	0.000	0.000
	Mobil.%	-0.153	0.611	**1.000**	0.016	-0.008	-0.012	0.025	0.025	0.025	-0.025	0.012	-0.163	-0.163	0.163
	S=, kg/t	-0.049	0.012	0.016	**1.000**	0.991	0.973	0.996	0.996	0.996	-0.996	-0.038	0.008	0.008	-0.008
	CO3=, kg/t	0.078	-0.020	-0.008	0.991	**1.000**	0.978	0.993	0.993	0.993	-0.993	0.016	0.030	0.030	-0.030
	Ai, mg	0.065	-0.035	-0.012	0.973	0.978	**1.000**	0.985	0.985	0.985	-0.985	0.040	0.000	0.000	0.000
	A-EAF, %	0.000	0.000	0.025	0.996	0.993	0.985	**1.000**	1.000	1.000	-1.000	0.000	0.000	0.000	0.000
	A-RF,%	0.000	0.000	0.025	0.996	0.993	0.985	1.000	**1.000**	1.000	-1.000	0.000	0.000	0.000	0.000
	A-OF,%	0.000	0.000	0.025	0.996	0.993	0.985	1.000	1.000	**1.000**	-1.000	0.000	0.000	0.000	0.000
	A-RES,%	0.000	0.000	-0.025	-0.996	-0.993	-0.985	-1.000	-1.000	-1.000	**1.000**	0.000	0.000	0.000	0.000
	Bğ.i, mg	0.618	-0.158	0.012	-0.038	0.016	0.040	0.000	0.000	0.000	0.000	**1.000**	-0.578	-0.578	0.578
	Bğ.-EAF,%	0.000	0.000	-0.163	0.008	0.030	0.000	0.000	0.000	0.000	0.000	-0.578	**1.000**	1.000	-1.000
	Bğ-L-RF,%	0.000	0.000	-0.163	0.008	0.030	0.000	0.000	0.000	0.000	0.000	-0.578	1.000	**1.000**	-1.000
	Bğ-OF,%	0.000	0.000	0.163	-0.008	-0.030	0.000	0.000	0.000	0.000	0.000	0.578	-1.000	-1.000	**1.000**

a. This matrix is not positive definite.

APPENDIX-20: Metal Concentrations Obtained by Using Marble Dust and Compared with EPA Standards and Turkish Regulation of Water Pollution Control

	EPA Standards	Turkish Reg of Water Pollution Control				CONCENTRATIONS (MG/L)																		
	National Primary Drinking Water Regulations for inorganic chemicals (mg/l)	Water Classes of TRWPC (mg/l)																						
		I. Class Very Clean	2. Class Less Polluted	3. Class Much Polluted	4. Class Extremely Polluted	MD1.1	MD1.2	MD1.5	MD1.10	MD2.1	MD2.2	MD2.5	MD2.10	MD3.1	MD3.2	MD3.5	MD3.10	MD4.1	MD4.2	MD4.5	MD4.10	MD5.1	MD5.2	MD5.5	MD5.10	
Al		0,3	0,3	1	>1	0,000	0,000	0,000	0,000	0,043	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,117	0,130	0,105	0,075	0,000	0,000	0,000	0,000	Al
As	0,01	0,02	0,05	0,1	>0,1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	As
Ba	2	1	2	2	>2	0,050	0,058	0,045	0,049	0,033	0,035	0,032	0,018	0,025	0,013	0,013	0,004	0,030	0,041	0,032	0,036	0,031	0,029	0,021	0,025	Ba
Ca						747,798	780,275	734,671	704,490	802,967	722,603	777,328	787,860	603,749	631,100	570,500	566,800	551,414	524,753	502,907	527,275	614,487	568,976	586,122	567,089	Ca
Cd	0,005	0,003	0,005	0,01	>0,01	0,249	0,129	0,043	0,061	3,350	2,675	1,547	1,576	2,129	2,529	1,992	1,657	0,554	0,464	0,412	0,273	1,086	1,350	0,903	0,668	Cd
Cr	0,1	0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,009	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Cr
Cu	1,3	0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,021	0,003	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Cu
Fe		0,3	1	5	>5	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Fe
K						0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,555	0,842	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	K
Mo						0,004	0,005	0,000	0,000	0,006	0,000	0,005	0,005	0,000	0,006	0,002	0,000	0,000	0,000	0,000	0,000	0,000	0,005	0,000	0,000	Mo
Na						23,245	22,727	23,724	26,142	24,829	33,366	27,706	24,441	24,726	19,580	20,450	25,300	25,400	28,181	23,085	28,980	26,956	23,392	21,582	18,358	Na
Ni		0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Ni
Pb	0,015	0,01	0,02	0,05	>0,05	0,000	0,000	0,000	0,000	2,616	2,048	3,413	3,335	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Pb
Sb	0,006					0,000	0,000	0,000	0,000	0,005	0,014	0,000	0,000	0,000	0,000	0,020	0,041	0,059	0,059	0,039	0,036	0,010	0,017	0,000	0,036	Sb
Zn		0,2	0,5	2	>2	42,744	7,089	0,000	1,210	366,216	300,354	186,542	158,365	109,173	119,258	86,819	68,412	14,629	10,876	8,957	8,904	70,291	83,636	53,522	23,790	Zn

APPENDIX-21: Metal Concentrations Obtained by Using Ash and Compared with EPA Standards and Turkish Regulation of Water Pollution Control

	EPA Standards	Turkish Reg of Water Pollution Control				CONCENTRATIONS (MG/L)																		
	National Primary Drinking Water Regulations for inorganic chemicals (mg/l)	Water Classes of TRWPC (mg/l)																						
		I. Class Very Clean	2. Class Less Polluted	3. Class Much Polluted	4. Class Extremely Polluted	A1.1	A1.2	A1.5	A1.10	A2.1	A2.2	A2.5	A2.10	A3.1	A3.2	A3.5	A3.10	A4.1	A4.2	A4.5	A4.10	A5.1	A5.2	A5.5	A5.10	
Al		0,3	0,3	1	>1	0,000	0,000	0,000	0,000	0,000	0,000	0,287	0,116	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Al**
As	0,01	0,02	0,05	0,1	>0,1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**As**
Ba	2	1	2	2	>2	0,032	0,189	3,630	0,092	0,034	0,045	0,078	0,098	0,000	0,000	0,000	0,000	0,040	0,043	0,047	0,052	0,000	0,015	0,032	0,029	**Ba**
Ca						784,002	832,182	814,957	853,780	744,971	765,838	763,115	766,295	200,900	117,300	56,147	30,982	600,644	592,904	594,492	565,777	585,823	550,781	579,647	0,000	**Ca**
Cd	0,005	0,003	0,005	0,01	>0,01	0,457	0,341	0,000	0,000	3,337	2,804	1,726	0,280	1,750	0,704	0,020	0,182	0,247	0,079	0,021	0,008	0,969	0,660	0,089	0,014	**Cd**
Cr	0,1	0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Cr**
Cu	1,3	0,02	0,05	0,2	>0,2	0,017	0,000	0,000	0,000	0,003	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Cu**
Fe		0,3	1	5	>5	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Fe**
K						0,517	0,000	1,075	3,866	0,000	0,000	3,261	6,558	0,000	0,000	0,000	0,000	0,000	0,000	1,855	3,478	0,000	0,000	3,175	5,081	**K**
Mo						0,005	0,005	0,016	0,025	0,000	0,007	0,009	0,133	0,000	0,009	0,000	0,015	0,000	0,000	0,005	0,000	0,000	0,000	0,000	0,000	**Mo**
Na						44,100	27,634	26,415	27,672	33,096	34,899	36,668	30,237	3,090	1,167	0,000	0,000	28,457	29,926	30,006	26,869	21,884	20,649	22,810	20,691	**Na**
Ni		0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Ni**
Pb	0,015	0,01	0,02	0,05	>0,05	1,330	0,405	1,134	0,000	1,549	1,514	0,984	0,264	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Pb**
Sb	0,006					0,000	0,000	0,000	0,051	0,000	0,025	0,000	0,000	0,056	0,057	0,075	0,088	0,000	0,027	0,024	0,000	0,000	0,000	0,000	0,000	**Sb**
Zn		0,2	0,5	2	>2	93,286	57,077	0,000	0,000	328,104	264,962	105,580	11,340	65,309	18,482	0,000	2,346	4,957	0,504	0,000	0,000	43,099	22,563	1,129	0,000	**Zn**

APPENDIX-22: Metal Concentrations obtained by Using Cement and Compared with EPA Standards and Turkish Regulation of Water Pollution Control

	EPA Standards	Turkish Reg of Water Pollution Control				CONCENTRATIONS (MG/L)																		
	National Primary Drinking Water Regulations for inorganic chemicals (mg/l)	Water Classes of TRWPC (mg/l)																						
		I. Class Very Clean	2. Class Less Polluted	3. Class Much Polluted	4. Class Extremely Polluted	C1.1	C1.2	C1.5	C1.10	C2.1	C2.2	C2.5	C2.10	C3.1	C3.2	C3.5	C3.10	C4.1	C4.2	C4.5	C4.10	C5.1	C5.2	C5.5	C5.10	
Al		0,3	0,3	1	>1	0,000	0,000	0,000	0,000	0,050	0,019	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,032	Al
As	0,01	0,02	0,05	0,1	>0,1	0,000	0,084	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	As
Ba	2	1	2	2	>2	0,091	0,135	0,082	0,069	0,050	0,033	0,095	0,000	0,000	0,000	0,000	0,000	0,040	0,043	0,048	0,048	0,025	0,039	0,046	0,049	Ba
Ca						838,374	828,903	804,726	811,148	738,352	778,235	797,778	69,791	293,700	367,500	266,500	220,200	537,380	577,670	600,185	577,842	627,048	617,410	565,672	624,792	Ca
Cd	0,005	0,003	0,005	0,01	>0,01	0,150	0,000	0,000	0,000	3,058	2,039	0,015	0,000	0,700	0,359	0,032	0,543	0,075	0,021	0,000	0,000	0,466	0,053	0,005	0,000	Cd
Cr	0,1	0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,027	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Cr
Cu	1,3	0,02	0,05	0,2	>0,2	0,000	0,010	0,003	0,029	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Cu
Fe		0,3	1	5	>5	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Fe
K						0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,670	2,947	1,828	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	K
Mo						0,000	0,010	0,008	0,017	0,009	0,000	0,008	1,017	0,007	0,010	0,026	0,013	0,000	0,006	0,000	0,009	0,000	0,000	0,008	0,005	Mo
Na						28,674	36,957	36,159	46,560	28,887	47,167	29,303	0,000	6,518	10,020	6,660	4,511	25,888	23,535	28,512	42,435	28,880	19,453	24,365	37,578	Na
Ni		0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Ni
Pb	0,015	0,01	0,02	0,05	>0,05	0,000	3,241	0,000	0,000	1,631	1,856	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	Pb
Sb	0,006					0,000	0,100	0,026	0,041	0,000	0,000	0,000	0,067	0,094	0,085	0,056	0,052	0,010	0,000	0,028	0,029	0,000	0,000	0,037	0,039	Sb
Zn		0,2	0,5	2	>2	14,039	0,000	0,000	0,000	228,091	73,238	0,505	0,000	20,101	4,701	0,000	5,719	1,031	0,000	0,000	0,000	11,370	1,332	0,000	0,000	Zn

APPENDIX-23: Metal Concentrations Obtained by Using Bentonite and Compared with EPA Standards and Turkish Regulation of Water Pollution Control

	EPA Standards	Turkish Reg of Water Pollution Control				CONCENTRATIONS (MG/L)																		
	National Primary Drinking Water Regulations for inorganic chemicals (mg/l)	Water Classes of TRWPC (mg/l)																						
		I. Class Very Clean	2. Class Less Polluted	3. Class Much Polluted	4. Class Extremely Polluted	B1.1	B1.2	B1.5	B1.10	B2.1	B2.2	B2.5	B2.10	B3.1	B3.2	B3.5	B3.10	B4.1	B4.2	B4.5	B4.10	B5.1	B5.2	B5.5	B5.10	
Al		0,3	0,3	1	>1	4,269	3,708	1,511	3,812	0,234	0,257	0,062	0,241	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Al**
As	0,01	0,02	0,05	0,1	>0,1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**As**
Ba	2	1	2	2	>2	0,033	0,024	0,027	0,019	0,034	0,028	0,031	0,033	0,017	0,000	0,000	0,000	0,022	0,015	0,021	0,019	0,027	0,019	0,024	0,026	**Ba**
Ca						801,263	764,468	817,557	730,047	764,802	750,192	768,552	764,935	581,600	523,700	469,700	404,200	492,657	502,362	461,557	446,558	480,976	386,434	498,837	426,819	**Ca**
Cd	0,005	0,003	0,005	0,01	>0,01	0,636	0,619	0,937	0,545	3,757	3,459	3,611	3,647	0,202	3,032	3,346	2,923	0,473	0,517	0,463	0,476	1,136	1,219	1,104	1,234	**Cd**
Cr	0,1	0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Cr**
Cu	1,3	0,02	0,05	0,2	>0,2	1,010	0,843	0,461	0,757	0,000	0,007	0,005	0,004	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Cu**
Fe		0,3	1	5	>5	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Fe**
K						0,490	0,483	1,812	0,000	0,317	0,000	0,000	0,000	9,383	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**K**
Mo						0,007	0,000	0,007	0,000	0,006	0,026	0,008	0,000	0,014	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Mo**
Na						24,697	30,046	35,753	19,942	27,820	36,351	35,462	45,249	29,940	19,730	13,720	9,608	20,887	23,435	17,134	18,498	17,811	12,990	16,874	13,225	**Na**
Ni		0,02	0,05	0,2	>0,2	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Ni**
Pb	0,015	0,01	0,02	0,05	>0,05	2,224	2,100	1,776	2,204	3,716	1,728	1,540	1,749	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	**Pb**
Sb	0,006					0,000	0,000	0,000	0,000	0,000	0,000	0,013	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,043	0,065	0,065	0,068	**Sb**
Zn		0,2	0,5	2	>2	118,661	113,777	198,668	102,039	359,208	378,634	381,326	359,698	4,523	149,982	169,885	181,820	17,335	21,818	14,913	12,747	77,437	82,140	82,353	82,028	**Zn**

APPENDIX-24: The Correlation of Samples and Marble Dust

Correlations

		Additive rate, %	Time, d	Tot. S, %	Pyr. S=, %	Inert C, %	AP, kg/ton	NP, kg/ton	NP/AP	Add Tot. S,%	Add Pyr. S=	Add Inert C	Add AP	Add NP	Add NP/AP	Mixed tot. S=	Mixed pyr. S=	Mixed inert C	Mixed AP	Mixed NP	Mixed NP/AP	% Vol Leached	pH	EC	SO4, mg/l
Additive rate, %	r	1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	1,000**	1,000**	1,000**	1,000**	1,000**	,498**	-0,075	-0,039	,757**	-0,039	,746**	,500**	0,017	,241**	0,056	0,056
	p		1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,146	0,450	0,000	0,449	0,000	0,000	0,738	0,000	0,275	0,280
Time, d	r		1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	,559**	,692**	-,202**	0,000
	p			1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	1,000
Tot. S, %	r			1	,973**	,371**	,974**	,413**	-,741**	0,000	0,000	0,000	0,000	0,000	0,000	,996**	,972**	,230**	,972**	,262**	-,422**	,232**	,266**	-,410**	0,022
	p				0,000	0,000	0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,673
Pyr. S=, %	r				1	,522**	1,000**	,548**	-,582**	0,000	0,000	0,000	0,000	0,000	0,000	,970**	,999**	,323**	,999**	,347**	-,379**	,211**	,300**	-,444**	0,034
	p					0,000	0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,507
Inert C, %	r					1	,521**	,965**	,324**	0,000	0,000	0,000	0,000	0,000	0,000	,370**	,521**	,619**	,521**	,612**	-,236**	0,049	,299**	-,204**	-,388**
	p						0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,348	0,000	0,000	0,000
AP, kg/ton	r						1	,549**	-,583**	0,000	0,000	0,000	0,000	0,000	0,000	,970**	,999**	,323**	,999**	,348**	-,380**	,211**	,301**	-,444**	0,033
	p							0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,519
NP, kg/ton	r							1	,240**	0,000	0,000	0,000	0,000	0,000	0,000	,412**	,547**	,597**	,548**	,634**	-,279**	0,052	,328**	-,210**	-,434**
	p								0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,315	0,000	0,000	0,000
NP/AP	r								1	0,000	0,000	0,000	0,000	0,000	0,000	-,738**	-,581**	,200**	-,582**	,152**	,317**	-,205**	-0,059	,225**	-,178**
	p									1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,003	0,000	0,000	0,254	0,000	0,001
Add Tot. S,%	r									1	1,000**	1,000**	1,000**	1,000**	,498**	-0,075	-0,039	,757**	-0,039	,746**	,500**	0,017	,241**	0,056	0,056
	p										0,000	0,000	0,000	0,000	0,000	0,146	0,450	0,000	0,449	0,000	0,000	0,738	0,000	0,275	0,280
Add Pyr. S=	r										1	1,000**	1,000**	1,000**	,498**	-0,075	-0,039	,757**	-0,039	,746**	,500**	0,017	,241**	0,056	0,056
	p											0,000	0,000	0,000	0,000	0,146	0,450	0,000	0,449	0,000	0,000	0,738	0,000	0,275	0,280
Add Inert C	r											1	1,000**	1,000**	,498**	-0,075	-0,039	,757**	-0,039	,746**	,500**	0,017	,241**	0,056	0,056
	p												0,000	0,000	0,000	0,146	0,450	0,000	0,449	0,000	0,000	0,738	0,000	0,275	0,280
Add AP	r												1	1,000**	,498**	-0,075	-0,039	,757**	-0,039	,746**	,500**	0,017	,241**	0,056	0,056
	p													0,000	0,000	0,146	0,450	0,000	0,449	0,000	0,000	0,738	0,000	0,275	0,280
Add NP	r													1	,498**	-0,075	-0,039	,757**	-0,039	,746**	,500**	0,017	,241**	0,056	0,056
	p														0,000	0,146	0,450	0,000	0,449	0,000	0,000	0,738	0,000	0,275	0,280
Add NP/AP	r														1	-0,038	-0,020	,262**	-0,020	,257**	,174**	-0,041	,292**	0,039	0,043
	p															0,469	0,706	0,000	0,705	0,000	0,001	0,432	0,000	0,448	0,401
Mixed tot. S=	r															1	,973**	,172**	,973**	,205**	-,443**	,230**	,253**	-,411**	0,013
	p																0,000	0,001	0,000	0,000	0,000	0,000	0,000	0,000	0,797
Mixed pyr. S=	r																1	,293**	1,000**	,318**	-,384**	,210**	,296**	-,444**	0,026
	p																	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,618
Mixed inert C	r																	1	,293**	,986**	,270**	0,046	,340**	-0,091	-,192**
	p																		0,000	0,000	0,000	0,371	0,000	0,078	0,000
Mixed AP	r																		1	,318**	-,384**	,210**	,297**	-,444**	0,025
	p																			0,000	0,000	0,000	0,000	0,000	0,632
Mixed NP	r																			1	,235**	0,049	,361**	-0,098	-,228**
	p																				0,000	0,345	0,000	0,058	0,000
Mixed NP/AP	r																				1	-0,087	0,079	,107*	,273**
	p																					0,093	0,128	0,038	0,000
% Vol Leached	r																					1	,631**	-,222**	0,001
	p																						0,000	0,000	0,978
pH	r																						1	-,322**	-0,054
	p																							0,000	0,293
EC	r																							1	-,127*
	p																								0,014
SO4, mg/l	r																								1
	p																								

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

APPENDIX-25: The Correlation of Samples and Ash

Correlations

		Additive rate, %	Time, d	Tot. S, %	Pyr. S=, %	Inert C, %	AP, kg/ton	NP, kg/ton	NP/AP	Add Tot. S,%	Add Pyr. S=	Add Inert C	Add AP	Add NP	Add NP/AP	Mixed tot. S=	Mixed pyr. S=	Mixed inert C	Mixed AP	Mixed NP	Mixed NP/AP	%Vol Leached	pH	EC	SO4, mg/l
Additive rate, %	r	1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	1,000**	1,000**	1,000**	1,000**	1,000**	,498**	-0,055	-0,038	,366**	-0,038	,352**	,433**	-0,016	,583**	,180**	-,136**
	p		1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,285	0,463	0,000	0,462	0,000	0,000	0,758	0,000	0,000	0,009
Time, d	r		1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	,468**	,473**	-0,094	0,000
	p			1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,069	1,000
Tot. S, %	r			1	,973**	,371**	,974**	,413**	-,741**	0,000	0,000	0,000	0,000	0,000	0,000	,998**	,972**	,343**	,972**	,384**	-,592**	,148**	,327**	-,495**	0,084
	p				0,000	0,000	0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,004	0,000	0,000	0,105
Pyr. S=, %	r				1	,522**	1,000**	,548**	-,582**	0,000	0,000	0,000	0,000	0,000	0,000	,971**	,999**	,482**	,999**	,509**	-,507**	,141**	,383**	-,515**	,109*
	p					0,000	0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,006	0,000	0,000	0,035
Inert C, %	r					1	,521**	,965**	,324**	0,000	0,000	0,000	0,000	0,000	0,000	,370**	,521**	,923**	,521**	,897**	-,104*	0,044	,397**	-,305**	-,336**
	p						0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,043	0,393	0,000	0,000	0,000
AP, kg/ton	r						1	,549**	-,583**	0,000	0,000	0,000	0,000	0,000	0,000	,971**	,999**	,481**	,999**	,510**	-,507**	,141**	,383**	-,515**	,108*
	p							0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,006	0,000	0,000	0,037
NP, kg/ton	r							1	,240**	0,000	0,000	0,000	0,000	0,000	0,000	,412**	,547**	,891**	,548**	,929**	-,167**	0,050	,415**	-,323**	-,368**
	p								0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,001	0,337	0,000	0,000	0,000
NP/AP	r								1	0,000	0,000	0,000	0,000	0,000	0,000	-,739**	-,581**	,299**	-,582**	,223**	,580**	-,118*	-0,039	,272**	-,195**
	p									1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,022	0,448	0,000	0,000
Add Tot. S,%	r									1	1,000**	1,000**	1,000**	1,000**	,498**	-0,055	-0,038	,366**	-0,038	,352**	,433**	-0,016	,583**	,180**	-,136**
	p										0,000	0,000	0,000	0,000	0,000	0,285	0,463	0,000	0,462	0,000	0,000	0,758	0,000	0,000	0,009
Add Pyr. S=	r										1	1,000**	1,000**	1,000**	,498**	-0,055	-0,038	,366**	-0,038	,352**	,433**	-0,016	,583**	,180**	-,136**
	p											0,000	0,000	0,000	0,000	0,285	0,463	0,000	0,462	0,000	0,000	0,758	0,000	0,000	0,009
Add Inert C	r											1	1,000**	1,000**	,498**	-0,055	-0,038	,366**	-0,038	,352**	,433**	-0,016	,583**	,180**	-,136**
	p												0,000	0,000	0,000	0,285	0,463	0,000	0,462	0,000	0,000	0,758	0,000	0,000	0,009
Add AP	r												1	1,000**	,498**	-0,055	-0,038	,366**	-0,038	,352**	,433**	-0,016	,583**	,180**	-,136**
	p													0,000	0,000	0,285	0,463	0,000	0,462	0,000	0,000	0,758	0,000	0,000	0,009
Add NP	r													1	,498**	-0,055	-0,038	,366**	-0,038	,352**	,433**	-0,016	,583**	,180**	-,136**
	p														0,000	0,285	0,463	0,000	0,462	0,000	0,000	0,758	0,000	0,000	0,009
Add NP/AP	r														1	-0,031	-0,019	,121*	-0,019	,116*	,152**	-0,003	,371**	0,072	-0,054
	p															0,555	0,711	0,019	0,711	0,025	0,003	0,947	0,000	0,161	0,301
Mixed tot. S=	r															1	,973**	,323**	,974**	,365**	-,601**	,150**	,298**	-,501**	0,082
	p																0,000	0,000	0,000	0,000	0,000	0,003	0,000	0,000	0,115
Mixed pyr. S=	r																1	,468**	1,000**	,496**	-,510**	,143**	,364**	-,518**	,104*
	p																	0,000	0,000	0,000	0,000	0,006	0,000	0,000	0,045
Mixed inert C	r																	1	,467**	,970**	0,087	0,036	,576**	-,214**	-,361**
	p																		0,000	0,000	0,091	0,484	0,000	0,000	0,000
Mixed AP	r																		1	,497**	-,511**	,143**	,364**	-,518**	,103*
	p																			0,000	0,000	0,006	0,000	0,000	0,046
Mixed NP	r																			1	0,023	0,041	,587**	-,234**	-,392**
	p																				0,653	0,425	0,000	0,000	0,000
Mixed NP/AP	r																				1	-0,077	,260**	,404**	0,026
	p																					0,137	0,000	0,000	0,614
%Vol Leached	r																					1	,394**	-0,088	-0,004
	p																						0,000	0,090	0,935
pH	r																						1	-,130*	-0,082
	p																							0,012	0,114
EC	r																							1	-0,085
	p																								0,100
SO4, mg/l	r																								1
	p																								

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

APPENDIX-26: The Correlation of Samples and Cement

Correlations

		Additive rate, %	Time, d	Tot. S, %	Pyr. S=, %	Inert C, %	AP, kg/ton	NP, kg/ton	NP/AP	Add Tot. S,%	Add Pyr. S=	Add Inert C	Add AP	Add NP	Add NP/AP	Mixed tot. S=	Mixed pyr. S=	Mixed inert C	Mixed AP	Mixed NP	Mixed NP/AP	%Vol Leached	pH	EC	SO4, mg/l
Additive rate, %	r	1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	1,000**	1,000**	1,000**	1,000**	1,000**	,498**	-0,068	-0,040	,341**	-0,040	,327**	,427**	-0,043	,826**	,374**	0,050
	p		1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,188	0,446	0,000	0,445	0,000	0,000	0,408	0,000	0,000	0,335
Time, d	r		1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	,112*	,143**	-0,069	0,000
	p			1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,030	0,006	0,180	1,000
Tot. S, %	r			1	,973**	,371**	,974**	,413**	-,741**	0,000	0,000	0,000	0,000	0,000	0,000	,997**	,972**	,347**	,972**	,388**	-,591**	0,066	,176**	-,489**	-0,006
	p				0,000	0,000	0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,199	0,001	0,000	0,913
Pyr. S=, %	r				1	,522**	1,000**	,548**	-,582**	0,000	0,000	0,000	0,000	0,000	0,000	,970**	,999**	,487**	,999**	,515**	-,505**	0,062	,210**	-,468**	0,064
	p					0,000	0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,235	0,000	0,000	0,214
Inert C, %	r					1	,521**	,965**	,324**	0,000	0,000	0,000	0,000	0,000	0,000	,370**	,521**	,934**	,521**	,906**	-,101*	0,014	,202**	-,134**	-,163**
	p						0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,050	0,783	0,000	0,010	0,001
AP, kg/ton	r						1	,549**	-,583**	0,000	0,000	0,000	0,000	0,000	0,000	,971**	,999**	,487**	,999**	,515**	-,506**	0,062	,210**	-,468**	0,066
	p							0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,232	0,000	0,000	0,205
NP, kg/ton	r							1	,240**	0,000	0,000	0,000	0,000	0,000	0,000	,412**	,547**	,901**	,548**	,939**	-,164**	0,039	,209**	-,157**	-0,081
	p								0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,001	0,456	0,000	0,002	0,117
NP/AP	r								1	0,000	0,000	0,000	0,000	0,000	0,000	-,738**	-,581**	,302**	-,582**	,226**	,582**	-0,061	-0,021	,394**	-0,003
	p									1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,235	0,684	0,000	0,954
Add Tot. S,%	r									1	1,000**	1,000**	1,000**	1,000**	,498**	-0,068	-0,040	,341**	-0,040	,327**	,427**	-0,043	,826**	,374**	0,050
	p										0,000	0,000	0,000	0,000	0,000	0,188	0,446	0,000	0,445	0,000	0,000	0,408	0,000	0,000	0,335
Add Pyr. S=	r										1	1,000**	1,000**	1,000**	,498**	-0,068	-0,040	,341**	-0,040	,327**	,427**	-0,043	,826**	,374**	0,050
	p											0,000	0,000	0,000	0,000	0,188	0,446	0,000	0,445	0,000	0,000	0,408	0,000	0,000	0,335
Add Inert C	r											1	1,000**	1,000**	,498**	-0,068	-0,040	,341**	-0,040	,327**	,427**	-0,043	,826**	,374**	0,050
	p												0,000	0,000	0,000	0,188	0,446	0,000	0,445	0,000	0,000	0,408	0,000	0,000	0,335
Add AP	r												1	1,000**	,498**	-0,068	-0,040	,341**	-0,040	,327**	,427**	-0,043	,826**	,374**	0,050
	p													0,000	0,000	0,188	0,446	0,000	0,445	0,000	0,000	0,408	0,000	0,000	0,335
Add NP	r													1	,498**	-0,068	-0,040	,341**	-0,040	,327**	,427**	-0,043	,826**	,374**	0,050
	p														0,000	0,188	0,446	0,000	0,445	0,000	0,000	0,408	0,000	0,000	0,335
Add NP/AP	r														1	-0,035	-0,020	,112*	-0,020	,107*	,149**	-0,001	,605**	,199**	,121*
	p															0,498	0,704	0,029	0,703	0,038	0,004	0,990	0,000	0,000	0,020
Mixed tot. S=	r															1	,973**	,323**	,973**	,365**	-,605**	0,069	,120*	-,514**	-0,021
	p																0,000	0,000	0,000	0,000	0,000	0,183	0,020	0,000	0,679
Mixed pyr. S=	r																1	,474**	1,000**	,502**	-,509**	0,063	,179**	-,484**	0,049
	p																	0,000	0,000	0,000	0,000	0,222	0,000	0,000	0,348
Mixed inert C	r																	1	,473**	,969**	0,076	-0,011	,446**	-0,001	-,145**
	p																		0,000	0,000	0,144	0,835	0,000	0,978	0,005
Mixed AP	r																		1	,502**	-,510**	0,064	,179**	-,484**	0,050
	p																			0,000	0,000	0,219	0,000	0,000	0,335
Mixed NP	r																			1	0,011	0,013	,442**	-0,030	-0,071
	p																				0,825	0,808	0,000	0,565	0,171
Mixed NP/AP	r																				1	-0,079	,289**	,420**	,135**
	p																					0,126	0,000	0,000	0,009
%Vol Leached	r																					1	0,028	-0,047	0,043
	p																						0,589	0,361	0,405
pH	r																						1	,245**	,125*
	p																							0,000	0,015
EC	r																							1	-0,004
	p																								0,945
SO4, mg/l	r																								1
	p																								

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

APPENDIX-27: The Correlation of Samples and Bentonite

Correlations

		Additive rate, %	Time, d	Tot. S, %	Pyr. S=, %	Inert C, %	AP, kg/ton	NP, kg/ton	NP/AP	Add Tot. S,%	Add Pyr. S=	Add Inert C	Add AP	Add NP	Add NP/AP	Mixed tot. S=	Mixed pyr. S=	Mixed inert C	Mixed AP	Mixed NP	Mixed NP/AP	%Vol Leached	pH	EC	SO4, mg/l
Additive rate, %	r	1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	1,000**	1,000**	1,000**	1,000**	1,000**	,498**	-0,072	-0,039	-0,033	-0,039	-0,037	0,047	-0,008	0,006	,129*	,475**
	p		1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,164	0,451	0,524	0,450	0,478	0,360	0,873	0,908	0,012	0,000
Time, d	r		1	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,094	,545**	-,216**	0,000
	p			1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	0,070	0,000	0,000	1,000
Tot. S, %	r			1	,973**	,371**	,974**	,413**	-,741**	0,000	0,000	0,000	0,000	0,000	0,000	,997**	,972**	,371**	,972**	,413**	-,756**	0,061	,506**	-,520**	-,464**
	p				0,000	0,000	0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,236	0,000	0,000	0,000
Pyr. S=, %	r				1	,522**	1,000**	,548**	-,582**	0,000	0,000	0,000	0,000	0,000	0,000	,970**	,999**	,521**	,999**	,547**	-,598**	0,054	,523**	-,526**	-,349**
	p					0,000	0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,295	0,000	0,000	0,000
Inert C, %	r					1	,521**	,965**	,324**	0,000	0,000	0,000	0,000	0,000	0,000	,370**	,521**	,999**	,521**	,964**	,290**	0,009	,625**	-,240**	,145**
	p						0,000	0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,868	0,000	0,000	0,005
AP, kg/ton	r						1	,549**	-,583**	0,000	0,000	0,000	0,000	0,000	0,000	,970**	,999**	,521**	,999**	,548**	-,599**	0,055	,524**	-,526**	-,348**
	p							0,000	0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,291	0,000	0,000	0,000
NP, kg/ton	r							1	,240**	0,000	0,000	0,000	0,000	0,000	0,000	,412**	,547**	,964**	,548**	,999**	,206**	0,034	,667**	-,267**	,181**
	p								0,000	1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,518	0,000	0,000	0,000
NP/AP	r								1	0,000	0,000	0,000	0,000	0,000	0,000	-,738**	-,581**	,323**	-,582**	,240**	,996**	-0,062	-,138**	,340**	,602**
	p									1,000	1,000	1,000	1,000	1,000	1,000	0,000	0,000	0,000	0,000	0,000	0,000	0,228	0,007	0,000	0,000
Add Tot. S,%	r									1	1,000**	1,000**	1,000**	1,000**	,498**	-0,072	-0,039	-0,033	-0,039	-0,037	0,047	-0,008	0,006	,129*	,475**
	p										0,000	0,000	0,000	0,000	0,000	0,164	0,451	0,524	0,450	0,478	0,360	0,873	0,908	0,012	0,000
Add Pyr. S=	r										1	1,000**	1,000**	1,000**	,498**	-0,072	-0,039	-0,033	-0,039	-0,037	0,047	-0,008	0,006	,129*	,475**
	p											0,000	0,000	0,000	0,000	0,164	0,451	0,524	0,450	0,478	0,360	0,873	0,908	0,012	0,000
Add Inert C	r											1	1,000**	1,000**	,498**	-0,072	-0,039	-0,033	-0,039	-0,037	0,047	-0,008	0,006	,129*	,475**
	p												0,000	0,000	0,000	0,164	0,451	0,524	0,450	0,478	0,360	0,873	0,908	0,012	0,000
Add AP	r												1	1,000**	,498**	-0,072	-0,039	-0,033	-0,039	-0,037	0,047	-0,008	0,006	,129*	,475**
	p													0,000	0,000	0,164	0,451	0,524	0,450	0,478	0,360	0,873	0,908	0,012	0,000
Add NP	r													1	,498**	-0,072	-0,039	-0,033	-0,039	-0,037	0,047	-0,008	0,006	,129*	,475**
	p														0,000	0,164	0,451	0,524	0,450	0,478	0,360	0,873	0,908	0,012	0,000
Add NP/AP	r														1	-0,036	-0,020	-0,020	-0,020	-0,022	0,017	0,036	0,065	,131*	,372**
	p															0,482	0,706	0,700	0,706	0,675	0,750	0,493	0,211	0,011	0,000
Mixed tot. S=	r															1	,973**	,373**	,973**	,414**	-,755**	0,062	,503**	-,526**	-,494**
	p																0,000	0,000	0,000	0,000	0,000	0,228	0,000	0,000	0,000
Mixed pyr. S=	r																1	,522**	1,000**	,549**	-,598**	0,055	,522**	-,529**	-,367**
	p																	0,000	0,000	0,000	0,000	0,287	0,000	0,000	0,000
Mixed inert C	r																	1	,522**	,965**	,290**	0,009	,624**	-,244**	,118*
	p																		0,000	0,000	0,000	0,862	0,000	0,000	0,022
Mixed AP	r																		1	,549**	-,599**	0,055	,523**	-,529**	-,366**
	p																			0,000	0,000	0,284	0,000	0,000	0,000
Mixed NP	r																			1	,205**	0,034	,665**	-,271**	,153**
	p																				0,000	0,508	0,000	0,000	0,003
Mixed NP/AP	r																				1	-0,063	-,169**	,354**	,623**
	p																					0,226	0,001	0,000	0,000
%Vol Leached	r																					1	,143**	-0,090	0,014
	p																						0,005	0,081	0,780
pH	r																						1	-,463**	-,108*
	p																							0,000	0,037
EC	r																							1	,239**
	p																								0,000
SO4, mg/l	r																								1
	p																								

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

APPENDIX-28: TAD Results of Waste Samples and Compared with Earth's Crust Level and SQuiRTs Chart

	TOTAL ACID DIGESTION (ppm)						*Earth's crust Average. ppm dw	BACKGROUND[1]		DUTCH STANDARDS[2]		ECO-SSL[3]				
Elements	**K1**	**K2**	**K3**	**K4**	**K5**	**K6**		MEAN	RANGE	TARGET	INTERVENTION	Avian	Invert s	Mammal s	Plant s	Microbe s
Al	1.311.06	883.56	2.878.71	370.26	1.150.48	15.669.64	82.300	47000	0.5->100000						50	600
As	**3.248.45**	**4.772.08**	**2.856.23**	**7.643.35**	**6.349.44**	**2.372.66**	1.8	5.2	bdl*-97	0.9	55	43	60	5.7	18	100
Ba	108.49	81.32	37.70	6.21	28.39	**555.91**	425	440	10-5000	160	625		330	1.04	500	3000
Ca	**93.488.97**	**55.873.76**	**58.669.49**	**46.042.52**	**57.230.88**	**46.295.80**	41.500									
Cd	**37.50**	**305.45**	**322.71**	**264.00**	**282.14**	**152.38**	0.15			0.8	12	0.77	20	0.00222	4	20
Cr	5.46	1.54	8.98	1.57	4.56	59.75	102	<37	1-<2000	<0.038 L**	<220 L	26	< 0.4	34	< 1	<10
Cu	**829.38**	**1.394.77**	**2.031.70**	**718.14**	**1.184.68**	**2.638.74**	60	17	bdl-700	3.4 L	96	28	50	5.4	70	100
Fe	**83.340.52**	**114.287.47**	**98.268.41**	**210.112.02**	**181.303.06**	**172.891.65**	56.300	18000	0.01->100000							200
K	2.682.12	2.337.33	915.47	224.68	664.76	12.254.55	20.900									
Mo	**2.64**	**3.34**	**2.66**	**1.25**	0.70	-	1.2	0.59	bdl-15	3	190 L				2	200
Na	4.180.77	3.751.25	3.480.29	3.293.99	3.557.52	3.823.77	23.600									
Ni	-	2.04	14.66	24.83	19.16	10.39	84	13	bdl-700	0.026 L	100 L	210	200	13.6	30	90
Pb	**56.698.38**	**99.173.08**	**40.339.66**	**23.323.02**	**42.084.38**	**28.131.91**	14	16	bdl-700	55 L	530	11	500	0.0537	50	900
Sb	**292.84**	**851.03**	**215.36**	**246.18**	**310.50**	**47.00**	0.2	0.48	bdl-8.8	3	15		78	0.142	5	
Zn	**8.829.41**	**45.481.17**	**52.293.12**	**38.996.21**	**43.075.96**	**68.545.37**	70	48	bdl-2900	16 L	350 L	46	6.62		50	100

*bdl: Below Detection Limit

** L : Environmental Risk Limit

1: USGS Prof. Paper 1270. 1984.

2: Dutch Standards. Ecotoxicological Serious Risk Concentrations for soil. sediment and (ground) water: updated proposals for first series of compounds (RIVM)

3: ECO-SSL: ECOTOX/Ecological Soil Screening Levels (from EPA)

APPENDIX-29: TAD Results of Binding Materials and Compared with Earth's Crust Level and SQuiRTs Chart

	BINDING MATERIALS (ppm)				*Earth's crust Average. ppm dw	BACKGROUND		DUTCH STANDARTS		ECO-SSL				
Elements	**MARBLE DUST**	**CEMENT**	**ASH**	**BENTONITE**		MEAN	RANGE	TARGET	INTERVENTION	Avian	Inverts	Mammals	Plants	Microbes
Al	8.45	2.131.46	2.840.38	8.354.44	82.300	47000	0.5->100000						50	600
As	-	**4.81**	-	-	1.80	5.2	Bdl*-97	0.9	55	43	60	5.7	18	100
Ba	9.74	33.20	29.85	162.95	425	440	10-5000	160	625		330	1.04	500	3000
Ca	-	-	-	10.375.42	41.500									
Cd	-	-	0.07	-	0.15			0.8	12	0.77	20	0.00222	4	20
Cr	0.25	4.46	20.57	13.28	102	<37	1-<2000	<0.038 L**	<220 L	26	< 0.4	34	< 1	<10
Cu	0.58	0.58	2.71	34.17	60	17	bdl-700	3.4 L	96	28	50	5.4	70	100
Fe	-	1.369.77	2.272.44	8.697.08	56.300	18000	0.01->100000							200
K	-	765.45	345.48	1.186.14	20.900									
Mo	0.11	0.15	**1.60**	**1.78**	1.20	0.59	bdl-15	3	190 L				2	200
Na	455.58	463.61	413.24	3.216.95	23.600									
Ni	-	2.70	10.18	-	84	13	bdl-700	0.026 L	100 L	210	200	13.6	30	90
Pb	-	-	-	-	14	16	bdl-700	55 L	530	11	500	0.0537	50	900
Sb	**0.62**	**0.47**	**0.65**	-	0.20	0.48	bdl-8.8	3	15		78	0.142	5	
Zn	-	-	-	-	70	48	bdl-2900	16 L	350 L	46	6.62		50	100

*bdl: Below Detection Limit

** L : Environmental Risk Limit

1: USGS Prof. Paper 1270. 1984.

2: Dutch Standards. Ecotoxicological Serious Risk Concentrations for soil. sediment and (ground) water: updated proposals for first series of compounds (RIVM)

3: ECO-SSL: ECOTOX/Ecological Soil Screening Levels (from EPA)