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# Thickener Water Neutralization by Mid-Bottom and Fly Ash of Thermal Power Plants and CO<sub>2</sub>: Organic Humate Mud of AMD Treatment for Remediation of Agricultural Fields

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Yıldırım İsmail Tosun

Additional information is available at the end of the chapter

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## Abstract

Coal mining sites and copper sulphide mines caused polluting acidic mine waters. Acidic mine drainage (AMD) into the natural streams and agricultural field irrigation waters causes environmental pollution with dissolved contents having heavy metals or acidic aqueous solutions of habitats and living fish in the local ponds and irrigation ponds. It is necessary to collect the polluted mine waters in the impermeable ponds and treat or neutralize the acidic character by the aeration treatment and subsequently discharge to the stream waters. This study introduced chemical neutralization and aeration treatment of polluted acidic waters in Şırnak Coal Mine site and Siirt Copper Concentrator site as happens in wastewaters of chemical industries and textile processing plants. The construction engineering of collector ponds was also so much critical in the point of cost of a case remediation model and muddy fertilization by Şırnak Thermal Power Plant waste, bottom ash, and fly ash in agricultural fields soil in Şırnak Coal Mine site, and how these facts may affect the possibility of remediation in the future were discussed. Organic fertilizer matter of fumatic acid and humic acid containing humate formed. Soil remediation process for both muddy bottom precipitates of treatment pools and aeration pools was collected and treated by CO<sub>2</sub> saturated waters. The comparison of the common methods is described and discussed with fly ash utilization and CO<sub>2</sub> gas of power plants containing alkali matter improved neutralization and carbon matter of soils.

**Keywords:** acid mine drainage, geochemistry, soil remediation, restoration, construction

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## 1. Introduction

Acid mine drainage brings out great environmental issue of acidic metallic sulfate rich wastewaters. Those type wastewaters are also the wastewaters of a variety of industrial

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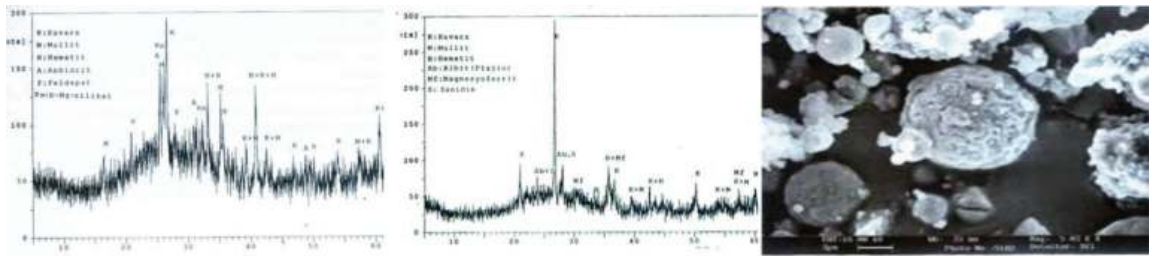
operations such as galvanizing, leaching, and the scrubbing of flue gases at thermal power plants [1–5]. The fundamental reasons of such wastewaters are under the agricultural and environmental concern occurring in the mining industry. Waters draining active and abandoned mines and mine wastes are often below pH 4 as low as sulphatic polluted (extremely so acidic). Such waters typically cause an additional risk to the environment by the fact that they often contain elevated concentrations of metals (iron, aluminium and manganese, zinc and copper, possibly Hg and Pb, and other heavy metals) and metalloids (arsenic and sulfur). The environmental issue caused by mine water discharges is difficult to manage accurately. It is generally preferable to prevent acidic water source by collector pools and settling the mud, although not always pragmatic, to preclude the formation of acidic mine drainage (AMD) in the first instance. Such techniques are known collectively as bsource control the precautive measures (**Figure 1**) and will be described only briefly [6–9].

In the formation of AMD, both oxygen and water affect to metal dissolution. The proposed precautions follow that by excluding either of these, it is necessary to prevent or minimize AMD production. The common method is practiced by sealing hazardous sites. The oxygen available in the slurry is utilized by oxidizing bacteria present, and completion of dissolved  $O_2$  by mass transfer, and diffusion is delayed by sealing the wastewaters. This is seen in the location of all contaminated seepage waters. Water storage was used for disposing and storing mine tailings that are potentially acid producing [10]. However, the main goal is to reduce the contact between the minerals and dissolved oxygen. Wastewater is chemically covered, or their reactivity is decreased by covering the waste material with a layer of sediment clay or organic material, beneficial on oxygen elimination and improved carbon dioxide gas diffuse [11–13].

The additives such as clay bentonite or diatomite provide protective cover on the tailings because of the actions of slurry mixing (**Figure 2**). Clay top covers of reactive wastes and sulphidic mineral mixtures may cause clayish organic layer. The sealing layer that covers the waste slime is usually constructed from clay. In wet and dry conditions, drying and cracking of the cover might present less effective precaution at the urbanization zones [14, 15].



**Figure 1.** The lake area of AMD in Çan and satellite image AMD lake in the Sırnak Coal Mine Site, pool remediation [9].



**Figure 2.** The X-ray diffractometer diagrams of Orhaneli and Seyitömer Fly Ash, SEM picture of fly ash in the Şırmak Coal Mine Site [6, 9].

The unsettling rust color of the water also served to make acid mine drainage an easy/prime target for environmental agencies around the world. However, when mines are closed and abandoned, and pumps are turned off, the rebound of the water table can lead to contaminated groundwater being discharged, sometimes in a catastrophic event such as the one that happened at the Wheal Jane mine in 1992 when a range of contaminants entered the environment [1, 5–14, 16]. As the water that refills the mine dissolves any acidic salts that have built up on the pore spaces of the exposed walls and ceilings of underground chambers.

Another suggested approach for minimizing AMD production is to blend acid-generating and acid-consuming materials, producing environmentally benign composites [16, 17]. A variant on this case is to add solid sorbents such as phosphates salts, fly ash, and apatite to acidic mine waste in order to precipitate iron (III) as ferric phosphate, thereby reducing its potential to act as an oxidant of sulfide minerals. The magnesium or calcium salts, phosphate minerals, or availability of soluble phosphate (together with hydrogen peroxide) eliminates oxidation of pyrite, producing ferric iron, which reacts with the phosphate to produce a surface protective coating of ferric ion [18]. An alternative technique involving the formation of an iron oxide/silica coating on pyrite surfaces has also been described. The kinetics of microorganism growth and act was critical in a month time period and over. However, certain time of season period of temperature and oxidation time was observed as followed 6 months' time duration by moisture even in the drought zone.

The lithotrophic iron- and sulfur-oxidizing bacteria had a main role in generating acidic waters in various laboratory tests and geothermal springs. The inhibitors or conditions eliminated their activities in mineral slimes and tailings. The anionic surfactants such as sodium dodecyl sulfate (SDS) are highly toxic to this group of bacteria [12, 13]. Chemolithotrophic thiobacillus type organisms needed low pH under 2 and higher temperatures for thermophilics for sulfuric acid production in the commence of oxidation reactions on complex sulphide ores.

However, the effectiveness of biocide applications has been found to be highly variable affording, at best, only short-term control of the problem and requiring repeated applications

of the chemicals [19]. While the practical difficulties prevailed in inhibiting the formation of AMD at source, often, the method is to minimize the impact that this polluting water has on receiving streams and rivers, and the wider environment; such an approach involves. It has been divided into active and passive processes. In general, concerned main effect of alkali materials is to neutralize acidic mine waters and precipitation of metal salts, by-product mud to the use of natural reconstruction of ecology in this studied project. The passive irrigation channels and pools were feasible for high flow rate slurries in the site requiring relatively little maintenance than active systems. In truth, the practiced passive treatment method in the projected site required a certain amount of maintenance costs.

## 2. Utility of fly ash and mid-bottom ash

Fly ash is formed by keeping the particles in the flue gases in the electric filters while burning the pulverized coal in the thermal power plant boilers alone. It is possible to obtain the following three different yields from the coal. Base Ash, which is relatively coarse and cannot be transported by flue gas. Mid Ash, which burned in cyclone type boilers. Fly Ash, which is very fine grained and transported with flue gases. The fly ashes are collected mechanically and electrostatically and stored in the vicinity of the plant or in other convenient places. For the purpose of collecting ash, the ashes accumulate in large areas and become a problem for the plant management.

The amount of fly ash yielded in the world is about 600 million tons per year. Almost 26 thermal power plants are currently operating in Turkey, including Afşin-Elbistan, Çatalağzı, Kangal, Kemerköy, Orhaneli, Seyitömer, Soma, Tunçbilek, Yatağan, and Yeniköy. The average annual fly ash production from these plants is about 13 million tons, but the annual rate varies with the introduction of natural gas power plants. One way of reducing the country's external dependence on energy production is to use low-calorie lignite coals in thermal power plants, which cannot be used in other parts of the industry. Therefore, the annual fly ash amounts are expected to increase further in the future. The X-ray diffractogram of the mineralogical composition of the Orhaneli Thermal Power Plant fly ash is given below. According to this, it is understood that the main phase of the Orhaneli fly ash is the glassy phase. In addition to the glassy phase, it is also found that there are crystallized phases such as quartz, mullite, hematite, anhydrite, sanidine, and K-Fe silicate. The main phase is the glassy phase in the X-ray diffractogram of the Orhanli fly ash, the background is generally in a high position. However, especially, in the  $23-27^{\circ}2\theta$ , the background showed a significant increase. In the chemical analysis, as the  $\text{SiO}_2$  48.53% and  $\text{Al}_2\text{O}_3$  24.61% were found in the volumetric cluster, the shift toward  $27^{\circ}2\theta$  was more  $\text{Al}_2\text{O}_3$  and CaO (9.48%) (Table 1). The X-ray diffractogram of the mineralogical composition of the Seyitömer Thermal Power Plant fly ash is given in Figure 2. As can be seen in the volcanic core, there are primarily glassy phases, quartz, mullite, magnesioferrite, hematite crystals, and alkali feldspars as minor. In the X-ray diffractogram of the Seyitömer fly ash, the glassy phase gave the maximum between 22 and 25, and the view

	Afsin Elbistan	Orhaneli	Yatağan	Seyitömer	Şırnak	ASTM C616 F	ASTM C616 C
SiO <sub>2</sub>	34.11	48.71	52.3	54.11	40.71		
Al <sub>2</sub> O <sub>3</sub>	10.58	24.53	23.2	20.58	11.53		
Fe <sub>2</sub> O <sub>3</sub>	4.33	7.62	5.9	9.33	5.62		
S + A + F	74.52	81.46	81.7	84.52	88.6	≥70	≥50
CaO	24.72	9.56	10.1	4.72	19.56		
MgO	3.33	2.41	2.4	4.33	2.41	≤5	≤5
SO <sub>4</sub>	2.72	3.02	1.5	0.72	1.02	≤5	≤5
KO	1.10	2.44	2.8	2.10	2.44		
Na <sub>2</sub> O	0.57	0.37	1.9	0.67	0.55		
Ignition Loss	4.22	1.74	0.9	3.22	4.74	≤ 6 ≤ 10(TSE639)	≤ 6 ≤ 10(TSE639)
Cl	0.006	0.005	0.0	0.006	0.0		
Free CaO	1.72	1.13	0.3	1.72	3.13		
React. SiO <sub>2</sub>	19.8	34.12	30.1	39.8	34.12		
React. CaO	13.16	6.72	7.1	2.16	12.72		

**Table 1.** The chemical analysis of utilized fly ash in the clarification of water pool in the Şırnak Coal Mine Site, fishery pool remediation [6, 9].

was glassy rich. In this case, the vitreous phase shows a siliceous character due to the quartz crystal being close to the maximum peak (**Figure 2**) [6, 9].

As a result of the morphological examination of the Orhanli flywheel, it was observed that the majority of spheroids ranging in size from 0.5 to 15 µ were regular spherical particles. Full spherical vitreous solid particles come into play due to the rapid cooling of the droplets that form as a result of the majority (clay) of the minerals in the coal due to the high temperature reached during the burning of the car. In addition to these, plospores with a hollow cavity and a cluster of microspheres are also encountered. In addition, conchoidal quartz crystals, surface anhydrite-coated particles, and fine prismatic mullite crystals have been identified in the microstructure. The result of the separation of the reactive glassy phase after the dissolution of the mullitic crystals in the ash acid has been revealed. The finely dispersed mullite is formed by partial crystallization of the vitreous phase consisting of aluminosilicate; in the senosphere, Quartz crystals have been added to the volatile compounds during their burning due to their high thermal stability, leaving the environment and partially protecting the original structures (conkoidal). Some spheres have accumulated anhydrous (cubic) and hematite (fine crystallized) deposits on the surface. The chemical characteristics of Şırnak and other fly ash and mid-bottom ash are illustrated in **Figure 3** used in AMD remediation. The increased iron and zinc contents of fly ash for neutralization decreased the effectivity in waste treatment due to acidic manner of composition dissolved in wastewater slurries by diminishing alkali reactions in the pool, while lighter heavy metals such as Pb and Zn should preferred in neutralization act on wastewaters in Şırnak Coal Mine site [6, 9].



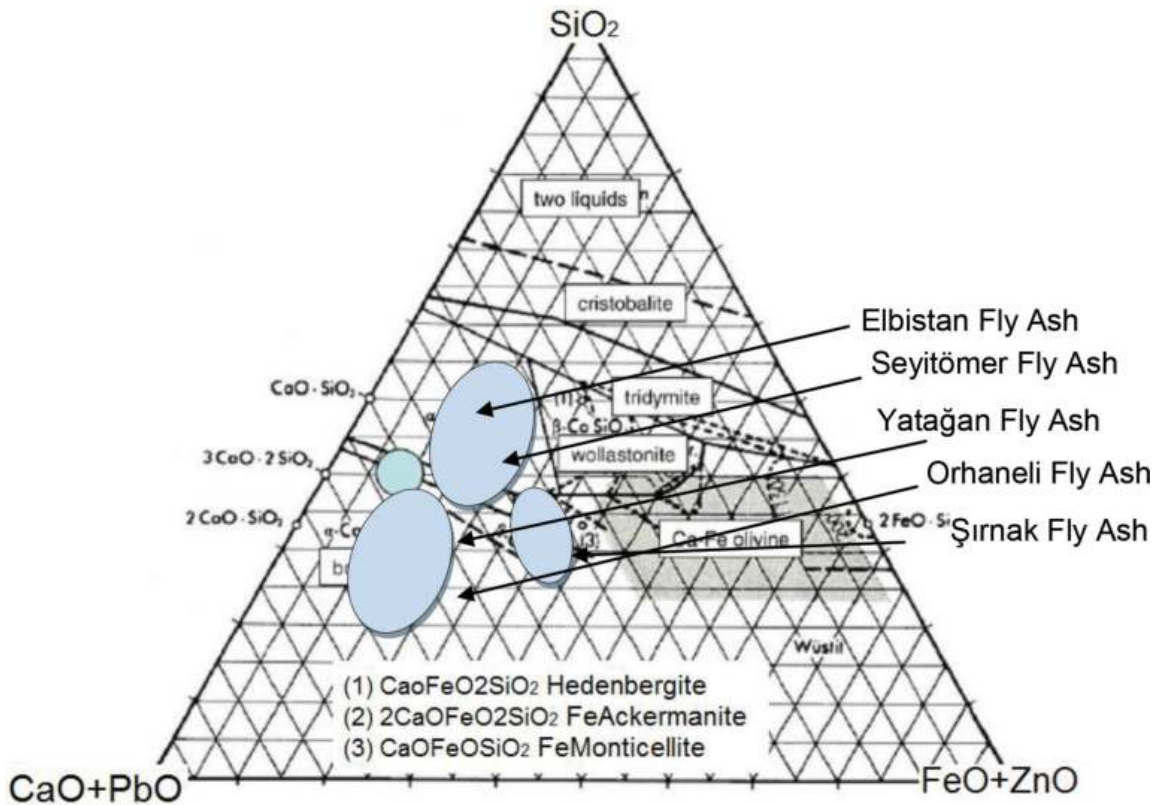


Figure 3. The chemical phase diagram of Şırnak Coal Mid Ash and Fly Ash used in remediation.

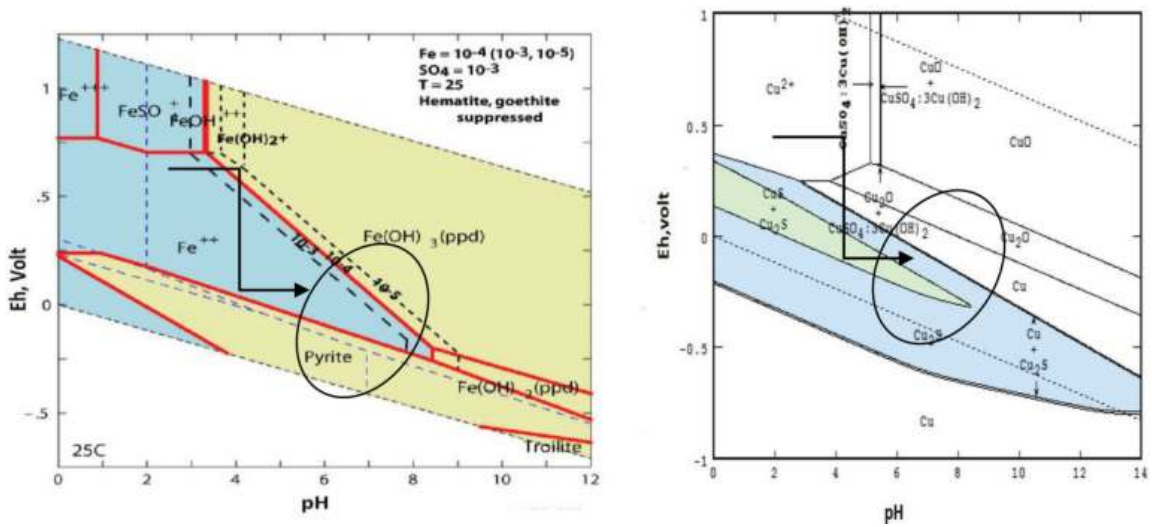
### 3. AMD waste treatment

The chemical reactions are following the paths as seen in **Figure 4**. The Fe and Cu sulfur matter oxidation potential for the first are shown, respectively. Many aquifers have oxidation states low enough to reach the threshold for these reactions to occur.

The value of pH required to induce precipitation may increase by neutralization in aqueous euphotropic waters and lake. However, despite the general importance of pH in an AMD treatment systems, it is not the only fundamental neutralization for metal removal, but also ionic strength, temperature, Eh, and concentrations of suitable complexing agents may change the precipitation. Treatment sludges therefore include the well-known crystalline form of goethite but consist mainly of highly amorphous oxy and hydroxyl iron oxides.

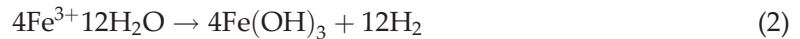
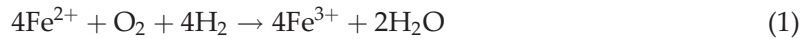
#### 3.1. Active technology

The common method used to treat acidic effluents is an active treatment process involving neutralization work reagent [20–25]. Addition of an alkali to AMD wastewaters easily changes the pH and commence of chemical oxidation on active aeration. While addition of a chemical promoter such as hydrogen peroxide is also beneficial, it causes the common metals present in solution to precipitate as hydroxides and carbonates. The active neutralization by alkali



**Figure 4.** The Eh-pH phase diagrams in the Fe-S-O-H and Cu-S-O-H system with lg [Fe], lg [S] and Eh as coordinates at the pH 5 and pH 7.5 [19].

matters is governed by the reactions given below Eqs. (1) and (2), as respected oxidation ferrous iron to ferric state was rate controlled on the concentration in the solute. The direct neutralization could be managed by settling of wastewaters during clarification by alkali sorbents (**Figures 5 and 6**). The lamelle settlers provide much settling area per flow rate wastewaters containing less solids.

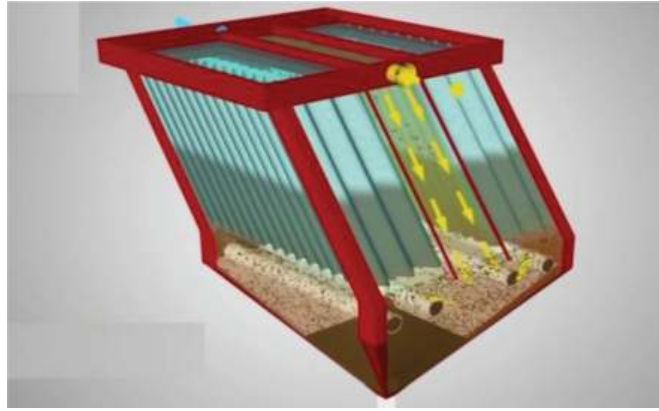


### 3.2. Passive technology

Ammonification occurs as an alkali yield process. Due to the lack of materials such as nitrate, the nitrification and ammonification are so slow and have minor importance in AMD waters and environments [26–32]. However, since both ferric iron and sulfate tend to be highly



**Figure 5.** The thickener clarification of AMD water in the Sınak Coal Mine Site for fishery pool remediation e<sup>-</sup>.

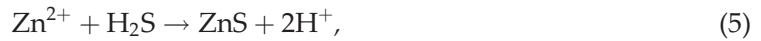


**Figure 6.** The Lamelle Thickening in AMD Water Treatment.

abundant in AMD seepage, alkali resulting from the reduction of these two species, a weak base (bicarbonate) and producing a strong base (hydroxyl ions), also generate net alkalinity (Eq. 3). The indirect acid production was relatively high at higher pH levels over 5 with dissolution of heavy metals in sulphide minerals, and neutralization by alkali matters governs the dissolution by the reactions given below:



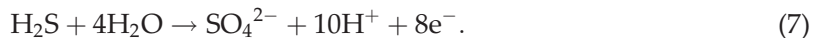
The sulfide produced is strongly reactive toward heavy metals as given in Eqs. (4) and (5):



which form very insoluble sulfide compounds. FeS is unstable relative to pyrite and the further reaction, which is an oxidation of  $\text{S}^{2-}$  to  $\text{S}^0$ , as given in Eq. (6):



generated in the late muds close to the settled mud–water interface. ZnS and PbS, in the sulphide complex structure, are much stable and retain S in the  $-2$  state. However, the sulfate part of reaction (Eqs. (7) and (8)) may cause redox effect an oxidation. Then

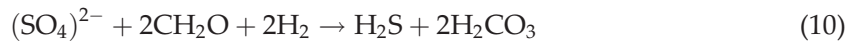


The precipitation of ferric iron does not decrease solution acidity, and the reverted ferrous iron as indicated in Eq. (9) generally is supplied by inorganic surface.



Bacteria that catalyze the dissimilatory reduction of sulfate to sulfide generate alkalinity by transforming a strong acid (sulfuric) into a relatively weak acid (hydrogen sulfide; Eq. (10)).





Besides the neutralization of AMD, the passive act results an increase in pH, the reduction of sulfate is an important mechanism in eliminating toxic metals from AMD seepage, since as many (e.g., lead, zinc, copper, and cadmium) form highly insoluble sulfides (e.g., Eq. (11)).

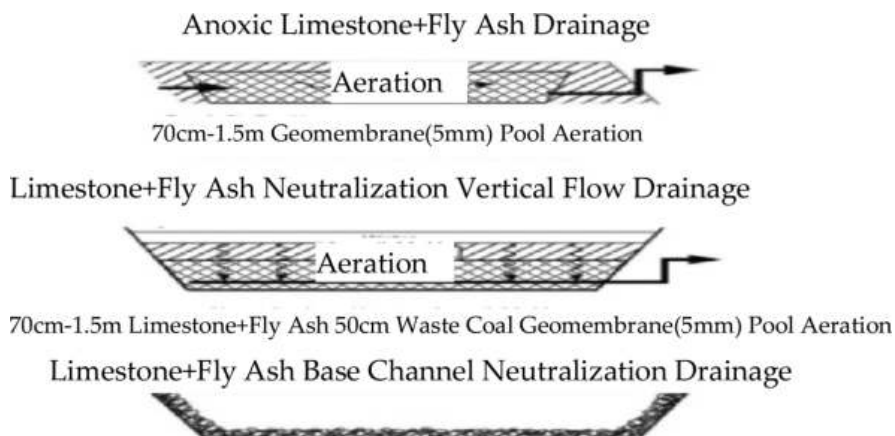


Biological oxidation of ferrous iron to ferric (which is highly insoluble above pH 2.5) is the other major metal-immobilizing process that occurs in aerobic wetlands and bioreactors. As shown in **Figure 7**, most microorganisms' act is a slow passive system. The constructed wetlands or compost bioreactors have been unfeasible for high flow rated wastes in full-scale. The basic advantage of passive bioremediation is relatively low maintenance costs. Due to the fact that the mud products of sludge are retained within the wetland sediments, the treatment handling is expensive. The landfill area available to install is higher than chemical treatment systems, and the long-term accumulation of wastes within the pools is uncertain [2, 33–37].

Passive bioremediation systems that utilize a combination of aerobic and anaerobic wetlands have been used for full-scale treatment of AMD. An example is the acid reduction using microbiology (ARUM) system [7, 9, 38–41]. Bioremediation and anoxic treatment of Şirnak Coal Mine acidic waters were carried out by limestone, fly ash, and waste coal layer aeration pools as illustrated in **Figure 7** [7, 9]. While there is insufficient alkalinity in the mine water to prevent a significant fall in pH, the kinetics of oxidation is controlled by the Eq. (12):

$$\frac{dC(\text{Fe}_2\text{O}_3)}{dt} = k^{1/2} \text{CO}_2 C(\text{Fe})^{2+} C(\text{SO}_4)^{2-} \quad (12)$$

This iron is oxidized and precipitated and followed by AMD passes first through ARUM cells, alkali and sulfide are generated. The ARUM systems showed to be effective in treating AMD in high latitude and subtropical locations [7, 42]. The passive treatment plant at the Wheal Jane site is also a composite system. The by-product of AMD treatment, zinc sulfide produced fed into the pool and reduced into the metallic zinc product from the plant [36, 43–45].



**Figure 7.** The Methods of Passive Limestone and Fly ash Use in AMD water Neutralization.

Sulfate-reducing bacteria (SRB) are heterotrophic bacteria and, the iron-oxidizing acidophiles, require provision of organic material such as carbon and sulfur. Hydrogen in the form of ethanol may substitute as energy for sulfate reduction and reductive act in acidic mine drainage waters as given in Eq. (13).



The use of hydrogen is advantageous instead of high sulfate loadings and results in lesser bacterial organic biomass contamination. However, hydrogen use in natural full scale, at high flow rated wastewaters, may not be feasible. In both cases, carbon dioxide is also produced, and some SRB can fix this as their source of carbon [46–50].

#### **4. Projected case for Şırnak coal site and Siirt copper mine AMD treatment: Organic soil mud**

This investigation of water clarification, neutralization, and organic humate mud yield was extremely useful in wastewater management strategies by reclaiming existing agricultural irrigation and water logged areas. The problems of water use and quality mostly exist in the irrigated areas like in South Eastern rocky plains of Şırnak, Turkey. The climate change and groundwater changes generally results in over irrigation, seepage losses through channel and distributions, poor water management practices, and inadequate control of drainage system. Analysis of high water table in water logged areas and drainage of irrigated areas have not been paid adequate attention in the planning and management of water resources, partly due to lack of requisite data and partly due to flood and contamination in the country. In order to develop suitable water management strategies, the area needed to control the extent of contamination and waste logging in the area. Geographic information system (GIS) may facilitate the reconstruction of the ecological environment but also to accommodate the sustainable development of the water resources and wastewater. For the treatment of wastewaters seepages, leaks of municipal wastes were planned to treat by neutralization at first. Clarification was designed by followed neutralization employed on ash and local limestones in thickeners. The local pools could be beneficial later for humate anaerobic digestion on the quality of humate mud yield. However, all these process units were needed to control metal contents in the water paths and muddy wastes.

##### **4.1. Thickening neutralization by fly ash**

Acid mine drainage brings out great environmental issue of acidic metallic sulfate rich wastewaters. Those type wastewaters are also the by-products of a variety of industrial operations such as galvanizing, leaching, and the scrubbing of flue gases at thermal power plants (**Figure 8**). The major producer of such wastewaters is under the agricultural and environmental concern occurring in the coal and copper mining. In particular, abandoned mines seepage waters and copper mines wastewaters are often acidic. Those wastewaters cause an extra risk to the environment. They often contain high concentrations of metals (iron, lead, cadmium,



Figure 8. The satellite image of MD clarified water pool in the Sirnak Coal Mine Site, fishery pool remediation.

zinc, aluminium, manganese, and rarely other heavy metals) and hazardous arsenic. AMD (Figure 9) waters damage as mine effluents. Although the true scale of the environmental pollution is caused by mine wastewaters, fly ash use on common discharges is difficult to assess accurately.

Acidic metal-rich waters may also form in spoil heaps and mineral tailings, essentially by the same biologically driven reactions as in mine shafts and adits. Due to the more disaggregated (and more concentrated, in the case of tailings) nature of the acid-generating minerals in these

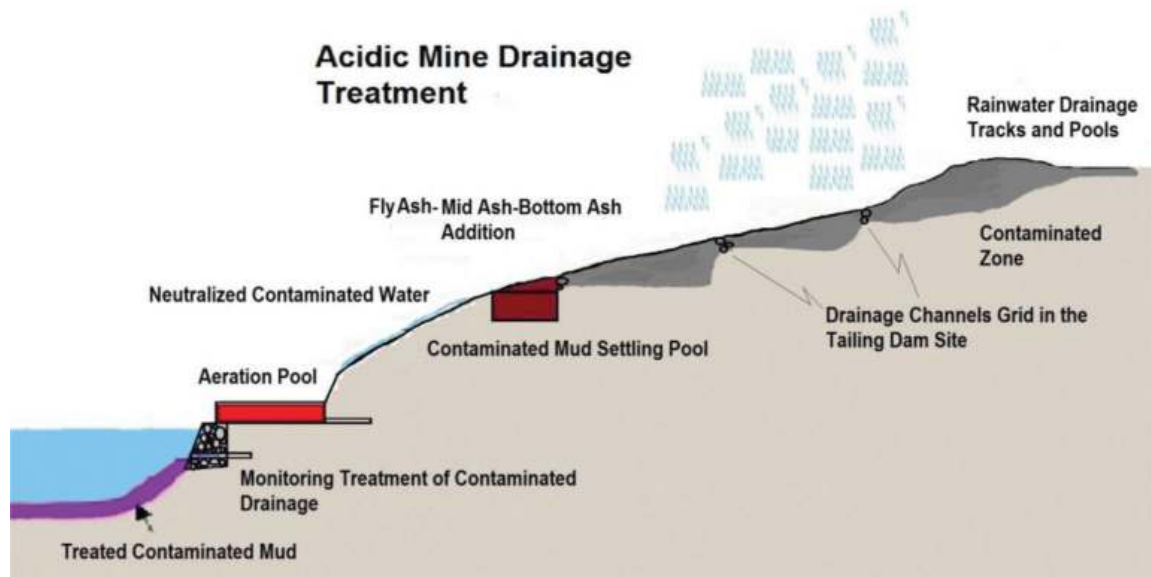


Figure 9. Acid mine drainage, contaminated water treatment by fly ash and neutralization by fly ash and mid-bottom ash of thermal power plants.

waste materials, the scanning electron microscopy pictures showed the Ca ferrites and active lime powders, which were effective in neutralizations.

AMD flowed from seepage channels was more aggressive than the discharges from the concentrator and ore stock site. Another critical concern was the potential of controlling the long-term contamination of agricultural irrigation water and soil contamination. The treatment of AMD waters in cycling manner between the slime ponds would continue for many years after the asphaltite extraction in mines stopped and tailing dams demolished. Although the neutralization pH of these waters was simple and above 6, particularly at the cycling depth (where dissolved oxygen concentrations was low), the metals such as the iron, zinc, and aluminium were dissolved and also the fly ash and bottom ash yielded local area as waste [9]. The ash reacted on neutralization caused reduced ( $Fe^{2+}$  and  $Mn^{2+}$ ) ionic states in anoxic AMD waters, and these forms of the metals were much stable at higher pH than the fully oxidized ( $Fe^{3+}$  and  $Mn^{4+}$ ) ions. The higher content of fly ash resulted in the AMD streams remained neutral-to-alkaline. Net acidity in AMD needs to be offset against any alkalinity of fly ash presented this was chiefly in the form of bicarbonate ( $HCO_3^-$ ) deriving from the dissolution of basic minerals (e.g., calcium carbonate), though, as noted below, biological processes may also generate alkalinity in AMD streams.

**4.2. Thickener sedimentation**

Fly ash slurries were collected in water pools and pumped to clarifiers for settlement and separation from alkali solutions as paste fine materials sedimentation and the settling of solid matter occur as below (Figure 10):

$$v_t = g \left( \frac{\rho_s - 1}{18\mu} \right) d_p^2 \quad Re \leq 2 \tag{14}$$

$$v_t = 0,13 (g(\rho_s - 1))^{0,72} d_p^{1,18} \mu^{0,45} \quad 2 < Re < 500 \tag{15}$$

$$v_t = 1,74 (g(\rho_s - 1) d_p)^{0,5} \quad Re \geq 500 \tag{16}$$

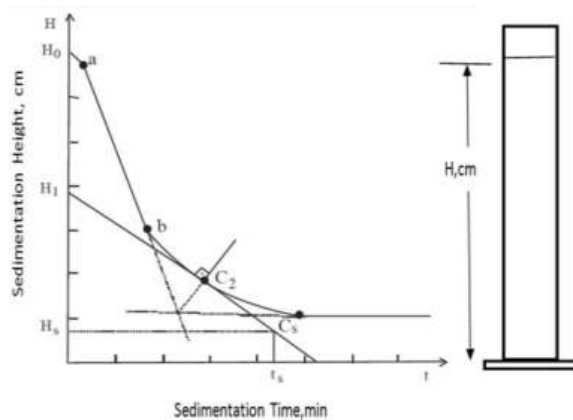


Figure 10. The settlement rate in thickener, sedimentation column used in settlement test.

$$\mathfrak{R} = \frac{v_t d_p}{\mu} \tag{17}$$

Where  $v_t$  is the terminal settling velocity of the particle in thickener,  $g$  is the gravity acceleration,  $\rho_s$  is the specific gravity of settling particle in thickener,  $d_p$  is the diameter of settling particle in thickener,  $\mu$  is the kinematic viscosity of fluid as water,  $\mathfrak{R}$  is the Reynolds parameter of fluid flow as given in Eq. 12, and the sedimentation in laminal thickener occurs as given below as illustrated in **Figure 11**.

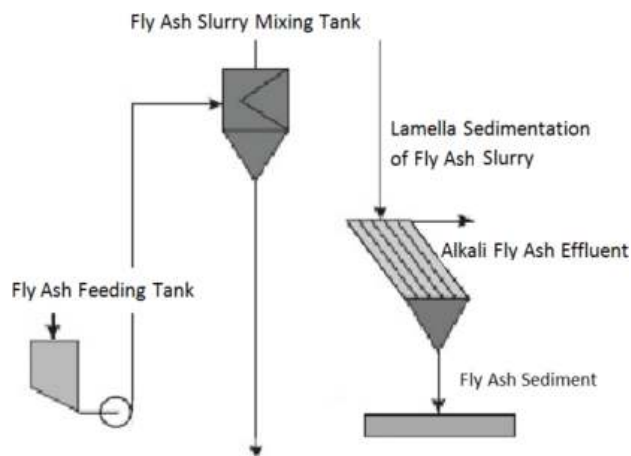
$$H = \frac{Q}{A} * t_s \left( \frac{1}{\rho_l} + \frac{x}{\rho_s} \right) \tag{18}$$

$H$  is the height of sedimentation of particles in thickener,  $t_s$  is the sedimentation time of settling particle in thickener,  $Q$  is the flow rate of solid matter in thickener,  $\rho_s$  is the specific gravity of settling particle in thickener,  $\rho_s$  is the specific gravity of liquid as water,  $x$  is the solid/liquid ratio in thickener feed.

Acid mine/rock drainage is a rampant problem in the world today. The screens illustrated in **Figure 10** and hydrolic clarifiers were tested (**Figure 11**) for the sediments in acid mine drainage treatment at an abandoned mine in the Şırnak. In this project, simple hydraulic clarifier may also provide neutralization reaction. It was very difficult for the government to enforce AMD treatment for the acid rock drainage at the Şırnak Coal Mine site. The conventional clarifier (**Figure 12**) and paste thickener (**Figure 13**) were also tested for fly ash neutralization.

Acid mine/rock drainage waters could be neutralized by fly ash and limestone waste fine in paste thickeners at longer times than conventional thickeners. The produced paste tailings occur reaction products and as mud as part of the chemical weathering process, but it is significantly used by mining, as filler material **Figure 14**.

AMD waters in Şırnak Coal Mine’s lake created a sulfuric acid effluent. The sulfuric acid dissolved and leached out the metals that are in the site rocks and coal pyrite metals, creating



**Figure 11.** The lamella clarification of fly ah slurries in the Şırnak Coal mining AMD.



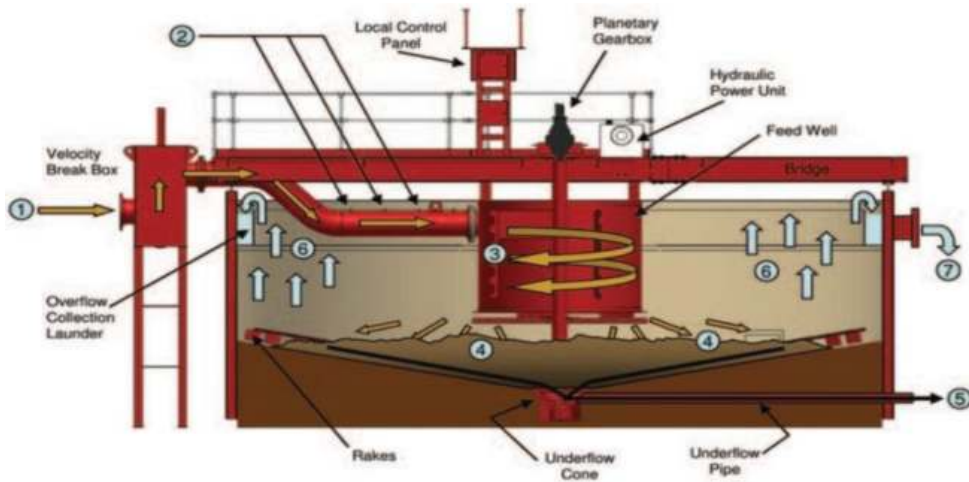


Figure 12. The WesTech thickener for fly ash and mid ash for clarification remediation in the Sirnak Coal Mine Site, fishery pool remediation.

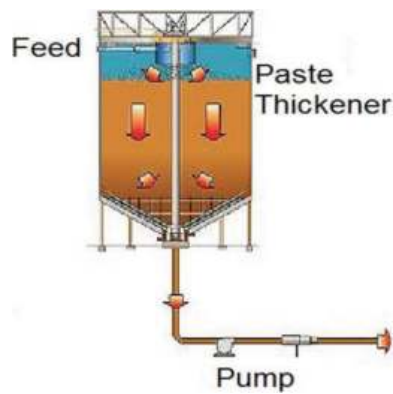


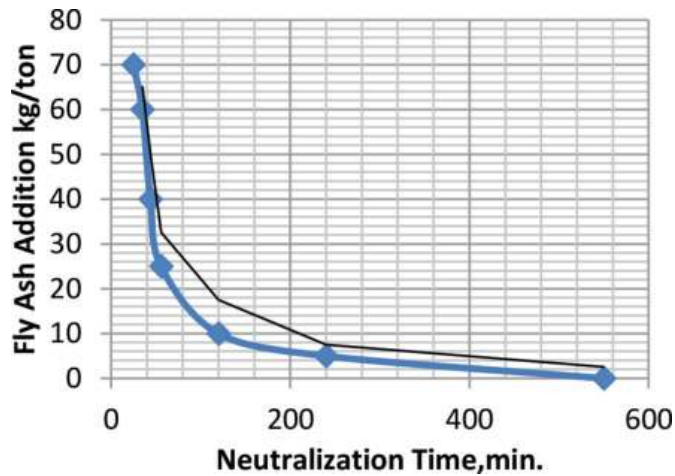
Figure 13. The Eimco paste thickener for fly ash and mid ash for clarification remediation.



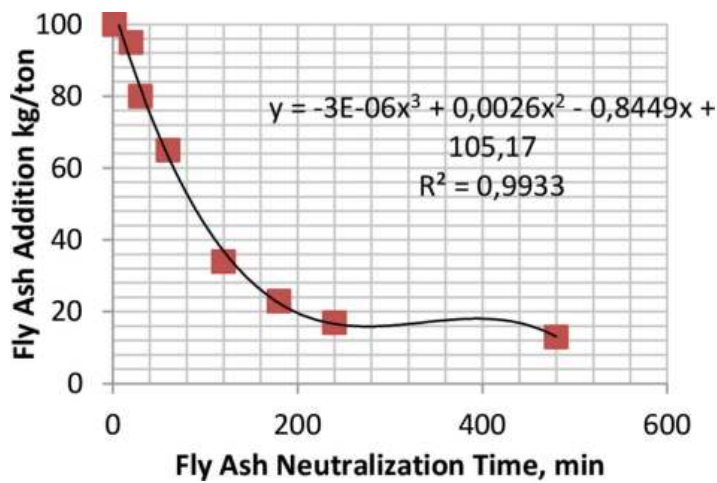
Figure 14. Paste thickening of treated neutralized effluent in the Coal mining AMD.

high concentrations of dissolved metals such as iron, zinc, copper, arsenic, and cadmium. As the water is exposed to aeration and fly ash neutralization as changing amount of 10–100 kg/ton of effluent was effective as illustrated in **Figures 15** and **16**.

Acidic mine drainage waters were treated by fly ash and limestone in paste thickeners, and Şırnak fly ash and mid ash of thermal power station were used at equal weight rates between 10 and 100 kg/ton of AMD water. Some part of the rock weathering process was reacted very slow in the season of winter but in summer term, the reaction kinetics were higher, but the treatment neutralization occurred higher than in winter term due to temperature of AMD waters. Significantly, as water comes in contact with the fly ash and mid ash, it neutralized to pH 6. The neutralized waters contained dissolved metal contents such as Zn and Fe and effluents containing alkali K, and phosphate metals that are beneficial for organic soils. The unsettling muddy rust color of the water also served to make organic matter for agricultural



**Figure 15.** Effect of Fly Ash and Lime Use in Neutralization of AMD in the Şırnak Coal Mine Site.

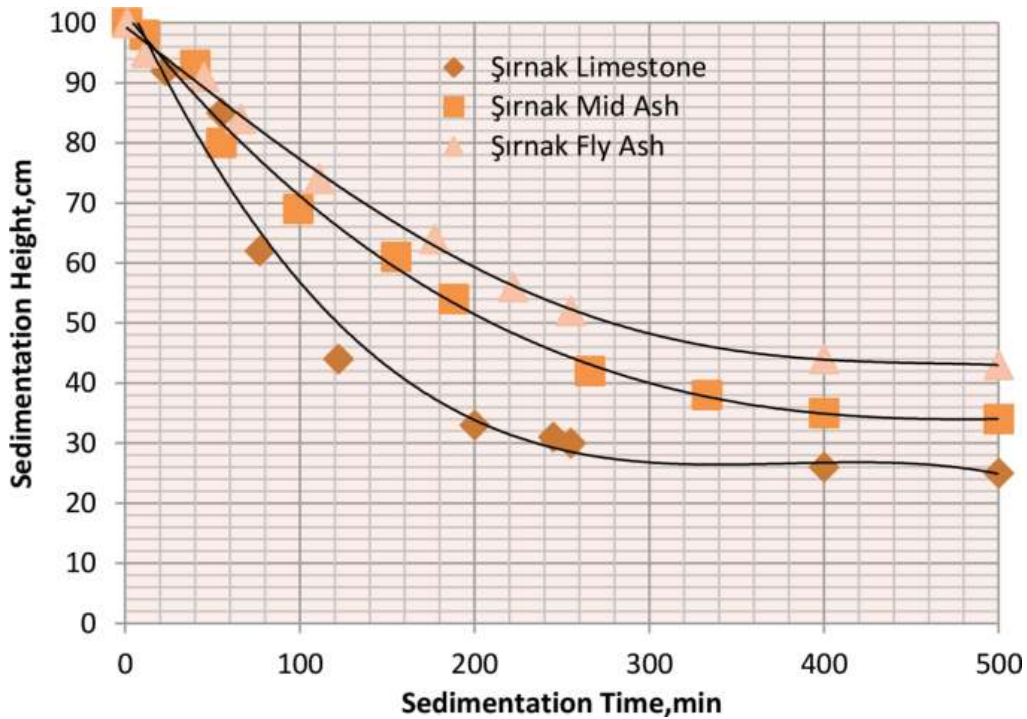


**Figure 16.** Effect of Fly Ash Use in Neutralization of AMD in the Şırnak Coal Mine Site.

irrigation waters in Şırnak Coal Mine site area. The settlement of muddy rust colored treated water occurred as illustrated in **Figure 16**. In brief, the major high-rate oxidation caused was the highly oxidation of iron pyrite ( $\text{FeS}_2$ ) and other sulphidic minerals. As a consequence of the mining and processing of copper ores and coals, many metals (e.g., iron, zinc, and copper) were associated with sphalerite and pyrite in the Şırnak Coal Mining and Siirt Copper Mine. Additionally, coal deposits contain variable (generally, 1–20%) amounts of pyritic-sulfur (a generic term that includes other iron sulfide minerals such as marcasite) as well as organic sulfur. As seen in **Figure 17**, common neutralization treatment is carried out by limestone, lime, and caustic lime, but local wastes such as fly ash or mid-bottom ash of thermal power plants using desulfurization.

When the pyrite oxidized in coal tailings slimes and slurry in the dumping area and slime pond in Şırnak, lack of oxygen occurred in the pond, making the water contaminated for farming and aquatic life. Moreover, the rust and heavy metals in the water make it impossible life limiting fishing [51–64].

The regeneration of ferric iron was the key reaction in promoting acidic media contamination during oxidation of the pyrite mineral in asphaltite slime pond at pH values above 4. This commenced mediated chemically or biologically, as below pH 5, abiotic iron oxidation is negligible [1–5, 65–75], and the activities of moderately and extremely acidophilic iron-oxidizing bacteria had a main role with a lack of oxygen in the slime pond. The contaminated water cycled by the neutralization unit to pond for treatment of acid mine drainage seepage. The sand separation followed neutralization was applied by Derrick classifiers and aeration of

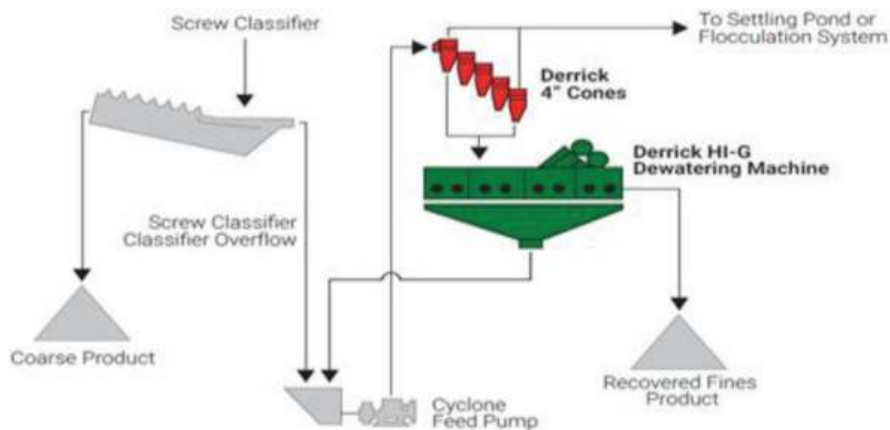


**Figure 17.** Effect of Fly Ash Use in Sedimentation of AMD in the Şırnak Coal Mine Site.

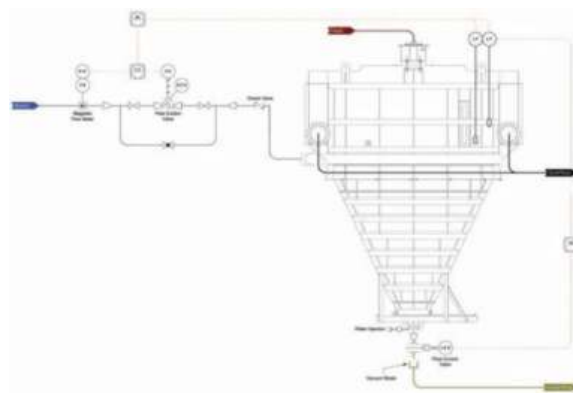
wastewaters carried out in the Eriez floaters and thickeners as illustrated in **Figures 18** and **19** [61, 62].

Acid mine drainage (AMD) neutralized by flay ash and alkali matters followed the formation settled mud in the classifiers in cycling slime pond in coal mine. Although this is generally of humate mud yield was also circulated to collect the mud in the slime pond by asphaltite slime had an active on fertilizer production by carbon and water tables are kept artificially low by pumping. This initial drainage water tends to be more potentially polluting (in terms of acidity and metal content) than AMD that is discharged subsequently [22, 76–77].

In this treatment, study of coal mine AMD treatment by use of fly ash and mid ash managed the neutralization by sediments such as jarosites and gypsum depending on oxygen content. The precipitation of jarosite and göthite clusters observed as given in the Eqs. 19 and 20 showed the reactions occurred between pH 3 and 6. As illustrated in **Figures 20** and **21**, the alkali reactions followed the paths over the arrows down till the lack of oxygen side at the bottom of wastewaters level. The alkali pH created much precipitation and jelatizing of sediments and deteriorating solid/liquid neutralization reactions in the thickeners.



**Figure 18.** The Derrick classifier for mud humate yield for clarification remediation [61].



**Figure 19.** The classifier for mud digestion for AMD treatment in the Şırnak [62].

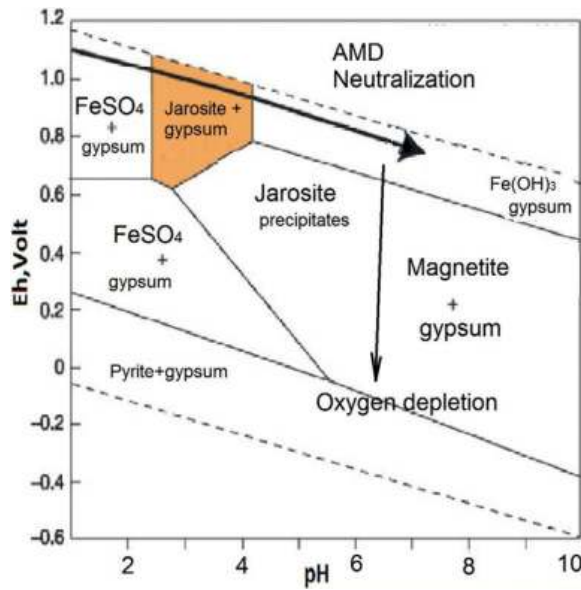


Figure 20. The Eh-pH phase diagrams in the Fe-S-O-H and Cu-S-O-H system.

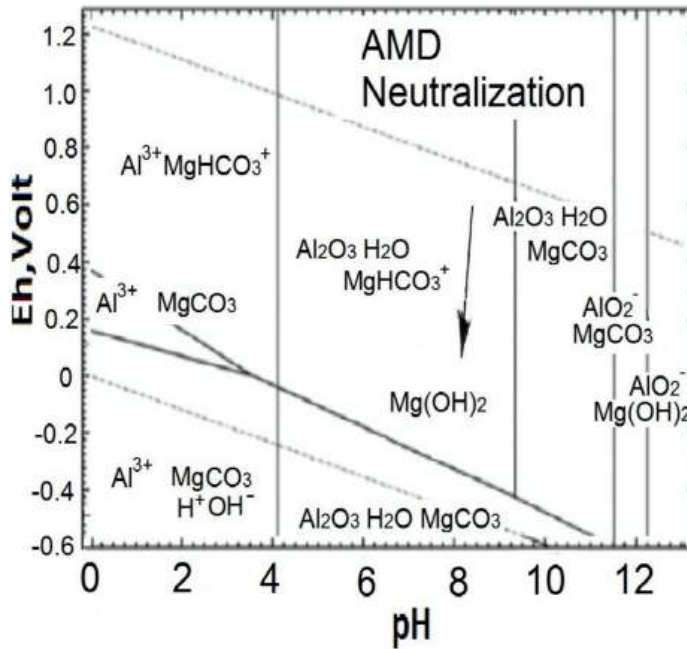


Figure 21. The Eh-pH phase diagrams with the fly ash clay and Al, Mg-OH, and CO<sub>2</sub>-OH system.

### 4.3. Humate mud yield and soil remediation

In this treatment, study of coal mine AMD treatment by use of fly ash and mid-bottom ash managed the neutralization by sediments and solids were analyzed by ASTM Soil Test standards as given in Table 2. The results of treated wastewater muds are given in Table 3.

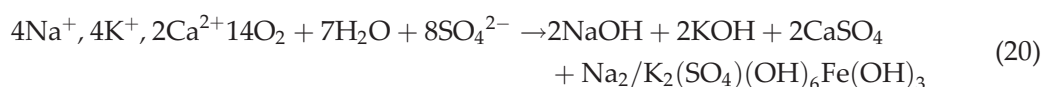
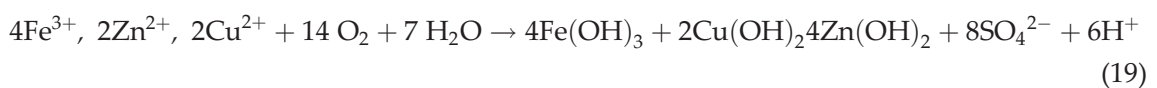


Analysis	Method
pH	Water
Lime requirement	Mehlich buffer
Extractable P, K, Ca, and Mg	Mehlich 3 (ICP)
Cation Exchange Capacity (CEC)	Summation
Organic matter	Loss on Ignition
Total C	Combustion
Nitrate N	Specific Ion Electrode
Ammonium N	Specific Ion Electrode
Total N	Combustion
Soluble salts	Electrical Conductivity (1:2)
Total sorbed Cu, Zn, Pb, Ni, Cd, Cr, Mo	EPA Method 3050B/3051 + 6010
Particle size analysis	Hydrometer method
As	EPA Method 3050B/3051 + 6010
Se	EPA Method 3050B/3051 + 6010
Hg	EPA Method 7473
Calcium carbonate equivalency (CCE)	ASTM Method C 25

**Table 2.** List of the standard soil-testing methods used soil remediations.

Humate waste sludge was treated by densification and CO<sub>2</sub> gas or biogas digestion in the concrete column pools sequentially with the flow sheet as given in **Figure 22**.

The plots treated with poultry manure (N-based) and TSP, without digestion amendment, had DPS values of 0.84 and 0.93, respectively, as given in **Table 3** in which these treatments could contribute humate content with significant amounts of P in runoff by anaerobic digestion by own biogas. The kinetic rate of digestion was greatly depended on active sludge carbon content and temperature. During digestion of a month, period time might not sufficient for fertile quality of mud, and organic manure carbon matter in 0.1% alkaline. Amendment with digestion and manure decreased the N and the TSP values by 86% (N-based) and 82% (P-based) relative to the same treatments without digestion amendment, respectively. Similarly, N and DPS values of the manure-treated mud decreased by 83% (N-based) and 82% (P-based), respectively.



The metal contents were higher with treatment of fly ash and bottom ash use in neutralization muds. The low power requirements of aeration limestone channel treatment made much

	Bottom ash + 50% soil	Manure	Humate	Fly ash + 50% Soil	Avgamasya soil	AMD treated limestone	AMD bottom ash
<b>pH</b>	6.8	8.2	7.9	5.6	6.8	7.2	7.9
<b>Total C</b>	32.0	54.7	56.6	13.9	34.7	16.6	13.9
<b>Total N</b>	0.4	7.0	9.03	0.7	8.0	1.03	0.7
<b>% Solids</b>	27.0 + 4.2	13.4 + 1.6	15.4 + 3.4	40.6 + 6.2	15.4 + 3.4	40.6 + 6.2	40.6 + 6.2
<b>Total P</b>	18.9 + 3.8	38.7 + 2.3	24.1 + 4.2	4.69 + 0.7	24.1 + 4.2	4.69 + 0.7	4.69 + 0.7
<b>Total Al</b>	0.94 + 0.1	9.37 + 0.4	9.26 + 1.4	107 + 8.3	9.26 + 1.4	107 + 8.3	107 + 8.3
<b>Total Fe</b>	1.53 + 0.3	24.3 + 3.1	32.8 + 6.4	6.08 + 0.4	32.8 + 6.4	6.08 + 0.4	6.08 + 0.4
<b>Oxalate P</b>	10.4 + 1.2	26.4 + 3.9	28.5 + 3.2	4.33 + 0.8	28.5 + 3.2	4.33 + 0.8	4.33 + 0.8
<b>Oxalate Al</b>	0.79 + 0.1	6.50 + 0.9	7.41 + 0.6	84.3 + 6.2	7.41 + 0.6	84.3 + 6.2	84.3 + 6.2
<b>Oxalate Fe</b>	10.82 + 3.3	19.4 + 2.3	24.7 + 4.2	5.16 + 1.0	3.82 + 1.3	4.22 + 1.3	5.16 + 1.0
<b>Fe strip P</b>	1.34 + 0.3	6.42 + 1.2	1.05 + 0.2	nd <sup>d</sup>	1.05 + 0.2	nd <sup>d</sup>	nd <sup>d</sup>
<b>WEP<sup>a</sup></b>	0.85 + 0.1	2.59 + 0.6	0.34 + 0.1	nd <sup>d</sup>	0.85 + 0.1	nd <sup>d</sup>	nd <sup>d</sup>
<b>PSI<sup>b</sup></b>	22	1.44	0.7	33	11	6	43

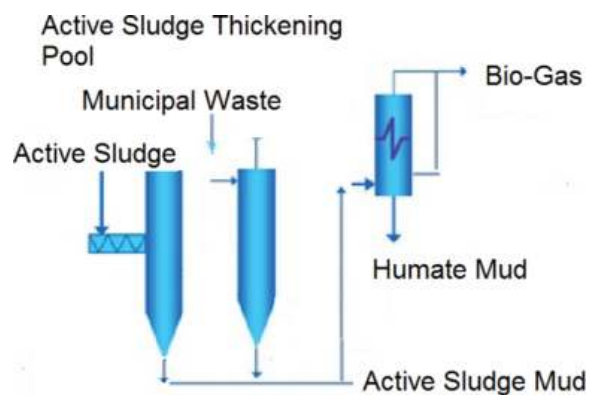
<sup>a</sup> Water extractable P.

<sup>b</sup> Phosphorus saturation index.

<sup>c</sup> Not applicable.

<sup>d</sup> Not determined.

**Table 3.** Selected chemical properties of remediation product sediment muds and soils in the Şırnak Coal Mine Site.



**Figure 22.** Selected chemical digestion of mud for remediation product sediment muds and soils in the Şırnak Coal Mine Site.

feasible neutralization for disseminated asphaltite extraction and slimes in many locations of Şırnak. The distribution of asphaltite slime ponds allowed to cycling at low flow rates in neutralization and required less cost. However, the pool settlers had a lower capacity and could not remove any of the heavy metals in the cycling itself. For concentrator tailing ponds, the larger flows in cycling manner removed the heavy metals by filtration treatment system. It was necessary to employ a more active and filtration application for heavy metal contents

followed thickening treatment system so the humate mud contained less dissolved metal contamination.

## 5. Projected flow sheet

Şırnak Coal Mine drainage water was not always strictly acidic. The projected neutralization plant to develop treatment for neutral mine drainage water that contained a fairly normal pH around 6 but contained high amount of heavy metals at the concentrations in the cycling slime waters over 200 mg/Lt Fe and over 45 mg/Lt Zn higher Pb and Cd and other contaminants that needed to be removed in order to farming requirements in this project. In the asphaltite slime water cycling with less acidic, the use of lime was not required to settle out the iron. In heavy dense settling and neutralization process, hydrogen peroxide or caustic lime could be concerned potentially use, but locally cheap alkali was concerned. However, without the lime and fly ash, the thickener bed was bound higher, and settling rate was decreased relatively as low as 5% solids. The proposed design flow sheet is illustrated in **Figure 20** on the fly ash content paste thickening proposed on the solid content in wastewater flow. In the copper mine site of Siirt, there was necessary to use collector pools and paste thickeners due to high solid content over 13%. In fact, in many cases, the thickener itself might not be necessary. The projected design considered the use of a recirculating-type clarifier or a solid contact clarifier.

For large acid mine flows, the projected fly ash treatment has developed as the following flow sheet proposed by this study shown in **Figure 23**. As an equipment manufacturer specializing in liquid/solids separation, WesTech has designed and installed many acid mine drainage treatment systems. Lack of digestion at a month caused wet acidic mud, and organic fuming matter was lower than 20% in 1% K-alkali test. Amendment with digestion and manure addition at 2 months' period increased the N and TSP by 86% (N-based) and 82% (P-based) relative to the same treatments at 1 month digestion amendment, respectively. The metal contents of humate mud were critical for organic farming and agricultural irrigation practice in the region.

37 mg/Lt Cu, 52 mg/Lt Zn, and about 141 mg/Lt Fe concentration as wastewater contaminants caused by acidic mine drainage waters of coal mine extraction site due to wet soils and environment and stream water channels determined as concentrated and polluted load. The pollutant load and pollutant concentrations changed widely and treated in the channel streams by fly ash and limestones used for various purposes. The thickening capacity was designed by flow of 2–3 Lt/s wastewater stream at 4–7% solid contents. The design capacity of the wastewater treatment plant resulted the lower metal contents in water analysis as clarified waters, but lead and zinc levels were still higher for fishing. The agricultural irrigation was managed by this water. The thickening output water oxygen demands were net below 10 and 10 COD and BOD levels (BOD, kg/day) and at the digestion, carbon dioxide and biogas entrance to the digestion treatment plant were expressed by the mud pollution load to be found as the product of the multiplication. The design capacity depends on the number of sequential kinetic rates of the mud content and temperature at the digestion pool depending on the pool conditions. The pollution loads of return currents were greatly affected much. Mud

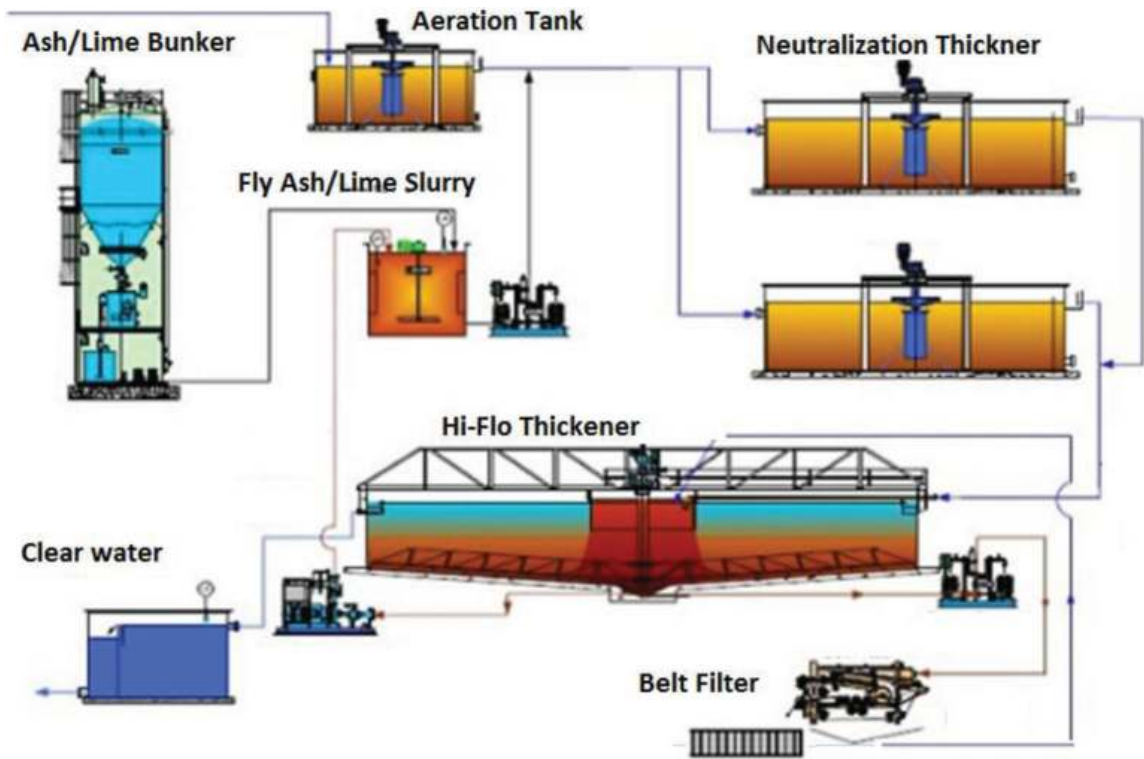


Figure 23. Projected Neutralization and Treatment Plant for AMD waters in Şırnak Coal Mine Site.

quality increased at humate value of organic dissolution, and phosphor level was measured at dry seasons with 30 BOD level on the summer times at temperatures over  $27^{\circ}\text{C}$ .

Neutralization and settling step in the treatment process managed the water clarification and removing the nonsoluble iron from the liquid. Heavy metal contents in the clarified stream decreased by ideal neutralization, allowing fly ash use to slow the settling rates down as necessary neutralization time. It is obviously critical to add neutralization ultrafine waste ash or fly ash into the HDS clarifier.

## 6. Conclusions

In this area, the hydrological characteristics of the Şırnak city were critical for the effect of waste characteristics on the pictured coal site and city. The hydrological features of the urbanization and countryside for agricultural irrigation with new settlements need modeling regarding available water source. The hydrological property of settlement areas with dense populated areas should be determined by geographic information systems (GIS) techniques. The main purpose of this municipal wastewaters and acidic waters treatment was to investigate the effect on settlement on the basic hydrological structure by studying the characteristics of the ground topography, ground water elevation, slope, and viewing. GIS techniques were used in the creation of the thematic maps and in the analysis of the parameters. The GIS study

models created, the available water source changed, and a stream network model was provided sufficient source control at the Şırnak province. GIS data maps followed planning of wastewater treatment plant made it possible to obtain more qualified data by enabling the use of humate mud production regarding metal contents in this research.

The AMD waters during the coal mining in the open pits and underground in Şırnak and copper AMD waters in Siirt copper mining and concentrator are polluting nature. This type of wastewater is acidic and contains heavy metals, which cause environmental pollution such as ferric iron and zinc and copper metals at 230, 122, and 57 mg/l, respectively. For this reason, the release of acidic mine drainage (AMD) waters into the irrigation waters of natural rivers and agricultural areas can cause great threat to the habitats and fish in the local streams and in the local lakes. AMD waters must be collected in the impermeable projected ponds and require neutral characterization and ventilation by acidic neutralization.

A more useful treatment method projected using local limestones, and fly and mid-bottom ash of thermal power stations used for desulfurization was so effective among the known remediation technologies that rely on biological activities and produced beneficial potassium and phosphate fertilizing mud.

Within these major treatments, there are processes that may be described as either active or passive neutralization by fly ash and mid-bottom ash with limestones of Şırnak at equal rates of 60 kg/l AMD water. This choice projected in Şırnak coal mining and Siirt copper mining site could remediate AMD waters following neutralization at economical and environmental stages.

The true environmental cost of this remediation system was low at apparent study with investment cost of about \$2 million. One of limiting operational costs was the amount of the transport of liming materials, often low distances from source to mine sites with a \$21 per ton alkali. In the Siirt copper open pit mining site in Sirvan, large acidic seepage volumes as tailing wastewaters could be treated by active chemical reactions of neutralization, made low acidic or neutral waters. The land surface area and topography brought out passive remediation systems in Siirt copper mine. However, similar treatment in the coal mining in Şırnak became significant at high costs of lime addition and treatment of sludge disposal. The higher land areas required for passive treatments made dramatically at smaller area by densing on small collector ponds optimizing biological processes, for example, packed bed bioreactors for removing iron from acidic mine waters following discharge, which were effective than aerobic wetlands [3, 9].

The projected passive pool systems also required a certain amount of management and would eventually fill with accumulated ferric mud (aerobic wetlands) and fertile muds. The long-term stabilities of these materials were certain, but since as the composted effluents in some pools might contain toxic elements (arsenic and cadmium such as 10 mg/l and 56 mg/l, respectively), their storage or disposal required careful consideration.

The sustainability of the projected remediation system was a great fact that was becoming increasingly critical in decision making. One of the problems here was that the products of AMD remediation have not been perceived as a resource. Recently, an iron oxide sludge recovered from a drainage channel at an abandoned coal mine in Şırnak coal site could be used to manufacture fertilize mud in a commercially packed bag.



The Cu and Zn metals could also be recovered by electrolysis as by products from AMD waters [9]. The treatment of AMD from metal mines in Siirt copper concentrator could provide some financial return on the investment and running costs of remediation. Ultimately, legislation was a prominent fact to become the dominant factor in determining which kind of remediation method could be used in local needs. The projected thickener neutralization of pond effluents might become increasingly beneficial to dispose of the base metals in sludges and sediments avoiding storage problems. There were high possibilities for their recovery and recycling.

The ecological limits for agricultural irrigation waters of wheat in Şırnak at the 50 mg/lit concentrations of metal sulfate that could be discharged from treatment plants needed the choice of two-stage systems as one that effectively removes sulfate as well as metals and acidity from mine waters, and the other stage may decrease the metal concentrations by water and effluent mixing. The problem of what to do about the pollution threat posed by AMD certainly brings to a certain treatment using fly ash and waste limestone forever in coal and copper mining activities at environmental concern.

## Author details

Yıldırım İsmail Tosun

Address all correspondence to: yildirimismailtosun@gmail.com

Mining Engineering Department, Şırnak University, Şırnak, Turkey

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