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TREATMENT OF ACIDIC MINE WATERS BY THE NEUTRALIZATION PROCESS

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ABSTRACT – Mine water is one of the biggest challenges facing the global mining industry. This water is primarily produced by the oxidation of sulfide minerals when exposed to air, water, and microbial activity in active or abandoned mines containing polymetallic sulfide ores or coal mines. It is characterized by high acidity, with a pH value usually below 4, which usually indicates high concentrations of sulfates and dissolved metal ions. There are two different treatment strategies: removing toxic metals and reducing the acidity of mine water. Processes for neutralization of acid mine waters with lime are the most commonly used. This process has low operating costs. untreated acid mine water is used, and the regulation of the pH value with lime leads to the precipitation of insoluble metal hydroxides.

Keywords: Acid Mine Waters, Sulphide Minerals, Neutralization, Lime.

INTRODUCTION

Mine waters represent one of the global mining industry's most significant challenges. These waters are primarily formed by the oxidation of sulphide minerals when they are exposed to air, water, and microbiological activity in active or abandoned mines of polymetallic sulphide ores, coal mines [1-4]. It is characterized by high acidity, which confirms the pH value, which is usually below 4, which generally confirms the high concentration of sulfates and dissolved metal ions [5].

Discharge of mine water without prior treatment leads to contamination of nearby water sources, flora, and fauna. This has serious negative impacts on biodiversity and causes high levels of metal ions in soil to reach the top of the food chain, ultimately creating a risk to human health. Therefore, the treatment of water in question is one of the most important topics in the field of environmental protection. During the past decades, researchers have made every effort to purify these waters by reducing acidity and removing metal ions to reduce their negative impact on the environment and human health [6]. Available treatment methods have confirmed that lime neutralization is a frequently applied and inexpensive technique. However, the main disadvantage of the

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mentioned method is the creation of a large amount of sludge, which does not favor the comprehensive utilization of useful metals and sulfates from treated waters [7]. Other conventional approaches such as ion exchange [8], chemical precipitation [9], adsorption [10], membrane separation techniques [11, 12], electrochemical processes (electrodialysis, electrocoagulation, electrokinetic) are also often used to treat mine waters [13], with most of these techniques mainly focusing on the neutralization of acidity, metal ions and sulfates in the treated waters rather than the valorization of useful and high-value components adequately.

FORMATION OF MINE WATERS

Mine waters are highly acidic, which confirms the pH value, which is usually below 4 and they are one of the main pollutants of the environment. Generally, they are formed by the oxidation of sulphide minerals due to exposure to air, water, and microbial activity [14, 15].

Pyrite is one of the most abundant and widespread sulphide minerals and is widely considered to be the dominant cause of acid mine waters (AMD) formation [16, 17]. Moreover, arsenopyrite, chalcopyrite, galena, pyrrhotite, and sphalerite also contribute to AMD formation [18]. A series of chemical reactions involved in the formation of AMD is shown in Figure 1 [19]. Pyrite exposed to water and air is first oxidized, releasing H^+, SO_4^{2-}, and Fe^{2+} ions on the surface, and the Fe^{2+} ions continue to be further oxidized to Fe^{3+} in water exposed to air. At low pH, Fe^{3+} ions will be hydrolyzed and precipitated to form $Fe(OH)_3$ precipitate, while some Fe^{3+} ions can continue to oxidize pyrite to produce sulfate and acid, leading to the formation of AMD [15, 20].

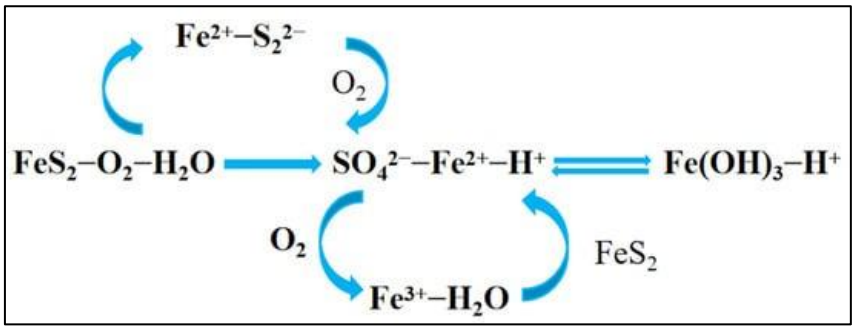

Figure 1 Chemical reactions are associated with the formation of AMD [19]

CHEMICAL COMPOSITION AMD

The chemical composition of mine waters is determined by the composition of ores and ore minerals. Deposits of different mineral raw materials are characterized by different chemical compositions of groundwater. In addition to the mineralogical composition, general structural-geological, modern climatic, and other factors, the formation of the chemical composition of groundwater of mineral deposits is influenced by various processes that take place in different geochemical environments. [21]

Geochemical processes take place in three natural geochemical environments: oxidizing, reducing, and metamorphic. The formation of the chemical composition of natural waters, and therefore of groundwater in ore deposits, takes place under the influence of basic geochemical processes: sulfuric-acidic, oxygenic, carbon dioxide, and hydrolytic.

Sulfuric acid processes are the leading processes for the decomposition of sulphide minerals. It is most active in the oxidation zone of sulfide-type copper deposits and polymetallic ores, enriched with Fe and Cu disulfides. Depending on the character of the reactions taking place, the sulfuric-acid process can have an oxidizing or reducing character. These processes significantly affect the migration ability of elements, their dispersion, and concentration. [22] Table 1 shows the chemical composition of the accumulated mine water. The pH value of acidic mine waters ranges from 2 to 4.

Table 1 An example of the chemical composition of accumulated mine water in an inactive open pit [25]

Element	Zn	Cd	Cr	Cu	Ni	Fe	Pb	As	Hg
mg/l	12.82	0.12	0.06	29.56	0.62	149.28	0.16	<0.020	<0.0005

BASIC PRINCIPLES OF THE NEUTRALIZATION PROCESS

The most commonly used method is neutralization with lime in neutralization reactors. High efficiency in removing dissolved heavy metals and low operating costs make this method the most commonly applied. Lime treatment consists of regulating the pH value of untreated water to a value at which metal pollutants are insoluble, which leads to the precipitation of metal hydroxides. After that, these sediments are separated to obtain purified wastewater that meets the regional criteria for discharge into the recipient.

Each metal in solution contributes to a certain acidity of acid mine waters, and in addition, each metal precipitates at a certain pH value, Table 1. Many metals have amphoteric properties, and their solubility decreases with an increase in pH up to a certain limit value, above which their solubility increases again, due to the formation of soluble complexes. Table 2 shows that most of the metal cations present in acid mine water can be settled if the pH of these waters is increased to a pH of around 9.5.

The solid/liquid separation forms sludge, which, depending on the applied process, can contain from 1 to 30% of solid matter. This sludge must be disposed of outside the system in an environmentally acceptable manner [23].

The advantages of the technology of treating acidic mine waters with lime are its effectiveness for the treatment of highly acidic waters, its simplicity, it has been checked and tested. The water after neutralization is of such quality that it can be directly discharged into the receiver. Changing the quality and quantity of acid mine waters can be easily adjusted by adjusting the basic parameters of the operation [24].

Disadvantages of the technology of treatment of acidic mine waters with lime are high maintenance costs, the resulting sludge is chemically unstable, complex, has a low density, and is gelatinous, which poses a problem during its disposal, and has no

commercial value. The precipitation of metal ions such as Mn requires a high pH value, which can interfere with the precipitation of other metal hydroxides, e.g., Al.

Table 2 The theoretical value of pH at which the solubility of metal hydroxide is minimal [24]

Metal cations that precipitate as hydroxides	Precipitation of hydroxide	pH value that corresponds to the minimum solubility of metal hydroxide/L
Fe^{3+}	$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow$	~ 3,5
Sb^{2+}		~ 4,2
Al^{3+}	$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \downarrow$	~ 4,5
Pb^{2+}	$Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2 \downarrow$	~ 6,5
Cu^{2+}	$Cu^{2+} + 2OH^- \rightarrow Cu(OH)_2 \downarrow$	~ 7,0
Fe^{2+}	$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \downarrow$	~ 8,0
Zn^{2+}	$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$	~ 8,5
Ni^{2+}	$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \downarrow$	~ 9,3
Cd^{2+}		~ 10,0
Mn^{2+}		~ 10,6
Co^{2+}	$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \downarrow$	

The basis of the neutralization of acidic mine waters with lime is the insolubility of heavy metals in a basic medium. Metal ions Fe, Zn, Cu, Al, Pb, etc., are deposited up to a pH value of 9.5, while Mn and Cd require a higher pH value (pH=10.5-11).

Metal deposits that occur in all processes of lime processing represent waste, better known as waste sludge, which is hazardous waste and should be handled according to legal regulations. Given that the costs of sludge disposal can be significant, the volumetric amount of sludge must be minimal.

CONCLUSION

The main sources of acid mine waters are mines and process tailings, ore, and mining operations related to ore extraction. The main pathway for the release of acidity, metals, and metalloids into the environment is water. Acid mine waters represent a major environmental problem caused by mining. Acid mine water is unique among industrial pollutants because of its leaching capacity, which is enhanced by bacterial activity and is self-perpetuating. Processes for treating acidic mine waters with lime have advantages and disadvantages. They can be simple with older processing methods or complex with modern and efficient systems. Older methods are less efficient and do not have good control over the processing system. While modern processes require huge capital investments, they are significantly more efficient regarding lime use and waste treatment.

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