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ANOXIC LIMESTONE DRAINAGE (ALD) TO TREAT ACID MINE WATER (AMD)

Summary. As a consequence of the weathering the pirite is combined together with the oxygen and water, Acid Mine Drainage is produced, with rather low pH and disolved metals. In order to treat the polluted water it could be good to increase its alkalinity. There are several ways to increase the water alkalinity. One of them is the ALD, limestone beds buried through which the polluted water flows, in which carbonates are dissolved, (mostly calcium carbonate), in a media lacking of oxygen.

BEZTLENOWE FILTRY WĘGLANOWE DLA KWAŚNYCH WÓD KOPALNIANYCH

Streszczenie. Wietrzenie pirytu przy dostępie tlenu i wody wywołuje zjawisko określane jako Acid Mine Drainage, oznaczające silne zakwaszenie wód kopalnianych przy równoczesnym wzbogaceniu ich w jony metali. Oczyszczanie takich wód wymaga podwyższenia ich alkaliczności. Jedna z używanych w tym celu metod opiera się na zastosowaniu usytuowanych pod ziemią beztlenowych filtrów węglanowych (ALD). Przepływajaca przez nie woda wzbogacana jest w węglany, przy równoczesnym niedostatku tlenu.

1. Introduction

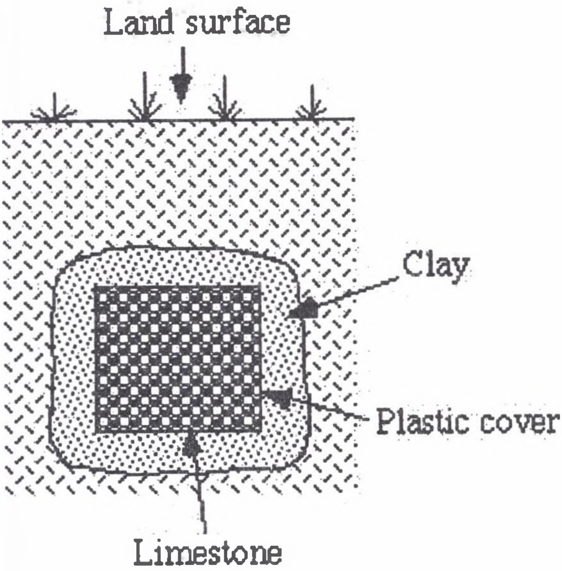
It is common in some mining types, mainly in mining of materials containing sulphurs, that diverse reactions take place, essentially oxidation of certain minerals (generally pyrite) present in mine, in mining desposals, etc. These reactions give place in one kine of waters that we called Acid Mine Drainage, characterized by their low pH that makes them strongly corrosive, so that this it dissolves several minerals, reaching high concentrations of dissolved pollutants (iron, aluminum, manganese, calcium magnesium, sulfates, etc).

2. Systems of passive treatment

The idea of the systems of passive treatment is trying to reproduce in built systems the reactions that produce the improvement of the quality of the water, taking place the precipitate solids in a place dedicated to this end, instead of precipitate in natural one. It is attempted, also in some cases, to promote the performance of certain bacterias and plants that help to these processes, to reduce the acidity, and to air the fluid, so that the conditions Eh - pH change until they are unstable the dissolved forms of the pollutants , forming its solids precipitate. It is beneficial for the quality of the Acid Mine Drainage to increase the alkalinity, facilitating, on one hand, to counteract the acidity of the system and to produce the deposition of pollutants, and, on the other hand, the presence of alkalinity prevents against possible descents of the pH. There are some possibilities to increase the alkalinity of the water, in a large part of the cases, additions of chemical reagents to increase the water's alcalinity is not feasible, due to their continuous and high cost. In the systems of passive treatment it is tried that they originate, among other, processes of bacterial reduction of sulfates, or breakup of calcareous stone (cheaper than the chemical reagents) to produce alkalinity. The disolution of minerals carbonated as the limestone is, in principle, a good form of elevating the alkalinity of the system, but they have the disadvantage that the limestone is recovered of precipitate solids, avoiding that the process continues, since the breakup of the limestone is a superficial process [18].

2.1. ALD systems

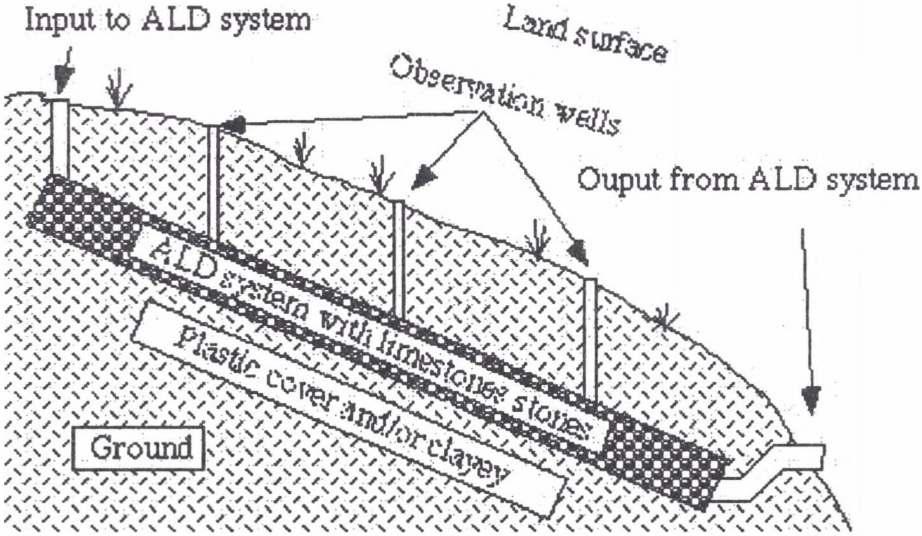
When the concentrations of ferric iron, aluminum and oxygen are very low, it can be used the systems ALD (that next will describe) to add alkalinity to the system. It is important that the water to try in systems ALD possesses low concentrations of ferric iron, aluminum and I oxygen, because otherwise they can take place precipitate of FeOOH and Al(OH)3 that would impede the correct operation of the system. The systems ALD is a channel (generally paralepipédicos) buried of limestone, through those which the water flows without the oxygen entrance is allowed, which would produce the cover of the limestone for precipitate of iron; this channel is usually recovered by plastics and for waterproof clay, to 1 or 2 meters deep, and, lastly a layer of vegetable earth that allows that the vegetable cover is developed on the system (Fig. 1).



Rys. 1. Schematyczny przekrój poprzeczny filtra ALD
Fig. 1. Schematic traverse section of a system ALD

In the event of being present in the system, oxygen, ferric iron or aluminum could take place precipitate that on one hand they inhibit the performance of the limestone (recovering it), and for the other one, they can cork the treatment system. The very quick operation of an ALD that receives Fe3+, Al3+ or dissolved oxygen, can be spectacular (the total deposition of these metals in the system of the ALD) [19], but its long term effectiveness is questionable [7].

The first time that the technology ALD was suggested, was when Turner and McCoy [24] showed that if the Acid Mine Drainage don't contain disolved could be treat, flowing through the limestone channel covered by plastic. The efluente of this first system system had alkaline conditions. The metallic pollutants precipitate quickly under these alkaline than in the initials ones. Since Turner and McCoy made public their discovery in 1.990, dozens of systems of treatment of this type have been built. The name that has been given to this method, is that of ALD or ALDs. In this systems the mine water is made pass through a channel of calcareous gravel avoiding the oxygen presence [7]. It seems to exist a direct relationship between the quantity of alkalinity generated by the system ALD, and the partial pressure of CO2 inside the system. In the ALD built in the Northwest of Pennsylvania, concentrations of dioxide of carbon (CO2) bigger 600 times that the normal levels in the atmosphere have been measured. This increases the solubility of the limestone, making that the efluent waters are very alkaline. Under the partial pressure of CO2 of 0'0003 atm. (atmospheric pressure) the breakup of CaCO3 in pure water is of approximately 60 mg/l of alkalinity. As CaCO3 eq.to measure that the partial pressure of CO2 increases, the alkalinity that can be dissolved in the water increases. Theoretically, in a total atmosphere (100%) of CO2, the water in contact with calcareous stone would reach alkalinity bigger than 1000 mg/l [18]. The high concentration of CO2, and the high solubility of CaCO3 observed in the built ALD, indicate that the system works as a closed system. Some systems ALD has been built using powdered limestone and small gravell but they have not been effective, by obstruction problems. It is important to use limestone with high content of CaCO3 in ALD systems, because it is much more reagent that the MgCO3 or the CaMg (CO3)2. The calcareous stone used in the ALD that have had good results, had between 85% and 95% of content of CaCO3. The system ALD should be sealed trying that the entrance of atmospheric oxygen is minimum and the accumulation of carbonic anhydride is maximum [7]. The ALD should be designed in form that the limestone is constantly flooded of water. The clay and plastic recover, and the entrance and exit pipes should be designed yhinking in this conditions (Fig. 2).



Rys. 2. Schematyczny przekrój podłużny filtra ALD
Fig. 2. Schematic traverse section of a system ALD

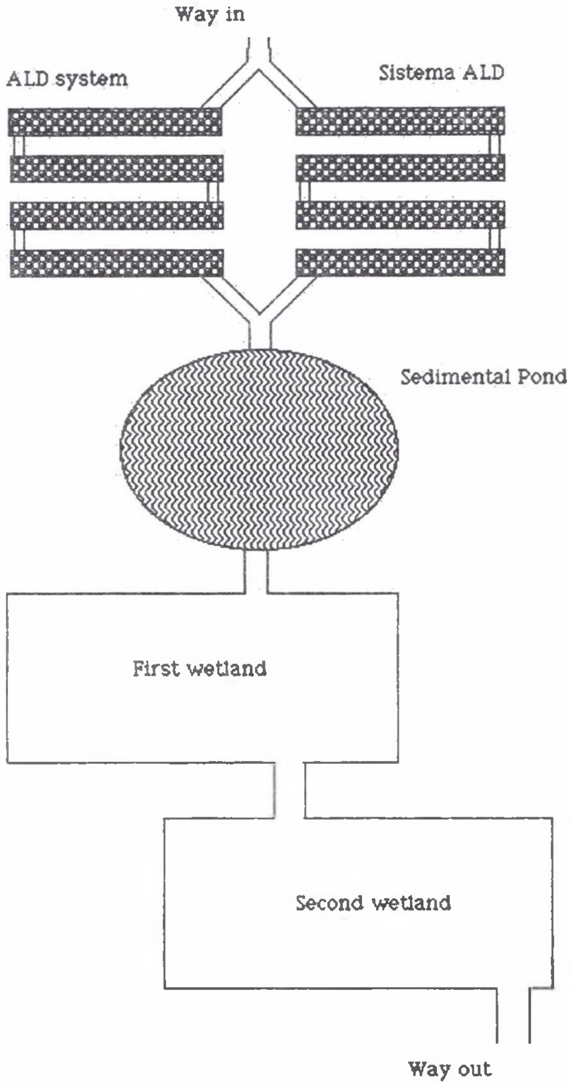
We should not forget that the ALD only adds alkalinity to the water, and they should continue (in space sequence) for an aerobic system in which the pollutants precipitate starting from reactions of oxidation and of hidrólisis [7].

2.2. ALD dimensions

It seems that the form of the ALD is not excessively important to get good results. The experiments that are carrying out in the laboratory seem to indicate that they need approximately 12 hours of contact between the Acid Mine Drainage and the limestone in an ALD to correct the maximum concentration of alkalinity. To get these 12 hours of contact between the mine waters and the limestone are needed about 3000 kg of calcareous stone for each l/min of mine waters. An ALD that contains 90% of CaCO3 of limestone produces 275 mg/l of alkalinity (maximum concentration observed in an ALD) it dissolves every 10 years 1 600 kg. of limestone for each l/min of flow of mine waters. To build an ALD that has enough calcareous stone as to work during 30 years, the system has to have about 7 800 Kg of limestone for each l/min of flow to try. In this calculation it is accepted that the Acid Mine Drainage doesn't have aluminum neither ferric iron. The presence of these ions would produce quick recover of the limestone and problems of bogging (seen previously) [7].

3. Passive systems of treatment associated to the ALD

One of the possible systems of passive treatment is, as we have seen, the ALD. The ALD operating ideally only produces the increase of the pH (until approaching to the neuter one) and the increment of the concentration of calcium and of the alkalinity. The following step would be to aireate the water and to retain it enough time in a sedimental pond to precipitate great proportion of pollutants. If after de sedimental pond the generated alkalinity has not been enough, it is not possible to add another ALD in series, due to the oxygen presence [7] in the water. But it would exist in general the possibility to build in series a substratum pantanal fermented with mushrooms. This kind of wetlands is characterized because in them reactions of reduction of the sulfates take place (bacterially catallyzed), at level of the substratum (anaerobic) that elevates the alkalinity of the means. In case the water already has enough alkalinity, but that it has not precipitated all the pollutants, it is possible to build in series an aerobic wetland, in which diverse reactions of oxidation and hidrólisis are promoted which will produce the precipitation of pollutants. An appropriate combination of the passive technologies of treatment of Acid Mine Drainage, dimensioning appropriately each one of them and adapting them to the available land, will create the convenient improvement of the quality from the waters to the smallest possible price (Fig. 3).



Rys. 3. Schemat koncepcyjny układu złożonego z dwóch systemów ALD
Fig. 3. Outline of an imaginary system combineed of two ALD systems

3.1. Wetlands to treat Acid Mine Drainage

In the artificial wetlands are planted those plants whose activity is favorable to the treatment of waters. Such it is the case, for example, of the *Typha* (denominated popularly pure or cat tails [4]), *Equisetum* (denominated horse line popularly), or mosses of the type *Sphagnum*. The idea of promoting the life of some of these plants in wetlands of acid waters comes from the discovery of a group of investigators of the Wright State University that, studying an area in Ohio, discovered *Sphagnum recurvum* living in waters with a pH of 2,5. While the water circulated on this plants, its characteristics improved: the pH increased, until 4,6, and the quantity of iron, magnesium, sulfate, calcium and dissolved manganese, descended [5]. The treatments of the Acid Mine Drainage in wetlands were developed, initially, as a result of observations carried out in natural wetlands, and they were continued by rehearsals to scale pilot that culminated in the development to real scale of wetlands, of which it has already been built a great variety in mining areas of the U.S.A. and many more for the treatment of urban waters [4]. The wetlands that have been built, tries to reproduce the existent conditions in the natural wetlands [9], in those that physical, chemical and biological processes are developed that improve the quality of the water notably. The built wetlands generally consists, of a series rafts, not very deep, to facilitate a better control of the flow of water that should take place homogeneously in the whole flooded surface [4]. In many cases the natural wetlands could be used to try Acid Mine Drainage, but many times the law it protects these wetlands, and it is not possible their use with these ends [5], for what usually appeals to the creation of artificial wetlands. The existence of an area anaerobia, in the button of organic matter of the wetland, benefits to the treatment of the Acid Mine Drainage [17]. It is believed that the potential of neutralization of the organic layer (mushrooms) recently implanted it is of the order of 3,5 equivalent% CaCO3. In the area of entrance of water to the wetland, if the pH is low (like it is usually it), the life that is developed in the wetland is minimum, but as the water advances on the wetland, the pH ascends, and it improves the quality of the water, that which allows that more varied vegetation is developed. The oxygen dissolved in the water favors the characteristics of the wetland, when improving the conditions that will allow the development of the life of plants and animals [21]. It has been demonstrated, in experimental wetlands that a certain quantity of calcareous gravell, at level of the silt, it is usually beneficial to the treatment process. This seems to indicate that the calcareous gravell is dissolved in the means, improving its characteristics [17]. The percentage of eliminated iron, so much in natural wetlands as built, varies between 28% and 99%, during the initial stage, after the construction of the wetland. While the vegetation reaches its development, the quantity of eliminated iron it is generally located between 30% and 50%. Once the vegetation is developed the quantity of eliminated iron totally it is increased, reaching values between the 50 and 90% [4]. The accumulation of solid material forces to clean and to restore the wetland, after a time, since they are formed barriers that don't allow the appropriate flow of the waters [10]. The quality of the water efluente of the wetlands doesn't reach, usually, the wanted quality, for that ,ussually, a supplementary chemical treatment is needed, after the wetland treatment [4], [12]. This chemical tratment have a cost a lot smaller than the one that would be required without the construction of the wetland. Most of the times the investment costs, in the treatment in wetlands, recover in a year of operation of the wetland, as consequence of the descent of costs in the chemical treatment [4].In the wetlands with Typha better results have been observed that in the wetlands of Sphagnum [5]. It is maybe for that reason that they are much more numerous the wetlands in which the Typha is planted. It is considered that the Typha is tolerant to waters with pH of 2,0 at 8,5, iron concentrations of up to 150 mg/l and of manganese of up to 50 mg/l. The recommended thickness of the sheet of water in wetlands is from 5 to 15 cm [4].

3.2. Processes that take place in wetlands

The wetlands generates favorable environment for the existence of communities of microorganisms with great number of individuals, as algae, protozoos and bacterias [10], that absorb certain polluting substances, to obtain energy and foods for their vital cycle [9]. The natural processes that take place in wetlands include: adsorption and ionic exchange, bioacumulaci¢n, bacterial oxidation and abiotic, sedimentation, neutralization, reduction of sulfates and possible formation of carbonated minerals [4]. In most of the built wetlands, the main mechanism of the retreat of the metals seems to be the bacterial catalytic oxidation of the iron. Then the subsequent hidrolisis precipitates the metal, in form of orange layer that recovers the surface of the substratum quickly [4]. The processes of adsorption, exchange of ions, and formation of complex in the organic matter of the wetland also play a very important paper in the retreat of metals of the polluted water [13]. During the first months of operation of the wetland, these effects help to compensate the fact that the vegetable activity is not still considerable. The phenomenons that take place in the wetlands are related with four components: the vegetation, the water, the microorganisms and the substratum. The animals, so much vertebrate as spineless, have a paper limited in the transformation of pollutants. The main effect of the vegetation is the one of creating support for the microscopic life, when allowing that the colonies of microorganisms are located on its surface (high specific surface), and they are located on the level of the floor [9]. Once it has been gotten that the wetland supports a beneficial bacterial life for the process of treatment of the sour waters, we could think about how to improve the support, so that this bacterial life evolves in an appropriate way. One of the possibilities to increase this support can be to add to the wetland organic matter, besides facilitating the appropriate means to certain vegetable life. The aquatic plants are accustomed to live in anaerobic conditions, picking up the air of the atmosphere and transporting it until the roots, around which an aerobic area is believed [10]. Apparently the plants with denser fibrous structure are those that better oxygenate the substratum [21]. The aireacion of the sustrato is favored, also, for the great quantity of surface that occupies the wetland [4] and for vegetation liberating oxygen for the roots. In the wetland, the water flows through plants, and of substratum formed for compound organic that serve from sustenance to colonies of bacterias which improve the quality of the water. It has been demonstrated, in laboratory that the bacterias present in wetlands are tolerant with high concentrations of heavy metals. The caracteristics of the water, of this substratum, are notably different to the characteristics of the water of the rest of the wetland; for example, the water among the pores of the substratum usually has a superior pH, between 3 and 5 units, to that of the water of the surface of the wetland, and a concentration of smaller dissolved iron that that of the water of the surface of the wetland [13]. Therefore, it is positive to promote a turbulent flow of the water locally, with the help of barriers, or even trunks, to improve the contact between the water and this substratum, and to avoid that they are formed preferential channels of flow of water. The effect of the bacterias oxidizers of the manganese begins to be appreciable, in the manganese concentrations, when the pH is superior at 6. The manganese deposition varies among very wide margins (between 8% and 98%), the evidences seem to point out that the iron concentration should descend first. Some materials, like the selenium for example, are absorbed selectively by some plants, but they are also absorbed by the substratum. Habitually, only 4%-5% of the incorporate nutrients to the system, they are incorporate to plants or animals [10]. The accumulation of metals for diverse plants is different, for example the Sphagnum has a great power of absorption of the dissolved iron. Still in presence of moderate concentrations of this, it absorbs such a quantity of iron that petrifies and dies [4]. The Thypa is quite less efficient in the absorption of metals, but it doesn't usually die petrified by excess of accumulated iron [13]. Some authors have calculated, in a wetland that received water with a content of 10 iron mg/l, a bioacumulaci¢n of 19.506mg of iron for each gram (weigh in dry) of Typha. The bioacumulaci¢n of the manganese for the Typha is always much smaller. Kepler, vide [13], measured bioacumulaciones of 56.000 manganese mg for kg (weigh in dry) of algae. But the algae biomass is very limited in wetlands, for that that its contribution to the retreat of metals of the water, it usually is not considerable [13]. The effectiveness of the wetland will depend, directly, of the capacity to create favorable atmospheres for the development of these microorganismos[9]. The bacterial reduction of the sulfates, and the formation of metallic sulfurs, in a rich substratum in organic matter, can contribute significantly to improve the quality of the water. The process taking place, is the inverse one to the oxidation of the pyrite, with acidity decrease. The evidence exists, in the study of the anaerobic part of the wetlands, that the ferric ion reduces to ferrous, which reacts to produce pyrite. As we have seen the processes of retreat of metals dissolved in acid waters passing through wetlands, are many and varied: [4] * Direct consum for plants, * Adsorption and ionic exchange with alive or dead organic matter, * Adsorption and ionic exchange with inorganic substratum, and * Microbiologic or chemical transformations (assimilation, reduction or oxidation). In a carried out study, starting from data acquired in several wetlands, it has been demonstrated that, except for very strange exceptions, the quality of the water tried in wetlands, it has been improved [12]. Some authors affirm that to treat each liter for minute of polluted water, are needed from 5 to 15 m2 of wetland [14], [6]. To make an idea of the land occupied by the wetlands we can say that, to retire of the water an iron kg a day 100 m2 of wetland are needed, and to retire a kg every day of manganese 500 m2 of wetland are needed. To retire of the water a kg of net acidity a day (the net acidity includes several parameters of quality of the water) they are needed between 200 and 500 m2 of wetland.

3.3. Advantages, disadvantages and costs

In general the polluted waters (also the Acid Mine Drainage) can be treated in wetlands. The treatment of waters in wetlands offers some advantages, regarding other treatment methods, like: under operation cost (cheaper than the chemical treatment) and not very high construction cost; effectiveness treatment of the water and, mainly that doesn't require chemical reagents. Also, they can combine with recess areas, creating to their surrounding parks, to go for a walk, to practice jogging, to make picnic or simply to relax [10] and they can allow the development of certain animal species. From this point of view, the wetland can be considered as a very interesting by-product. But they also have some disadvantages. For example they occupy a big extension of land; the wanted operation is not immediate, it is necessary to wait that the system is balanced, and that the good development of the life is reached; precise periodically of restructurings and adjustments; due to the accumulation of solid material, the precise wetland of periodic cleanings; and it is possible that it can create an undesirable ecosystem (mosquitos, rats, etc) [10].

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Omówienie

Wietrzenie pirytu przy dostępie tlenu i wody wywołuje zjawisko określane jako Acid Mine Drainage, oznaczające silne zakwaszenie wód kopalnianych, przy równoczesnym wzbogaceniu ich w jony metali. Jedną z metod jego likwidacji jest stosowanie systemów, w których przy współudziale bakterii następuje redukcja zawartych w wodzie siarczanów. W celu podwyższania alkaliczności stosowane są także filtry wykonane z pokruszonych skał węglanowych. W przypadkach niskich stężeń żelaza, glinu i tlenu podwyższanie alkaliczności wody może odbywać się przy użyciu beztlenowych filtrów węglanowych (ALD). Są one wykonane jako usytuowane pod ziemią kanały wypełnione kruszywem węglanowym. Kontakt wody przepływającej przez filtr zachodzi w warunkach beztlenowych. System ALD działa wyłącznie na zasadzie podwyższania pH wody oraz podwyższania w niej stężenia wapnia. Następnym etapem oczyszczania skojarzonym z ALD może być natlenianie wody i zatrzymywanie jej w stawie osadowym. Dla dalszego alkalizowania odczynu wody można stosować oczyszczanie naturalne (fitobiologiczne). Używane w tym celu rośliny to m.in.: *Typha*, *Equisetum*, *Sphagnum*. Uważa się, że usunięcie jednego kilograma żelaza na dzień wymaga około 100 m^2 powierzchni oczyszczalni; kilograma manganu natomiast - od 200 do 500 m^2.