Mining Waste and Wetlands

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PREFACE

This thesis is part of the MSc programme School of Applied Geosciences and Mining (SAGM) at Luleå University of Technology.

I would like to thank Luleå University of Technology for the opportunity to study here.

Also I would like to express my gratitude to my supervisor Anders Widerlund for proposing me this project, his help and his comments on my work.

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ABSTRACT

Today mining operations have produced minerals and metals that are widely used in different daily processes. However, most of the operations leave or have left behind waste that create a serious ecological problem – formation of acid rock drainage (ARD), which can result in release of heavy metals to surface waters. Acid mine drainage is currently a very important problem, since AMD can leach toxic concentrations of metals and waters polluted by AMD are very difficult to clean up.

The fact that wetlands intentionally or unintentionally can be used for the treatment of polluted waters is widely known. The main task of wetland treatment is to improve water quality in drainage basins, and the quality of the groundwater.

This thesis describes the study of wetland treatment and processes that can be used for the treatment of metal polluted waters in wetlands.
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1 INTRODUCTION

1.1 Influence of the mining industry on the biosphere

The mining industry is technologically interconnected to human processes influencing the environment for the purpose of supporting energy and primary resources of the various spheres of economic activities. All excavation methods of deposits have an effect on the biosphere, and involve practically all its components: water and air, earth surface resources and the floral and animal world. During mining activities, the areas disturbed by mine opening, waste bank and waste material of the processing increase and add up to the adverse impact on the surrounding environment.

Drainage of deposits and pollution of drainage and waste water reaching lakes and streams drastically change the hydrogeological and hydrological conditions in the region of a deposit. As a result, the quality of ground and surface waters deteriorates. The atmosphere is polluted by emissions from different sources, including excavations, waste rock and manufacturing industry. The conditions for the growth of plants, habitation of animals and human lives essentially worsen as a result of the complex influence on the specified compartments of the biosphere. The resources of the earth which are exposed to the greatest influence concerning the elements of biosphere are those with little or no ability to natural renewal in the future. Their protection must imply a scientifically proved and economically justified maintenance and an integrated approach of use. Land reclamation covers the problem of landscape redevelopment and restoration of its productivity, ecological integrity, and economic and aesthetic value (Internet 1).

1.2 Classification of the influence of mining activities on the environment

It is more expedient to classify the influence of mining activities on an environment for separate compartments of the biosphere. The basic kinds and results of the influence of mining activities on the biosphere are presented in Table 1 (Internet 1).

<table>
<thead>
<tr>
<th>COMPARTMENT OF THE BIOSPHERE</th>
<th>INFLUENCE ON COMPARTMENT OF THE BIOSPHERE</th>
<th>RESULT OF INFLUENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground water</td>
<td>Drainage of deposits, pollution of waste and drainage water.</td>
<td>Depletion of stock of ground and surface water. Effects on hydro-geological and hydrological maintenance of water basin.</td>
</tr>
<tr>
<td>Surface water</td>
<td>Drainage and transport of surface waters and streams, pollution of drainage and waste water reaching lakes and streams.</td>
<td>Pollution of water pool by waste and drainage waters. Deterioration of waters as a result of adverse changes of hydro-chemical and biological modes of surface and ground waters.</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Emissions of dust and gases into the</td>
<td>Pollution (dust and gases) of the atmos-</td>
</tr>
<tr>
<td>COMPARTMENT OF THE BIOSPHERE</td>
<td>INFLUENCE ON COMPARTMENT OF THE BIOSPHERE</td>
<td>RESULT OF INFLUENCE</td>
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<tr>
<td>------------------------------</td>
<td>------------------------------------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Soil</td>
<td>Mine excavations, construction of dumps, slurry dumps, tailings dumps, storage reservoirs.</td>
<td>Disturbance of ground surface. Effect on soil cover. Changes of the conditions of ground and surface water. Sedimentation of dust and chemical compounds owing to emissions to the atmosphere. Erosion processes.</td>
</tr>
<tr>
<td>Flora and fauna</td>
<td>Industrial construction, forest devastations, effect on soil cover, effect on ground and surface water, emission of dust and gases to the atmosphere, effect of industrial noise.</td>
<td>Deterioration of conditions of growth of wood, land vegetation and water flora and fauna. Migration and reduction of the number of wild animals. Oppression and reduction of wild-growing plants.</td>
</tr>
</tbody>
</table>
2 MINING WASTE – THEORETICAL BACKGROUND

2.1 Objectives

Future exploitation of ore reserves discovered during exploration demands technical and environmental knowledge. Mining operations are connected to occupation of large areas of land, production of dust and large amounts of mine waste. The fundamental mine waste environmental problems are:

- Mine waste often contains metal sulphides
- Sulphides oxidise when exposed to oxygen and water
- Sulphide oxidation creates an acidic metal-laden leachate water
- Large amounts of waste result in leachate generation over long periods of time

This waste needs to be managed using principles that control the environmental impact in both short and long term, as well as meet the safety requirements on the deposits over long periods of time. The respective time scales are on the order of hundreds or even thousand of years. Determination of convenient methods to decrease the problems related to mine waste disposal and finding solutions that work coherently with nature are very important tasks for today. In addition, enormous quantities of waste also create the problem of how to restore the landscape (Höglund, 2003). For example, 380 million tons of mining waste has been produced during the extraction of iron ore in Sweden. However these wastes pose far less risk to the environment than the waste from the extraction of sulphidic ores (Sjöblom, 2003).

2.2 Mine wastes produced

The major types of mine waste are: tailings sand and waste rock as illustrated in the mine production scheme (Figure 1).
The waste rock is the low-grade material that needs to be excavated to reach the ore body, and is not profitable to mine. The tailings sand is the gangue and other refuse material resulting from the washing, concentration, or treatment of ground ore that has been processed in an enrichment plant before deposition in waste deposits. Crushing and ore reduction to a fine powder is followed by a flotation process or extraction of valuable material by other means of separation. The crushing increases the surface area of rock material in the tailings sand, which may increase the oxidation rate (Höglund, 2003). The environmental problems associated with mining and mine wastes cause contamination of all media (air, ground water, soil, sediments, and surface water) resulting from a host of metals, primarily As, Cd, Cu, Mn, Mo, Pb, and Zn). These metals emanate from a wide variety of sources e.g., acid drainage from edits and sulfide bearing waste piles, exposed ore zones, heap-leach spoils, mine-waste piles and sediments, slag piles, fluvial tailings deposits, and tailings and waste rock piles (Internet 2).

Ore is mined in surface or underground operations. Often the ore first has to be uncovered by removing the surrounding waste rock. In Sweden, for example, the main mine products are iron ore and sulphidic ore. The sulphidic ore is processed in a concentrator, including such processes as crushing, grinding, gravimetric separation of Au and flotation. Flotation is a milling process by which some mineral particles are induced to become attached to bubbles and float, while others sink. In this way the valuable minerals are concentrated and separated from the worthless gangue. The product from the concentrator is transported to smelters for further treatment, where the use of water by weight in the production of metals is more than the weight of the ore grade material (Sjöblom, 2003).

Waste from extraction of iron and sulphidic ores can be divided into waste rock and tailings. Tailings are the material rejected from a mill after most of the recoverable valuable minerals have been extracted. Normally tailings consist of finely ground host rock, the gangue minerals that occur within the ore assemblage, and small amounts of ore materials that can not be re-
covered economically. Most mining tailings are deposited in impoundments. The impoundments are surrounded by retaining dams constructed of unconsolidated soil materials, waste rock or coarse-grained tailings. The design and construction of tailings impoundments must provide retention of tailings solids, protection from dam failure, and prevention of uncontrolled release of dissolved constituents from the impoundment to downstream groundwater and surface-water flow systems. In spite of the impoundment design improvement over the past century, there are today problems with the failure of retaining dams and release of tailings and tailings waters. The uncontrolled release of contaminated water from tailings impoundments can harm the quality of downstream water and destroy aquatic environments. The number of tailings dam failure has increased in recent years.

There is one more problem connected with tailings, – namely the discharge of contaminated water from intact tailings impoundments. The water discharged from tailings impoundments may contain high concentration of sulfate and dissolved metals derived from the oxidation of sulfide minerals. In that case the retaining dams may be designed to facilitate drainage to the adjacent surface water environment or into underlying permeable geological materials to raise the stability of the retaining dams. Exposure of sulfide materials from tailings to atmospheric oxygen, release of $H^+$, sulfate and dissolved metals to the pore water of the impoundments may be caused by the drainage of impoundments. This may cause degradation of groundwater and surface-water resources (Blowes et al., 2002).

For example, the failure of a tailings dam at the Boliden Apirsa’s Aznalcollar (Los Frailes) Ag-Cu-Pb-Zn mine near Seville, Spain, released approximately $5.5 \times 10^6$ m$^3$ of acidic water and $1.3 \times 10^6$ m$^3$ of heavy metal-bearing tailings (Hudson-Edwards, 2003).

It has been estimated that 18 billion m$^3$ of mine tailings are generated worldwide, every year. For example, the mass of tailings produced daily in Canada is estimated to be 950, 000 tones (Arctic Centre University of Lapland, 2000).

In Russia, the volume of tailings and sludge in tailings dumps are estimated to be 500 – 600 million m$^3$. In the Russian territories of the Barents Region the water is polluted by heavy metals, oil, organic compounds, chlorine and other toxins. The largest amount of wastewater is led to the water system in the Murmansk region – in 1993, 67 million m$^3$. The most polluted waters are near the metallurgical plants (Monchegorsk, Zapolyarnij and Nikel). The typical water pollutants from metallurgical and mining industries are heavy metals, mineral salts, sulphates and chlorides. In the Republic of Karelia the main water polluters are the pulp and paper industry, the aluminium plant in Nadvoitsy and a mining concentration plant in Kostamuksha. The amount of wastewater is 210, 4 million m$^3$. The pollutants consist mainly of organic compounds, oil, and compounds of nitrogen, copper and zinc. In the Archangelsk Oblast, the main polluters
of wastewaters are oil, nitrates, heavy metals and iron. The amount of wastewater in the Ar-
changelsk Oblast is 773 million m$^3$. In the Republic of Komi the main pollutant is the chlorine
bleaching used in the wood processing plant, the amount of waste waters is 650 million m$^3$ (Ar-
tic Centre University of Lapland, 2000).

In Sweden, there are approximately 250 million tons of waste rock and 400 million tons of
tailings from the mining of sulphidic ores. Sulphidic mine waste may give rise to acid mine
drainage which is one of the major environment problems associated with mining operations
(Sjöblom, 2003).

2.3 Acid Mine Drainage

Acid mine drainage is currently a very important problem in areas where there has been a
history of coal or hard-rock mining. Oxidation of exposed sulfide minerals in mine tailings and
waste rock releases toxic heavy metal ions and acidic hydrogen into surface and ground waters.
The water pollution problems that result from acid mine drainage and acid rock drainage are very
difficult to clean up. Acid mine drainage will go on for thousands of years once the chemical
and microbial processes that create acid mine drainage in exposed overburden are set into motion
(Internet 3).

Seepage of contaminated water from abandoned mines (known as acid mine drainage,
AMD) causes severe water pollution problems such as dead fish and aquatic insects, stunt plant
growth, corrosion of concrete and metal structures, high water treatment costs, and stream banks
and beds with bright, rusty, orange color. In addition, AMD can leach toxic concentrations of
metals like iron, and aluminum from mine waste, causing further contamination of creeks, rivers,
and ground water. For example, coal fields of the Appalachian Mountains in the eastern United
States are connected with the AMD problem. The major problem with AMD is the reaction be-
tween the mineral pyrite and water and oxygen. A series of chemical reactions occur, that create
the pollutants that appear in mine waters. The character of these reactions is dependent on the
specific geology and hydrology of a particular mine site (Internet 2). Acid mine drainage results
when the mineral pyrite (FeS$_2$) is exposed to air and water, resulting in the formation of sulfuric
acid and iron hydroxide. The overall equation for AMD formation is:

$$\text{FeS}_2 + \frac{15}{4}\text{O}_2 + \frac{5}{2}\text{H}_2\text{O} \rightarrow \text{FeOOH} + 2 \text{H}_2\text{SO}_4$$

Sulfuric acid ($\text{H}_2\text{SO}_4$) is a strong acid capable to create severe environmental degradation
regarding plants and animals. Iron hydroxide (Fe OOH) can form an orange or yellow sludge coating
the bottoms of streams, effectively extinguishing aquatic life (Internet 4).
2.4 Ways to minimize the generation of Acid Mine Drainage

2.4.1 Soil covering

The basic principle of the soil cover technique is to reduce the amount of oxygen that can penetrate into the waste, with regard to climatic conditions. In Sweden, for example, the most acid generating wastes need to be covered with a sophisticated sandwich-layer technique. First a sealing layer consisting of a compacted clayey till is placed on the tailings, followed by a protective layer of ordinary till. The sealing layer must provide capillary retention properties (pore size distribution of the soil material) since the sealing layer should maintain a high degree of water saturation during the whole year, including dry periods. Protection of the sealing layer from erosion, frost action and thawing, to enhance the retention of water, to supply a basis for establishing vegetation and to protect from spreading of dust are the main functions of the protective layer.

Oxygen penetration

Oxygen penetration in mine waste deposits can occur through different processes:

- Transportation of air into waste by convection (e.g. driven by wind).
  Can be important in waste rock deposits with coarse material.

- Transportation of air into waste by a chimney effect.
  Can occur in waste rock deposits which have large heaps where oxidation may be strong.

- Diffusion of air that can be take place as:
  - diffusion of oxygen gas in air-filled pores
  - diffusion of dissolved oxygen in water-saturated pores
  Diffusion is important in tailings which are denser and less permeable than waste rock. The diffusion rate in gas filled pores is about 10 000 times faster than that in water saturated pores.

- Transportation of oxygen dissolved in rainwater

The main task of design is to maintain a high degree of water saturation in the sealing layer. This will reduce the oxidation rate, and will preclude any significant oxidation. In addition, an oxygen diffusion rate of the same magnitude as the amount of oxygen supplied by percolation of rainwater will be obtained. To achieve this diffusion rate, the sealing layer must be water-saturated during the major part of the year and needs to be dimensioned for dry-year conditions. For that reason, a dense soil material must be used (for instance clayey till). Large amounts
of soil material are necessary for the covering of waste deposits, i.e. several million tones. Because of that reason, the local availability of soil material must be taken into account in the design and construction of cover layers. (Höglund, 2003)

**Water balance**

The main task of a soil cover is to minimize the infiltration of water, thus minimizing the production of drainage water in the underlying waste with regard to the water balance. The reasons to investigate the routing of water in the cover are (Carlson, 2002):

- to compare alternative design profiles and materials
- to understand how a cover will function and which water routing mechanisms are most important at the site
- to estimate flow rates so that the different components such as drainage systems can be sized properly
- to estimate the amount of drainage water that will form from the underlying waste

The capillary retention needs to be high for the sealing material and the protective soil needs to be applied in sufficient thickness to prevent drying out during the dry season. When a soil cover has the low-permeable properties of a sealing layer, the protective cover must be designed to allow for a controlled diversion of surplus water that infiltrates through the top, but cannot be transported through the sealing layer. This method usually can be used when water retention properties are required. The accumulation of drainage water in the protective cover contributes to the formation of ponds on the ground surface. With increasing size, such ponds will reach the brim and an overflow situation will occur that can cause rapid and severe erosion of the brinks of a deposit. The reason for the situation stated above is that pore-pressures increase in the cover soil, which reduces its shear strength to practically zero. The design of a bottom deposit must allow for the anticipated percolation through the sealing layer in order to give a correct water balance. A correct water balance corresponding to the local climatic conditions and to the design of a cover will provide long-term stability of the deposits (Höglund, 2003).

### 2.4.2 Water covering

The main principle of water covering is to limit the contact between the sulphidic tailings and atmospheric oxygen. The low solubility and slow diffusion of oxygen in water restricts the penetration of oxygen into deposited waste. With the objective of raising the water level, a dam must be constructed to contain the tailings (Höglund, 2003).
The water balance must be established for precipitation falling within the local runoff area, the inflow of surface water, evaporation, groundwater recharge and discharge. Water covers should be designed according to the local climatic and hydrological conditions (Höglund, 2003).

**Oxygen penetration**

The water in tailings ponds is often well oxygenated. However, the oxygen solubility in water is low and the diffusion rate of dissolved oxygen in water is slow. Therefore, the oxygen penetration into underlying tailings is still slow. The transportation of oxygen will be due to mixing of the free water body, caused by the action of wind. The resuspension of solid material from the bottom sediments may be caused by wind action (by wind-induced waves). This may increase the contact between oxygenated water and the fine-grained sulphide particles, which may cause an increased oxidation. To avoid this, the water depth must be dimensioned so that wave action does not reach the bottom sediments, i.e. if the water depth increases wave action will decrease. However, with increasing water depth the amount of water in the impoundment and the height of the dam increase. To prevent wave action it is possible to raise the water level and to establish vegetation in the pond. Vegetation will act as a breakwater and will increase the sedimentation of organic material, which will help in protecting the sulphide particles from resuspension and oxidation (Höglund, 2003).

### 2.5 Basic reactions and processes

#### 2.5.1 Oxidation by atmospheric oxygen

Ore enrichment processes extract and separate minerals of commercial value and exclude minerals that cannot be economically recovered. The chemical processes responsible for occurrence of acid mine drainage (AMD) can be exemplified by the oxidation of pyrite (FeS$_2$), which is the most abundant sulfide mineral in most tailings impoundments. In FeS$_2$, both the Fe and S atoms may be oxidized. Wherever pyrite can come into contact with oxygen and water a potential problem exists. This trio of pyrite, oxygen and water gets the ball rolling in the formation of AMD. When pyrite is initially exposed to oxygen and water the following reaction can occur:

$$\text{FeS}_2(s) + \frac{7}{2} \text{O}_2(g) + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+$$

(2.1)

The oxidation of pyrite is the result of the interactions of physical, chemical, and biological reactions, and can also occur in many environments free from mining activities. Due to greater air accessibility and greater sulphide surface area after the ore processing, pyrite oxidation becomes enhanced in mine waste deposits. Pyrite, oxygen, and water react to form dissolved fer-
rous iron ions, dissolved sulfate ions and acidity. Thus ferrous iron ions and acidic hydrogen ions are released into the waters draining through the mine tunnels or waste piles. When the pH of the solution exceeds 7, low concentrations are found of species derived from partial oxidation of sulfide-sulfur. The partial oxidation products are exposed and subsequently oxidized to SO$_4^{2-}$. The drainage is rich in Fe$^{2+}$ and SO$_4^{2-}$ as Fe$^{2+}$ and SO$_4^{2-}$ are fairly soluble and mobile.

The next step in the process is the oxidation of ferrous iron to ferric iron as shown in the following reaction (2.2) (Internet 2).

$$\text{Fe}^{2+} + \frac{1}{4} \text{O}_2(g) + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \quad (2.2)$$

Ferrous ($\text{Fe}^{2+}$) ions react with oxygen and acidic hydrogen ions to form ferric ($\text{Fe}^{3+}$) ions and water. Often this reaction doesn't happen to any great extent underground because of limited amounts of available oxygen. This reaction is pH dependent, with the reaction proceeding slowly under acidic conditions (pH 2-3) with no bacteria present, and several orders of magnitude faster at pH values near 5 (Höglund, 2003).

The next reaction describes how ferric ions may be hydrolyzed in water and precipitate as ferric Fe oxyhydroxide:

$$\text{Fe}^{3+} + 2 \text{H}_2\text{O} \rightarrow \text{FeOOH}_{(s)} + 3\text{H}^+ \quad (2.3)$$

This process releases even more hydrogen ions into the aquatic environment and further reduces the pH. The yellowish-orange precipitate of ferric hydroxide formed in this reaction turns the acidic runoff in the streams into an orange or red color, and covers the stream bed with a slimy coating. Aquatic life dwelling on the bottom channel of the stream is soon killed off. In the cases when pH is higher than 3.5 and when mixed with oxygenated groundwater or surface water, oxidation to Fe$^{3+}$ and precipitation of FeOOH$_{(s)}$ will occur (Internet 2).

By adding equations (2.1), (2.2) and (2.3), we obtain the overall reaction for pyrite oxidation, where acidic hydrogen ions are released into the water and stream beds are coated with ferric hydroxide:

$$\text{FeS}_2_{(s)} + \frac{15}{4} \text{O}_2(g) + \frac{5}{2} \text{H}_2\text{O} \rightarrow \text{FeOOH}_{(s)} + 2 \text{SO}_4^{2-} + 4\text{H}^+ \quad (2.4)$$

Equation (2.4) shows that four units of H$^+$ are formed for each unit of pyrite. In equation (1) the oxidation of sulphide to sulphate results in two units of H$^+$ and equation (2.4) shows that subsequent oxidation of ferrous iron to ferric iron followed by hydrolysis to precipitate FeOOH.
results in an additional two units of $H^+$. Pyrite oxidation depends on the chemical conditions in solution and at pyrite surfaces.

The following reaction shows how pyrite is oxidized by $Fe^{3+}$, which in turn is generated by oxidation of $Fe^{2+}$:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (2.5)$$

Ferric iron may contribute to the oxidative dissolution of sulphide minerals. Ferric iron is a strong oxidant of pyrite under low-pH conditions (below about 3.5), where oxidation of $Fe^{2+}$ to $Fe^{3+}$ is catalyzed by bacteria. The role of $Fe^{3+}$ in the oxidation of pyrite becomes less significant when pH increases because of a decline in the solubility of $Fe^{3+}$ and because the rate of pyrite oxidation by $O_2$ increases as the pH increases (Blowes et al., 2002).

Mine waste deposits contain an abundance of bacteria, which are very important in biomineralization, including: *Acidithiobacillus* (previously *Thiobacillus*) ferrooxidans, *Leptospirillum*, *Acidiphilium*, *Sulfobacillus*, *Ferroplasma*, *Sulfolobus*, *Metallosphaera*, and *Acidianus* (Internet 5).

The activity of bacteria accelerates the oxidation of sulfide and ferrous iron resulting in the generation of acidic drainage. Bacteria act as catalysts in both major types of sulphide oxidation reactions:

- sulfide mineral + oxygen + water = sulfate + acidity + metals
- sulfide mineral + ferric iron + water = sulfate + acidity + metals

*Thiobacillus* ferrooxidans can accelerate sulfide oxidation by orders of magnitude at acidic pH (Singer and Stumm, 1970).

### 2.5.2 Acid neutralization

Acid mine drainage introduces sulfuric acid and heavy metals into the environment. The environment can naturally assimilate some AMD through dilution, biological activity, and neutralization. The assimilation of AMD will depend on specific conditions such as drainage patterns and dilution, biological activity, and neutralizing capacity of the ore, waste material, tailings, and/or surrounding soils. Naturally occurring biological activity can to some extent attenuate metal concentrations by adsorption and precipitation of some metal species such as sulfates (Internet 6).

Limestone and other materials that produce alkalinity can affect the generation of AMD in two ways. If water flowing into pyritic materials is alkaline, alkaline conditions can be maintained in the pyritic material, the acid-generating reactions may be inhibited so that little or no
AMD forms. Alternatively, once AMD has formed, its interaction with alkaline materials may neutralize the acidity and promote the removal of Fe, Al and other metals. Hence, water with high SO$_4$ and low Fe may be indicative of earlier AMD generation (Internet 7).

Movement of acidic tailings water, generated in the unsaturated zone, is retarded with respect to groundwater velocity. A conceptual model describing acid neutralization in mine waste was proposed by Morin et al., (1998). The model was based on observations of water chemistry made in an aquifer underlying the tailings impoundment at the Nordic U mine site in Elliot Lake (Ontario), and from geochemical calculations based on these data. According to this model, a sequence of precipitation – dissolution reactions controls the pH of the porewater. This sequence includes the dissolution and precipitation of aluminosilicate minerals. The composition of the tailings shows that specific minerals neutralize the acidity. Aqueous geochemical modeling indicates that the series of reactions can be divided into equilibrium reactions and kinetically limited reactions. The process of carbonate and hydroxide dissolution is more rapid than the groundwater velocity. Because of that reason, these reactions can occur at equilibrium or near equilibrium. The dissolution of aluminosilicate minerals is kinetically limited (Jambor et al., 2003).

**2.5.3 Dissolution of carbonate minerals**

Mineral dissolution and precipitation of carbonate minerals partially regulate pH and alkalinity of natural waters, affecting the transport of organic and inorganic contaminants. Due to human pollution, the aquifers contain many hazardous metals. Seasonal cycles in pH and redox conditions, dissolving the carbonate host lattices, again releasing the trace metals into the aquifer, threaten ecosystems and human health (Internet 8).

Carbonate minerals in non-carbonate rock terrain may occur as carbonate detritus, fossil shells, and carbonate cements. In non-carbonate soils, when their concentration exceeds 1%, the water chemistry is mainly controlled by the carbonates. This fact is extremely important when one is concerned about the ability of the rock to neutralize acid mine waters, other acid waste waters, or acid rain (Internet 9).

Host rocks and ore deposits usually contain one or more of the following carbonates: calcite (CaCO$_3$), siderite (FeCO$_3$), ankerite (Ca (Fe, Mg) (CO$_3$)$_2$) and dolomite (Ca Mg (CO$_3$)$_2$). The dissolution of carbonate minerals is more effective when pH is below 5-5.5 (Jambor et al., 2003).

Calcite is the most rapidly reacting of the carbonate minerals existing in tailings impoundments. The dissolution of calcite can maintain the pH of tailings pore waters near neutral. Neutrality of pH will remain as long as sufficient amount calcite remains in the tailings. Calcite dissolves according to the reaction:
\[
\text{CaCO}_3(\text{s}) + H^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{HCO}_3^-(\text{aq})
\]

Because of calcite dissolution sulfide-mineral oxidation and the dissolution of less soluble minerals contained in the tailings can occur. As calcite has a high relative solubility, the contribution of other minerals to acid neutralization will be small. During oxidation of Fe sulfides, high concentrations of Fe (II) can combine with HCO$_3^-$ released by calcite dissolution to result the precipitation of secondary siderite:

\[
\text{Fe}^{2+}(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightarrow \text{FeCO}_3 + \text{H}^+(\text{aq})
\]

Because of depletion of calcite from the tailings, the pH will decrease to the next pH plateau where siderite will form the primary pH buffer. Primary and secondary siderite neutralizes acidity in tailings where this one carbonate mineral is present (Jambor et al., 2003).

\[
\text{FeCO}_3 + \text{H}^+(\text{aq}) \rightarrow \text{Fe}^{2+}(\text{aq}) + \text{HCO}_3^-(\text{aq})
\]

2.5.4 Oxyhydroxide precipitation and dissolution of aluminosilicate minerals

During carbonate dissolution, aluminosilicate dissolution provides Al ions to the solution, and Al-containing phases may precipitate. For example precipitation of gibbsite (Al(OH)$_3$):

\[
\text{Al}^{3+} + 3 \text{OH}^-(\text{aq}) \rightarrow \text{Al(OH)}_3(\text{s})
\]

Because of low concentrations and the difficulties in identifying Al precipitates, gibbsite can seldom be identified in the tailings environment. There is a hypothesis which is supported by the observation of two Al-bearing secondary minerals at Heath Steele tailings impoundments in New Brunswick (Jambor et al., 2003).

It was established that small amounts of an Al-bearing and pH buffering phase were formed in the tailings during an experiment. (Blowes et al., 2002)

One of the minerals was identified as alunogen (Al$_2$(SO$_4$)$_3$ x 17 H$_2$O). Dissolution of aluminosilicate minerals proceeds after depletion of primary carbonates and the easily soluble hydroxide and oxyhydroxide minerals. As dissolution of aluminosilicate is slow relative to the rate of groundwater flow, these reactions are kinetically limited (Jambor et al., 2003).
3 WETLANDS - THEORETICAL BACKGROUND

Wetlands are land areas that are wet during part or all of the year because of their location in the landscape. Wetlands are unique among major ecosystem groups on the earth depending on existing plants, water conditions and on geographic setting, and also due to the chemical, physical and biological changes that occur during flooding. Wetlands are found at topographic lows (depressions), in areas with high slopes and low permeability soils or between stream drainages where the land is flat and poorly drained. Distribution and differences in wetland type, vegetative composition, and soil type are caused primarily by geology, topography, and climate. Abundant supply of water is important for most forms of biological productivity. The wetland plants are adapted to take advantage of this abundant supply of water while overcoming the periodic shortage of other essential chemical elements such as oxygen. Besides jungle-like plants, wetlands are inhabited by a multitude of animals including mammals, birds, reptiles, amphibians and fish (Kadlec and Knight, 1996).

Adamus et al., (1987, 1990) have presented a list of the major functions and values of wetlands:

**Functions:**
- Groundwater recharge
- Groundwater discharge
- Floodwater alteration
- Sediment stabilization
- Sediment/toxicant retention
- Nutrient removal/transformation
- Production export
- Aquatic diversity/abundance
- Wildlife diversity/abundance

**Values:**
- Recreation
- Uniqueness/heritage values

The most important function of wetlands is water quality improvement. Because wetlands have a higher rate of biological activity than most ecosystems, they can transform many common pollutants that occur in conventional wastewaters into harmless by-products or essential nutrients that can be used for additional biological productivity. These transformations are accomplished by the use of natural energy sources such as solar radiation, wind, soil, plants, and animals. Wet-
lands are one of the least expensive treatment systems to operate and maintain. (Kadlec and Knight, 1996)

Wetlands provide effective, free treatment for many types of water pollution. Wetlands can effectively remove or convert large quantities of pollutants from point sources (industrial wastewater effluents) and non-point sources (mine, agricultural, and urban runoff). Sedimentation, natural filtration and other processes help clear the water of many pollutants (Hammer, 1989). Some pollutants are held for years in the roots of plants such as arrowhead, cattails, or reed canary grass. Sometimes these pollutants are later released by the plants and soil in the winter months when impacts to water quality will be greatly reduced. Wetland plants also filter sediments from water and help to stabilize the land around them (Internet 21). Wetland plants remove nutrients through absorption and assimilation for biomass production. Oxygen produced by plants increases the dissolved oxygen content of the water and also of the soil near the plant roots. (Hammer, 1989)

3.1 Wetland hydrology

The term wetland hydrology generally refers to the inflow and outflow of water through a wetland and its interaction with other site factors. Features of land having wetland hydrology are characterized by inundation or saturation of the upper part of the soil at a sufficient duration to create anaerobic conditions (Internet 7).

The formation, persistence, size, and function of wetlands are controlled by hydrologic processes. Hydrologic conditions also influence the soil and nutrients, which in turn influence the character of biota. Differences in wetland type are the product of the movement of water through or within the wetland, water quality, and the degree of natural or human-induced disturbance. The wetland soils and vegetation alter water velocities, flow paths, and chemistry. The hydrologic and water-quality functions of wetlands, that is, the roles wetlands play in changing the quantity or quality of water moving through them, are related to the wetland’s physical setting (Internet 15).

When topographic and hydrogeologic conditions are sufficient and a long-term source of water exists, wetland conditions occur. Topographic conditions refer to the presence of landsurface depressions in the drainage basin. Areas having fine textured surficial soils with low hydraulic conductivity, sufficient thickness to store water and the presence of impermeable bedrock near the land surface may favor the development of wetland hydrology.

A long-term source of water is a very important feature for the development of wetland conditions. The source of water may be precipitation, ground water discharge, surface water run-off during rainfall or snowmelt events, periodic flooding caused by elevated water levels in
nearby surface water bodies, groundwater inflow to the wetland, or a combination of any, or all, of these sources (Figure 2 and Internet 16). Wetlands lose water via streamflow, groundwater recharge, evaporation from standing water or saturated soils, and by transpiration from plants, surface water or groundwater outflow (Figure 2).

3.1.1 Wetland water mass balances

In treatment wetlands, wastewater additions are normally the dominant flow, but under some conditions, other transfers of water are also important. According to Kadlec and Knight (1996), the dynamic water budget for a wetland can be written:

$$Q_i - Q_o + Q_c - Q_b - Q_{gw} + Q_{sm} + PA - ETA = \frac{dV}{dt}$$

where

- $A =$ wetland top surface area, $m^2$
- $ET =$ evaporation rate, $m/d$
- $P =$ precipitation rate, $m/d$
- $Q_b =$ bank loss, $m^3/d$
- $Q_c =$ catchment runoff rate, $m^3/d$
- $Q_{gw} =$ infiltration to groundwater, $m^3/d$
\[ Q_i = \text{input wastewater flow rate, m}^3/\text{d} \]
\[ Q_0 = \text{output wastewater flow rate, m}^3/\text{d} \]
\[ Q_{sm} = \text{snowmelt rate, m}^3/\text{d} \]
\[ t = \text{time, d} \]
\[ V = \text{water storage in wetland, m}^3 \]

### 3.1.2 Snowmelt

In northern climates, snowmelt is one of the water mass balance components, which is used for flow and outflow measurements. The end-of-season snow pack is melted over time in rough proportion to the temperature excess above freezing. The determination of the \( Q_{sm} \) snowmelt rate is given by Chow:

\[
Q_{sm} = (0.0254)(0.03(T_{avg} - 24) + 0.02(T_{max} - 27)) \times A
\]

where 
\[ T_{avg} = \text{average daily temperature, °C} \]
\[ T_{max} = \text{maximum daily temperature, °C} \]
\[ A = \text{wetland top surface area, m}^2 \]

### 3.1.3 Water mass balance of estuaries

Estuaries receive freshwater from precipitation, ground-water discharge, streamflow, and overland flow (figure 3). Ground water discharges through shallow-water sediments of the estuary or through marsh soils and can affect the nutrient balance and salinity of the receiving waters. As the freshwater-saltwater interface moves down the estuary from the stream toward the sea, estuarine salinity decreases during periods of high stream flow (Figure 3).

As streamflow decreases, the estuarine salinity increases and the interface moves up the estuary. Water temporarily stored in flood-plain wetlands upstream of the estuary deposit sediment and nutrients. Subsequently, water leaving these wetlands exports decomposition products and organic detritus to the estuary. The decrease in flow velocity and temporary storage of water controls the size and time of freshwater inflow to estuaries (Internet 17).
3.1.4 Water mass balance impact on pollutant reduction

Water mass balancing can be used for purposes of contaminant mass balancing. The frequency of water quality sampling is generally influencing the time period over which averaging is done. Precipitation and evaporation rate are time variable transfers. But they combine over extended periods to either dilution or concentration of the wastewater during its passage through a wetland. Dilution, adverse effects on retention time and poor mass removals can be caused by heavy rainfall (Kadlec and Knight, 1996).

3.2 Mechanisms of metal immobilization in wetlands

Wetlands have been used for treatment of municipal wastewater (sewage), agricultural wastewater and runoff, industrial wastewater, and stormwater runoff from urban, suburban and rural areas. The removal of contaminants from the water is the main goal of wastewater treatment. The goal of wastewater treatment is the removal of contaminants from the water in order to decrease the possibility of detrimental impacts on humans and ecosystems. Many contaminants, including a wide variety of organic compounds and metals, are toxic to humans and other organisms (Internet 18).

A number of metals are required in small amounts for plant or animal growth. Some of these metals, such as copper, selenium, zinc, cadmium, mercury and lead are toxic at higher or even low concentrations, and can be found in industrial or other types of wastewaters. Cadmium, mercury and lead have a tendency to become concentrated at higher levels of the food chain that can lead to serious health hazards to higher organisms, including humans (Internet 18). The
processes of metal removal in wetlands include sedimentation, filtration, adsorption, complexation, precipitation, plant uptake, and microbially mediated reactions, such as oxidation sulphate reduction (Figure 4).

![Figure 4 Summary of the major physical, chemical and biological processes controlling contaminant removal in wetlands (Hammer, 1990)](image)

### 3.2.1 Sedimentation

Reducing the velocity of the water is one of the ecological functions of wetlands containing macrophytes. This process promotes the settling of the metals in wetlands. The settling rate of particles is proportional to the square of their diameter. The major problems of metal immobilization connected with sedimentation are the accumulation of metals in the ecosystem, the removal of newly formed sediments on a regular basis, and decrease of the total wetland basin volume (Sjöblom, 2003).

### 3.2.2 Adsorption and ion exchange

The process of adsorption on solid surfaces is very important for metal immobilization. The surface charge of a mineral surface is neutral when the pH is equal to the zero point of charge (ZPC), positively charged, when pH < ZPC, or negatively charged, when pH > ZPC. Therefore, metals are increasingly adsorbed more strongly at a higher pH in cationic forms, and metals are increased at a low pH in anionic forms. In more saline waters, cations and ions that are more abundant may out-compete trace metals for binding sites.

The adsorption edge is the pH interval where there is a rapid transition from dissolved to adsorbed metal. Different metals have different adsorption edges for the same mineral. The iden-
tity of the adsorption species, the water chemistry and the solid phase composition influence the position and width of the adsorption edge. Some aqueous phase components can have a negative influence on adsorption. For example, dissolved organic matter (DOM) can form soluble complexes with the dissolved metals. In ion exchange processes, ions on the solid substrate (e.g. clay, natural organic compounds) are replaced by ions from the surrounding solution. The cation exchange capacity of a material is to some extent determined by pH. The process of sorption includes both adsorption and ion exchange (Sjöblom, 2003).

3.2.3 Oxidation and hydrolysis

In acid mine drainage, Fe is often found in its ferrous form in contact with oxygen. This ferrous Fe will be oxidized to ferric Fe:

\[ 4 \text{Fe}^{2+} + \text{O}_2 (\text{aq}) + 4 \text{H}^+ \rightarrow 4 \text{Fe}^{3+} + 2 \text{H}_2\text{O} \]

This reaction is dependent on pH, temperature and the presence of microorganisms. The chemical oxidation will increase with increasing pH, and the chemical oxidation will be pH-independent at pH below 3.5. The ionization constant of water influences the temperature dependence of the process. The oxidation reaction may be catalyzed by iron-oxidizing bacteria, such as Thiobacillus ferrooxidans and Ferrobacillus ferrooxidans. At pH > 3.5, the ferric Fe will be hydrolyzed and precipitate as a ferric hydroxide according to the reaction:

\[ \text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 3\text{H}^+ \]

The liberation of H\(^+\) in this reaction means that pH of the solution will fall. The rate of ferrous Fe oxidation and hydrolysis is reduced when pH is low (Sjöblom, 2003).

3.2.4 Iron reduction

Iron is found in wetlands, primarily in its reduced form (ferrous). This element is more soluble and more rapidly available to organisms in reduced form. Reduced iron causes a grey-green coloration of mineral soils, instead of the normal red or brown color of oxidized (ferric) iron (Internet 19). In the wetlands, ferric iron is reduced according to the reaction:

\[ 4\text{Fe(OH)}_3 + \text{CH}_2\text{O} + 7\text{CO}_2 \rightarrow 4\text{Fe}^{2+} + 8\text{HCO}_3^- + 3\text{H}_2\text{O} \]
3.2.5 Sulfate reduction

Sulfur occurs in several different oxidation states in wetlands. Sulfur is released when wetland sediments are disturbed. Sulfate reduction is implemented by sulfate-reducing bacteria, such as Desulfomonas, Desulfotomaculum, and Desulfovibrio, which in the absence of oxygen use $\text{SO}_4^{2-}$ to mineralize low molecular weight organic compound according to the reaction:

$$\text{SO}_4^{2-} + 2 \text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2 \text{HCO}_3^- \quad (3.1)$$

Sulfate reduction can be effected by generation of bicarbonate alkalinity (equation 3.1), by removal of $\text{H}^+$ from solution and an increase of pH. Sulfate reduction will raise the pH of the surrounding water. Metals such as Cd, Cu, Hg, Pb and Zn form highly insoluble precipitates with sulfide according to the reactions:

$$\text{H}_2\text{S} \text{ (g)} \rightarrow \text{H}_2\text{S} \text{ (aq)} \rightarrow \text{H}_5 \text{ (aq)} \quad (3.2)$$

$$\text{H}_2\text{S} \text{ (aq)} \rightarrow \text{HS}^- + \text{H}^+ \quad (3.3)$$

$$\text{HS}^- + \text{Me}^{2+} \rightarrow \text{MeS} \text{ (s)} + \text{H}^+ \quad (3.4)$$

Many metals may co-precipitate with, or adsorb to, other sulfides formed (Sjöblom, 2003).

Nutrient removal

Nutrient removal in wetlands is caused by the flourishing plant growth and also by physical processes such as adsorption of nutrients on suspended sediments, precipitation and sedimentation. Plants and sediments are the major accumulators of nutrients in wetlands (Kadlec and Knight, 1996).

3.3 Ecological aspects.

3.3.1 Biological uptake of metals

Biological uptake is a very important pathway for contaminant removal in wetlands, including metals. Data on metal removal in constructed wetlands are mostly from systems treating acid mine drainage (Hammer, 1997). Investigations of mine drainage treatment in wetlands show that microorganisms may play an important role in trace metal accumulation in soil. Microorganisms may provide a measurable amount of contaminant uptake and storage (Sjöblom, 2003). Microbes in wetlands compete with cellulose and chitin as chelating surfaces for metal absorption, and metal-chelating materials such as clay, other ions, and pH affect the toxicity of heavy metals to microorganisms. Resistance to toxic metals is achieved by an increasing impermeability of the
cell and biochemical transformation of metals. This process protects the cell from toxic elements in its environment. Then follows detoxification of the cell environment by elimination of toxic metals or altering of metals to nontoxic forms. Transformations of toxic metals into nontoxic forms may be achieved intracellularly and/or extracellularly. Toxic metals may be oxidized, reduced, or methylated to produce less toxic compounds. Most heavy metals form insoluble sulfides, and sulfide production by the bacterium *Desulphovibrio desulphuricans*, the fungus *Poria vaillantii* and some strains of the yeast *Saccharomyces cerevisiae* precipitate metals from solution. Microorganisms increase their tolerance to toxic metals through many processes and simultaneously immobilize, precipitate and bind contaminants in treatment processes for polluted water (Hammer, 1997).

Aquatic macrophytes have different growth forms (figure 5). There are the freely floating macrophytes, which accumulate metals and nutrients from the water phase, and the rooted macrophytes, which accumulate metals and nutrients from the sediments (Internet 18).

![Figure 5 Different growth forms of aquatic macrophytes](image)

The water, sediments and plants in wetlands receiving urban runoff contain higher levels of heavy metals than wetlands not receiving urban runoff. Large aquatic plants e.g. *Typha latifolia*, *Iris pseudacornis* and *Phragmitis australis* are known to accumulate heavy metals in their tissues (Internet 20).

Systems with humic substrates are potentially effective because of the already mentioned ion exchange capacity. However, the ion exchange capacity of humic materials or mosses has a limited functional longevity. A *Sphagnum* bed with an area of 1600 m$^2$ and a depth of 30 cm treating a mine drainage flow of 40 L/min and an iron concentration of 200 mg/L may be saturated in only 2.2 years (Hammer, 1997).
Plants of *Sphagnum fallax* and *Sphagnum henryense* can grow in solutions with Fe concentrations up to several mg/l, but at concentrations of 100 mg/l or more, they turn brown and stop growing (Sjöblom, 2003).

Most constructed marshes are dominated by cattail (*Typha latofolia*) because of its relatively reactive surfaces in marshes and marsh wastewater treatment (Hammer, 1997). The tolerance of *Typha latofolia* to acid mine drainage has been investigated by Wenerick. *Typha* was found to be the most tolerant plant compared with other mosses. Aboveground plants of *Typha latofolia* were almost completely dead by the sixth week of exposure to synthetic AMD (pH 3.5, containing e.g. 78.8 mg/l Fe$^{2+}$, 10.0 mg/l Al$^{3+}$, and 5.2 mg/l Mn$^{2+}$) (Sjöblom, 2003).

The plant species, cattail (*Typha latofolia* and *T.angustifolia*) and alkali bulrush (*Scirpus robustus*), have been analyzed for uptake and accumulation of the metals Cd, Cr, Pb, Mn, Ni, and Zn. Leaf tissue in *Typha* took up 447 – 1200 mg Mn/kg dry wt (34 – 187% of the background soil level). Zink uptake in *Scirpus* and *Typha* was greatest in root parts, with a maximum observed Zn concentration of 81.3 mg/kg. Ni, and Zn were significant in *Scirpus* roots and various *Typha* parts (Hammer, 1997).

A number of physical, chemical and biological processes in constructed and natural wetlands are providing contaminant removal (Internet 18).

**Specific removal processes**

**Physical**
- Sedimentation
- Filtration
- Adsorption
- Volatilization

**Biological**
- Bacterial metabolism
- Plant metabolism
- Plant adsorption
- Natural Die-off

**Chemical**
- Precipitation
• Adsorption
• Hydrolysis
• Oxidation, Reduction

3.4 Effects of cold climate

The best conditions for wetland treatment are found in warm climates, but there are a number of wetland systems containing different kinds of wastewater and landfill leachate in cold temperature regions. Cold weather conditions affect wetland processes and treatment results, and influence all stages of the planning, design, construction, and maintenance of wetlands. The term cold climate refers to environments where the coldest and warmest months have mean temperatures below -3°C and above 10°C. This classification includes most of Canada, Alaska and northern U.S., Scandinavia, Eastern Europe, Russia, and northeastern China.

There are three major climate-dependent processes: ice formation, hydrology and hydraulics, and the thermal effects on biologically or microbiologically mediated treatment processes (Mulamoottil et al., 1998).

3.4.1 Ice formation

Energy accumulated in underlying soil during the warm season slows down ice formation. However, due to differences in density and convective losses, ice formation on the water surface starts when the water temperature reaches 3°C. Dead vegetation in wetlands collects drifting and falling snow that forms an insulating layer. Due to that reason, the water in natural swamps and marshes often does not freeze in winter. If snow accumulates before a significant ice layer is formed, subsequent freezing is greatly reduced. The presence of some ice can provide insulation, thereby slowing the cooling of the underlying water. In cases when the ice is held by vegetation, the water flow beneath the ice will be reduced when the ice layer thickens. This may lead to subsequent flooding, freezing, and hydraulic failure (Mulamoottil et al., 1998). For example, a Canadian water system with constructed wetlands was operated successfully by raising the water level at freezing time, thereby providing an ice cap to trap insulating air as the water level dropped (Herskowitz, 1986).

Calculation of energy balances and water temperatures are required to predict ice formation. Major factors to consider are the wetland dimensions, the temperature and loading rate of wastewater, the ambient air temperature and wind speed, and the depth and thermal conductivity of different layers (snow, ice, plant litter and soil, or other porous media) (Mulamoottil et al., 1998).
3.4.2 Hydrology and Hydraulic Conditions

Snow and ice influence the wetland water balance. The leachate flow mainly consists of the precipitation percolating through the landfill. The precipitation is higher in cold climatic regions than in warmer regions. Due to that reason landfill leachates are more diluted in cold climate. In cases when the snow melt percolates through the waste, the leachate production will increase when snow accumulation is high. Snow melting and increased leachate volume in the wetlands will decrease the hydraulic residence time in the treatment system and the concentration of pollutants will be diluted. The size of a landfill area and the wetland-to-catchments ratio are very important parameters for determining the magnitude of the influence of snow melting. If the ratio is small it may contribute to hydraulic overloading of subsurface horizontal-flow that will lead to short-circuiting.

Deposition of suspended solids within subsurface horizontal-flow systems clog the system and degradation products can accumulate in the filter with the mineral fraction of total suspended solids, especially Fe, Mn and Ca precipitates. These deposits can decrease the hydraulic conductivity. In cold periods, nutrient uptake, oxygen transport to the roots, and microbiological rhizosphere activity slow down. This can also lead to accumulation of total suspended solids (organic material) and decrease the hydraulic conductivity of the system. Soil microorganisms are surrounded by polysaccharide containing structures (glycocalyx) of bacterial origin. Environmental stress as a result of temperature changes can result in an increase of the glycocalyx production. The microorganisms and bacterial glycocalyx together form a highly organized matrix (biofilm). An increase of the biofilm thickness due to a fall in temperature and decreased oxygen availability in winter may lead to decreased hydraulic conductivity of subsurface horizontal-flow treatment wetlands (Kristiansen, 1981).

3.4.3 Biogeochemical processes

Nutrient uptake by plants and microbial transformations of wastewater components and plant litter depend on climatic conditions. Plant physiology, influenced by solar radiation and temperature, and microbial processes, influenced by temperature, are examples of direct effects. Biological, biochemical and biogeochemical processes also depend on indirect effects, influencing physical conditions, e.g., hydraulic residence time, oxygen availability, and freezing/thawing of soil. Decomposition of organic matter, nitrification, denitrification, and removal of pathogens are generally temperature dependent in all wastewater treatment processes. The removal processes influenced by temperature are shown in Table 2. The temperature effect in many full-scale constructed wetland systems is insignificant and the treatment performance decreases during the winter (Mulamoottil at al., 1998).
Table 2 Selected physical, chemical, and biological processes regulating nutrient removal in wetlands and expected influence of low temperature on the process.

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>EFFLUENT PARAMETERS</th>
<th>INFLUENCE OF LOW TEMPERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flocculation</td>
<td>Suspended solids, particulate organic C, N, and P</td>
<td>*</td>
</tr>
<tr>
<td>Sedimentation</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Filtration</td>
<td></td>
<td>*</td>
</tr>
<tr>
<td>Chemical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorption</td>
<td>Dissolved organic compounds, anions PO₄³⁻ NH₄⁻N, and metals</td>
<td>*</td>
</tr>
<tr>
<td>Precipitation</td>
<td>Inorganic P, sulfides, and metals</td>
<td>*</td>
</tr>
<tr>
<td>Volatilization</td>
<td>NH₄⁻N and volatile organic compounds</td>
<td>**</td>
</tr>
<tr>
<td>Microbiological</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Respiration</td>
<td>Biochemical oxygen demand, O₂, NO₃⁻N, SO₄²⁻, HCO₃⁻, and volatile fatty acids</td>
<td>***</td>
</tr>
<tr>
<td>Nitrification</td>
<td>NH₄⁺N</td>
<td>**</td>
</tr>
<tr>
<td>Denitrification</td>
<td>NO₃⁻N and NO₂⁻N</td>
<td>**</td>
</tr>
<tr>
<td>Mineralization</td>
<td>Organic N and P</td>
<td>*</td>
</tr>
<tr>
<td>Assimilation</td>
<td>Nutrients</td>
<td>**</td>
</tr>
<tr>
<td>Competition, dying</td>
<td>Pathogenic organisms</td>
<td>**</td>
</tr>
<tr>
<td>Biological(Plants)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Growth of uptake</td>
<td>Nutrients</td>
<td>***</td>
</tr>
<tr>
<td>Gas transport</td>
<td>O₂ and related reactions</td>
<td>***</td>
</tr>
</tbody>
</table>

Note:  * - Little, ** - Moderate, *** - Large influence of low temperature < 5°C (meaning low reaction rate due to low temperatures).

The temperature influence on biogeochemical processes (C, P, and N) is discussed by Reddy and Burgoon (1996). Due to increased temperature of the medium, many biochemical reactions and enzymatic reactions mediated by microbes proceed at a faster rate. Each microbial species and each strain has its own minimum, optimum, and maximum temperature for microbial activity. Such interactive factors as hydraulic loading, effluent quality, vegetation and soil/substrate within the wetland affect the optimal temperature for maximum microbial activity. Three types of relationships between the reactions rate constant, activation energy, and temperature given by van’t Hoff-Arrhenius equation are detected by Reddy and Burgoon (1996). The
temperature effect when the temperature of a given reaction increases by 10° C is shown as $Q_{10}$. This confirmation means that the reaction rate follows a simple exponential function of temperature. In most cases, biological reaction rates double ($Q_{10} = 2$) with a 10°C increase in temperature (Reddy and Burgoon, 1996).

The temperature dependence of reaction rate constants is expressed as (Mulamoottil at al., 1998)

$$k_{T1} = k_{T2} \times O^{(T1-T2)}$$

where $k_{T1}$, $k_{T2}$ are first order rate constants at temperatures T1 and T2, and $O$ is the temperature coefficient.
4 NATURAL AND CONSTRUCTED WETLANDS

4.1 Natural wetlands

Compared to constructed wetlands, natural wetlands are rarely used for the treatment of contaminated water bodies and wastewaters. This is because natural wetlands are protected by law in many countries, when they contain valuable biotopes (Sjöblom, 2003). To select a natural wetland for remediation it is necessary to estimate the wetland area and find a suitable wetland plant community type with sufficient area. A number of factors must be taken into account such as wastewater pre-treatment needs, flow control, mass and hydraulic loading rates and existing environmental resources in the wetland to control and minimize ecological alterations. The topography of natural wetlands varies with respect to morphology and size. The main task in engineering wetland treatment systems is to design a water conveyance and distribution system that uses a large portion of the wetland surface area. Natural wetlands can be used for remediation if there are natural wetland areas available to treat the anticipated flow to the necessary final effluent quality. The natural wetland area required for treatment can be determined based on the level of pre-treatment, flow rate, final effluent quality goals, and the type of natural wetland available. The wastewater must be pre-treated and the concentration of wastewater pollution should be reduced to action level before being introduced into natural wetlands (Kadlec and Knight, 1996). Natural wetlands can be used for the remediation of metal polluted water, for example, before the influence on the wetland’s ecosystem have been analysed in detail (Sjöblom, 2003). Effective pre-treatment is a very important factor in wetland treatment which provides a good influent quality and prevents an increase of acceptable pollutant levels, thus protecting the wetland (Kadlec and Knight, 1996).

There are situations when the effect of mine drainage treatment is less comparable with treatment of, for instance, municipal wastewater, containing high nutrient concentrations and biological oxygen demand. This situation occurs when the concentrations of metals in drainage do not reach harmful levels (Sjöblom, 2003).

The role of plants is significant in natural wetlands remediation. Increased water flows received by a natural wetland change its hydroperiod and thereby the influence on wetland plants. Regular or recurrent wastewater flows will alter the wetland hydroperiod, change the water regime and increase the duration of flooding. Only some subsets of the wetland plant species are adapted to these hydroperiod alterations (Duck Potato, Cattail, Buttonbush Shrub, Water Lily, and Hydrilla). Some natural wetland plant communities have been used for wastewater and stormwater recycling (Typha, Pontederia, Sagittaria, Scirpus, Sedges, Cephalanthus occiden-
Wetland tree species such as *Taxodium*, *Nyssa*, *sabal minor*, and *Malaleuca quinquinerva* are generally adapted to continuous inundation (Kadlec and Knight, 1996). In addition, in many cases the material for the construction of a treatment wetland (e.g. plants and peat) is sometimes harvested from natural wetlands (Sjöblom, 2003).

Fulfilment of all requirements, including soils, hydrology, water chemistry and ecology provides a natural wetland remediation (Kadlec and Knight, 1996).

### 4.2 Constructed wetlands

Today, we know about the great significance of wetlands in the global ecosystem. Wetlands are unique ecosystems on the planet for recycling of the essential elements of life (carbon, hydrogen, oxygen, nitrogen, and phosphorus). Wetlands naturally clean water, their soils and root mass of the plants work as filters to extract contaminants from water. Natural wetlands do not have the capacity to clean waters, contaminated by humans and the industry. Because of that reason, constructed wetlands are widely used in wetland treatment technology today (Internet 22).

Wetlands act in connection with other treatment elements. The basic functions of constructed wetlands are (Campbell and Ogden, 1999):

- Nutrient (nitrogen and phosphorus) removal and recycling
- Sedimentation
- Biochemical Oxygen Demand of organic compounds capable of being oxidized.
- Digestion and removal
- Metal precipitation
- Toxic compound degradation

#### 4.2.1 Design principles

Constructed wetlands should be designed to remove the biochemical oxygen demand (BOD), total suspended solids (TSS), nitrogen, phosphorus, metals, hydrocarbons, organic pollutants, pathogenic compounds, and viruses. The hydraulic capacity, residence time, areal loading rates, water temperature, and plant density are the wetland design components (Campbell and Ogden, 1999).

The constructed wetland system is divided into two general types: the Horizontal Flow System (HFS) and the Vertical Flow System (VFS). The HFS is divided into Surface Flow (SF) and Sub-surface Flow (SSF) systems. In the case of HFS, the wastewater flows horizontally from the feed inlet to the outlet. VFS are fed by wastewater from time to time and drain vertically through the drainage pipes (Internet 11). A SF system consists of a cell or cells with wastewater...
routed at shallow depths over a substrate supporting emergent vegetation. An SSF system consists of a cell or cells with wastewater routed through and below the surface of permeable substrate supporting emergent vegetation (Hammer, 1997).

The main distinctive feature of constructed treatment wetlands from natural treatment wetlands is the origin and their landform. The landform criteria have important significance in the design of wetlands (Kadlec and Knight, 1996).

A number of factors, such as the location of wastewater sources, geological, geotechnical, hydrological, and other environmental information, determine the site selection of a constructed wetland. According to Hammer (1997): “The site selection should clearly define the wastewater management objectives and the regulatory considerations, collect sufficient data to develop the preliminary design of a wetland system, investigate the environmental and social conditions and sensitivities to predict any adverse effects and provide mitigation, and obtain legal access to the site”.

4.2.2 Hydrology

Hydrology is a very important parameter in wetland design as hydraulic conditions affect many abiotic factors, including soil anarobiosis, nutrient availability, and, in coastal wetlands, salinity (Mitsch, 2000). The hydrologic conditions are controlled by climate, seasonal patterns of streamflow and runoff, tides, and possible groundwater influences, landscape position, topographic location, presence or absence of vegetation, type of soil, the hydrogeologic framework, the geochemistry of surface and ground water (Internet 12). Unsuitable hydrologic conditions can lead to failure of wetlands. Parameters such as hydroperiod, depth, seasonal pulses, hydraulic loading rates, and retention time are used to describe the hydraulic conditions (Mitsch, 2000).

The hydroperiod is the most basic design parameter for constructed wetlands because this determines the form, nature, and function of the wetland. Hydroperiod is defined as “the depth and duration of inundation measured over an annual wet or dry cycle”. Permissible high and low elevations of water will estimate the stormwater volume capacity of a wetland, the discharge structure, and bleed-down orifice elevations (Hammer, 1997).

In a constructed wastewater wetland, the water level is controlled by outflow structures that provide appropriate water depth (Mitsch, 2000). The duration and depth of flooding are important in determining the plant species appropriate to a constructed wetland and the influence on plant physiology due to concentration of soil oxygen, soil pH, and concentrations of toxic chemicals (Kadlec and Knight, 1996). Water depth causes different vegetation zones in a wet-
land, as deeper water may restrict oxygen from reaching the substrate. Also, water depth may affect the photosynthesis (Hammer, 1997).

At the start of wetland exploitation, it is necessary to maintain low water levels to avoid newly emerged plants. For example, this drawdown period may be required in cases when wetland plants from germinating seeds are used. But continuous flooding is needed for floating-leaved and submerged plants. The start-up period for plant establishment may take 2 to 3 years (Mitsch, 2000).

Storms and seasonal flood patterns seldom influence on constructed wastewater wetlands, although they can affect the operation of wetlands designed for the control of non-point source runoff (Mitsch, 2000). It is very important to take into account periodicity, duration, and seasonality of flooding during development, as wetland plants withstand flooding to various degrees (Hammer, 1990). During winter and spring, when there is less vegetation, storms and seasonal floods may create high pulses of different contaminants, for example drainage water loading. A good wetland design can benefit from these seasonal pulses for system accumulation and provide for excess wet weather storage (Mitsch, 2000).

The hydraulic loading rate (HLR) “refers to the loading of water volume per unit area basis. [loading = (parameter concentration)(water volume/area)]” (Internet 13). The HLR is defined as (Mitsch, 2000):

\[ q = \frac{Q}{A} \]

where \( q \) = inflowing hydraulic loading rate (HLR), the volume per unit time per unit area, which is equivalent to the depth of flooding over the treatment area per unit time (m day\(^{-1}\) or m yr\(^{-1}\))

\( Q \) = flow rate (m\(^3\) day\(^{-1}\) or m\(^3\) yr\(^{-1}\))

\( A \) = wetland surface area (m\(^2\))

The ability of a wetland to treat a given volume of water in a given time – the hydraulic residence time (HRT) - defines the hydraulic capacity of the wetland. An expected average time in which a molecule of water will flow from one end of the wetland to the other can be identified as HRT (Campbell and Ogden, 1999). HRT is a vital operational parameter for optimizing the performance of a wetland system. Hydraulic residence time (t) is defined as (Hammer, 1990):

\[ t = \frac{L W n d}{Q} \]

where \( L \) = length of system (parallel to flow direction) (m)

\( W \) = width of system (perpendicular to flow direction) (m)
4.2.3 Temperature

Almost all wastewater treatment processes are affected by temperature (Campbell and Ogden, 1999). Some biochemical processes, especially the microbially mediated nitrogen processes, are temperature sensitive (Kadlec and Knight, 1996). There is the problem to determine the potential thermal conditions of water during wastewater treatment processes of wetlands. According to Campbell and Ogden (1999), a simple description of a heat model for wetlands can be written:

\[ \Delta \text{heat} = \text{heat (in)} +/- \text{heat (air)} +/- \text{heat (ground)} – \text{heat (out)} \]

where

\( \Delta \text{heat} \) = the change of heat in the wetland (in BTUs or calories)

heat (in) = heat content of the influent water

heat (air) = heat lost or gained to the air

heat (ground) = heat lost or gained from the ground under the wetlands

heat (out) = heat content of the effluent water

However, there is a complication in determining the heat transfer coefficient for losses to the air and ground because heat transfer is affected by snow cover, ice, and layers of dead vegetation. A heat-loss model, proposed by Sherwood C. Reed can be written (Campbell and Ogden, 1999):

\[ \text{heat loss/gain to air} = \text{surface area} \times U_{\text{air}} \times (T_{\text{water}} – T_{\text{air}}) \times \text{HRT} \]

where

surface area = area of the wetlands

\( U_{\text{air}} = 0.052 \) BTU / ft\(^2\) – °F – hr

T water = temperature of water entering the wetlands (°F)

Tair = air temperature (°F)

HRT = hydraulic residence time (hours)
4.2.4 Design goals

The research has been extensive with a large amount of published articles about optimal design of constructed wetlands. In sympathy with the guidelines proposed by Mitch, it is possible to establish the main purposes of successful constructed wetlands design (Mitsch, 2000).

- The design of constructed wetlands should be simple, because design complexity may create failure.
- The design of wetlands must be concerted with climatic conditions, especially for the extremes of weather and climate.
- The design of wetlands must be concerted with the natural topography of the site.
- Constructed wetlands should look like natural wetlands, without rectangular basins, rigid structures and channels, and regular morphology.
- Wetlands systems require time for wetland processes to commence before the optimal performance is reached.
- The main task of design is function. If the design results do not agree with the basic planning, but the overall function of the wetland is acceptable, then the system has not failed.
- Wetlands should be designed according to a variety of wetland types and configurations, and to a variety of local, native plant species, taking into account the type of wastewater.
- A constructed wetland should be designed to take advantage of the natural features of the site and to minimize their disturbance.
5 CASE STUDIES

Two cases will be described in the following, which demonstrate the use of wetlands for reclamation of AMD. The first is a case with a natural wetland: Kristineberg – Vormbäcken (Sweden). The second is a case with constructed wetlands: Dunka Mine (Minnesota).

5.1 Immobilization of metals along a mining region recipient (the river Vormbäcken)

Metal immobilization in wetlands situated around river Vormbäcken (northern Sweden) and adjoining rivers and lakes has been studied during two years. The Kristineberg mine and its tailings ponds are located in the upper part of the catchment area of Vormbäcken. The catchment area is underlain by granite, metarhyolites, metatonalite, metagranodiorite, metaargilite, and metagraywacke. The wetland environment was investigated by comparing the water chemistry at two stations situated on opposite sides of the wetland.

Table 3. Characteristics of the Vormbäcken system

| Wetland size | The first wetland is situated more or less immediately downstream of the sampling station Aspliden; its size is approximately 4 km$^2$. The second wetland is situated between the sampling stations Rökå and Mickeldammet; its size is approximately 6 km$^2$. |
| Altitude | 230 - 360 meters above sea level |
| Water flow | The river water flow slows down, and more finely grained sediments may accumulate on the bottom. The highest water flow recorded for Vormbäcken was measured at Brännfors (catchment area 188 km$^2$) in June (4.72 m$^3$/s) and in October (1.57 m$^3$/s). |
| Species | Wetlands are dominated by aquatic macrophytes such as reed (Phragmites australis), sedges (Carex spp.), horsetail (Equisetum fluviatile), and cotton grasses (Eriophorum spp.). |
| pH | pH was always measured at the in situ temperature. The pH value varied between 5 and 7, enough to permit substantial adsorption of, for example, Cu and Pb to both natural particles and Fe oxyhydroxides present. During the spring months the pH values recorded along Vormbäcken were close to neutral. During the rest of the year, pH was estimated as relatively constant along the river, except in October, when pH fell by more than one unit. |
| Incoming metals | Zn, Cu, Cd, Al, Mn, As, and Fe. |

The goal of this investigation was to quantify metal immobilization and any seasonal changes in natural wetlands surrounding a small river that is the recipient of treated water from a metal mine. Metal immobilization in wetlands has been studied by comparing variations in metal concentrations existing along the wetland system, together with variations in the concentration of SO$_4^{2-}$.

According to A.A Milne, the concentrations of Zn, Cu, Cd, and Pb did not decrease more than 5%. Loadings of these metals contributed by tributaries could be detected due to the high pH in these tributaries. The flow rate is too rapid compared to the time required for physical...
(sedimentation), chemical (adsorption, precipitation), and biological (uptake, sulfate reduction) immobilization processes to occur. For this reason, the wetlands were inefficient traps for Zn, Cu, Cd and Pb. For As the catchment is the most important source. Fe is influenced by the efficiency of the metal immobilization process. In spring, part of the river and the substrate normally acting as an adsorbent were frozen. Due to large water flows during snowmelt, the adsorption time was reduced when metal transport is most intense in the system (Sjöblom, 2003).

5.2 Use of constructed wetlands to remove nickel and copper from Dunka mine drainage

Drainage from the mineralized Duluth Complex stockpiles located at Dunka Mine in northeastern Minnesota contains elevated concentrations of nickel (Ni), copper (Cu), cobalt (Co), and zinc (Zn), and has increased metal concentrations of nearby receiving waters to levels up to 400 times the natural background concentrations. At this mine an igneous intrusion overlies the taconite ore and must be removed and stockpiled. A feasibility study that analyzed treatment options ranging from a full-scale treatment plant to various passive treatment alternatives was conducted (Mulamoottil, 1998).

The metal retention capacity of each wetland was estimated to determine if wetland treatment was a viable treatment alternative.

Table 4. Characteristics of the Dunka mine wetlands system.

<table>
<thead>
<tr>
<th>Wetland size</th>
<th>The wetlands range in size from 1 to 20 ha, with average depths ranging from 0.2 to 1.2 m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water flow</td>
<td>The average daily water flow recorded for the EM-8 wetland with a catchment area of 20 ha is 14 (L/s)</td>
</tr>
<tr>
<td>Species</td>
<td>During the investigation natural vegetation such as cattails (Typha), sedges (Carex sp.), and grasses (Calamagrostis sp.) were used.</td>
</tr>
<tr>
<td>pH</td>
<td>The pH ranged from 5.25 to 7.45</td>
</tr>
<tr>
<td>Incoming metals</td>
<td>Ni, Cu, Co, Zn</td>
</tr>
</tbody>
</table>

Limited diffuse drainage seepage occurs along the toe of some stockpiles, but it was not a major contributor to overall load to the watershed. Seeps begin to flow during spring thaw in April and flow continuously until freeze up at the end of November. Peat depth, number and spacing of sampling stations were selected in view of the capability of each of the wetlands. The variation of metal concentrations depended on the proximity of the sites to existing stockpile drainage. Cu concentrations ranged from 40 to 724 mg/kg, and Ni ranged from 19 to 740 mg/kg. The wetland area that received drainage from stockpiles had metal concentrations greater than
100 mg/kg, and significantly reduced removal potential. Because of low degree of decomposition (decomposed peat is more fibrous) flow resistance through the peat was reduced. This increased the hydraulic conductivity with the result that more stockpile drainage could contact the peat. To estimate the Ni retention capacity, laboratory and field studies were used. The maximum Ni concentration measured in field samples was 6400 mg/kg, while concentrations as high as 20,000 mg/kg were measured in laboratory experiments. From this data the total removal potential of each area was estimated. The active removal depth of 20 cm was determined with respect to that most flow in peatlands occurs across and within 30 cm of the surface. Using data collected from a white cedar peatland area it was determined that metal concentrations decrease with depth and that more than 80 % of the metal removal occurred in the upper 20 cm. Using data for the annual Ni loading, a wetland lifetime ranging from 20 to several hundred years was estimated.
6 CONCLUSIONS

This thesis gives a structural description of wetlands and some processes that are vital for the treatment of metal-polluted waters in wetlands. A number of factors affecting the productivity and useful lifetimes of treatment wetlands are also described. The sources of acid mine drainage (AMD) and ways to minimize production of AMD such as soil covering and water covering is discussed based on previous research results.

The main goal of the thesis is to describe if wetlands are effective to use as a remediation method, which processes contribute to their efficiency and what limitations may prevent treatment performance. For consideration of this problem, natural and constructed wetlands have been studied.

Natural wetlands can be used as an effective remediation method which provides good water quality and prevents the development of unacceptable pollutant levels. A number of factors such as climatic conditions, wastewater pre-treatment needs, flow control, mass and hydraulic loading rates, design of conveyance and distribution systems, existing environmental resources in the wetland water, and plant species control ecological alterations in wetlands.

A good design of a constructed wetland system contributes to high quality of treatment with expected results. Such parameters as site selection, hydraulic and climatic conditions, hydroperiod, hydraulic loading rate, hydraulic residence time, and plant ability play very significant roles in wetland design and construction.

However, the following limitations may reduce the effectiveness of wetland treatment processes:

- Temperature and flow deviations influence wetland processes and may reduce the removal rates of contaminants in wetlands.
- Cold climatic conditions can slow down or inhibit plant growth, slow remediation implementation, reduce the rate of contaminant breakdown in wetlands, and increase the period of treatment.
- The removal mechanisms in a wetland can be overloaded by high inflows of water.
- Dry-weather periods can damage plants and significantly limit wetland processes.
- Small wetland areas are not suitable for implementation of remediation.
- Employing specific plant species for phytoremediation can be difficult due to adaptability problems.
- High concentrations of contaminants may create plant toxicity effects.
- Remediation connected with factors such as contamination depth, for example where fast-growing, deep-rooted trees are used to remediate contaminated groundwater.
• Wetland ageing may induce a decrease of contaminant removal rates over time.

This thesis also presents the results from two case studies aimed at investigating metal immobilization in a natural wetland (Kristineberg – Vormbäcken in Sweden) and in a constructed wetland (Dunka Mine in northeastern Minnesota).

The results from the Kristineberg site show that the immobilization of Zn, Cu, Cd, Al, Mn, As, and Fe along a mining region recipient (the river Vormbäcken) did not decrease metal concentrations more than 5% due to high pH, rapid flow rate, and climatic conditions.

The results of the investigation of metal removal (Ni, Cu, Co, Zn) from the Dunka Mine drainage are regarded as successful. However, some treatment limitations are indicated. Increasing drainage flow during spring thaw until freeze-up at the end of November contributed to the overall load to the watershed. Using data collected during an investigation of the site, it was determined that metal concentrations decreased with depth, and that wetland lifetime probably ranges from 20 to several hundred years.
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