



**UNIVERSITY OF
BIRMINGHAM**

**The Performance of an Ultrasound
Flotation System for Heavy Metal
Removal from Acid Mine Drainage
in Wheal Jane Mine**

by

FAIZAL WAN ISHAK

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School of Chemical Engineering,
University of Birmingham,
Birmingham
B15 2TT

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ABSTRACT

The aim of this study is to compare the effect of the ultrasound on the removal of heavy metals (Iron, Zinc and Copper) from Acid Mine Drainage (AMD) using a Denver Cell flotation. Samples from the Wheal Jane mine site, Cornwall, which contain high loadings (32 ppm of iron, 35 ppm zinc) of heavy metals, were chosen for this study. Synthetic AMD and individual metal solutions are used in the initial experiments to optimise the flotation process condition prior to using real AMD.

Initial flotation results with column and Denver flotation units were compared before ultrasound was added to the process flow sheet. The Denver flotation unit gave better metal removal compared to the traditional column flotation unit and successfully removed the metals (optimum removal 100% copper, 99% iron and 96% zinc) and hence was selected for the ultrasound test programme.

Three different process methods, ultrasound treatment followed by Denver flotation cell, Denver flotation cell alone and ultrasonic applied simultaneously with Denver flotation cell were tested for every sample. Ultrasound pre-treatment enhances the metal removal when coupled with the flotation system. In the early stages of the treatment (first 2 minutes of flotation time), up to a 10% increase in metal removal (iron, zinc) compared to the Denver cell alone was achieved by using ultrasound treatment. This could prove to be a significant improvement in removal efficiency at the early stages of separation. The correct pH for the metal to precipitate and the optimum dosage of suitable frother however are also major contributors to the success of this technique.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrophotometry
AMD	Acid Mine Drainage
AMW	Acid Mine Water
ALD	Anoxic Limestone Drains
Bdet	Benzenediamidoethanethiol Dianion
BOD	Biological Oxygen Demand
CAF	Cavitation Air Flotation
CF	Centrifugal Flotation
COD	Chemical Oxygen Demand
Armac	Cocoalkyl Amine Thioacetate
CW	Constructed Wetland
CCC	Critical Coalescence Concentration
CV	Coefficient of Variation
DAF	Dissolved Air Flotation
EC	European Countries
EF	Electro-Flotation
EQS	Environment Quality Standards
HIC	High Intensity Conditioning
IAF	Induced Air Flotation
JF	Jet Flotation
KAX	Amyl Xanthate
LD	Lime Dosed
LF	Lime Free
PPTP	Pilot Scheme Passive Treatment Plant
PAC	Polyaluminium Chloride
rAMD	Real Acid Mine Drainage

RSD	Relative Standard Deviation
SAPS	Successive Alkalinity Producing Systems
SRB	Sulfate Reducing Bacteria
SS	Suspended Solids
sAMD	Synthetic Acid Mine Drainage
TDS	Total Dissolved Solids
TVSS	Total Volatile Suspended Solids

UNITS

w/w	weight per weight
$\mu\text{g/L}$	microgram per litre
L/s	litre per second
ppm	parts per million
rpm	rotation per minutes

Chapter 1. Introduction

1.1. Overview

Wastewater treatment is an important component in the sustainable development of countries, and can play a key role in maintaining the quality of clean water to every human life. However, every system developed to treat wastewater has to consider the operational cost and carrying capacity at every discharge point to be practically applied in an industrial context.

The past decade has seen the rapid development of wastewater treatment systems. Various technology and methods have been developed to meet the water quality criteria and at the same time attempts have been made to minimize the capital and operational cost. Manufacturing and mineral processing industries use a large amount of water for processing and cleaning purposes, and the water often needs to be treated before release into the discharge stream or recycled. The treatment of the water does not contribute to the capital production of the industries, but the quality and purity of the treated water is very important to the sustainable management of industry. However, higher cost of treatment and combined with higher quality treated water requirements will increase the overall production cost. Low cost treatment options with subsequent low quality of treated water can result in disciplinary action or sanctions from the local authority.

Manufacturers have to balance between cost of the treatment and the quality of the treated water produced by each plant based on a number of criteria.

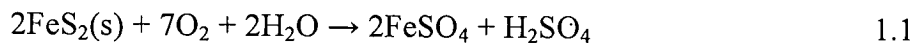
1.2. Acid Mine Drainage

Abandoned mines are another major source of environmental pollution especially mine water entering local streams and rivers. Metal sulphides that have been left at the mine are exposed to water and air and generate soluble metal sulphates. The metal sulphides are dissolved and generate sulphuric acid. Sulphuric acid then dissolves other minerals via an indirect leaching process.

Mine drainage may be categorized as follows:

1. Alkaline
2. Saline
3. Alkaline and ferruginous
4. Acid and ferruginous

It is type 4 that is of greatest importance in the UK. Acid Mine Drainage (AMD) is formed by the oxidation of sulphide minerals within the exposed rock face of an abandoned mining operation.



Equation 1.1 has become the common generic representative to describe AMD formation although not all the AMD is acidic as some is almost neutral or alkaline, depending on the local geology of the mine.

Wheal Jane Mine is a very famous case study in the UK showing the impact of AMD. The mine was rich with tin in 1700. Around 1885, the tin mine became uneconomical to exploit exclusively for tin, but Wheal Jane was still able to continue activities for associated minerals. The mine was completely shut down in 1992 when the world tin price collapsed. The abandoned mine slowly flooded and was then overloaded by heavy rain and at one stage, it breached its barrier and overflowed into the nearest river, Carnon Valley and eventually Falmouth Bay. This phenomenon affected the surrounding habitat causing great environmental damage. After this incident caused international news, remediation measures were installed in 1994.

1.3. Treatment of AMD

The treatment of the AMD can be generally divided into two different methods:

1. Passive treatment
2. Active treatment.

1.3.1 Passive Treatment

Passive treatment – a treatment that involves the application of geochemical or biological based systems. Bacteria are commonly used to break down the sulphur related bond. Aeration constantly needs to be applied to the pond to maintain the bacteria populations. This method was chosen because of the low cost and ease of maintenance. However, this treatment method needs a very big area for pond treatment and normally only caters for less than 5000m³ per day of flow rate water. Also they are usually used in combination with other remediation techniques.

Types of Passive treatment system include:

1. Aerobic Wetlands
2. Anaerobic Organic Substrate System
3. Anoxic Limestone Drains (ALD's)
4. Successive Alkalinity Producing System, and
5. Rock Filters

1.3.1.1 Aerobic Wetlands

Wetlands systems affect a separation by the aerobic oxidation of the metal contamination, forming insoluble metal oxide, hydroxide and oxyhydroxide precipitate. The vegetation in the wetland will promote the aerobic oxidation of the metal contaminants. Oxygen from the plant roots diffuses into the surrounding substrate and creates a localised oxygenated zone in

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which metal precipitation is promoted. The formation of insoluble iron compounds is promoted by the microbial activity associated with the substrate.

As an aerobic wetland is only efficient in processing net alkaline waters, an acid generating reaction and the wetland system must be continually monitored to ensure that excessive acidification does not impair the pH dependent contaminant removal process, although the pH of the inflow improved by pre-treatment in other passive systems upstream of the aerobic wetland.

1.3.1.2 Anaerobic Organic Substrate System

A non-compacted layer of substrate between 30 and 45 cm thick for encouraging bacteria growth is built for this system. Limestone may be artificially added or naturally present within the substrate. Sulphate reducing bacteria facilitate the precipitation of the dissolved metal content out of solution. The bacteria employ the sulphate to oxidise organic matter, resulting in the production of bicarbonate and hydrogen sulphide.

1.3.1.3 Anoxic Limestone Drains (ALDs)

Alkalinity is being promoted within the AMD and incurs a lower overall cost than the anaerobic wetlands. Limestone channels are buried beneath several metres of liquid clay and an additional layer of plastic is usually

present to prevent gas escape. The channel dimensions may vary according to available space between 1 and 20 metre wide.

Dissolved aluminium and iron will be precipitated out upon contact with limestone to form insoluble hydroxide compounds. However, precipitation of the insoluble hydroxide may decrease the overall efficiency of the drain either through armouring the limestone surface with $\text{Fe}(\text{OH})_3$ precipitates or plugging the drain with gelatinous $\text{Al}(\text{OH})_3$.

1.3.1.4 Successive Alkalinity Producing Systems (SAPS)

Limestone beds covered with an organic substrate or compost are built for this system. Anaerobic microbial conversion and limestone dissolution neutralised the inflow. Iron-reducers, sulphate-reducers and ammonifiers are the bacteria groups present with the latter group thought to be primarily responsible for microbial alkalinity generation.

1.3.1.5 Rock Filters

A rock filter is an aerobic treatment process where an algal growth is encouraged through which the AMD percolates. An alkaline environment helps to promote manganese removal at pH values above 10 (Gazea et al. 1996). Rock filters may be considered, therefore, as a final polishing stage employed together with aerobic and anaerobic treatment.

1.3.2 Active Treatment

Active treatment - a treatment for bigger capacity of flow rates needs to have rapid kinetics and is usually assisted by chemicals, usually lime for neutralization and precipitation. Sometimes flocculants could be added to speed up the precipitation settling process. For the high degree of contamination water and high volume of wastewater, this method has proven to be effective. However, the application of lime, a non-renewable material will create a huge amount of sludge. Equipment and chemical usage also needs to be monitored very closely.

Types of Active treatment system include:

1. Neutralization / Precipitation
2. Lagooning
3. Ion Exchange, and
4. Electrolysis

1.3.2.1 Neutralization

This method was reported have been used as early as the 1920's. Limestone, lime, sodium hydroxide, sodium bicarbonate and magnesia are the reagents normally used in this process. The reagent causes the dissolved metal content to precipitate out as metal hydroxide sludge, principally $\text{Fe}(\text{OH})_3$. The characteristic of the resultant metal hydroxide sludge depends

on the initial neutralizing reagent used. This process is the most essential requirement in the active treatment of AMD.

1.3.2.2 Lagooning

Oxidative conversion of iron sulphate ($\text{Fe}(\text{SO}_4)$) content to form insoluble $\text{Fe}(\text{OH})_3$ will occur during prolonged lagooning of AMD. A significant large area is needed to build the lagoon.

1.3.2.3 Ion Exchange

Ion exchange involves the removal of certain ions by contact with an anion exchange resin such as amberlite. Aeration and clarification processes will follow as latter stages of the AMD treatment. Industrial minerals such as clay waste, vermiculite, zeolite and cat litter have all been assessed for their ability to control acidity and absorb cations. Another source of material investigated for this role was polyacrylamide polymers.

1.3.2.4 Electrolysis

This process involves the precipitation of dissolved metals on electrodes. Iron metal is employed as an anode coupling with a sulphide/granite cathode and an AMD leachate with an electrochemical cell. Zinc also could be used as the cathode with an aluminium anode.

1.4. Motivation for Research

AMD at the Wheal Jane site has become a very popular case study among researchers. Various treatment methodologies have been proposed and some have been implemented to reduce the impact of the contaminated water on the local environment. So far, however, there has been little research and discussion regarding applications of new active treatment technology for the AMD treatment. Most studies on Wheal Jane have only been carried out in the passive treatment area. This thesis investigates active treatment (e.g. froth flotation) techniques for AMD treatment. The data from this research could also be used in other aspects of wastewater treatment that relate to heavy metal disposal e.g. metal refinery waste disposal and the remediation of AMD at disused coal mines.

1.5. Focus and Aim

The aim of this study was to find an alternative low cost and rapid technique to remove soluble heavy metals (Cu, Zn, Fe) from wastewater. This research will focus on the application of several froth flotation techniques (Denver cell, column flotation) to optimize metal removal. Both synthetic and real AMD from Wheal Jane was used as the wastewater sample for this study. Chemicals other than lime were used for pH adjustment prior to flotation. The best available frothers will be tested to obtain the maximum removal with the chosen equipment(s). Initial tests

will be conducted with synthetic AMD samples to gather all optimum experimental conditions before real AMD samples are collected from site and used with the optimum machine parameters (e.g frother type, dosage, agitation speed and pH conditions).

1.6. Outline of Thesis Structure

The thesis begins with an introduction (chapter 1) and follows with a brief literature review (chapter 2). The experiment methodology will be described in chapter 3.

Chapter 4 begins with a study into using column flotation as a means of metal removal for AMD. The column was used to remove precipitated metals from single solutions of copper, zinc and iron. After identifying the optimum pH for precipitation using NaOH as a neutralization agent, column tests were undertaken. With all the optimum parameters defined for the individual metal systems, experiments were carried out on synthetic mixed metal solutions.

Chapter 5 used all the optimum parameters and reagents determined in chapter 4 but used a Denver cell unit as the flotation device. Optimum operation conditions, (flotation time and impeller speed) for the Denver cell unit were identified with single metal solutions. Synthetic mixed metal solutions were then processed under the optimum conditions. Results from

chapters 4 and 5 have been compared for the maximum removal of every metal. The best and most cost effective methods for flotation will be used in the next set of experiments.

Chapter 6 describes the use of selected flotation devices and operating parameters from chapters 4 and 5, combined with ultrasonic pre-treatment. Every sample was pre-treated with ultrasound before undergoing the normal flotation process. All the optimum conditions for the device were maintained and both single and mixed solutions were tested.

Chapter 7 used the flotation device and ultrasonic application simultaneously. All the previous optimum parameters were used in these experiments. Results for the metal removal from this chapter have been compared with data from chapter 6.

Chapter 8 used the selected method in chapter 7 with a real AMD sample from Wheal Jane Mine. Initial experiments used all the optimum conditions. The parameters are expected to be different using a real AMD sample as there are many other metals other than copper, zinc and iron present. Optimum conditions, especially the frother concentration for the real sample were finalized at the end of the experimental regime.

Finally, conclusions for the all experiments in the thesis will be outlined in the final chapter along with recommendations for future work.