Freie Universität Berlin
Fachbereich Geowissenschaften

PhD Thesis

An Evaluation Of The Current Situation Of Cyanide Waste Disposal And Treatment Methods

A dissertation for the academic title of
Doctor rerum naturalium

Presented by
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2013

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Date of Defense: 31/05/2013

Declaration

I hereby declare that, except for those portions of this work taken from other sources that have been duely cited, this dissertation is the product of my personal endeavor.

This work has neither in partial nor in total been submitted to any academic institution as a requirement for the completion of an academic program prior to this date.

Augustine Mahbu Ntemi

Berlin, 21.01.2013

Dedication

To my parents, Mr. Jacob Ngwang Ntemi and Mrs. Magdalene Lem Ntemi, whose love and guidance have shaped the person I am.

To my wife Mrs. Mbongha Mahbu Terese-Clare née Acho, and my son Nfor Shallom Mahbu for that special quality which they have brought to my life

To my brothers and sisters (Hycenthine, Roland, Leo, Theophile and Cynthia). I will like to thank you all for the support I have received during this period.

Acknowledgement

This work has benefitted from contributions of various sorts: academic, moral, financial etc. My journey after I obtained a master degree to this date of submitting a doctoral thesis has been a thriller. In the darkest moments of life we appreciate the best in those around us. I will like to express special thanks to,

Prof. Dr. mult. Dr. h. c. Konstantin Terytze for the exceptional professionalism he has demonstrated during this research period, both academically and morally.

Prof. Dr. Michael Schneider for assisting in assessing and directing this dissertation.

Prof. Dr. Habil. Bernhard Pracejus of the Sultan Qaboos University of Oman, for his great intuition during this research project. Your academic and moral contributions are unquantifiable.

Dr. Thorsten Spirgath of SpiCon Consulting for his insightful contributions especially in the area of sampling techniques and qualitative analysis.

Dr. Michael Quednau of SpiCon Consulting for his contributions in experimental trials, results analyses and in describing the interactions of chemicals and metals at mine sites.

Mrs. Jana Wazeck of n-Mining Gbr. for her support both during and after our stay at n-Mining. Your suggestions on many of my worries were very helpful.

A special thanks goes to my wife Mrs. Mbongha Mahbu Terese Clare née Acho for all the sacrifices she has made which permitted me to build both the moral and physical stamina which I needed most during this period.

Abstract

The application of cyanide in mineral extraction processes in especially pristine environments poses great pollution problems to adjacent ecosystems. This is due to the amount (98%) of cyanide lost to cyanicides in the process, and the complexity and extreme toxicity of the cyanide wastes produced. In isolation, currently applied treatment processes are limited by one or a combination of any of the following; the volume of the waste, the viscosity of the waste (slurry or solution), the cyanide species present (free cyanides, cyanide complexes strong or weak, sulphur compounds (thiocyanate, etc.), possible break down compounds (ammonia, nitrites and nitrates) and the economics of the process (running cost, especially cost of reagents).

Our ability to modify the genes of microorganisms (bioaugmentation) and to enhance their ability (biostimulation) to perform selected tasks due to advances in engineering/biotechnology is providing new opportunities in the efforts at treating these wastes. Favorable present and projected prices for especially scarce earth metals make the extraction of metals from process effluents a profitable venture, not only because of the extra win from the sales of these metals but also that poisonous/heavy metals are taken out, thereby reducing the amount of the hard-to-treat cyanide-metal complexes in process effluents. This reduction in cyanide metal complexes enhances the performances of cyanide treatment processes.

Irrespective of the treatment method/process applied, a residual ends up in the environment. How this residual is fit for biological degradation should be part of the aim of treatment processes. This work is a detail look at presently applied treatment processes and recommends that treatment processes should not only be focused on reducing the total amount of cyanides but should also be seen as preparatory steps for the eventual disposal of the residual to the environment. The extraction of heavy/poisonous metals and the avoidance to create other toxic non-cyanide containing compounds should be vital components of treatment processes. In this regard, the potential for dead cell surfaces acting as ion exchange sites does not only become relevant for cyanide degradation but these can be applied to simultaneously harvest especially rare earth metals

While biodegradation is proposed to be the final step in treatment processes, treatment should begin with measures to reduce the amount of cyanide waste produced, especially the quantity of cyanide lost to cyanicides and the use of appropriate treatment processes to reduce the amounts of heavy metals and other toxic wastes in the treatment effluents. This is because, other non-cyanide containing toxic compounds like ammonia can be lethal to microorganisms and the presence of toxic heavy metals can inhibit the ability of microorganisms to degrade these residuals.

Zusammenfassung

Die Anwendung von Zyanid im Mineralgewinnungsprozess birgt große Umweltverschmutzung Probleme für angrenzende Ökosysteme, besonders in unberührter Umgebung. Grund dafür ist die Menge von Zyanid, die während des Prozesses an Zyanizide verloren geht (98 %), sowie die Komplexität und die hohe Giftigkeit der anfallenden Zyanidabfälle. Im Zusammenhang mit der Abscheidung sind aktuell angewandte Behandlungsprozesse limitiert durch einen oder mehrere der folgenden Faktoren: Das Volumen des Abfalls, die Viskosität des Abfalls (schlackig oder gelöst), die vorliegenden Zyanidarten (freie Zyanide, starke oder schwache Zyanidkomplexe, Schwefelverbindungen/Thiozyanide, etc.), mögliche Zerfallsverbindungen (Ammonium, Nitrite und Nitrate) und die ökonomischen Aspekte des Prozesses (laufende Kosten, besonders Kosten der Reagenzien).

Die durch Fortschritte in der Technik und Biotechnik entstandene Möglichkeit, die Gene von Mikroorganismen zu verändern (Bioaugmentation) und die Möglichkeit, deren Fähigkeiten, bestimmte Aufgaben zu Erfüllen, zu steigern (Biostimulation) erschließt neue Handlungsspielräume in den Bemühungen, diese Abfälle zu behandeln. Vorteilhafte jetzige und zu erwartende Preise besonders für seltene Erdmetalle machen die Gewinnung von Metall aus Prozessabwässern zu einer gewinnbringenden Unternehmung, nicht nur wegen des Profits aus dem Verkauf dieser Metalle, sondern auch durch die Tatsache, dass giftige Metalle/Schwermetalle entfernt werden und somit die Menge an schwer behandelbaren Zyanid-Metall-Komplexen im Prozessabwasser reduziert wird.

Unabhängig von der angewandten Behandlungsmethode bleibt ein Residuum übrig, das in die Umwelt entlassen wird. Inwiefern dieses Residuum für den biologischen Abbau geeignet ist, sollte eine Rolle für die Zielsetzung des Prozesses spielen. Diese Arbeit ist eine detaillierte Betrachtung gegenwärtig angewandter Gewinnungsprozesse und empfiehlt, den Behandlungsprozess nicht nur auf die Reduzierung der Menge des anfallenden Abfalls auszurichten sondern auch, diesen Prozess als vorbereitenden Schritt für die anstehende Entsorgung des Residuums in die Umwelt zu sehen. Die Extraktion von giftigen Metallen/Schwermetallen und die Vermeidung von anderen giftigen nicht-Zyanidverbindungen sollten zentrale Komponenten im Behandlungsprozess sein. In dieser Hinsicht wird nicht nur das

Potential der Oberfläche toter Zellen als Ionentauscherstellen relevant für den Abbau von Zyanid, darüber hinaus können diese auch angewandt werden, gleichzeitig seltenen Erdmetalle zu gewinnen.

Abstrait

L’usage du cyanure dans la procédure d’extraction des mines, plus précisément dans les milieux pristine provoque des sérieux dommages à l’écosystème environnant. Ceci est dû d’une part au taux élevé (98%) de cyanure perdu au profit des cyanicides, et d’autre part à la complexité et à l’extrême toxicité des déchets de cyanure résultant de la procédure. Les techniques de traitement usuelles sont limitées par l’une ou la combinaison des causes ci-après; la quantité de déchets, la viscosité des déchets (slurry or solution), la classe de cyanure présente (cyanures libres, cyanure forts et faibles, composés sulfuriques (thiocyanates), etc….), des probables composés (ammonium, nitrites et nitrates) et le coût économique de la procédure.

Notre capacité à modifier les gènes des microorganismes (par la procédure de bio-augmentation) et à augmenter leur capacité (bio-stimulation) à exécuter des tâches précises grâce à des avancées dans les domaines de Biotechnologie offre des nouvelles opportunités de traitement de ces déchets. Les prix réels et estimés des métaux issus des terres rares font de leur extraction (process effluents) une aventure onéreuse, non seulement à cause du profit supplémentaire provenant des ventes, mais également parce que les métaux lourds et à risque sont extraits dans la même procédure, réduisant de facto le taux d’agrégats des métaux de cyanure qui généralement sont difficiles à traiter. Cette réduction du taux d’agrégats de métaux de cyanure rend la procédure de traitement de cyanure plus efficace.

Néanmoins, quelle que soit la technique de traitement, une quantité résiduelle s’échappe presque inévitablement dans l’environnement. La procédure de traitement devrait tenir compte de la biodégradabilité de ce résiduel qui s’échappe dans l’environnement. Le présent travail jette un regard détaillé sur les pratiques courantes de traitement et recommande que chaque procédure devrait se concentrer non seulement sur la réduction du taux de cyanure, mais penser en amont comment disposer du résiduel toxique susmentionné. Extraire les métaux lourds ou toxiques et éviter d’en créer des dérivés toxiques devraient être partie intégrante de toute procédure de traitement. A cet effet, le potentiel des surfaces à cellule morte agissant comme des sites d’échange d’ions devient non seulement important pour la dégradation du cyanure mais peut être appliqué dans le processus de recouvrement des métaux des terres rares.

Avec la biodégradation comme dernière étape dans la procédure de traitement, la première étape devrait commencer avec des mesures de réduction de déchets de cyanure. Plus précisément la quantité de cyanure perdue au profit des cyanicides doit être réduite et l'usage des techniques de traitement appropriées afin de réduire le taux de métaux lourds et autres déchets toxiques doit être encouragé. Ceci s'explique par le fait que d'autres déchets toxiques (ne contenant pas de cyanure) tels que l'ammonium peuvent être nocifs aux microorganismes et la présence des métaux lourds et toxiques peut affecter la capacité des microorganismes à dégrader ces résidus.

Table of Contents

List of tables

List of figures

List of Abbreviations and Units

%	Percentage
ºC	Degree centigrade
Å	Angstrom
Ag	Silver
AMD	Acid Mine Drainage
Atm	Atmosphere
ATCC	American Type Culture Collection
Au	Gold
AVR	Acidification-Volatilization-recovery
BMD	biological degradation method
Ca	Calcium
CA	Activated carbon
Cal/gm	Calories per gram of mole
Cd	Cadmium
CI	Carbon-In-Pulp
CM	Chemical method
CNO	Cyanate
$\mathrm{CN_{total}}$	Total cyanide
CN	Cyanide ion
Co	Cobalt
Cs	Caesium
Cu	Copper
DOC	Dissolved Oxygen Concentration

DSM	Deutsche Sammlung Von Mikroorganismen
DVB	Dyvinylbenzene
EDR	Electrodialysis Reversal
Eo	Redox potential
E_n	Energy
Fe	Iron
Fig	Figure
g/t	gram per tonne
HCN	Free cyanide
Hg	Mercury
INCO	International Nickel cooperation
K	Kelvin
K	Potassium
Kg	kilogram
Kg/t	kilogram per tonne
KPa	Kilo Pascal
Li	Lithium
M	Mass
m^2/g	meter square per gram
m^3	meters cube
Mg	Magnesium
mg	milligram
mg/l	milligrams per liter
Mn	Manganese
Na	Sodium

Ni	Nickel
Nm	nanometers
P	Phosphorous
pH	Acidity or basicity of solution
pKa	Dissociation constant
PM	Physical method
ppm	parts per million
SAC	Strong Acid Cation
SAD	Strong Acid Dissociable
SAR	Systematic acquired resistance
SBC	Strong Base Cation
SCNO	Thiocyanates
UV	Ultraviolet
V	Volts
Vis	Visible
WAC	Weak Acid Cation
WAD	Weak Acid Dissociable
WBA	Weak Base Anion
Zn	Zinc

Chapter 1

Introduction

1.1 Statement Of The Problem

The history of gold is intertwined in the evolutionary process of human civilization. In ancient times gold was given as gifts to royalties, later it was used as a currency and presently it is used amongst others as jewelry and in nano-sizes in the high tech industry. Due to its increasing relevance, production techniques have evolved optimizing recovery rates from host ores. The major metallurgical processes for gold recovery from ores include gravity concentration, flotation and leaching. Of greatest significance to the gold extraction process was the development of cyanidation or the McArthur-Forrest process in Glasgow-Scotland by John Seward MacArthur and the brothers Dr. Robert and Dr. William Forrest in 1887 (Knight 2005, Jason 2007). This leaching process doubled the recovery rate of gold from ores from 40-50% to 85-95% establishing gold leaching using cyanide as a lixiviant as the dominant metallurgical process for gold extraction (Larmour-Ship, et al. 2005). This method is especially good given that gold has a very small concentration in the earth's crust, 0.005g/t (Wong & Arund 2009) compared to 0.07g/t for silver and 50g/t for copper. The cheap price of cyanide makes this process economically favorable compared to other extraction methods. Notwithstanding, the success of this process is shrouded in controversies associated with the accompanying polluting effects of the environment by cyanide (McCulloch & Young, 2004; Böhm, 2000; Cyanide-Free Romania, 2008; Oelsner et al. 2001). The reactivity of cyanide is a major hindrance to efforts to design a cyanide degradation process. Being a versatile ligand, the cyanide anion reacts with almost every metal or compound it encounters generating a residual cocktail of cyanide complexes. Over the years there has been great research into the development of alternative lixiviants such as thiourea and thiosulfate (Gos & Rubo, 2001). Experiments with these alternative lixiviants showed great potential in metal recovery as possible alternatives to cyanide in the mining of gold but due to extreme reagent consumption and the cost of purchasing and handling these alternatives, the use of cyanide remains the best available cost effective gold recovery method even after factoring the cost of cyanide waste treatment (Huiatt 1984).

Presently, cyanide is used in mining (gold, silver), processing industries (McCulloch & Young 2004, Greenpeace 2008), electroplating industry (MIGA 2008), food processing industry (MIGA 2008), jewelry manufacturing (C. EPA 2002), petrochemical industry, plating shops in the automobile industry (Pargaa et al. 2003), aluminum smelting (Gagnon et al. 2004), manufactured gas plant and coal coking plant sites (Mansfeldt, et al. 2004) and other industries. Added to this list are naturally occurring cyanides in plants, with the most important group being the rose family including almond tree and legumes (Oelsner et al. 2001). Cassava also contains high quantities of these cyanogenic glycosides (Asegbeloyin & Onyimonyi 2007, Kobawila, et al. 2005). Effluents from these industries contain cyanide as the principal toxin. For eventual discharge to the environment, these cyanide-laden effluents are required to be ridden bare of cyanide or be treated to minimize cyanide concentration to accepted benchmarks (Rodrigo et al. 2005). Due to their high toxicity, in Germany the maximum concentration of free cyanide in surface water is 0.01mg/l and 0.5mg/l for sewage water (Kiran & Chandrajit, 2011), while the American Health Service cites 0.01mg/l as guideline and 0.2mg/l as permissible limit for cyanide in effluent (Dash et al. 2006). For industries using cyanide, effluent treatment cost is having negative effects at various levels. Pressure from increasingly stringent environmental laws prohibiting/limiting the use of cyanide in response to a public anti-cyanide campaign (Yarar, 2001) has sometimes forced associated companies out of business. Examples of mine closures as a consequence of stringent environmental laws include; Ok Tedt mine in Papua New Guinea (Corbett 2003), and Eldorado gold mine in Esme Kisladag, Turkey (Hatch Associates 2003). Also, there is a complete ban on the use of cyanide for gold mining in most of central Europe, Greece and Turkey, and in the American state of Montana (Riani, et al. 2007). Unfortunately, the cyanide pollution story is often only in relation to cyanide use in the mining industry with the potential of resulting in a ‘frightfully costly’ neglect of its use and pollution in the non mining sector consuming 80% of cyanide produced globally (Clarke & Morna 2009).

Simplistically, three treatment methods can be identified with varying degrees of merits and demerits. These include,

- The chemical method (CM). These methods are very fast and also very expensive. These are mainly oxidation reactions.

- Physical method (PM). These methods are very fast, very environmentally unfriendly and also very expensive. These are accomplished by dilution, membranes, electrowinning, and hydrolysis/distillation (Young & Jordan 1995)
- Biological degradation method (BDM). This method is less expensive and time consuming (Saarela & Toivo 2004). '*The chemical and physical methods tend to be complex and costly. Biological treatment, however, is becoming less costly with advances in biotechnology and can be just as effective*' (Jason 2007) There is reasonable evidence to show that biological detoxification of cyanide waste is more successful than the widely used chemical method (Sobolewski 2000).

In practice these three major groups are further divided into five subgroups based on methods similarities in chemistry and procedure. These five groups are, the adsorption method, the physical method, the complexation method, the oxidation method and the biological method.

Driven by the quest to increase profits, some proposed detoxification technologies have not received the desired attention from major cyanide users. These methods looked only at managing the negative publicity associated with cyanide use without any consideration of the profitability or economics of the processes.

The PMs are generally redundant as they are mainly separation technologies. The chemistry of the cyanide ion is left intact and therefore the level of toxicity is not affected. Because they are simple and cheap, they are popular and widespread. Physical methods are limited by the bulk of waste produced.

A relative ignorance in the past of the long-term environmental fate of cyano-toxins (cyanide and its derivatives) meant that the choice of treatment method was limited only by industry profit margin. Toxicity to humans was the main consideration. This criterion for selection of cyanide treatment process favored CMs. Products of the CM (e.g. cyanates, thiocyanates e.t.c) are very less toxic to humans and aquatic life than their predecessors. Despite the CMs being expensive, their speed (almost spontaneous in character, encouraged by the chemistry of the cyanide ion) safes time, permitting large quantities of cyanide ladened wastes to be processed in short time frames ensuring rapidity of general production, which guarantees process profitability.

An alternative but often-sidelined procedure is BDM. Despite being very promising from test trials, it has not received as much attention as the CM or the PM. It is a compromise of the PMs and CMs, satisfying both industrial and environmental concerns. A major disadvantage of the BDM is that, its slowness permits a cumulative accumulation of large quantities of cyanide bearing effluents (Teixeira et al. 2005). BDMs require more storage facility, eventually retarding overall industry production rate. This research aims at diagnosing the various major treatment techniques of cyanide/cyanide-complexes, emphasizing their economic and environmental advantages. Of special consideration will be the future of the biodegradation method. Inspiration for this BDM emanates from the following facts,

- That bustling communities of organisms flourish in environments with otherwise lethal concentrations of cyanide. Examples of such environments will be tailing ponds (May & John, 2001).
- That there exist a great number of fauna and flora that synthesize and/or metabolize cyanide (Raybuck A. S., 1992; Huertas M.-J. , et al., 2006; Miller & Conn, 1980; Blumenthal et al. 1968; Castric & Strobel, 1969). *'A microorganism can metabolize cyanide only when, in addition to a biodegradative pathway to convert cyanide into an assimilable product (NH4+), it also harbors a cyanide-resistance mechanism (a cyanide-insensitive oxidase)*' (Igeno et al. 2007)
- That some organisms can feed solely on cyanide, using it as their sole nitrogen or carbon source (Harris & Knowles, 1983; Sartaj M. , 2008; Meyers et al. 1991; Luque-Almagro, et al., 2005)
- That there exist organisms that utilize energy released from chemical reactions to fix elements for their use or to make those elements available for use by other organisms. Examples include the Thermodesulfobacterium and Thermodesulfovibrion that have their maximum growth rates at temperatures in excess of 65°C. These communities are associated with high temperature environments such as geothermal vents (Doshi 2006). Also Acidothiobacillus ferrooxidans and acidothiobacillus thiooxidans (Reith, et al. 2007)
- That thriving communities of anaerobic prokaryotes exist in extreme conditions (e.g. in hot hydrothermal vents deep down the floors of the Pacific and the Atlantic oceans) forming ecosystems analogous to our system of

> plants and animals but powered exclusively by geothermal energy instead of light as in ours. '*There are lithotrophic species that can feed on a plain diet of inorganic nutrients, getting their carbon from* CO_2*, and relying on* H_2S *to fuel their energy needs or on* H_2*, or* Fe^{2+}*, or elemental sulfur, or any of a host of other chemicals that occur in the environment*' (Bruce 2002). The versatility in the feeding habits of bacteria is an asset to be explored for any success in designing a biomimetic cyanide biodegradation system.

A microscopic diagnosis of these facts is hoped will provide a clearer understanding of how these organisms operate in such extreme environments thereby providing answers to questions paramount to the design of any BDM. These questions include, how do these communities inoculate themselves against cyanide poisoning? How do they feed? For organisms that synthesize and/or metabolize cyanide, how do they achieve immunity from cyanide? Will understanding and controlling the physicochemical parameters governing these processes provide enough information for the design of a biological degradation process or will there be a need to borrow from the PMs and CMs, i.e. to design a multilevel process combining both biodegradation and other methods to achieve the complete degradation of even the most stable cyanide complexes.

Finally, a major oversight in the legislation regulating cyanide use and disposal has hampered the race for the development of innovative cyanide treatment techniques. Without any comprehensive and/or conclusive studies on the polluting potential and the long term fate of cyanide derivatives including its oxides (e.g. cyanates) and thiols (e.g. thiocyanate) which are more persistent in the environment (Yarar 2001), these are considered less hazardous and therefore are not properly catered for within the law. These compounds are considered comparatively less harmful and this has resulted in a gap in the legislation (Yarar 2001) offering major cyanide users a leeway out from stringent laws governing cyanide use and disposal. These derivatives are not required to be tested for in mine waste control practices and no mention is made at what concentrations these are toxic. '*Despite the risks posed by these cyanide-related breakdown compounds, regulatory agencies do not require mine operators to monitor this group of chemicals in mining-related waters. Therefore, while much of the cyanide used at mining sites does break down fairly readily, either as a result of* *natural degradation or the various treatment processes sometimes employed, significant amounts of the original cyanide form potentially toxic compounds remain unaccounted for in the monitoring of mining operations'* (R. Moran 1998). *'Contrary to much of the literature published in mining and regulatory documents, not all of the cyanide used in mineral processing breaks down quickly into largely harmless substances. Many of the breakdown compounds, while generally less toxic than the original cyanide, are known to be toxic to aquatic organisms, and may persist in the environment for significant periods of time. Some of these toxic breakdown forms include the free cyanides, metal-cyanide complexes, organic-cyanide compounds, cyanogen chloride, cyanates, thiocyanates, chloramines, and ammonia. Unfortunately, many of these chemical species are not detected in the routine laboratory analyses normally performed on mining-related waters. Thus, it is often assumed that they do not exist. For many reasons, national and international regulatory (and lending) agencies do not require monitoring for many of these chemical species'* (R. E. Moran 2000).

In strong cyano-metal complexes, the cyanide ion is so strongly bonded to the metal such that it is hardly detected. Because the cyanide ion is not detected it is considered as not present and consequently the complex is considered not toxic to humans and other organisms (Fallon et al. 1991). This is faulty given what we now know about natural attenuation processes for cyanide degradation (Gagnon et al. 2004). There is evidence to show that despite these products of cyanide treatment processes being considered less toxic they can persist in the environment for over long periods of time. Da Rosa & Lynn in 1997 stated, that under favourable alkaline conditions cyanide can persist in ground water, mine tailings and in abandoned leach heaps for over a century (Eisler & Wiemeyer 2004). Depending on the pH and redox potential of a system the half-life of a cyanide complex can extern from a few days to a few thousand years (Meehan, S., 2001). The half-life of cyanide complexes increases exponentially with an increase in pH and/or redox potential. However, the cyanide ion (CN^-) or free cyanide (HCN) is not believed to persist in the environment as they readily form less toxic compounds with other elements (Logsdon et al. 1999). Therefore, the phrase 'environmental persistence' should be cautiously used when discussing cyanides and cyanide derivatives. Their ability to persist in the environment over long periods of time makes these compounds dangerous as they gradually accumulate in the tissues of plants and other aquatic inhabitants and may even become poisonous to these (R. Moran 1998, M. P. MPC 2000). The degree of contamination of ground water or pollution due to cyanide depends heavily on the solubility and mobility of iron-cyanide complexes whose solubility depends on a variety of physical and chemical processes including oxidation-reduction, precipitation–dissolution, sorption–desorption, complexation with inorganic ions, and chemical or microbial decomposition (Mansfeldt et al. 2004). The solubility of Iron–cyanide complexes increases with decreases in soil pH and redox potential. All the methods of cyanide degradation perform one of the following (Rodrigo et al. 2005),

I. Dilution of the cyanide.
II. Removal of toxic forms from solution.
III. Conversion of toxic cyanide forms into non/less toxic forms.

As it will be discussed later, dilution as a method of cyanide waste treatment is not allowed, the complete removal of toxic cyanide from solution is economically not feasible leaving only the third option of converting toxic cyanide into non/less toxic forms.

1.2 Research Motivation

Motivation for this research is two fold, economic (as seen in increases in the price of gold (Taylor 2010)) and environmental.

The existence of a great number of fauna and flora that synthesis/metabolize cyanide compounds for various reasons is evidence that these posses an inherent inoculation for cyanide poisoning. Many plants including Cassava (Nhassico, et al. 2008) produce cyanide (through hydrolysis of cyanogenic glycosides (Miller & Conn 1980)) as a defense against predating herbivores, insects, and pathogens. Some millipedes have been seen to release hydrogen cyanide in defense against predators (Nhassico, et al. 2008, Logsdon et al. 1999). Producing and storing cyanide will not be possible without this internal inoculation for cyanide. The interest/motivation to design a biodegradation or a multiple stage treatment process culminating with biodegradation has been encouraged by the following facts,

- That there exist a number of bacteria that can feed solely on cyanide, using it as their sole carbon and/or nitrogen source (M.-J. Huertas, et al. 2006).

- That there exist a number of non-cyanogenic plants and fungi capable of withstanding varying concentrations of cyanide implies that these either posses a cyanide destroying substance (enzymes) or mechanism.

- Present methods for the destruction of cyanide and/or cyanide complexes involve the application of otherwise environmentally hazardous chemicals. Often, the cyanide is not destroyed but is converted to ‘less’ toxic forms.

- In plants, systemic acquired resistance (SAR) is a “whole-plant” resistance response that occurs following an earlier localized exposure to a pathogen. SAR is analogous to the innate immune system found in animals, and there is evidence that SAR in plants and innate immunity in animals may be evolutionarily conserved.

- That there exist a number of natural processes through which cyanide can be reduced in the environment.

- That there exists cyanide treatment processes which can upgrade the physical and chemical properties of cyanide wastes to enhance their biodegradability.

1.3 Research Objective

The objective of this work is to present a detail look of the various methods (physical, chemical and biological) for treating cyanide wastes and their derivatives and to propose a cyanide treatment plan that is both economically and environmentally acceptable. It must be noted that not every treatment process can be discussed here but that an example of every method will be presented. The reason being that some treatment methods have many processes that have the same goal and an attempt to treat all the processes will result in repetitions.

Chapter 2

Chemistry Of Cyanides

2.1 What Is Cyanide?

The term cyanide is a generic name for all substances containing the Carbon-Nitrogen triple bond group (Logsdon et al. 1999, Taebi, Bafqi & Sataj 2006). These compounds are unique because of the presence of the carbon-nitrogen triple bond (C≡N) group (Canada 1999). They occur in many forms including free cyanides, complexed cyanides (metallocyanides), and organic cyanides (nitriles). They can be of either natural or anthropogenic origins, and are believed to predate live on earth (Logsdon et al. 1999). In nature, cyanide occurs for example as cyanogenic glycosides which when hydrolyzed or digested produce hydrogen cyanide. In the gaseous/liquid form, the cyanide ion combines with hydrogen ion to form an extremely toxic gas hydrogen cyanide, which smells like almonds, and not all individuals can detect the odor. Both HCN gas and liquid are colorless (ICMI 2011). HCN is miscible in water and ethanol but its solubility decreases with an increase in temperature and under highly saline conditions (ICMI 2011). HCN liquid is very stable until when exposed to the environment where it rapidly evaporates as gaseous hydrogen cyanide. The rapid evaporation of cyanide is due to the low boiling point of pure hydrogen cyanide which is 26°C. At this temperature hydrogen cyanide has a vapor pressure of 0.99atm that is higher than the vapor pressure of water 0.34atm at this same temperature. This implies that, hydrogen cyanide can be taken out of solution by increasing the temperature or by reducing the pressure. Because of this, the location of tailings dams at high elevations in hot climates is a dangerous/risky practice. Evaporation of hydrogen cyanide from solutions can be increased by agitation. Agitation in effect increases the air/solution contact interface (Young & Jordan 1995).

2.2 Classification Of Cyanides

Most classifications of cyanides have three main categories; free cyanides, weak acid dissociable cyanides (WADs) and strong acid dissociable cyanides (SADs) (Botz M. , 1999; Latkowska & Figa, 2007; Huiatt, 1984; Traub, et al. 2001) fig 2.2.

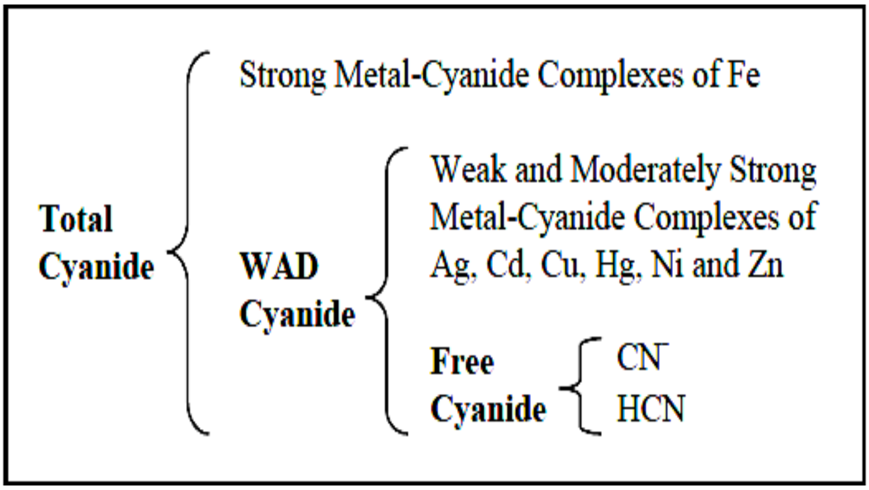


Fig 2.2: Classes of Cyanides (M. Botz 1999).

The German Standard Methods (DEV,) of 1981 and 1988, only differentiates between the easily releasable cyanides (Hydrocyanic acid, their alkali and alkaline earth salts, including cyanide complexes of Cd, Cu, Ag and Zn) and the strong complexes (cyanide complexes of iron, cobalt and gold), with the complexes of nickel thought to occupy an intermediate position between those two groups (Oelsner et al. 2001) and it is not expected to easily release cyanides. The amount of cyanide in a given system is the total of all the species in these categories present. Therefore, the phrase total-cyanides includes free cyanides, WADs and (SADs) not including the nittrles ((R-CN), (acetonitrile and benzonitrile)), cyanate ion (OCN^-), thiocyanate ions ($SCNO^-$) and cyanogen chloride (ClCN) (Oelsner et al. 2001). The term free cyanide is used to express the sum total of the molecular hydrogen cyanide (HCN) plus the ionic cyanide (CN^-) present. The chemical names for hydrogen cyanide (HCN) include hydrogen cyanide, hydrocyanic acid and prussic acid. When dissolved in a solution, hydrogen cyanide can exist depending on the pH and redox potential either in the free or complex form.

Scott 1984 has a much more detailed grouping of the cyanide species. He comes up with five categories grouping composed of; 1) free cyanides, 2) simple compounds (further divided into readily soluble and relatively insoluble), 3) weak complexes, 4) moderately strong complexes, 5) strong complexes. (Table 2.2)

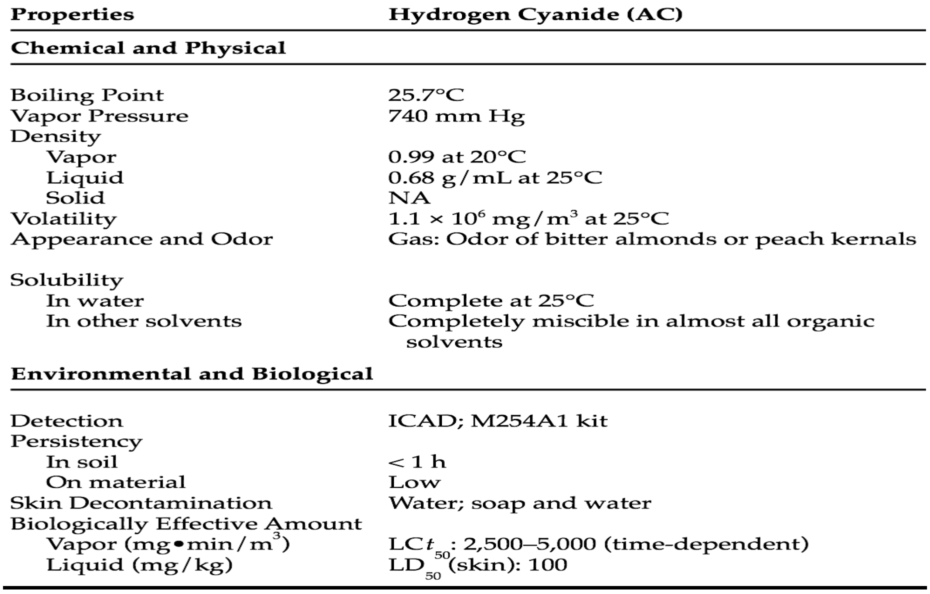
Table 2.2: Relative Stability of Cyanide Complexes (Scott 1984).

Terms	**Forms of cyanide**
Free Cyanide	CN^- and HCN
Simple Cyanides	(1) Readily Soluble, [NaCN, KCN, $Ca(CN)_2$, $Hg(CN)_2$]
	(2)Relatively insoluble, [$Zn(CN)_2$, $Cd(CN)_2$, CuCN, $Ni(CN)_2$, $Ag(CN)_2$]
Weak Complexes	$Zn(CN)_4^{2-}$, $Cd(CN)_4^{2-}$, $Cd(CN)_3^{1-}$
Moderately strong complexes	$Cu(CN)_2^{1-}$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$, $Ag(CN)_2^{1-}$
Strong Complexes	$Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$

Moving from top to bottom in the list, there is an increase in the stability of the compounds. As the stability of the cyanide compounds increases there a reduction in their ability to release/form free cyanide in solution. This is an advantage if cyanide mobility is be to halted, but it becomes a disadvantage in cyanide waste treatment/remediation as the cyanide ions (CN^-) are tightly held in extremely stable complexes such as ferrous [$Fe(CN)_6^{4-}$] and ferric [$Fe(CN)_6^{3-}$] cyano-complexes requiring more effort to dislodge them from these complexes.

2.3 Properties Of Cyanides

Table 2.3: Physical, Chemical and Biological Properties of Free Cyanide (Baskin, James, et al. 2008).



Properties	**Hydrogen Cyanide (AC)**
Chemical and Physical	
Boiling Point	25.7°C
Vapor Pressure	740 mm Hg
Density	
Vapor	0.99 at 20°C
Liquid	0.68 g/mL at 25°C
Solid	NA
Volatility	1.1×10^6 mg/m^3 at 25°C
Appearance and Odor	Gas: Odor of bitter almonds or peach kernals
Solubility	
In water	Complete at 25°C
In other solvents	Completely miscible in almost all organic solvents
Environmental and Biological	
Detection	ICAD; M254A1 kit
Persistency	
In soil	< 1 h
On material	Low
Skin Decontamination	Water; soap and water
Biologically Effective Amount	
Vapor ($mg \bullet min/m^3$)	LCt_{50}: 2,500–5,000 (time-dependent)
Liquid (mg/kg)	LD_{50}(skin): 100

Free Cyanides

This term refers to both the cyanide ion (CN^-) and hydrogen cyanide (HCN) either in the gaseous or liquid phase. This is the most toxic form of cyanide in either the liquid or gaseous phases. It is simply a word to describe the cyanide ion (CN^-) dissolved in water and any hydrogen cyanide (HCN) formed as a result. In solution, the relationship between CN^- and HCN is governed by the pH of the solution. This relationship is described by the following equation,

$$CN^- + H_2O \leftrightarrow HCN + OH^- \qquad \text{--------eqn2.3a}$$

The concentrations of CN^- and HCN are at equilibrium when the pH of the solution is between 9.3 and 9.5 (ICMI 2011), which is equal to the pKa of HCN. Oelsner et al 2001, quoted 9.2 as the pH at which equilibrium is established between HCN and CN^- in solution. Caution should be exercised when quoting the pH value at which equilibrium is attained as this value also depends on other factors such as the concentration of dissolved solids in the solution (R. E. Moran 2000). As the pH drops below 9.36 the concentration of HCN progressively increases with further drops in pH. This is because, as the pH drops there is stoichiometrically sufficient amount of hydrogen ions to favour formation of HCN. Likewise is there an increase in CN^- as the pH increases further above 9.36 (fig 2.3). This is also as a result of a deficiency in the amount of hydrogen ion available for any formation of HCN so CN^- dominates (Logsdon et al. 1999).

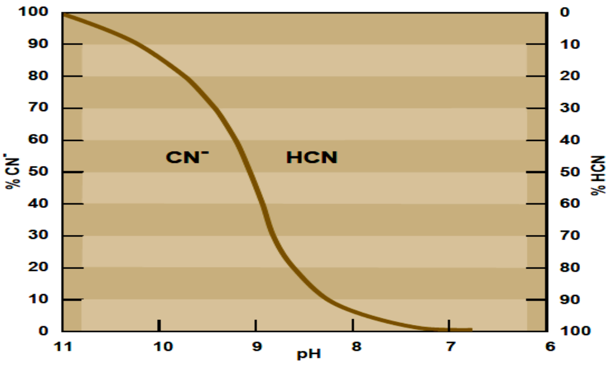


Figure 2.3: Relationship between cyanide ion and free cyanide as a function of pH (25°) (Logsdon et al. 1999).

The relationship between HCN and CN^- in solution is very important as it governs the availability of cyanides in ground and surface water bodies. Natural water bodies often have pH values of between 6 and 8.5, (streams and ground water bodies which have been polluted by acid mine drainage have pH values lower than 4.5) implying that the dominant species in such systems will be HCN which is volatile and readily escapes shortly after formation thereby reducing the concentration of cyanides in open water bodies. Anyway, this view is currently under great review as a research by the US geological survey has daunting evidence showing that the reduction of free cyanide amounts in open/ground water is due to a greater extent to the fact that they are converted to other compounds and are either precipitated or adsorbed onto other mineral surfaces as oppose to being simply evaporated (R. E. Moran 2000). This view is further supported by Boadi et al 2009 where they stated that, '*the availability of metals would stabilize cyanide in the metallic complex forms and thereby cause its retention in the environments at temperatures far above ambient temperature*'. The escape of HCN into the atmosphere is a natural method by which cyanides are reduced from the environment. In other cases where the cyanide ion is desired to be dominant, as in the cyanidation process, the pH is kept far greater than 9.36 to achieve this. Solubility of free cyanides is high in water but this solubility decreases with increase in temperature and salinity.

Simple Cyanides

These are represented by the formula $A(CN)_x$. where A = to an alkali metal or a metal, and X = the valence of the alkali or metal and it is equal to the number of cyano groups present in the compound. Alkali cyanides ionize releasing cyanide ions according to the following reaction,

$$A(CN)_x \rightleftharpoons A^{+x} + x(CN)^- \qquad \text{---------eqn 2.3b}$$

These compounds are colorless, very toxic and very soluble with their solubility being pH dependent. Some of these compounds are relatively stable. After dissolution, the hydrolysis of the cyanide ion and subsequent behavior would be similar as in eqn 2.3a above. The salts of sodium, potassium and calcium are extremely toxic as they readily dissolve in water releasing HCN. Most operations requiring the application of HCN as a gas or liquid receive cyanide as salts of Na, K or Ca.

Alkali Metal-Cyano Complexes

These have a general formula of $A_{(y)}M(CN)_{(x)}$. Where A = alkali metal, y = number of alkali metals present, M = a heavy metal (e.g. ferrous or ferric iron, cadmium, copper, nickel, silver etc), and x = number of CN groups.
Where X = (the valency of A multiplied y) + (the valency of the heavy metal).
Unlike simple cyanides that dissociate yielding the cyanide ion (CN^-), the alkali metal cyanide complexes yield cyanide complexes of the heavy metal plus the alkali metals eqn 2.3c.

$$A_{(y)}M(CN)_{(x)} \rightleftharpoons {}_{y}A^{+x} + [M(CN)_{(x)}]^{-yw} \qquad \text{-----------eqn2.3c}$$

Where w = oxidation state of A in the original molecule.

Despite the use of a simple stoichiometric equation to demonstrate the dissociation of alkali-metal-cyanide complexes, there is believed to be other important intermediary reactions taking place that can function as rate determinants for the dissociation process (Huiatt 1984). One of such steps may prevent a rapid dissociation of the complex. The pH and the relative concentration of the reactants also influence the rate of dissociation.

Weak Acid Dissociable (WAD)

This class of cyanide complexes includes those of copper, nickel, Zinc, silver and cadmium. These are described as weak or moderately stable. In table 2.2, WADS have been further divided into either weak or moderately strong groups. These are described as weak acid dissociable because even at pH values of most natural waters they can dissociate sufficient enough to pose an environmental threat (ICMI 2011) by releasing toxic free cyanide and metal cations.

Strong Acid Dissociable (SAD)

This is a group of very stable cyanide-metal complexes. The group is composed of cyanide complexes of iron, cobalt, gold and mercury. These will remain stable at pH values where WADs will dissociate. Despite their high stability, the iron ferrous [$Fe(CN)_6^{4-}$] and ferric [$Fe(CN)_6^{3-}$] complexes dissociate on exposure to ultraviolet light. This photolytic degradation reverses in the absence of UV light (ICMI 2011). Like every other cyanide compound the stability of the SADs is pH dependent and so is their potential to pollute the environment.

Metal Cyanide Alkali/Heavy Metal Cation

Metal cyanide complexes have the potential to bond with other cations to form salt-like residues referred to as double salts. Double salts can be formed with alkali metals [e.g. potassium Ferro cyanide, $K_4Fe(CN)_6$] or with other heavy metals [e.g. copper Ferro cyanide $Cu_2Fe(CN)_6$]. The solubility of these compounds depends on the solubility of the metal cations and also on the solubility of the metal cyanide. Generally, alkali salts of iron cyanide are very soluble, dissociating in the process to release metal cyanide complexes, which can then release free cyanide. At some pH values heavy metal salts of some iron cyanides produce insoluble precipitates.

Thiocyanates

Thiocyanate (SCN^-) is formed by a reaction between the cyanide ion and sulfur. This compound dissociates under weak acidic conditions but it is not considered to be a WAD. The reason being that it is very reactive and behaves like the cyanide ion in forming complexes. Thiocyanate is believed to be 7x less toxic than cyanide and it irritates the lungs as it oxidizes to carbonate, sulphate and ammonia.

Cyanate

This is formed as a result of the oxidation of cyanide. The oxidation can be due to natural processes or from anthropogenic activities as during the application of cyanide remediation/treatment reagents. It is less toxic than cyanide and hydrolysis to ammonia and carbon dioxide.

Nitriles

This is a special class of cyanides made up of organic compounds possessing the cyanide ion (CN^-) group. A few of these compounds dissociate in water releasing cyanide ions or molecular HCN. Also belonging to this group are complex organic acids, alcohols, esters and amides possessing the cyanide radical. Unfortunately, except for a few of these the toxicity, persistence and chemistry of these nitriles in aquatic environments are not well known (A. EPA 1976).

Stability Of Cyanide Species

Knowing the stability of cyanide species is important especially when considering what treatment/remediation method to apply for a particular cyanide waste. This is because, species stability greatly influences both process kinetics and the applicability of certain methods (Scott 1984). This implies that there is no standard method or best method for cyanide waste treatment because choice of treatment method depends primarily on the dominant species present, which depends also on the ore mineralogy in the case of mine effluents.

Chapter 3

Toxicity Of Cyanides

Introduction

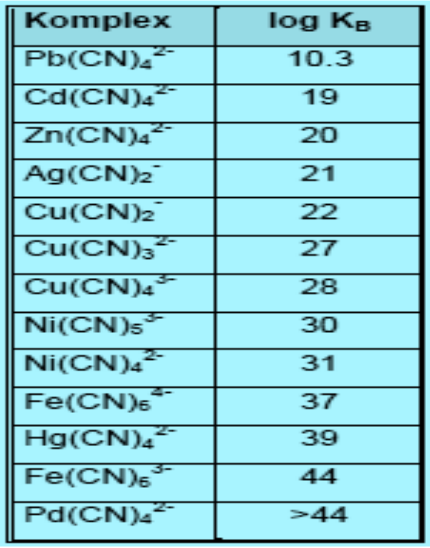
Global production of Hydrogen Cyanide is approximately 1.4 million metric tons of which 13% is used in gold mining for heap leaching (Trapp, et al. 2007, Australia Environment 2003) other reports put the percentage used in mining at 20% (Logsdon et al. 1999). Despite its varied application in a multitude of industrial processes, its highest exposure and contact with the external environment is when it is used in mining especially following spills from mines (Ok Tedt mine Papua new Guinea (Corbett 2003), Eldorado gold mine in Esme Kisladag, 1999 Turkey (Hatch Associates 2003, Eisler & Wiemeyer 2004) Baia Mare, Romania (Dzombac & Ghosh 2006)). From cyanidation stoichiometry the ratio of cyanide to gold during cyanidation is approximately 3 to 4 grams of cyanide to one tone of ore (Carrillo-Pedroza & Soria-Aguilar 2001). Practically, this is not the case as typical field estimates show that about 200 to 300 grams of cyanide are needed for each tone of ore. It can be argued that ores vary from each other in many categories. Notwithstanding there is great deviation of the actual process from stoichiometrically estimated amounts. A great majority of the cyanide is lost to cyanicides in side reactions that result in the formation of other cyanide complexes. In an attempt to reduce the amount of cyanide lost to cyanicides, the International Cyanide Management Code has imposed a limit of 50mg/l cyanide solution concentrate for gold mining (Riani, et al. 2007).

3.1 Uncertainties In Cyanide Toxicity

Discussions on the toxicity of cyanide compounds and their derivatives are often full of uncertainties and this is especially so when discussing the toxicity of cyanide in mine wastes. This is because, mine effluents/wastes are comprised of a cocktail of cyanide complexes (organic and inorganic) in a jumble with potentially toxic metals making the identification of a particular chemical responsible for a toxic effect a practical impossibility. As a consequence of this uncertainty it is common to find phrases such as '*Hydrogen cyanate and cyanate ions are significantly less toxic than HCN'*,'*Thiocyanate is relatively non-toxic when compared to cyanide*' (R. Moran 1998), and '*Complexed cyanide is also generally less toxic to microorganisms*' (Fallon, et al. 1991). Such phrases are dangerous and result in an oversight or neglect of potentially toxic cyanide derivatives.

When cyanides are released to the environment their ability to undergo a number of processes such as precipitation, dissolution, adsorption, oxidation, biodegradation e.t.c and including to complex with a variety of elements and compounds makes tracing their path in the soil, water or air very difficult to accomplish. These various processes occurring often simultaneously depending on the prevailing physical or chemical conditions end in either the degradation or attenuation of the cyanides. The toxicity of the cyanide species is a function of their readiness to dissociate releasing free cyanides into the air, soil and surface/ground water bodies. Readiness to dissociate reduces with increasing stability of the cyanide complex, from weak complexes through moderately strong complexes to strong complexes (Tables 2.2 and 3.1).

Table 3.1: Stability constants of Some Cyanide Compounds in Water at room Temperature (Hollemann & Wiberg, 1995 in (Oelsner et al. 2001)).



Komplex	log K_B
$Pb(CN)_4^{2-}$	10.3
$Cd(CN)_4^{2-}$	19
$Zn(CN)_4^{2-}$	20
$Ag(CN)_2^{-}$	21
$Cu(CN)_2^{-}$	22
$Cu(CN)_3^{2-}$	27
$Cu(CN)_4^{3-}$	28
$Ni(CN)_5^{3-}$	30
$Ni(CN)_4^{2-}$	31
$Fe(CN)_6^{4-}$	37
$Hg(CN)_4^{2-}$	39
$Fe(CN)_6^{3-}$	44
$Pd(CN)_4^{2-}$	>44

The stability constants for Ferric iron complex [$Fe(CN)_6^{3-}$] is 1044, and for ferrous iron [$Fe(CN)_6^{4-}$] is 1037. Because the stability constants of the complexes of lead, cadmium, silver, nickel and copper are lesser than those of iron, they are more likely to release HCN and therefore are more toxic than the iron complexes. Contrary to the view that the greater the stability constant of a cyanide complex the harder it is for it to release free toxic cyanide is the situation between Fe(II) and Fe(III). This is because the Fe(III) is a more versatile ligand making it kinetically labile under the same condition with Fe(II) and therefore more toxic (Oelsner et al. 2001).

The chemical and physical variables of mine environments are very complex as they can be altered by some of the very processes responsible for cyanide degradation/attenuation. A typical example is the fact that WADs cyano-complexes of copper and zinc are insoluble in water but are soluble in ammonia. Therefore the production of ammonia from natural attenuation processes will result in the dissolution of copper and zinc cyanide complexes. This results in an increase in the bioavailability and concentration of cyanide within a specific environment. This is also the case resulting from the formation of acid mine drainage (AMD), which results in a drop of the pH in the system causing some SADs and moderately strong metal-cyanide complexes to dissociate thereby increasing the amount of free cyanide in the system. Except volatilization of the freed cyanide from cyanide-metal complexes occurs, the released cyanides are still available for other chemical processes which may end in the formation of new cyanide species especially if the right conditions are present. This implies therefore that cyanide treatment processes based on the imposition of certain conditions are only valid as long as those conditions exist. This holds true for processes such as photolysis, precipitation and complexation amongst others. Several factors affect the rate of dissociation of cyanide species including; temperature, pH, total dissolved solids, concentration of the complex, atmospheric carbon dioxide, sunlight, air, percolation through the soil, agitation, bacterial degradation e.t.c.

3.1.1 Toxicity Of Cyanide Derivatives

Cyanide in the environment undergoes a great number of oxidation/reduction reactions with numerous chemicals in its vicinity resulting in the formation of cyanide related species of varying toxicity levels. Although most of these compounds are considered non-toxic, they become toxic at elevated concentrations. These compounds include:

Cyanates:

These are generally formed as intermediary products when cyanides react with oxidants such as ozone, hypochlorite, chlorine, hydrogen peroxide e.t.c, during oxidation processes aimed at degrading the cyanides. (Equations 8.2.1b & c, 8.2.2c and d, 8.3.1, 8.4.1a, 8.5.2a e.t.c.).

Cyanogen Chlorides

This is a class of toxic compounds formed as intermediaries during the chlorine oxidation of cyanides to cyanates. (Equations 8.2.1a, and 8.2.2a). When ammonia is present during the chlorination of cyanides another class of toxic cyanide-chlorine compounds called chloramines is produced. (Equations 8.2.1 i and j)

Thiocyanates ($SCNO^-$)

These are formed when cyanide reacts with sulphur or sulphur containing chemical species that are often present in mineral ores. Thiocyanates have been found to persist in acid mine drains for decades after the mines have been closed.

Cyanogens (NC-CN)

These are formed in acidic environments when free cyanide encounters oxidants such as oxidized copper minerals. Formation of cyanogens is not expected in alkaline conditions.

Nitrate And Ammonia.

The chemical dissociation of cyanides and the above mentioned cyanide derivatives often end with the generation of high concentrations of nitrates and ammonia. High concentrations of these are toxic to aquatic organisms.

3.2 Toxicity To Humans And Other Ecological Receptors.

Cyanide can be inhaled, taken orally (by drinking contaminated water or by eating cyanide contaminated food), and it can diffuse through the skin. In humans, cyanide prevents the uptake and subsequent transportation of oxygen to the cells, resulting in a bluish coloration of the skin from tissue hypoxia and cyanosis (Logsdon et al, 1999). Because iron which co-ordinates the uptake and transport of oxygen to the cells of body tissues is consumed by cyanide, the respiratory system fails, rapid breathing ensues which may result to convulsions, loss of consciousness, and suffocation if there is no medical intervention. However, the body can detoxify small concentrations of cyanide by converting it to cyanate that is less toxic. The cyanate is then excreted from the body and so cyanide does not accumulate in the body. Absorption through the skin is supported by the small size of hydrogen cyanide molecule and the fact that cyanide dissolves readily in lipids found on our bodies (Simeonova & Fishbein 2004). Cyanide is toxic to aquatic inhabitants and migratory birds. Concentrations of 20ppm to 40ppm in the air are toxic to most humans. When the concentration is 250ppm death occurs within minutes. Death occurs for humans with concentrations of 1 to 3 mg of cyanide per kg of body weight (Logsdon et al. 1999).

Chapter 4

Cyanidation

4.1 Introduction To Cyanidation

This is the process of extracting gold from its ores using cyanide as the lixivant in the presence of lime and oxygen (Wong & Arun, 2009; Eisler & Wiemeyer, 2004). The low cost and process simplicity (Zaoheng & Muhammed 1992; Trexler et al. 1990) of cyanidation compared to other metallurgical processes for gold extraction (Logsdon et al. 1999) makes the process very attractive to the mining industry. Cyanidation is also advantageous because of the selectivity of free cyanide for gold dissolution and the high stability of the resultant gold-cyanide complex (G. Deschenes 2005; Huiatt 1984). This is important especially as gold occurs often in combination with other elements in its host ores such as sylvanite ($AuAgTe_4$), Monbroyite ($AuTe_3$) and Calaverite ($AuTe_2$) in association with typically sulphide and copper minerals. In contrast to other gold complexes e.g. gold-chloride complex that tends to precipitate gold when it contacts sulphide minerals, the cyanide-gold complex is stable and does not release the gold.

In recent times, in response to increasingly stringent environmental regulations, fluctuating and often low prices of gold, and lower ore grade qualities, there has been growing research aimed at optimizing the cyanidation process (G. Deschenes 2005). In other cases, an increase in the price of gold has encouraged research to optimize extraction technologies (Eisler & Wiemeyer, 2004). Great advances have been made in the monitoring and control of reagents such as cyanide, oxygen and lead nitrate as well as improvements in equipment automation. Control and monitoring of reactants have been extensively studied as the rate of the cyanidation process is controlled by the rate of diffusion of reactants especially cyanide to the gold surface (Grunwell et.al 1997). Dissolution of gold depends on the cyanide concentration, availability of oxygen and pH of the solution (Huiatt 1984).

Once the ore is extracted, it is processed either in-situ or it is moved to a processing plant. At the processing plant, the ore is first comminuted (the finer the ore grain sizes after comminution the faster the rate of gold dissolution (Kyoseva et al. 2009)) and then concentrated by either flotation or centrifugal gravity concentration. The choice of the concentration method depends on the ore mineralogy. Methods of comminution and concentration depend heavily on the grade of the ore, quantity of ore, ore mineralogical and metallurgical properties.

Concentrating the ore has various advantages including that; 1) It helps to guarantee a high purity end product. Handling a small concentrated portion is cheaper and easier at every level of treatment. 2) Concentrating a sample helps in discarding the gangue. 3) The reduction of the gangue is vital in calculating the amounts of reactants needed at various levels of processing and the stress of dealing with the effects of possible side reactions. Some side reactions cause a general slow down of process kinetics, and/or consume reactants intended for different reactions. This results in an increase in the cost of production. Some of these reactions include, sulfide minerals reacting with cyanide to yield thiocyanates, gold adsorbing carbonates or acid consuming carbonates. The predominant importance of ore comminution is that it is cost saving.

4.1.1 Cyanide In Cyanidation

Field consumption of cyanide greatly deviates from estimations from the process stoichiometry partly amongst others due to the presence of cyanicides (Hutchison et al. 1984). At optimum conditions, a 0.05% sodium cyanide solution concentration dissolves fine grain gold particles at a rate of 3.25mg per square cm per hour at a pH of 10.3 (Wong & Arun 2009; Huiatt 1984). In mining operations cyanide concentrations of 0.01%f – 0.05% are typically used i.e. 100 to 500 parts per million (Logsdon et al. 1999). The addition of lime prevents hydrolysis of the cyanide, neutralizes any acids that may be present or be formed, decomposes any carbonates present, e.t.c. Competition for cyanide ions from other ionic species present and the need for extra cyanide to counteract the retarding effect resulting from coatings formed on gold grains due to the dissolution of metallic sulphides have been blamed for the excess cyanide consumption (G. Deschenes 2005). For the formation of iron complexes six parts of cyanide are required for one part of iron [$Fe(CN)_6^{-3}$, $Fe(CN)_6^{-2}$] implying a large consumption of cyanide species during the formation of iron-cyanide complexes. Three approaches are used to reduce the consumption of cyanide, thereby reducing cyanidation cost and cost of effluent treatment. These include (G. Deschenes 2005),

I. The use of online cyanide analyzers.
II. Oxygen enrichment of the pulp.
III. Addition of lead nitrate.

The main principles guiding cyanidation are that; in instances of low cyanide concentration the rate of gold dissolution is a function of cyanide concentration whereas in instances of high cyanide concentration dissolution rate is a function of oxygen concentration (G. Deschenes 2005). A simplified equation for the rate of dissolution of gold has been expressed mathematically (Zaoheng & Muhammed 1992, Habashi 1966),

$$\text{Rate} = \frac{2\text{ADcn}^{-}.\text{Do}\left[\text{CN}^{-}\right]\left[\text{O}_2\right]}{\delta\left[\text{Dcn}^{-}\left(\text{CN}^{-}\right)+4\text{Do}\left(\text{O}_2\right)\right]} \qquad \text{----------eqn 4.1.1a}$$

Where;
Dcn^{-} = Diffusion coefficient of cyanide.
D_o = Diffusion coefficient of oxygen.
б = Coefficient of diffusion film i.e. thickness of the boundary layer.
A = Surface area of reacting gold.

The variables included in the equation and some others not included in the equation will be further examined as gold cyanidation is influenced by many other factors. (Zaoheng & Mohammed 1992)

4.1.2 Gold Leaching

There are two main leaching methods. These are the heap leaching introduced in the 1970s and the agitated leaching. Their difference is basically where they are carried out and not in their chemistry. Heap leaching, is leaching done in the immediate vicinity of the ore extraction. With agitated leaching, the leaching is done in large tanks away from the site of the ore extraction. In fig 4.1.2, the alkaline cyanide solution is drip irrigated on the concentrated crushed ore body. As the solution percolates through the heap, it dissolves any gold grains and leaches them out. The alkaline cyanide solution dissolves the gold grains and the gold-cyanide complex collects at the bottom of the heap for extraction of gold by either adsorption onto carbon or by zinc precipitation. To prevent any pollution of the soil and subsequently the ground water in the area, the bottoms of the heaps are lined with thick impermeable plastics.

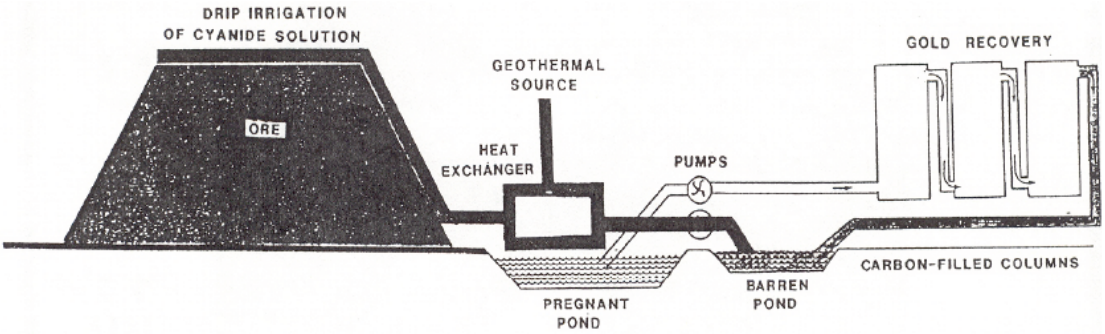


Fig 4.1.2: Idealized thermally enhanced, Heap Leach (Trexler et al. 1990).

The leachate is collected in the pregnant pond where it is pumped to the gold recovery chamber filled with activated carbon for the adsorption process or processed with zinc powder. The spent leachate is sent to the barren pond where more cyanide and alkaline solution is added for reuse. Not all of the total volume of the barren solution is been recirculated into the leaching process. This is because the barren solution contains a great amount of deleterious metals e.g. iron, copper, zinc, arsenic, nickel and antimony which if continuously recirculated into the system risk building up to concentrations that will greatly affect the efficiency of the cyanidation process by interfering with the dissolution and precipitation of gold. To avoid such a scenario a portion of the barren solution is bled off and discarded in tailing ponds or treated. The amount of barren solution bled off or discarded depends on the ore mineralogy (Scott 1984). In some instances, a portion of the barren solution is used to wash the leached rocks and filters to recover any gold that may be left and finally the rocks are washed with clean water before evacuation to tailings ponds. Cost reduction associated with heap leaching result from the facts that;

a. The ore is not required to be finely crushed. Heap leaching is done on rock sizes of ¾ inches; agitated leaching requires reduction to 200 meshes (0.002inches). Crushing is energy consuming therefore costly.

b. In agitated leaching, there is the need to separate the solids and the liquids after the leaching process. This is not required in heap leaching.

c. Tailings disposal costs associated with agitated leaching are quite high as the liquid wastes from leaching processes have to be held in large tanks before disposal and that is additional cost. This is not the case for heap leaching as these can be held in place.

There are also disadvantages associated with heap leaching including,

a. There must be sufficient porosity to ensure percolation of the lixiviant. The problem of porosity occurs when the ore has a high amount of clay content.

b. In areas with high rainfall, water input from rainfall can negatively affect the leaching process resulting in the need to treat and discharge process water.

c. In cold climates there can arise the problem of low recovery. This problem has been tackled by employing subsurface introduction of the lixiviant but this has only ameliorated the situation.

d. The melting of snow and ice can result in the accumulation of leach solutions. This can be solved using other diversion channels to transport the spent cyanide.

For agitated leaching, the ore is transported and leached in vessels within a processing plant. A major advantage of the outdoor heap leaching is the fact that there is hardly any oxygen depletion as the system is naturally aerated by atmospheric oxygen. In agitated leaching, the system is continuously agitated to ensure an even distribution of oxygen within the system. Not withstanding it is common practice in the mining industry to use agitated leaching for high-grade ores and heap leaching for low-grade ores (Wong & Arun 2009). Within the leaching systems there may be a number of side reactions but the target reaction is that between gold and cyanide. This is called the Elsner reaction with the following stoichiometry, equation 4.1.2a:

$$4Au + 8NaCN + O_2 + 2H_2O \rightarrow 4NaAu(CN)_2 + 4NaOH \text{ ------ eqn 4.1.2a}$$

Cyanidation is a heterogeneous reaction controlled by the diffusion of the most important reagents, oxygen and cyanide (O_2 and CN^-). The rate of gold dissolution correlates positively with the cyanide concentration until a maximum dissolution rate is reached beyond which occurs a slight decrease in the rate of cyanide dissolution. The formation of precipitates on the surface of the gold grains is significant in the cyanidation process as it is generally a rate-limiting step. Owing to the intra/inter mineralogical and metallurgical discrepancies within/between ore bodies, the Elsner reaction assumes that only gold, water and sodium cyanide are present. Cyanide forms complexes with elements such as copper, zinc, cobalt, nickel, sulfur, sulfide minerals e.t.c. Nickel further interferes with the precipitation of gold from the gold-cyanide leachate. Taking out or extraction of these elements before leaching ensures that cyanide is not consumed by other side reactions involving these elements. These reactions result in the formation of other cyanide complexes that tie up cyanide that would otherwise be available for gold dissolution. Of particular interest is the formation of copper cyanide complexes that are fairly stable. The stability of the copper complexes can cause operational as well as environmental problems as this will imply a much higher concentration of cyanides in tailing ponds (ICMI 2011). Without pretreatment cyanide will preferably leach sulfide minerals and this will enhance the oxidation of reduced sulfur species. Oxidation of these sulfur species results in an increase in acidity requiring the addition of more lime to neutralize the effect. The presence of copper in gold ores can greatly increase operational cost due to the extreme consumption of cyanide by copper. Compounds such as arsenic and antimony do not only form complexes with cyanide but their reactions require the presence of oxygen thereby reducing the amount of oxygen available for the Elsner reaction. There are some factors very important to the chemistry and/or safety of the Elsner reaction including pH, lead nitrate, oxygen concentration, sulphide minerals, and zinc (catalyst).

Precipitation Of Gold

The dominant methods for precipitating gold are the Merrill-Crowe process and Carbon-in-Pulp (CIP). The Merrill-Crowe process will be described when discussing the role of zinc in the cyanidation process (refer to section 4.1.3.1). The CIP process extracts gold by adsorption of the gold grains onto activated carbon. The gold is stripped off the carbon by washing with hot caustic cyanide solution and later electrowon from the stripped solution (Scott 1984). The disadvantages of CIP method compared to the Merrill-Crowe process are; the CIP process consumes a greater quantity of cyanide as there is no recycling of cyanide in this process and also that cyanide waste is a slurry and not a clear liquid as in the Merrill-Crowe process.

4.1.3 Factors Affecting Cyanidation

4.1.3.1 Zinc Powder

After the ore has been gotten rid of gold by leaching, the gold-cyanide concentrate leachate is ready for gold stripping but before stripping the leachate is de-aerated (Scott 1984). To strip the leachate of gold there are two main procedures applied to achieve this. The gold can either be precipitated out of the leachate by the addition of fine grain zinc powder (Merrill Crowe zinc precipitation process) or by adsorption of the gold onto activated carbon (CIP). The use of activated carbon has been shown to increase cyanide consumption as cyanide is oxidized at the surface of carbon (Deschenes et al. 2007). Precipitating gold by the addition of fine grain zinc particles is most commonly used in the gold mining industry. The reaction is as follows (eqn 4.1.3.1a),

$$2Au(CN)_2 + Zn \rightarrow 2Au + Zn(CN)_4^{-2} \qquad \text{------ eqn 4.1.3.1a}$$

This reaction is possible because zinc has a higher affinity for cyanide than gold, silver or copper. Therefore, on addition of zinc powder any of the metals with a lesser affinity for cyanide is precipitated out of the solution.

4.1.3.2 Effect Of pH

A major factor in the cyanidation process is the pH of the system. Deciphering the role played by pH in the relationship between hydrogen cyanide (HCN) gas and solution, this knowledge is used to keep HCN in solution where it takes part in the dissolution of gold as oppose to having it as a gas where it only does not escape from the system but also becomes poisonous to anybody in the vicinity of the leaching process. To avoid generating gaseous cyanide the pH of the system is maintained above 9.0. At a pH of 10.5 the rate of dissolution is maximum and at pH values above 10.5 the reaction rate begins to drop. Despite being aware of the rate drop above a 10,5 pH the system is often maintained at higher pH levels because of the risk associated with the formation of HCN gas that far outweighs any benefits of running the system at a risky pH margin. To maintain such a high pH, lime ($Ca(OH)_2$) or soda (NaOH) is added to the system. At pH values below 9.0, HCN escapes as a gas to the atmosphere reducing the available HCN for gold dissolution.

4.1.3.3 Effect Of Oxygen

From the Elsner equation, dissolved oxygen concentration is critical to the rate of gold dissolution. Oxygen can be supplied to the system as natural air, pure oxygen or as natural air enriched with pure oxygen. Addition of oxygen is more significant in increasing the rate of gold dissolution than addition of air or oxygen-air mixture (Davidson, et al. 1978). Oxygen sparging is done using special equipment.

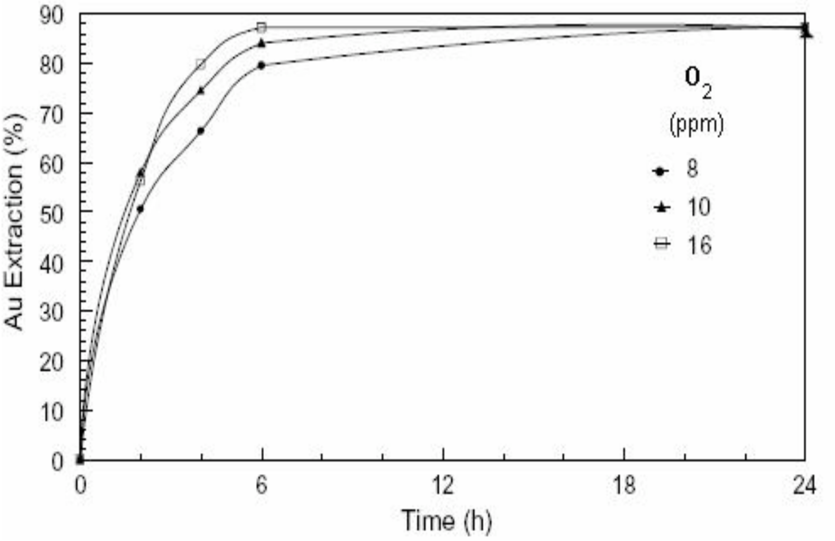


Fig 4.1.3.3a: Effect of oxygen addition on cyanidation, pH 11.2, 500ppm NaCN, 24 hour. (Deschenes et al. 2003)

The optimum concentration at a temperature of 20°C for dissolved oxygen in a cyanidation solution is 8.2mg/l (=8.2ppm) (Deschenes G. , 2005). However, the rate of gold dissolution greatly decreases when the dissolved oxygen concentration drops below 4ppm and increases significantly when the dissolved oxygen concentration is greater than 10ppm(Deschenes G. , 2005) (Fig 4.1.3.3a and fig 4.1.3.3b).

Increasing the oxygen concentration does not necessarily result in an increase in the rate of gold dissolution except in the presence of a reasonable amount of cyanide. Reasonable amount of cyanide here must be emphasized because if the concentration of cyanide is over increased the excess cyanide will only go to take part in the formation of undesired cyanide complexes. Increasing or decreasing the cyanide concentration from the required concentration needed for a particular ore type negatively affects the cyanidation process. In oxygen free environments there is no oxidation of minerals and any sulfides available are stable thermodynamically and are not readily soluble. The presence of oxygen especially as with rocks above the surface initiates a number of bio-geochemical processes which increase the potential for development of acid mine drainage (IGEI, 2006).

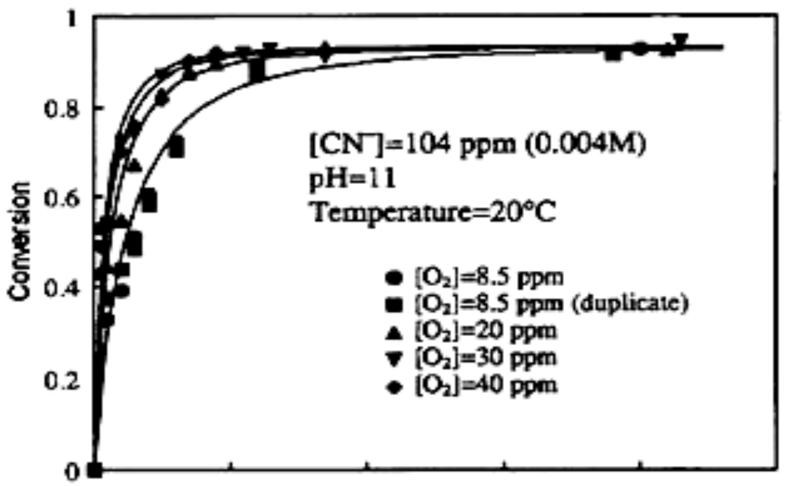


Fig 4.1.3.3b: Effect of dissolved oxygen concentration (DOC) on gold conversion. (Srithammavut 2008)

The practice of adding oxygen to a leaching system was started in the 1980's by a South African company, Air Products, and since then it is a common practice within the industry especially for indoor agitated leaching systems. Studies have shown that small increases in dissolved oxygen concentration have a greater impact on the gold dissolution rate as oppose to even greater percentage increases in the cyanide concentration. When oxygen is sufficiently supplied, it reduces the retention time and also lowers the cyanide consumption by the process. Pyritic ores consume more oxygen than other ores predominantly of albite, quartz and chlorite minerals. This shows that the oxygen demand is not the same for all ores, but that oxygen demand is a factor of the ore mineralogy. Studies on sulphidic ores showed that a 50% increase in oxygen concentration within the pulp positively impacted the rate of gold dissolution more as compared to a 147% increase in cyanide concentration (G. Deschenes, 2005).

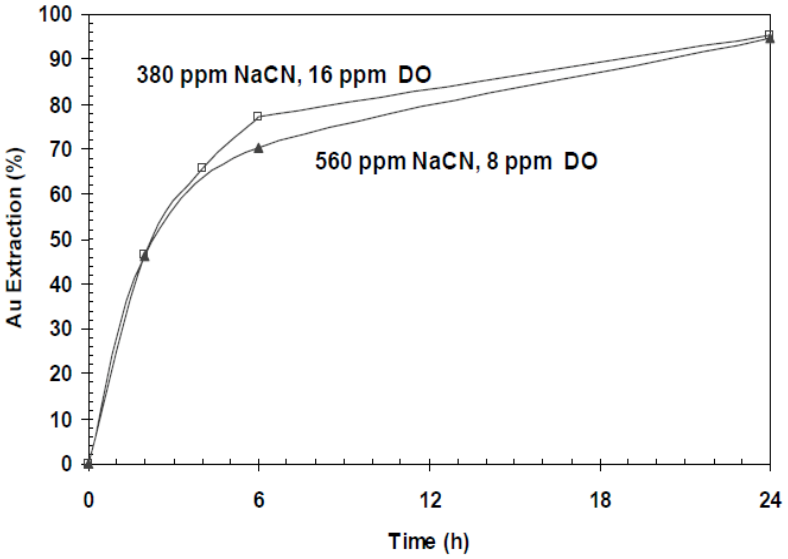


Fig 4.1.3.3c: Effect of oxygen and lead nitrate on gold leaching kinetics of an ore containing pyrite and pyrrhotite, cyanidation: pH 11.0. (G. Deschenes, 2005)

From fig 4.1.3.3c it can be seen that increasing the oxygen concentration increases the rate of cyanidation as oppose to increasing the cyanide concentration. The cyanidation of sulphidic gold ores is particularly problematic as there is competition for oxygen between the processes of sulphide minerals oxidation and gold dissolution. To avoid any reduction in gold dissolution/leaching due to reduced oxygen concentration in the pulp, typical dissolved oxygen concentrations are kept at between 12 and 18ppm by sparging. Sulphide ions form coatings on the surfaces of gold grains, and therefore oxidation of these ions to free these gold surfaces is important if the leaching rate is to be maintained.

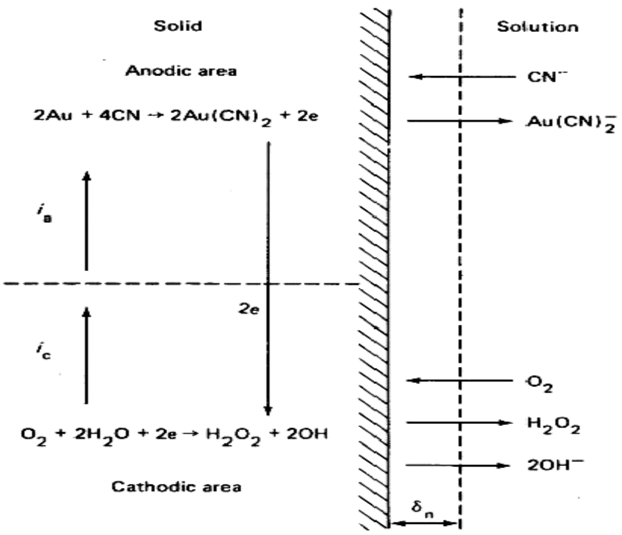


Fig 4.1.3.3d: Schematic representation of the local corrosion cell at a gold surface in contact with an oxygen-containing cyanide solution. Ia is the anodic current; Ic is the cathodic current and $б_n$ is the passive layer (Marsden & House,1992).

It can be concluded from the above diagram that, the presence of a passive layer between the reactant mixture (oxygen and cyanide) and the gold grains reduces/resists the ability for these to contact and also reduces the contact time thereby slowing down the cyanidation process.

4.1.3.4 Lead Nitrate

The application of a lead nitrate solution is of particular importance in the leaching of partially oxidized ores. Lead nitrate ($PbNO_3$) has been successfully applied as a catalyst for the dissolution of gold as it plays the following roles (G. Deschenes, 2005; Deschenes et al. 2007; Taylor, 2010),

1) It forms a coating around metallic sulphides thereby precipitating them and decreasing their dissolution. The sulphide minerals are precipitated as lead sulphide (Pbs). Therefore, the lead ion will react with the passive film (gold-sulphide) on the gold grains dissolving and precipitating the sulphides thereby exposing the gold surfaces for cyanide action (leaching) in the absence of further oxidation or dissolution of sulphides. This action has the following effects in a cyanidation process;
    - Reduces the dissolution of sulphide minerals.

- Reduces consumption of cyanide by sulphides.
- Reduces consumption of oxygen by sulphides

2) It enhances the dissolution of gold by.
    - Preventing/limiting the formation of a passivation film on the gold grains. This is done by preventing the dissolution of sulphide minerals, thus activating the gold surfaces.
    - Forming a precipitate on gold grains creating a corrosion pile making gold anodic and more incline to dissolve.
    - Depolarizing the reduction of oxygen.

In the absence of lead nitrate there is the deposition of a precipitate of various compounds including sulphides of cupper, silver, iron and calcium on the surface of gold grains. This slurry composed of a pyrite concentrate formed on the surface of gold grains is considerably reduced or even absent in the presence of lead nitrate.

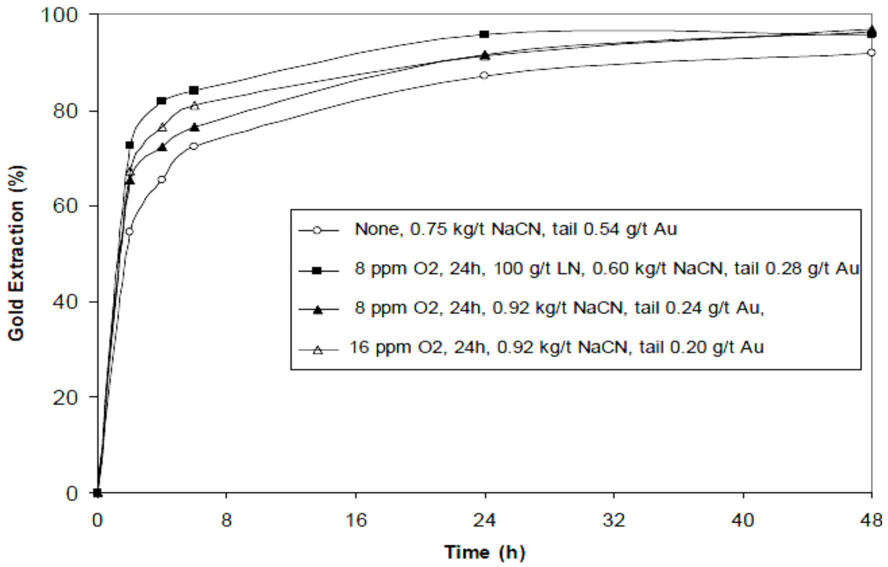


Figure 4.1.3.4a: Effect of a pre-treatment on gold leaching from a sulphide-bearing gold ore. Pretreatment: pH 11.3, 8ppm O_2; cyanidation: pH 11.3, 360ppm NaCN, 8ppm O_2. (G. Deschenes 2005).

As it can be seen in fig 4.1.3.4a above, the application of 100g of lead nitrate per tone of ore greatly increased the dissolution of gold during a 24 hours period. It was concluded, that in the absence of lead nitrate (without pre-treatment) gold forms a number of gold-sulphide species (G. Deschenes 2005). When the ore contains mainly realgar (As_4S_4 or AsS) there is a significant depositon of arsenic on the surface of the gold grains that disappears on addition of lead nitrate and is replaced by lead sulphide on the surface of gold grains. The deposited sulphide layer even though pre-dominantly of lead sulphide also contains many other sulphide species. Lead hydroxide ($Pb(HO)_2$) and iron-oxyhydroxide were found deposited on particles of some sulphides such as pyrite, pyrrhotite, arsenopyrite but not on chalcopyrite ($CuFeS_2$) and realgar (Deschenes et al. 2007), which may explain the passivation effect of this layer on the gold leaching process. The formation of a hydroxide layer on the sulphide minerals on addition of lead nitrate reduces the ability of these sulphides to scavange for cyanide ions resulting in a high availability of cyanide concentration for gold dissolution. In Deschenes 2005, it is suggested that lead sulphide might be a catalyst for sulphide oxidation to release lead ions which is recycled in the system to further react with sulphide ions. Fig 4.1.3.4b shows the combine effect of increased oxygen concentration and the presence of lead nitrate (G. Deschenes 2005).

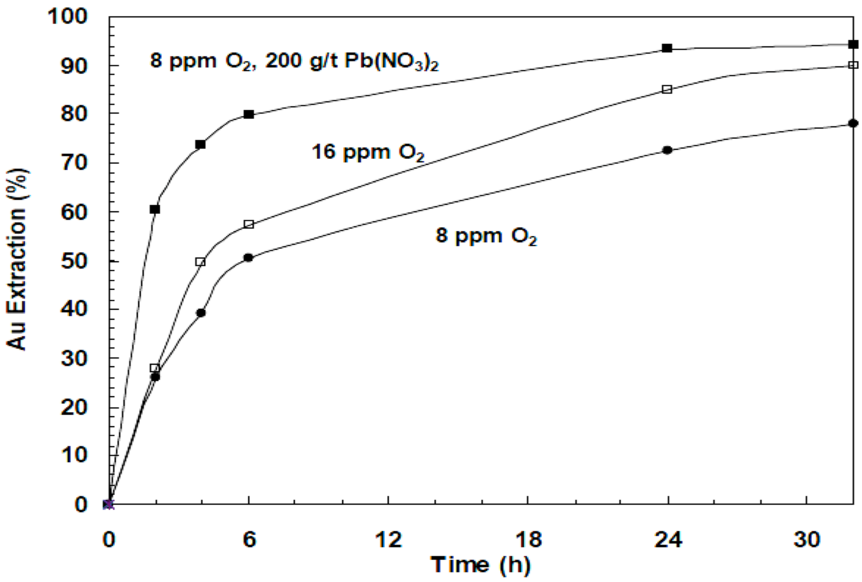


Fig 4.1.3.4b: Effect of lead nitrate and oxygen addition on the leaching of a pyrrhotite-bearing gold ore, with lead nitrate: pre-leaching pH 11.2, 0.5 h, 8ppm O_2; cyanidation: pH 11.2, 380ppm NaCN, 8ppm O_2. (G. Deschenes 2005).

4.1.3.5 Presence Of Sulphide Minerals

Gold ores often occur in association with sulphide minerals that pose a great amount of stress during the gold leaching process. While gold leaching of sulphidic ores is generally problematic, there is a great variation in the extern to which the various sulphidic minerals affect the leaching process. How the various minerals affect the gold leaching process is governed amongst others by their concentration in the ore, solubility and reactivity, which are themselves governed by other factors such as ambient pH, temperature, etc. At a pH of 12, orpiment, stibnite and realgar dissolve significantly but when the pH is 10, only orpiment dissolves considerately. Sulphide minerals are oxidized to thiocyanates in the presence of cyanide or react with oxygen yielding sulphites and sulphates that migrate to the surfaces of gold grains forming a passive layer. Sulphide ions can also be directly adsorbed on the surfaces of gold grains also forming a passive layer on the gold grains. Formation of a passive layer depends on the sulphide mineral type and amongst other factors the ambient oxygen concentration. This passive layer reduces reactants mass transfer to the gold surfaces thereby reducing the leaching kinetics (Deschenes et al. 2007). Experiments done on sulphidic ores showed that the application of lead nitrate reduced cyanide consumption by 25% (from 2.03kg/t to 1.52kg/t) as lead nitrate reduces the reactivity of sulphides (Deschenes et al. 2007). The reactivity of common sulphides is in this order, stibnite > orpiment > arsenopyrite > realgar. Ores containing 1.0% of pyrite or 5.7% of arsenopyrite have an insignificant or no noticeable effect on the gold leaching process. This is not the case for sulphidic ores containing any of the following, 1.0% of chalcopyrite, or 1.2% pyrrhotite or 0.5% realgar which have shown to greatly negatively affect the gold leaching process (G. Deschenes 2005). Based on the degree to which sulphidic minerals negatively affect the cyanidation process they have been loosely classified as follows; realgar (AsS) > pyrrhotite (FeS) > chalcopyrite ($CuFeS_2$). Arsenopyrite and pyrite only negatively affected the leaching process when the retention time is long or when they occur in very high concentrations.

Once sulphide ions are released from the sulphide minerals their oxidation to thiosulphate (eqn 4.1.3.5a) and sulphate (eqn 4.1.3.5b) ions is as follows (Deschenes et al. 2007),

$$2S^{2-} + 2O_2 + H_2O \rightarrow S_2O_3^{2-} + 2OH^- \qquad \text{------ eqn 4.1.3.5a}$$

$$S_2O_3^{2-} + 2OH^- + 2O_2 \rightarrow 2SO_4^{2-} + H_2O \qquad \text{------ eqn 4.1.3.5b}$$

Under leaching conditions and time scale, the oxidation of thiosulphate to sulphate is incomplete. On addition of lead nitrate the concentration of thiosulphate increased implying that the oxidation of sulphides to thiosulphates is favored against oxidation of thiosulphate to sulphate in the presence of lead nitrate. Thiosulphate reacts with cyanide following these paths:

$$CN^- + S_2O_3^{2-} \rightarrow CNS^- + SO_3^{2-} \qquad \text{------ eqn 4.1.3.5c}$$

Or

$$H_2O + 4CN^- + 3S_2O_3^{2-} \rightarrow 4CNS^- + 2SO_4^{2-} + 2OH^- \qquad \text{------ eqn 4.1.3.5d}$$

Notwithstanding cyanide may react on the surfaces of sulphide minerals. Consider the reaction on the surface of pyrrhotite. (Equation 4.1.3.5e)

$$Fe_7S_8 + CN^- \rightarrow 7FeS + CNS^- \qquad \text{------ eqn 4.1.3.5e}$$

Sulphidic minerals affect the leaching process by forming a partial sulphite layer around gold grains shielding them from contact with cyanide and subsequent dissolution. Increasing the lead nitrate concentration has proven successful in counteracting this coating effect by sulphide minerals. Lead nitrate as explained encourages formation of a lead hydroxide or oxy-hydroxide coat around the sulphide minerals preventing them from reacting with cyanide thereby consuming cyanide. Increasing the oxygen concentration can counter the coating effect also, but it is not effective against realgar. Therefore lead nitrate is preferred to oxygen when it comes to catering for the coating effect of sulphide minerals on the cyanidation process(G. Deschenes 2005). The case of stibnite is special as it retards the leaching process even when in very minute concentrations as low as 20ppm by forming an oxide (SbO_5) coat around gold grains. Lowering the pH to 10 and below treats a slurry containing stibnite. At this pH the solubility of stibnite is greatly reduced and therefore its ability to form a coat around gold grains is greatly reduced. Addition of lead nitrate is a better solution. Increasing the amount of dissolved oxygen in the slurry with stibnite increases the negative effect on the leaching process. Like stibnite, the passivation effect by antimony can be counteracted by adding lead nitrate or by lowering the pH.

The danger of reducing the pH is that the formation of free cyanide (HCN) is encouraged and the level in the reaction chamber can rise to dangerous levels. The addition of lead nitrate has shown to increase the leaching efficiency in the tank by 5% when only a small concentration of antimony was present. Oxidation of sulphides culminates with the production of acids thereby decreasing the pH and encouraging the formation of poisonous HCN. To inhibit this from happening there is the constant addition of excess alkali to maintain a pH high enough above the pH which hydrocyanic gas ($HCN_{\mathbf{gas}}$) forms.

Solubility of common sulphide minerals was found in decreasing order to be; pyrrhotite **>** marcasite **>** pyrite. Arsenic and antimony do not form stable complexes with cyanide. Based on how sulphide minerals affect the gold leaching process in the presence of increased oxygen they can be divided into three groups (G. Deschenes 2005); group one consists of minerals which negatively affect the gold leaching process. These include stibnite, chalcocite, and pyrrhotite. Group two consists of the following minerals pyrite, chalcopyrite, arsenopyrite and sphalerite. This group of minerals does not affect the gold leaching process. The last group is made up only of galena, which rather enhances the gold leaching process.

When the concentration of oxygen is 8ppm, galena and asernopyrite enhance the gold dissolution process (Fig 4.1.3.5). As the concentration of oxygen increases the rate of gold leaching reduces and it is almost zero when the concentration of oxygen reaches 32ppm. The initial increase in leaching is as a result of the addition of metal ions from galena and asernopyrite, but as the oxygen concentration increases, increased amounts of galena and arsenopyrite are dissolved which possibly results in the formation of a passive laver over the gold grains.

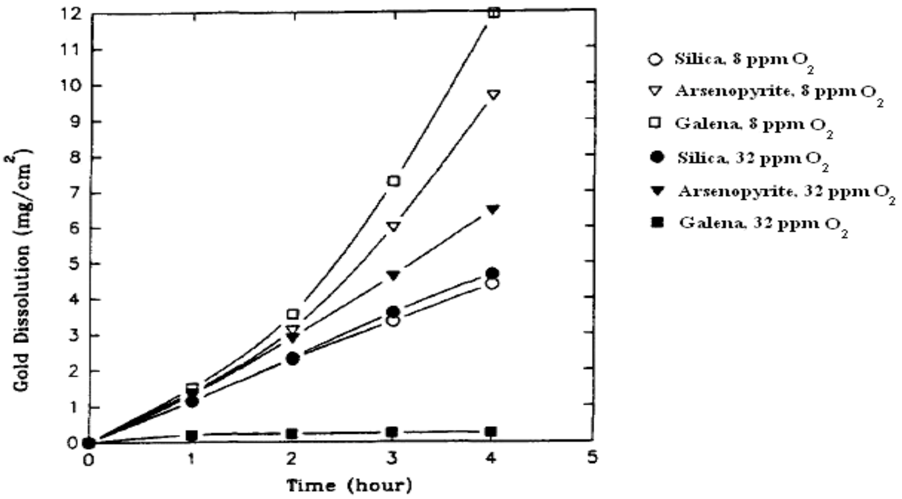


Fig 4.1.3.5: Effect of arsenopyrite, galena and oxygen on gold dissolution (Liu & Yen, 1994).

4.1.3.6 **Cyanide Concentration**

Stating a definite value as the concentration of cyanide required for the cyanidation process is tricky. This will depend above all on the metallurgy and the mineralogy of a particular ore, whether the ores are pretreated or not before leaching is carried out, etc. The ambient temperature and pressure are critical to the cyanidation process since these directly affect the dissolution of oxygen.

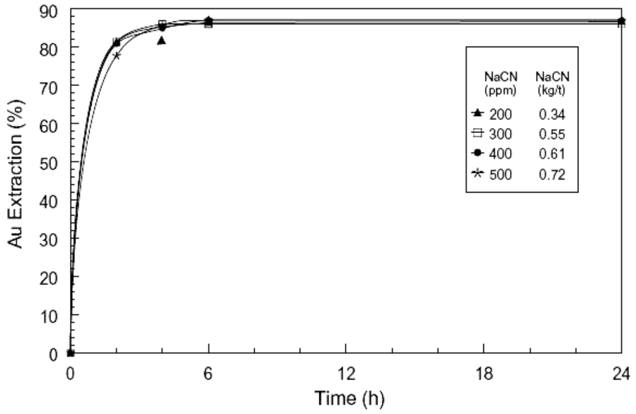


Figure 4.1.3.6: Effect of cyanide concentration on leaching. Pre-leaching: pH 11.2, 8ppm O_2, 100g/t $Pb(NO_3)_2$, 12 h; cyanide: pH 11.2, 10ppm O_2. (Deschenes et al. 2003)

If conditions favour oxygen dissolution then a lesser amount of cyanide is needed as oppose to when then conditions of temperature and pressure do not favour the dissolution of oxygen. In another scenario and given that every other factor is constant, it has been concluded by a number of researchers (Deschenes et al. 2003) that the cyanidation process is not very sensitive to slight variations of the concentration of free cyanide especially at elevated levels of cyanide concentration (Fig 4.1.3.6). From the graph it can be seen that at elevated cyanide concentration there is not much change in process dynamics in response to small changes in the concentration of cyanides. Any excess cyanide is only consumed by competing species especially soluble sulfides (Mardens & House, 1992). Habashi 1966, demonstrated that at low cyanide concentration the rate of gold dissolution was dependent only on the cyanide concentration but at high cyanide concentrations the rate of gold dissolution was dependent only on the concentration of dissolved oxygen. These conclusions can be derived from eqn 4.1.1a. At low cyanide concentrations the first portion of the denominator (Dcn$^-$(CN$^-$)) can be neglected, while at high cyanide concentration the second part of the denominator (4Do$^-$(O$^-$)) can be neglected.

Chapter 5

Adsorption Methods

5.1 Introduction

Adsorption is the ability of certain materials to retain molecules (gas, metallic ions, organic molecules, etc.) on their surfaces in a more or less reversible manner (Ghinwa & Bohumil 2009). It is a simple and low cost system for the extraction of heavy metals and other charged particles from solution (Eba, et al. 2010). This is the extraction of matter from one phase and concentrating/accumulating it on the surface of a second phase. This is also referred to as interface accumulation. In the process there is a mass transfer of the sorbate from the bulk liquid or gas phase to the surface of a sorbent that is a highly porous material. Resins, activated carbon and a host of other minerals are capable of adsorbing free and complexed cyanides (Young & Jordan 1995).

As a consequence of this mass transfer, the solid sorbent acquires superficial hydrophobic or hydrophilic properties, which modify the state of equilibrium (rate of diffusion or flocculation i.e. forming woolly cloudlike aggregations) in the medium (Ghinwa & Bohumil 2009). Adsorption of the sorbate on the sorbent is governed by physical and chemical interactions between the sorbate and the sorbent surface which depend on the characteristics (surface area, pore size distribution (PSD), and surface chemistry) of the adsorbent, and the characteristics (molecular weight and size, functional groups, polarity, solubility) of the adsorbate, and the physical and chemical properties of the solution (pH, temperature, presence of competitive solutes, ionic strength) (Kose, 2010). Adsorption of a sorbate at the surface of an adsorbent is governed by bonding forces resulting from electromagnetic interactions of the adsorbate atoms, molecules and ions, and the adsorbent surface (J. J. Weber, 1972; Weber & Vliet 1980). Compared to absorption, adsorption is more of a surface phenomenon. In absorption, matter changes phases. Both phenomena are described in the figure 5.1. Adsorption is effective for the removal of material in the solution phase that is neither volatile nor biodegradable. The material to be adsorbed is called the adsorbate while the material onto which it is adsorbed is called the adsorbent. Examples of adsorbents include activated carbon or ion exchange resin.

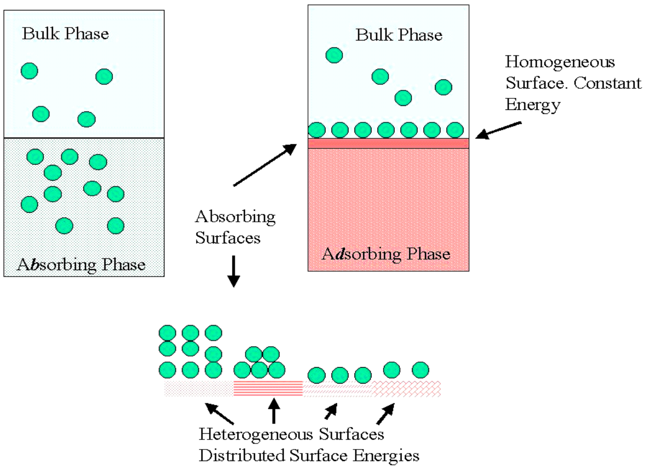


Figure 5.1: Differentiating between absorption and adsorption (CU 2010)

5.1.1 The Adsorptive Capacity Of Solid Sorbents

1) This depends on the developed surface area or specific surface area of the material (Naeem & Zafar 2009). The specific surface area of natural adsorbents varies depending on the physicochemical properties (pH value, nature of the bounded cations, surface saturation by organic molecules e.t.c.) of the liquid medium. Clays such as bentonites (monmorilonite) have surface areas accessible to most molecules. These clays have a surface area ranging from 40-800m^2/g. The adsorbtive capacity of these clays is quite variable as evident by the large range of the available surface area. Industrial adsorbents e.g. activated carbon present an even larger available surface area ranging between 600-1200m^2/g defined by extensive micro porosity. The lager the surface area of an adsorbent the higher is its adsorption capacity (Wang, et al. 2009). Other adsorbents such as metallic hydroxides develop very large surface areas that depend heavily on the pH value of the medium.

2) The nature of the adsorbent-adsorbate bond. This is the free energy of interaction between the adsorption sites and molecules on the surfaces.

3) The contact time between the solid and the solutes. At equilibrium there is constant movement of molecules between the bulk solution and the adsorbent surface. There is no universally accepted theory to explain the relationship between the number of molecules adsorbed and the number of molecules at equilibrium. The most accepted theory that attempts to explain this relationship for adsorption on activated

carbon is the Fruendlich equation (eqn 5.1.1a).

$$x/m = k(C_{eq})^{1/n} \qquad \text{----------------eqn 5.1.1a}$$

x/m = weight of the pollutant retained per unit weight of the adsorbent.

C_{eq} = Equilibrium concentration of pollutant molecules in the aqueous phase.

K and n = energy constants depending on the adsorbate-adsorbent couple at a given temperature.

During the adsorption process the adsorbate diffuses to the surface of the adsorbent where it is held onto the surface by weak forces of attraction while the carrier gas incase of a gaseous mixture passes by not being held on to the surfaces by those same forces keeping the target molecules on the adsorbent surface. During adsorption, there is first the diffusion of the adsorbate to the macropores, which are much larger and present a possibility for the adsorbate passing through without contact with the walls of the macropores. As the adsorbate moves further inwards the pores become smaller.

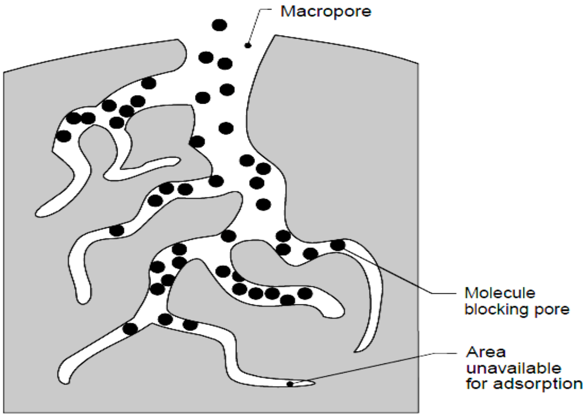


Figure 5.1.1: Vapour adsorbed into pores of adsorbent (APTI 2010).

They get attached to the pore walls and may block the passage of oncoming molecules to the inner spaces or the diameter of the molecules become equal to that of the pores and the pores become blocked. This results in micropores being blocked and not available for adsorption (fig 5.1.1).

5.1.2 Adsorption Steps

This is a three steps process. First, there is the transfer of the adsorbate from the bulk gas stream flowing through onto the external surface of the adsorbent material (step 1, fig 5.1.2). Secondly, the adsorbate diffuses from the external surface to the macropores then through the transitional pores to the micro pores (step 2, fig 5.1.2). Thirdly, there is adsorption of the adsorbate on to the surface of the micro pores (step 3 fig 5.1.2). Whereas the external surface presents an available surface area of a few square meters per gram, the micro pores have surface areas of hundreds of square meters per gram. This explains why most of the adsorbate is adsorbed in the micro pores.

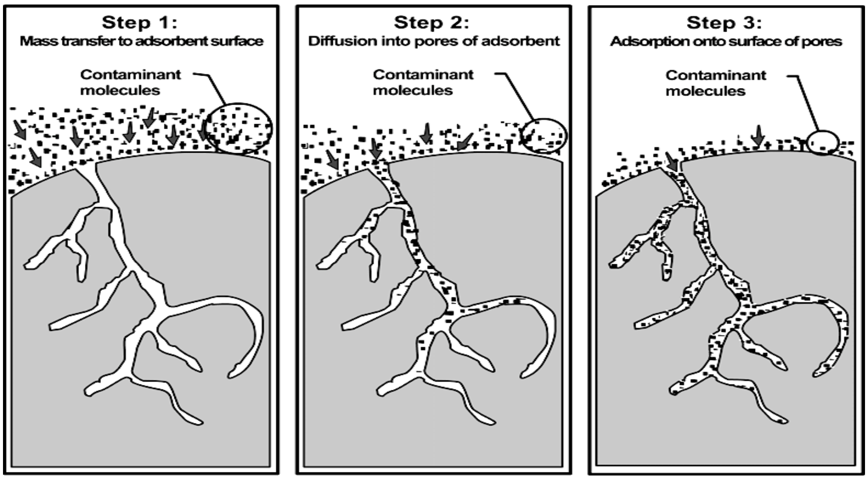


Figure 5.1.2: Illustrates the mass transfer, diffusion and adsorption processes. (APTI 2010).

Steps one and two occur as a result of the difference in adsorbate concentration in the bulk stream and that near the adsorbent surface. Step three is the actual attachment of the adsorbate to the wall of the adsorbent. Step three occurs faster than steps one and two.

5.1.3 Factors That Affect Adsorption Efficiency

5.1.3.1 Temperature

Increasing the temperature generally decreases the performance of an adsorption system. When the temperature is increased the vapour pressure of the adsorbate molecules and the energy level of the adsorbed molecules are increased. As a result, a proportion of the adsorbed molecules can posses an amount of energy enough to overcome the weak Van der Waals' forces attaching them to the surface of the adsorbent and will cause these molecules to move back to the gaseous phase. Adsorbate molecules in the gaseous phase will stay in the gaseous phase as they posses energy (vapour pressure) larger than the energy of the weak Van der Waals' forces working to attach them to the adsorbent surface. Adsorption is generally exothermic with heat release both for physical sorption and chemisorption. Increasing the temperature increases the rate at which molecules reach the surface, and therefore the cumulative energy released as molecules are adsorbed by the adsorbent. This increases the temperature of the adsorbent thereby reducing its adsorption capacity.

5.1.3.2 Solubility

Adsorption decreases with increasing solubility of adsorbate in the bulk. According to the Lindelius rule, which explains that binding at the solid (adsorbent) - solute (adsorbate) interphase competes with solute-solvent attraction. More to that, the solubility of a substance is affected by other variables. As the molecular weight of compounds increases, their solubility decreases. This implies that compounds with larger molecular weight are less soluble than those with lower molecular weights. Ionization also affects solubility as solubility decreases when compounds are uncharged. The polarity of a compound affects its solubility, and the solubility of compounds increases with increase in polarity.

5.1.3.3 pH

The pH of the medium affects both the surface charge of the adsorbent and that of the adsorbate. For organic materials adsorption increases with a decrease in pH.

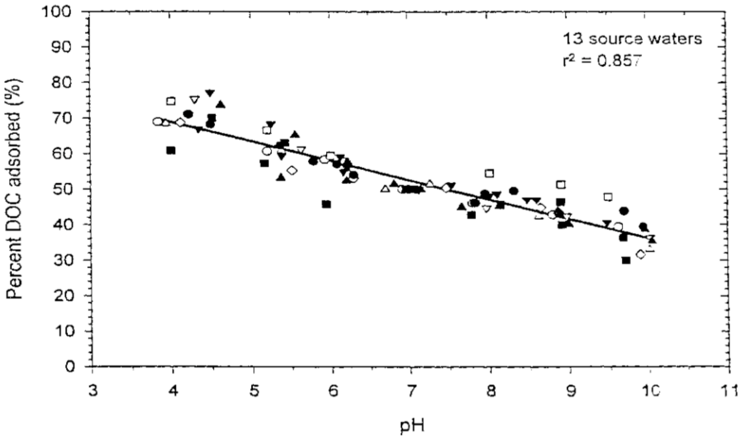


Figure 5.1.3.3: Impact of pH on percent DOC adsorbed for several waters (Snoeyink & Summers, 1999).

5.1.3 Humidity.

Increased humidity simply implies increase in the amount of water molecules in a system. When this happens, there will be the competition for adsorption sites between the adsorbate and the excess water molecules resulting in a drop in adsorption efficiency.

5.1.3.5 Presence Of Other Solutes.

The presence of other solutes especially organic compounds with high boiling points, particulate matter and other dissolved solutes can reduce adsorption efficiency. The presence of other solutes will result in a competition for adsorptions sites and this will mean reduced adsorption of the target compound (adsorbate), while particulate matter will either block pores or will be attached to adsorbent surface reducing the adsorption sites. When adsorption sites are covered by inert matter this is referred to as blinding or deactivation. To avoid blinding or deactivation, many industrial adsorption systems have a built in screening mechanism to take out particulate matter from the gas stream before it reaches the adsorbent.

5.1.3.6 Pressure

Any increase in pressure within the system increases adsorption as the partial pressure of the adsorbate is increased. This is true until a point where the internal energy of the molecules is greater than the energy exerted by the weak Van der Waals' forces. In this condition the adsorbate molecules are packed more tightly therefore increasing their chances of hitting available adsorption sites thereby increasing rate of adsorption.

5.1.3.7 Gas Velocity

The velocity at which an adsorbate molecule passes through the adsorbent bed determines the contact or residence time between the adsorbate and the adsorbent. When the velocity is low the contact time is high and so is the probability of a molecule reaching/contacting an available site for adsorption is increased.

5.1.4 Adsorption Types

There are four kinds of adsorption,

I. Exchange.
II. Physical.
III. Chemical.
IV. Specific

The adsorption type i.e. the nature of interaction between the adsorbate and the adsorbent is to a large extent determined by the characteristics of the intra-particle surface. This is logical as a greater portion of available adsorption sites are found in the intra-particle surface area. The adsorption capacity of an adsorbent depends largely on the total surface area available for adsorption and the nature of distribution of this surface area with respect to pore sizes. The larger the amount of surface area available assigned to micro pores the greater the adsorption capacity of the adsorbent. The term micropores here must be further examined. When the micropores are very small i.e. less than 10 Å (Å = Angstrom), the adsorption capacity of the adsorbent is reduced. It is very important that the micro pores be greater than 10 Å (for liquid phase adsorbates) for adsorption capacity to be enhanced. Therefore, it is necessary that the pore sizes be larger than the adsorbate molecules.

5.1.4.1 Exchange Adsorption

This type of adsorption is also referred to as ion exchange. Here, charged ionic species attach themselves electrostatically to sites of opposite charge on the adsorbent surface. Because, the force of attachment of ions here is proportional to the electronic charge of adsorbate species, species with larger electronic charges and therefore possessing a larger affinity for the same reaction site will displace species already occupying reaction sites but have lower electrostatic charges.

5.1.4.2 Physical Adsorption

In this type of adsorption, which is also referred to as Van der Waals' adsorption, the adsorbate molecules are attached to the adsorbent surfaces by intermolecular cohesion forces. The Van der Waals force involved in physical adsorption has two principal components, the London dispersion forces and the classical electrostatic forces. These Van der Waals's forces are electrostatic in nature resulting from the polarity of the gas molecules and the adsorbent surfaces. In physical sorption the molecules are not fixed to any specific site and therefore the adsorbate is relatively free to move on the surface. The nature of these electrostatic forces sometimes results in the stacking of adsorbate layers over one another.

The electrostatic effect causing the Van der Waals' forces of attraction depends on the polarity of both the gas molecules and the adsorbent surfaces i.e. the molecules of the solid surface. Irrespective of which state a molecule exists, it is either polar or nonpolar depending on its chemical structure. Polar molecules are molecules that have a separation of their positive and negative charges within them. They are referred to as permanently dipole e.g. water. Non-polar molecules have their positive and negative charges in one center and therefore have no permanent dipole. Most organic molecules are nonpolar. How the dipolar or nonpolar molecules interact with each other generates the Van der Waals' forces. Polar molecules are held together by the orientation effect. Because the positive charges of one molecule are separated from the negative charges, one end of the molecule is positively charged and the other end is negatively charged. Once two such molecules come close to one another the positive end of one molecule is attracted to the negative end of the other molecule. Therefore a charge on a molecule is attracted to the opposite charge on the adsorbent surface. This is used in the extraction of water vapour (polar) from the exhaust of car engines using polarized silica gels. Adsorption of a nonpolar molecule on to a nonpolar adsorbent surface is controlled by the dispersion effect. This is due to the fact that, nonpolar molecules do generate polarity by the distribution of their electrons around their nucleus but only that these are fluctuating and oscillating in character. Therefore, polarity is not permanent in nonpolar molecules. When two nonpolar molecules come close to each other, their total energy becomes reduced and they turn to distribute their charges in phase with each other. It is this ability for nonpolar substances to distribute their charges in an ordered manner that is referred to as the dispersion effect. An example of a nonpolar molecular attraction is seen in the adsorption of organic vapours on activated carbon. The third effect is called the induction effect. This is the scenario that occurs when a polar and a nonpolar substance come close to each other. The polar molecule induces polarity on the nonpolar substance. The energy for attraction here is defined by the energy of the induced polarity. Fig 5.1.4.2 is a demonstration of orientation, dispersion and induction effects.

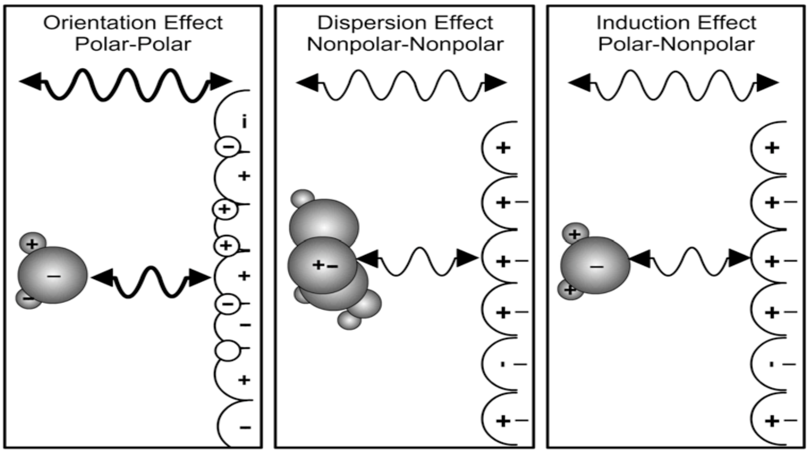


Figure 5.1.4.2: Physical forces causing adsorption. (APTI 2010)

The inductive effect is much smaller than the orientation and dispersion effects; therefore adsorption systems are designed to extract polar substances using polar adsorbents. In this way the forces of attraction between those adsorbent surface and the target molecules is stronger than between same molecules in the gas phases.

5.1.4.3 Chemical Adsorption

This is also referred to as chemisorption and it occurs due to chemical interactions between the adsorbate and the adsorbent. The adsorbate is held to the surface of the adsorbent by chemical bonds, which are stronger than electrostatic bonds of the Van der Waals forces in physical adsorption. There is also a possibility of attachment of adsorbate species to functional groups on the adsorbent surface not resulting in a transformation of the adsorbate. The adsorbate is fixed to a specific site and is not free to move. Such adsorbents can be constructed from either chemically active materials or from inert materials in which case the inert materials function as carriers of chemically active materials. An example of where the adsorbent is active is the case where an adsorbent is constructed from iron chips to extract hydrogen sulphide gas from gas streams.

Table 5.1.4.3: Characteristics of chemisorptions and physical sorption (APTI 2010).

Summary of the characteristics of chemisorptions and physical sorption	
Chemisorption	Physical sorption
Releases high heat, 10 cal/gm mole	Releases low heat, 0.1 cal/gm mole
Forms a chemical compound	Gas retained by dipolar interaction
Desorption is difficult	Desorption easy
Adsorbate recovery impossible	Adsorbate recovery easy

The hydrogen sulphide gas reacts with the iron and is taken out of the gas stream. In another case, an adsorbent can be constructed from activated carbon (which is inert) but it will be impregnated with a chemically active substance e.g. potassium iodide in this case to extract mercury from a gas stream. Table 5.1.4.3 is a summary of physical and chemical sorptions characteristics.

5.1.4.4 Specific Adsorption

The bond strength in specific adsorption lies between those of physical and those of chemisorption. Specific adsorption is when a particular adsorbate is singled out for adsorption. The affinity of a particular adsorbate for a particular reaction site on an adsorbent surface is determined by its dispersion energy, the electrostatic forces affecting it, forces acting on it due to chemisorption and its interaction with any surface functional groups present.

Conclusion;

The degree to which a substance can be adsorbed depends on its solvophobicity (dislike for the solvent phase) or lyophobocity (insolubility in the solvent phase). The greater the solvophobicity of an adsorbate in a solvent the easier it is for it to be adsorbed. As the solvophobicity of an adsorbate in a solvent increases so thus the bond strength between the adsorbate and the solvent reduce, implying that only a comparatively small amount of energy is needed to separate the adsorbate from the solvent. The greater the solubility of a compound in a solvent the harder it is to adsorb such a compound (J. J. Weber, 1972).

Irrespective of whether adsorption is physical or chemical, it is often exothermic. This is so because, upon adsorption on to the surface of the adsorbent the fast moving gas (adsorbate) molecules give up their kinetic energy in the form of heat. In the case of physical sorption the amount of energy given up is proportional to the heat of condensation whereas for chemisorption it is a balance of the energy required for bonding and that of condensation.

Reversibility of adsorption depends on whether it is physical adsorption or chemisorption. Physical adsorption is easily reversible while chemisorption is often not reversible. Increasing the temperature in the system or decreasing the pressure within the absorbent layers in the system are often enough to reverse physical adsorption. Chemisorption stops when all active sites are consumed but physical adsorption continues resulting in multiple layers of adsorbed molecules. Once adsorption is completed the adsorbent (mineral, activated carbon or resin) is taken out of the solution by screening, gravity separation or flotation for concentration of the adsorbed species. After concentration, the cyanide is reactivated and recycled for reuse.

5.1.5 Adsorption Of Cyanides

The adsorption of free cyanides (Deveci et al. 2006; Naeem & Zafar, 2009; Weisse & Venkat, 1988) at near neutral pH values, and complexed cyanides (Ketcha et al.2010) on activated carbon, on metal-impregnated activated carbon and on other naturally occurring materials such as zeolites, clays, alumina etc (Naeem & Zafar 2009) have been extensively studied. Activated carbon is a general term for a large group of amorphous carbon-based materials characteristically highly porous and having a large surface area. Molecular size pores and capillaries within the carbon granules resulting from defined pyrolytic and oxidation treatment processes of selected materials account for those unique characteristics. The level of success seen in the adsorption of cyano-metal complexes has not been matched by adsorption of free cyanides (Deveci, et al. 2006). Little success has been recorded for the adsorption of free cyanide giving a probable explanation for why there has not been much interest from major stakeholders of the cyanide branch for this technology. Adsorption on activated carbon is controlled by the following, ion exchange, solvation, chelation and coulombic interactions (Young & Jordan 1995).

Cyanide loss in the presence of activated carbon is not always due to adsorption. Gray 1999 reported that activated carbon catalyses the oxidation of cyanide to cyanate and also acts as a catalyst for the decomposition of the cyanate formed.

Both the physical adsorption of cyanides on activated carbon (Milenković, Rajaković & Stoiljković 2004)) and the chemisorption of cyanides on impregnated activated carbon have been successful. Reactivity of the adsorbent surface is due to the oxygenation of functional groups present on these surfaces. The active surface properties of the adsorbent are attributed to the functional groups and the internal surface areas. The activated carbon is impregnated with salts that form stable complexes with cyanide ions. Salts of many elements form stable complexes with cyanide ions but preference is given to metals which form weak acid dissociable cyanide-metal complexes e.g. copper, nickel, silver e.t.c, as oppose to ferric salts which form an even stronger complex. Usage of ferric salts for impregnation of activated must be well thought through. Iron complexes with cyanide are very unstable when exposed to UV light. In the presence of UV light iron complexes undergo photolysis releasing poisonous $HCN_{(gas)}$. Therefore, only in the absence of UV light should ferric salts of cyanide be employed for the adsorption of cyanide (Milenković et al. 2004). '*Mass of bonded CN per unit mass of AC during the testing time (mCN) is a complex function of specific surface AC (S), impregnant mass per unit mass of AC – impregnation index (I), temperature (t), granulating composition of AC (G), nature of impregnant, initial concentration of CN in to water (C0), mass of AC per unit volume of cyanide solution (M), medium pH, in other words mCN=f(S,I,t,g,C0,M,pH)*' (Milenković et al. 2004). The adsorption of cyanide-complexes onto activated carbon has been successfully applied in the gold mining industry in the carbon-in-bulb (CIP) process (Fleming & Nicole 1984). In this process, the cyanide-gold complex is selectively extracted out of a solution mix from the leachate of the cyanidation process. As reported by Fleming & Nicole 1984, a major importance of the adsorption process is that, it locks up cyanide in the plant. Compared to the ion exchange process, adsorption of cyanides onto activated carbon is a slow process.

Table 5.1.5a: Effect of cyanide concentration and pH value on the loading of gold and copper. (Fleming & Nicole 1984).

Copper in solution	NaCN added ppm	pH value	Gold on carbon	Coper on carbon
0	0	10,5	44000	0
0	0	5,0	67400	0
0	300	10,5	34500	0
0	300	5,5	60000	0
80	300	10,5	33460	600
80	300	5,0	19800	50900

Using the adsorption of gold-cyanide complex as an example for the use of the adsorption process as a method for the treatment or pretreatment of cyanide waste, it was observed that the presence of other metal cyanide complexes in solution had an affect on the adsorption of gold-cyanide complex. Characteristic of the cyanidation leachate is the presence of metal complexes of copper, nickel, cobalt, iron etc.

Copper complexes and to a lesser extern nickel complexes have been found to have an effect on the adsorption of the gold-complex. In some instances the adsorption of the copper-squeezes gold cyanide off the carbon. Copper has the greatest effect, but this depends on two parameters, the pH of the medium and the concentration of free cyanide. Using a solution containing 9.2ppm gold, the pH, the concentrations of copper and free cyanide were varied and the adsorption of gold-cyanide complex was measured, table 5.1.5a (Fleming & Nicole, 1984).

Decreasing the pH of the solution and the concentration of free cyanide favors the adsorption of gold. At a pH of 5.0, the adsorption of copper increases at the expense of gold-cyanide adsorption (Fleming & Nicole 1984).

Naeem & Zafar (2009) studied the adsorption of cyanide on alumina with respect to the influence of temperature, agitation time, pH and initial cyanide concentration at 313K. The adsorption of cyanide between a time interval of 5minutes and 24hours was as shown in fig 5.1.5. From both curves it was concluded that the absence of any meaningful adsorption rate changes was probably due to both surface precipitation and ion exchange occurring simultaneously with ion exchange masking any fluctuations in adsorption rates over time.

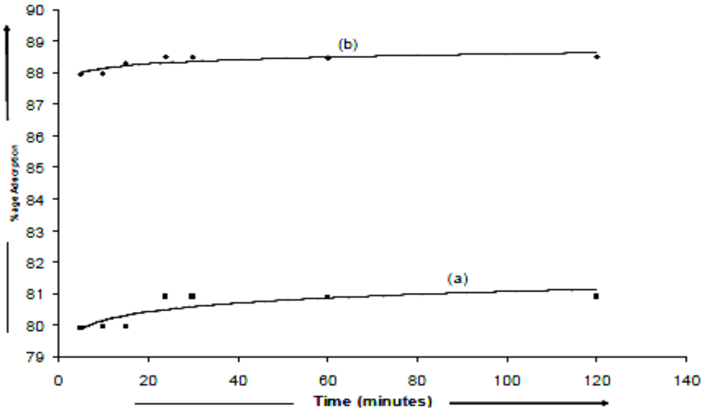


Figure 5.1.5: Effect of shaking time on %age Adsorption at (a) 10ppm, (b) 40ppm for CN- adsorption on Alumina. (Naeem & Zafar 2009). (Y axis= % adsorption and X axis = time (minutes))

It was also concluded that, the initial cyanide concentration did not play a great role and therefore not a consequential factor in cyanide adsorption rate.

From table 5.1.5b, it can be seen that at a near neutral pH of 7.34, the adsorption was maximum. It showed the same pattern between pH values of 7.0 and 8.0. The rate of adsorption increased with increasing temperature. When the pH is increased two things occur, first the surface of the alumina becomes increasingly positively charged and secondly a reduction in pH implies increased hydrogen ion concentration which compete with metal ions for binding sites and some metal ions are desorbed by hydrogen ions.

Table 5.1.5b: Effect of pH on Adsorption of CN^- on Alumina at 313K (Naeem & Zafar 2009).

pH	Amount of CN^- taken (ppm)	Amount of CN^- at equilibrium (ppm)	Amount of CN^- adsorbed (ppm)	Adsorption (%)
3.02	10.00	2.46	7.54	75.40
6.25	10.00	1.60	8.40	84.00
7.34	10.00	1.15	8.85	88.50
9.05	10.00	2.02	7.98	79.80
12.08	10.00	2.07	7.30	73.00

At pH values of 9.0 and above cyanide adsorption decreased probably as a result of the formation of soluble cyanide-metal complexes that are kept dissolved in solution.

5.1.6 Preparation Of Activated Carbon (AC)

Activated carbon can be produced from any solid carbon based materials including peat, wood, nutshells, bone, and e.t.c. (Saad 2007).

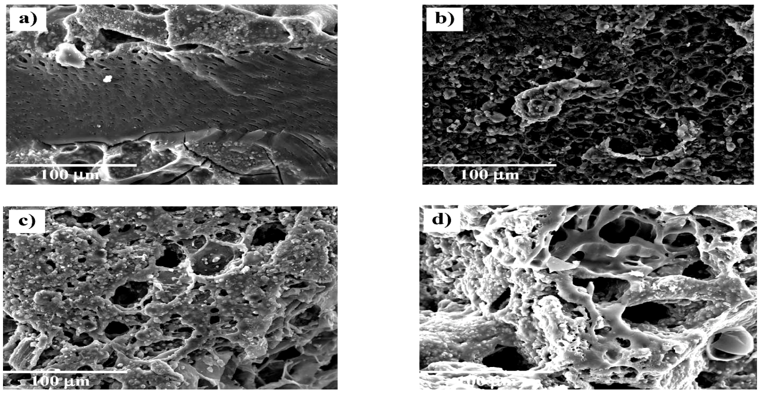


Figure 5.1.6: Scanning electron micrograph of (a) char without activation and char activated by (b) CO2, (c) H3PO4, and (d) KOH (Viboon, et al. 2008).

To be activated, these materials are thermally treated with steam at temperatures greater than 900°C or with acid at temperatures over 450°C. Activation creates pores of various size ranges in the carbon, increasing the surface area available for adsorption to greater than 1500m^2/g. There is sufficient literature on the production of activated carbon (Saad, 2007). The physical and chemical characteristics of activated carbon are not the same for all.

These properties are amongst others a function of the base material from which they are produced, the conditions under which they are prepared and the chemicals that were used for the activation of the carbon after pyrolysis (Fig 5.1.6). As a consequence of their varied properties they can be employed in different processes.

Activated carbon can be used as fine size powder, coarse grains, pellets, or extrudates. Activated carbon can take the form of fibres, flexible or hard solids, mesocarbon microbeads, forms and aerosol (Saad 2007). Rates of adsorption vary for different forms of activated carbon mainly based on the surface functional groups present and the size of the carbon grains. Adsorption is much faster on granulated or fine grain AC because diffusion problems due to difficulties in accessibility to micro and mesopores are not encountered here (Radovic, 1985). This is not the case for large size grains as the greater portion of the active sites are relatively further away from the external sufaces thereby imposing a longer distance for diffusion before reaching those active sites.

5.1.6.1 Surface Chemistry Of Activated Carbon (AC)

The surface chemistry of ACs is controlled by the functional groups present in the carbonaceous adsorbent. These functional groups are important for the adsorption process as they influence reactivity of the AC. The functional groups on the surface of ACs can be modified by any of the following processes oxidation, amination, heat treatment and impregnation of inorganic compounds.

5.2 Ion Exchange

This is the exchange of ions between an ion exchange material and a process solution flowing through the ion exchange material (GLM 2010). *'Ion exchange is a process in which mobile ions from an external solution are exchanged for ions that are electrostatically bound to the functional groups contained within a solid matrix'* (IAEA 2002). The material is constructed such that it can selectively absorb either cations or anions from a solution in contact with it and in exchange, this material releases 'counter ions' from its ion exchange sites (Osmonics 1997).

As the solution flows through the ion exchange material, ions in the solution are been exchanged with ions of the ion exchange material. This process goes on until all the exchange sites on the ion exchanger are exhausted, at which point the ion exchanger is removed for regeneration with appropriate chemicals. These ion exchange materials are called resins.

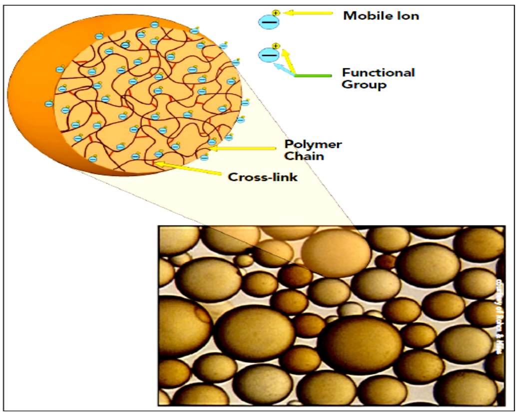


Figure 5.2: Ion exchange Resin Bead Structure (GLM 2010).

The term resin is a generic term for a class of highly porous beads that can be synthetic, co-polymers or natural substances (organic) matrixes impregnated with active sites and can perform ion exchange (Fig 5.2).

These active groups have the ability of exchanging some of their ions for other ions in solutions flowing through pores within the beads. The essential issue is that the polarities of the exchanged ions should be of the same type. This implies that cations are exchanged for cations and anions are exchanged for anions. There is no physical alteration to the ion exchange material during the ion exchange process. The active groups are composed of insoluble acids or bases containing salts that are also insoluble. Their insolubility enables them to either exchange positively charged ions in the case of cation exchangers or negatively charged ions in the case of anion exchangers. There are many naturally occurring substances (proteins, cellulose, living cells and soil particles) that possess this ability to exchange ions

This phenomenon of ion exchange between ions in an external solution and the loosely bound ions in the solid phase was first observed and reported by two British agricultural chemists Harry Thompson and John Way in 1850. They observed that when they ran a fertilizer solution containing ammonia through a soil column containing calcium, the ammonia was retained in the soil while calcium ions in the soil were ejected with the effluent. This and other observations that they made are the fundamentals on which ion exchange is built. The other observations were (DeSilva, 1999):

a. That the exchange ions involved ions of similar valence or ionic charge i.e. their valency.

b. That some ions were more readily exchanged than others.
c. The presence of aluminum silicates in the soil gave it ion exchange characteristics.
d. The ion exchange mechanism was different from the adsorption mechanism.

These observations became significant and prepared for commercialization when a German chemist, Eichorn, proved that the ion exchange mechanism was a reversible process. Commercialization went into effect with the use of the process for water softening by trading Mg^{2+} and Ca^{2+} ions for Na^{+} ions by Gans in 1905 (GLM 2010). Gans used synthetic alumino silicate cation exchangers that he named zeolite.

Resins are effective for water softening and for the removal of dissolved ions at low concentrations (GLM 2010).

5.2.1 Construction Of Ion Exchange Resins

Ion exchangers are produced in a two-step process. First, there is the production of a hard porous bead in a suspension polymerization process using styrene and divinylbenzene (DVB). A mixture of styrene and divinylbenzene is placed in a reaction chamber equipped with an agitator. Added to this mixture in the reaction chamber is an equal amount of water. To prevent the agglomeration of the reactants a surfactant (these are substances which influence the properties of surfaces and interfaces e.g. by lowering the surface tension, the interfacial tension between two liquids, or that between a liquid and a solid) is added. The presence of the surfactant ensures that the reactants remain dispersed. As the agitator begins mixing the reactants, there is the formation of large globules. To reduce the size of the globules formed, the rate of agitation is increased until the desired size of globules to be used as ion exchange beads is obtained. The range is often between size 16 US mesh = 1.18mm and size 50 US mesh = 0.31mm (DeSilva, 1999), or 0.5 to 1.0mm in diameter (NZIC 2010). Once the desired bead size has been obtained polymerization is initiated by addition of benzoyl peroxide causing the styrene/divinylbezene molecules to coagulate forming small beads. The physical hardness/stability of the beads is thanks to the cross-linkages formed by DVB. It is also thanks to these linkages that the beads are insoluble. Styrene forms the chains while divinylbenzene forms the crosslinks.

The second step involves activation of those beads. Activation imparts onto the beads the ability to exchange ions by attaching active functional groups to them. These active groups have electrical charges that can either be negative or positive.

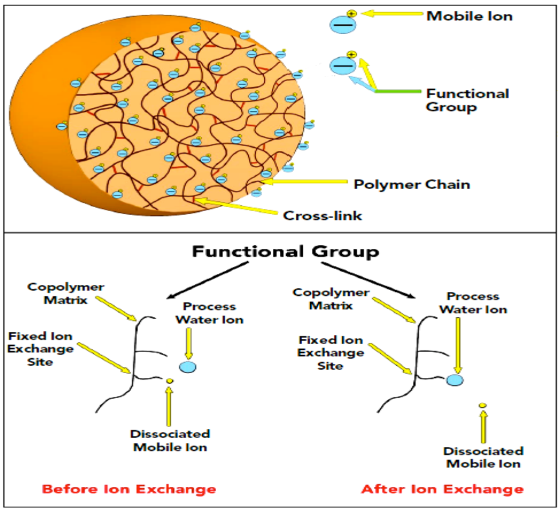


Figure 5.2.1: Ion Exchange Before and After (GLM 2010).

The charges of the active groups are countered/neutralized by loosely bound ions with opposite electrostatic charges of the same magnitude except for weak base resins, which do not have the mobile ion component of the active group. The loosely bonded ions on the active sites are the ions that are exchanged in ion exchange processes. Positively charged sodium ions are commonly used to coat cation exchange resins. Negatively charged chloride or hydroxide ions are commonly used to coat anion exchange resins. Mixed bed resins combine both positive and negative ions. Once in solution, ions dissociate from the functional groups and become mobile and can be exchanged for other ions in the solution (Fig 5.2.1). When not in solution the cations colored yellow in fig 5.2.1 remain attached to the functional groups. In solution these ions dissociate themselves from the functional groups and get into solution making the functional groups temporally negatively charged and open to attraction and bonding with any loose cations in solution.

5.2.2 How Resins Work

If a resin has more affinity for ion B than for ion A which is attached to its functional group, and ion B is dissolved in a solution flowing through it, an exchange reaction occurs which can be represented as thus;

$$AR + B^{n\pm} \leftrightarrow BR + A^{n\pm}$$

Where,

AR = Resin containing A ions before ion exchange.

B = B ions dissolved in solution.

BR = Resin containing B ions after ion exchange.

n± = number of ions with charge positive (+) or negative (-).

Initially there will be a tendency for the reaction to move to the right but as the resin approaches its exchange capacity level i.e. exhaustion, it will exist more in the form BR. Looking at the equation above, regeneration is achieved by shifting the reaction to the left. A mass transfer equation expressing the reaction can be represented as follows (eqn 5.2.2a).

$$\frac{[BR][A]}{[AR][B]} = \sigma \text{ -------------Eqn 5.2.2a}$$

Where σ, is the equilibrium quotient specific for that pair of ions and for that type of resin. From eqn 5.2.2a it can be deduced that increasing the concentration of the A ions will regenerate AR as B ions are eluded into solution and AR can be reused. Ions are not selected for exchange solely on their valency but also on their ability to reach exchange sites within the resin. It has been observed that upon hydration a number of ions swell, thereby increasing in ionic radius and reducing their chances of migrating or diffusing to ion exchange sites within the resin (GLM 2010). This factor also influences the contact time between the active group and the ion in solution. The faster an ion can reached ion exchange sites the longer the contact time it will have with the functional group thereby increasing the chances of it been exchanged.

The movement of ions between resin and solution during ion exchange can be summarized as follows,

i. The ions in solution to be exchanged diffuse from the solution to the external surface of the resin.

ii. Since 99.9% of ion exchange occurs within the internal pores of the resin, for any significant ion exchange to occur, those ions must diffuse further inwards to the exchange sites.

iii. Once these ions get to the ion exchange sites, ion exchange occurs and the mobile components of these exchange sites are released into the bulk solution.

iv. The released ions begin their outward diffusion to the external surface of the resin.

v. Once on the surface of the resins the ions then migrate to the bulk solution.

5.2.3 Types Of Resins

Resins are classified based on the strength (strong or weak) and charge (positive or negative) of their functional groups as these two factors determine which ions a resin can take out of a solution.

The beads of strong acid cation (SAC) resins, strong base anion (SBA) resins and weak acid cation (WAC) resins have two components, a fix or a mobile ion exchange site and a mobile ion (Fig 5.2.1 and fig 5.2.3a),

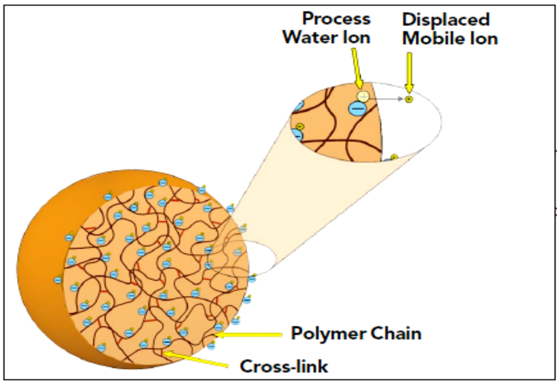


Figure 5.2.3a: Ion Exchange at Functional Group (GLM 2010).

The beads of weak base anion resins have only a single part referred to as a free base (GLM 2010) (Fig 5.2.3b). Functional groups are described as weak or strong based on their readiness to dissociate in solution releasing free ions open for exchange. Whereas the functional groups of strong resins completely dissociate in solution releasing ions for exchange, the functional groups of weak resins either may not dissociate at all (as for WBA) or may only partially dissociate (as with WAC) therefore releasing only a small amount of ions for exchange.

The form of a resin is defined by the mobile ion on the functional group. In the case when there is no functional group as with WBA resins they are referred to as free base resins. When the functional group contains sodium, hydrogen, hydroxide, chloride it is referred to as sodium base, hydrogen base, hydroxide base, and chloride base respectively.

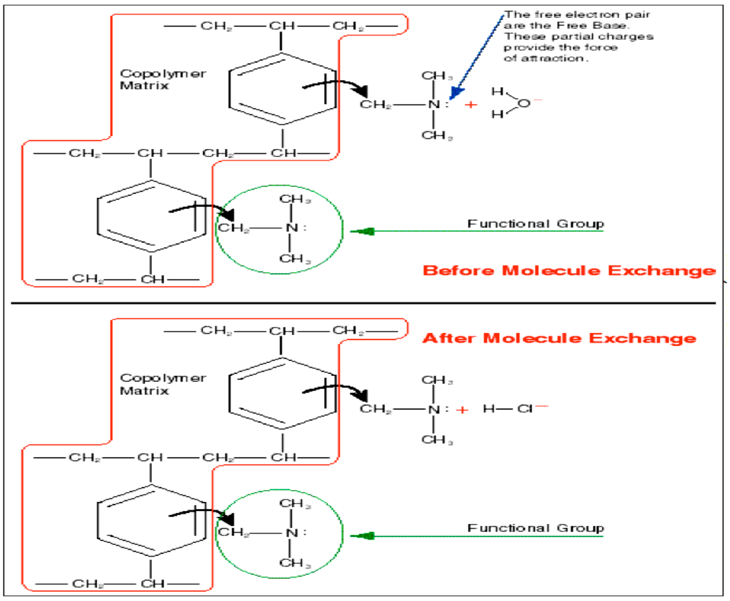


Figure 5.2.3b: WBA Free Base Functional Group Before and After Molecule Exchange. (GLM 2010)

They are manufactured in this form and it is left to the end user to attach the appropriate mobile ion base on the purpose for which it to be used. Table 5.2.3 shows examples of different resin forms.

Table 5.2.3: Resin forms (GLM 2010)

Resin Type	Mobile Ion	Form
SAC	H^+	Hydrogen
SAC	Na^+	Sodium
WAC	H^+	Hydrogen
SBA	OH	Hydroxide
SBA	Cl	Chloride
WBA	None	Free Base

5.2.3.1 Strong Acid Cations (SAC) Resins

These are resulting from the treatment of polystyrene/DVB beads with concentrated sulphuric (H_2SO_4) acid. This treatment method referred to as sulfonation, can either use concentrated sulphuric acid or some other acid as chlorosulphonic acid which is even more efficient (Ling et al. 2001), or silica sulfuric acid ($SiOSO_3H$) (Sulkowski, et al. 2009) which introduces active sulfonic acid (anionic group) groups which are permanently negatively charged (Elabd & Napadensky 2004) and having a high affinity for cations. The trick is to attach a cation for which the active group has a lesser affinity for than the affinity it has for the ionic species intended to be taken out of solution.

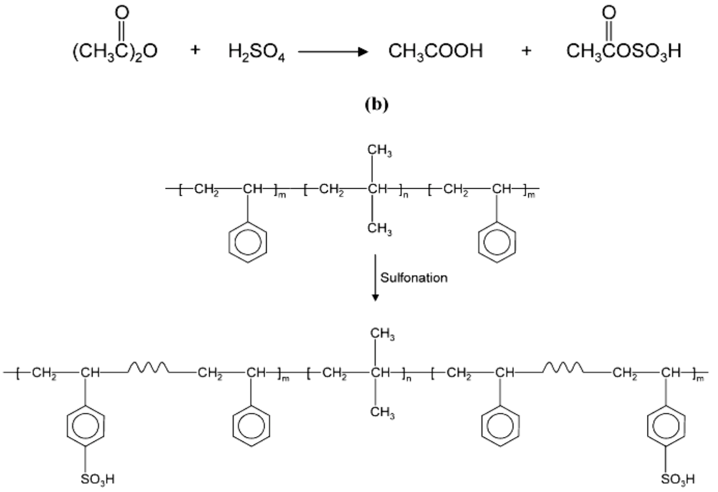


Figure 5.2.3.1: Sulfonation reactions: (a) preparation of sulfonating agent (acetyl sulfate): acetic anhydride reacts with sulfuric acid to form acetyl sulfate and acetic acid, (b) sulfonation reaction: Poly styrene-isobutylene-styrene (SIBS) reacts with acetyl sulfate to form Sulfonated Poly styrene-isobutylene-styrene (S-SIBS), where the styrene block is randomly sulfonated (sulfonic acid substituted in the para-position of the aromatic rings).(Elabd & Napadensky 2004)

When a solution carrying an ionic species for which the active group has a greater affinity for is passed through the resin, those ions are taken out of the solution and attached to the sites where the ions for which the active groups have a lesser affinity for have been given off and are now existing in solution attached to sites from where the preferred ions have been taken out from. These resins convert neutral salts into their corresponding acids.

It is very important to ensure during activation that the active groups are spread allover the beads, in the interior as well as on the surfaces. The degree of sulfonation, which determines their ion-exchage capacity, is governed by a number of parameters including physical (Temperature, time of sulfonation) and chemical (percentage of divinylbenzene as this controls the degree of cross linking and consequently the pore sizes) factors during the polymerization process (Toro et al. 2009). Transportation of the sulfonating agents into the interior is controlled by a number of different diffusion mechanisms and the internal pore sizes (Toro et al. 2009). The sulfonic acid species (SO_3H) is the active group. The hydrogen of the sulfonic acid can be replaced with sodium by passing a solution of concentrated sodium chloride (NaCl). Below is a list of the order of increasing affinity for some common cations (NZIC 2010).

Affinity for cations

$Hg^{2+} < Li^+ < H^+ < Na^+ < K^+ \approx NH4^+ < Cd^{2+} < Cs^+ < Ag^+ < Mn^{2+} < Mg^{2+}$ $Hg^{2+} < Li^+ < H^+ < Na^+ < K^+ \approx NH4^+ < Cd^{2+} < Cs^+ < Ag^+ < Mn^{2+} < Mg^{2+}$

Properly spreading the exchange sites is important as almost 99% of ion exchange occurs within the pores in the beads. Through sulfonation, the hardness/strength of the beads is increased, as well as their hydrophilicity and proton conductivity (Elabd & Napadensky 2004) making the beads more suitable for ion exchange. Phase segregation occurs at a nano scale in ion containing polymers, such as in polystyrene after sulfonation. The electrostatic interaction between ion pairs or groups result in ion rich and ion poor zones within the polymer. Increasing the sulfonic acid content in the polymer converts it from an insulator to a conductor. This occurs because as the sulfonic acid concentration increases, isolated pockets of active groups become linked within the polymer.

Strong acid cation resins are very robust. They can operate effectively over a wide pH range. Thy can handle almost all salts and they need substantial amount of regenerants. They are effective for softening applications, as the first unit in a two-bed demineralizer or as the cation component of a mixed bed system (DeSilva 1999).

5.2.3.2 Weak Acid Cations (WAC) Resin

Unlike strong acid cation resins that have sulfonic acid as their active ingredient, weak acid cation resins have carboxylic groups as their active ingredients. These resins neutralize strong bases. These resins are highly efficient and require a much lesser amount of regenerant. They require a 100% volume of the stoichiometric amount of regenerant as compared to 200 – 300% of regenerant needed by strong acid cation resins (DeSilva 1999). Their ion exchange capacity reduces as the effluent flow rate increases, as the system temperature reduces, and as the ratio of hardness to alkalinity reduces below 1.0. When used in combination with strong acid cation resins, they are first in contact with the solution so that they can treat cations associated with alkalinity and the remaining cations are handled by the strong acid cation resin. The effluent acid from strong acid cation resin processes can be applied in regenerating weak acid cation resins making them cheap to manage.

5.2.3.3 Strong Base Anion (SBA) Resins

Two functional groups are involved in the activation of poly styrene-divinylbenzene polymers to strong base anion resins. The first step is chloromethylation and then amination. Differentiation of resins begins during the production of the beads. The mixture of styrene and divinylebenzene used for the production of beads to be activated as strong base anion resins has a mush lesser amount of divinylbemzene. As a consequence the beads are more porous than beads used for the production of cation exchangers. Strong base anion resins neutralize their salts into their corresponding bases.

In the first level of activation, there is the attachment of a chloromethyl group to each benzene ring of the bead structure. The methyllated beads undergo amination where they are reacted with amines. The amines are the anions to be exchanged. A most often-used amine group is trimethylamine (TMA). Based on the type of amine used during activation two types of strong base anion resins can be distinguished. The first type has three methyl groups while the second group has only two methyl groups as one is replaced with an ethanol group.

Type ones is good for the removal of all anions in waters. Irrespective of whether they contain the hydroxide or chloride groups. These swell enormously than the second type and they are also hard to regenerate. Type ones are more temperature resistant and should be used when the alkalinity is very high or when dealing with silica waters i.e. water containing high levels of silica.

The second type of strong base anion resins are good for the removal of all anions from water but are less effective for the removal of carbon dioxide and silica when the weak acid ions constitute more than 30% of total anions. Generally, these are best for waters with free mineral acid chlorides and sulphates. Below is a list of common anions that can be attached as the mobile ions to the functional group in order of increasing affinity.

Affinity for anions

$OH^{-} \approx F^{-} < HCO^{3-} < Cl^{-} < Br^{-} < NO^{3-} < HSO^{4-} < PO4^{3-} < CrO4^{2-} < SO4^{2-}$

This implies a fluoride ion in solution will be exchanged for a hydroxide ion on the functional group, as well as a bromide ion in solution will be exchanged for a chloride attached to the functional and so on.

5.2.3.4 Weak Base Anion (WBA) Resins

The functional group here is polyamine. These act as acid adsorbers removing strong acids in effluent streams. These resins do not have the mobile part of the functional group and have only one part called a free base (Fig 5.2.3a). Regeneration of these resins requires stoichiometric amounts of regenerant bases such as sodium hydroxide to restore their active sites to free base form. Regeneration is basically by neutralizing the acids accumulated on the resin. Therefore, simply adjusting or altering the pH achieves regeneration of weak base resins. Weak base anion resins should be used for removing sulphates, chlorides, or in situations where the need to eliminate alkalinity or silica is not required.

5.2.4 Ion Exchange Treatment Of Cyanides

Cyanide complexes dissolved in water forming salt waters. Also, Cyanide complex anions such as $Cu(CN)^{-2}$, $Zn(CN)^{-2}$, $Ni(CN)_4^{-2}$, or free cyanide (CN^{-}) dissociate in water. Often than not the cyanide ion is so tightly bonded to the metal ions that they remain bonded. A strong base resin with a quaternary ammonium functional group having a permanent positive charge can be used to take out these cyanide species from the solution. The ion exchange process responsible for the adsorption of cyanide metal complexes can be represented as follows using zinc cyanide complex as an example.

$\lceil 2(N^+R_3X^-)+ Zn(CN)_4^{-2} \leftrightarrow \lceil (N^+R_3)_2Zn(CN)_4^{-2} + 2X^-$ ------eqn 5.2.4a

Where;

$\lceil$ = Resin matrix

N^+R_3 = Functional group.

X^- = Mobile portion of functional group used for ion exchange often a mono valent anion e.g. hydroxide ion (OH^-).

The use of strong and weak base resin scavengers for cyanide-metal complexes is not a recent practice (EPA, 1981). The extraction of cyanide-cobalt complex (cobalt cyanide) from uranium processing tailings has been studied as far back as 1953 (Preuss, 1953) which also lead to the development of another strong base resin IRA958 by Rohm and Haas for the recovery of iron cyanide complexes (Nesbitt, 1999). It has been observed that while the adsorption or ion exchange processes may be fast, a major problem was the slow kinetics of the desorption process. Emphasis then was shifted to adjusting the resin pore sizes to accommodate the iron cyanide molecule sizes and reinforcing the resin matrix (Nesbitt, 1999)**.** The sheer size of the iron molecule and the strength of its ionic charge needed to be considered. Regeneration of the resin was easy as sodium chloride could be used. The strong electro negativity of the chloride ion is capable of displacing the iron cyanide complex. Anion exchange resins have been used for the extraction of anionic nickel cyanide complex (eqn 5.2.4b).

$2[(Resin^+)(OH^-)] + [Ni(CN)_4^{-2}] \rightarrow (Resin^+)_2[Ni(CN)_4]^{2-} + 2OH^-$ ------ eqn 5.2.4b

5.2.5 Selectivity Of Ions

Knowing that a typical cyanide waste contains a cocktail of cyanide metal complexes, the next issue is how these complexes can be separated using resins. Selectivity for ions depends on the functional group used for the resin production, i.e. whether it is a tri-methyl ammonium group or a tri-ethyl ammonium group that is used. Tri-methyl ammonium functional groups have a greater affinity for multi-valence cyanide complexes e.g. $Fe(CN)_6^{3-}$,$Cu(CN)_4^{3-}$, while the tri-ethyl ammonium functional group has more affinity for mono- and divalent metal cyanides e.g. $Au(CN)_2^{1-}$, $Ni(CN)_4^{2-}$ (Strangfeld, 2000; Nesbitt, 1999). It was also noticed that the rate of ion exchange for free cyanides was heavily dependent on the concentration of the solution. The higher the free cyanide solution concentration the faster the rate of ion exchange. This was not the case for cyanide metal complexes. The rate of ion exchange for cyanide metal complexes did not depend on the concentration of the solution. This means ion exchange or adsorption of cyano-metal complexes can be done even when the concentration of the complexes is very minute (Strangfeld, 2000).

Advantages And Disadvantages Of Ion Exchange

i. Advantages of ion exchange method

1) No formation of new products.
2) Very compact.
3) Easy recovery of metals.
4) More versatile than other methods.

ii. Disadvantage of ion exchange method

1) A major problem with this method has been disposal of the spent solution from the process. Currently there are many methods for treating these spent solutions.

Chapter 6

Physical Methods

6.1 Dilution

Dilution neither separates nor destroys cyanides. In this method toxic cyanide wastes are simply diluted, producing an effluent that has a very minute concentration of cyanides below discharge limits. This cyanide treatment method is very cheap and simple, as it does not involve the application of other chemicals or energy. Unfortunately this method does not reduce the total amount of cyanides released to the environment. These cyanides, once released to the environment are susceptible to natural attenuation processes such as adsorption and precipitation that have the potential of concentrating these toxic cyanide species in surface and ground waters. This method is often used as a standby method to meet discharge standards.

6.2 Electrowinning

Introduction

This is an electrolytic process employed for the recovery of metals from their dissolved state e.g. in rinse waters. Traditionally, this process has been used only for metal recovery from rinse waters. A typical electrolytic unit has three main components, an electrolytic cell, a rectifier and a pump. The electrolytic cell (fig 6.2) is constructed such that, the cathodes and the anodes are arranged in an alternating order and the cell is sometimes equipped with devices such as air spargers and flow dispersers to assist in the circulation of the solution within the cell. When in action, the positive ions (cations) move to the cathode and are plated on it. As the build up of the metals on the cathode increases so does the rate of deposition of new metals on the cathode decreases.

The deposition rate reduces until a point is reached that deposition is negligible and the cathode is removed for the extraction of the metals thereby recycling the cathode. At the anode, other rinse water components are been oxidized.

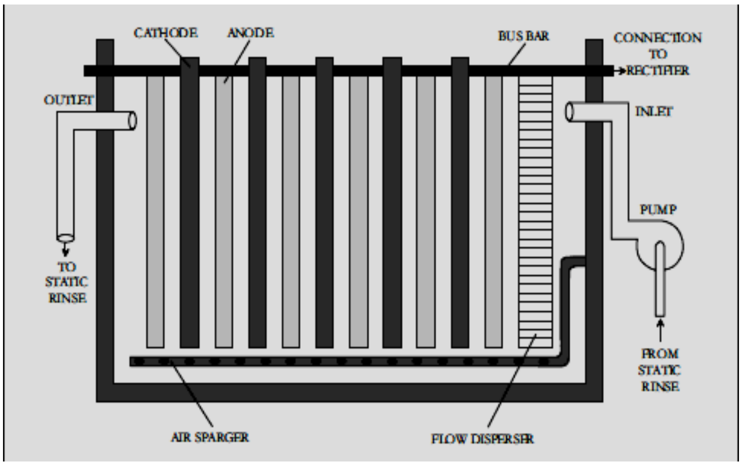


Figure 6.2: Cross-section of electrowinning unit (MPPPPMF, 1997).

6.2.1 Cyanide Treatment By Electrowinning

Electrowinning also known as electrolytic/electrochemical metal recovery is effective in the remediation of WADs and SADs. In the process, cyanide ions in a complex are destroyed at the anode while the freed metals are been collected at the cathode (Saarela & Toivo, 2004). In electrowinning, an electric potential is applied across two electrodes immersed in a cyanide-metal-complex bearing solution (in this case it is the electrolyte). As the electric potential is applied, the metals are stripped-off from their corresponding complexes with cyanides, leaving free cyanide ions which are attracted due to their negative charge to the positively charged electrode (anode). Under appropriate electric potential conditions, the dissolved metal ions (cations) migrate to the negative electrode (cathode) where they are reduced and deposited/plated in metallic form onto the cathode and the negative ions (anions) are oxidized at the positively charged anode (Wang et al. 2006; LightEnvironmental, 2011).

An electric potential is obtained within the cell by application of a direct current through the cathode and the anode. When an electric potential is applied to a solution containing WADs and SADs the metals dissociate from the cyanide complexes following equation (eqn 6.2.1a) but this is not possible for thiocyanates.

$$M(CN)_x^{y-x} + ye^- \rightarrow M^\circ + xCN^- \qquad \text{------ eqn 6.2.1a}$$

Where;

M = metal ion.

Y = Valence of metal ion.

X = number of cyanide ions in the complex

Considering an electrolyte containing silver cyanide $Ag(CN)_3$, there are the following reactions at the anode and at the cathode.

Anodic reactions:

Oxidation of free cyanides at the anode (eqn 6.2.1b).

$$CN^- + 2OH^- \rightarrow CNO^- + H_2O + 2e^- \quad \text{------eqn 6.2.1b}$$

Oxidation of Wads at the anode (eqn 6.2.1c).

$$[Ag(CN)_2]^{2-} + 6OH^- \rightarrow Ag^{2+} + 3CNO^- + 3H_2O + 5e^- \quad \text{------ eqn 6.2.1c}$$

Cathodic reactions:

Reduction of metals at the cathode (eqn 6.2.1d)

$$Ag^{2+} + 2e^- \rightarrow Ag_{(s)} \quad \text{------ eqn 6.2.1d}$$

oxidation at the anode (eqn 6.2.1e)

$$2CNO^- + 4OH^- \rightarrow 2CO_{2(g)} + N_{2(g)} + 2H_2O + 6e^- \quad \text{------ eqn 6.2.1e}$$

Copper Electrowinning (Davies et al. 1998))

Reactions at the anode:

$$4NaOH \rightarrow O_{2(g)} + 2H_2O + 4Na^+ + 4\ e^- \quad \text{---------- eqn 6.2.1f}$$

Membrane: $4Na^+_{(anolyte)} \rightarrow 4Na^+_{(catholyte)}$

Reactions at the Cathode:

$$4\ Na^+ + 4\ Na_2Cu(CN)_3 + 4\ e^- \rightarrow 4\ Cu^\circ + 12\ NaCN_{(aq)} \quad \text{------ eqn 6.2.1g}$$

Overall reaction:

$$4\ Na_2Cu(CN)_3 + 4\ NaOH \rightarrow O_{2(g)} + 2H_2O + 4\ Cu^\circ + 12\ NaCN_{(aq)} \quad \text{-- eqn 6.2.1h}$$

In the process of copper electrowinning, there is the liberation of free cyanides. The liberated free cyanides are oxidized at the anode to cyanates and then to carbon dioxide and nitrogen, (Lemos et al. 2006; Naga & Volesky, 2009; MPPPPMF, 1997) however the presence of a strong oxidizer as nitric poses some problems (Wang et al. 2006). Electrowinning as a method for cyanide treatment is hardly sufficient to meet discharge limits and therefore it is only used to reduce the amount of cyanide in an effluent before the application of other methods which can handle spent solutions or rinses with very low cyanide concentrations (Cushnie, 1994).

In the cyanidation process a major problem is the loss of cyanide, as it bonds more readily with copper than with metalic gold. Regeneration of the cyanide lost to cyanide-copper complexation is vital for the cyanidation process as the cost of cyanide is the highest cost incurred in the process (Lemos et al. 2006). Initially electrowinning was used for recovering metals from mine effluents but gradually its application was extended to the oxidation of cyanides and even to recycle cyanides for reuse compensating for the cyanide lost to copper-cyanide complexion during the cyanidation process.

Cathodic reactions for a copper cyano-complex (Sobral et al. 2002);

$$Cu(CN)_3^{2-} + e^- \rightarrow Cu^\circ + 3CN^- \quad Eo = -1.09V \quad \text{------ eqn 6.2.1i}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad Eo = -0.83V \quad \text{------ eqn 6.2.1j}$$

The following reactions occur at the anode;

$$Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^- \quad Eo = 0.36V \quad \text{------ eqn 6.2.1k}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \quad Eo = 0.40V \quad \text{------ eqn 6.2.1l}$$

Eqn 6.2.1l is allowed to occur in processes that are aimed at oxidizing the free cyanides generated in eqn 6.2.1i. In situations where the cyanide generated at the cathode is intended for reuse, another chemical which oxidizes at a potential less (eqn 6.2.1k) than that of oxygen generation (eqn 6.2.1l) thereby mitigating the generation of oxygen which migrates to the cathode, oxidizing the CN^- released there. Such a chemical can be a ferrous cyano-complex that is oxidized to a ferric cyano-complex (eqn 6.2.1k) (Sobral et al. 2002).

Disadvantages Of The Electrowinning Process

There are problems associated with the treatment of solutions with very low cyano-metal-complex concentrations. However, the mass transfer rate reduces as the concentration gradient reduces, thereby reducing the rate of plating of metals on the cathode (Sobral et al. 2002). A reduction in the plating-out of the metals from the solution implies a lower efficiency of the process. Another problem is that the CN^- concentration in the vicinity of the cathode increases significantly, retarding the reduction process and even possibly changing the order of the metal complex to a higher value that hinders the plating of metal ions on to the cathode (Naga & Volesky, 2009; Sobral et al. 2002).

These problems are resolved through the application of cathodes with very large surfaces (flow-through processes) or by increasing turbulence (flow-by processes) in the solution close to the cathode (Naga & Volesky, 2009; Sobral et al. 2002).

6.2.1.1 Flow-By Processes

1) Forced flow cell.

In this cell type, agitation of the electrolyte around the cathode is through mechanical or physical methods. Proper agitation of the electrolyte can be attained either by bubbling air through the electrolyte using a pump or by creating holes at the bottom of the cell, or through the application of static mixers. This cell can hardly be good for cyanide oxidation because of the periodic removal of the cathode for stripping which makes continuous application difficult to attain. Also the process cannot handle solutions of low concentrations.

2) Rotating Cathodes.

Like in the forced-flow cell, agitation is necessary to increase process efficiency with the difference here being that, agitation is by the brisk movement of the cathode (Naga & Volesky, 2009). The cathode is designed to be mobile thereby agitating the solution in the process. Often, the cathode is designed to be rotating. Unlike the forced flow cell, the rotating cathode cell can be operated continuously by modeling the movement of the rods such that collision of the cathode rods occurs stripping off metals plated on them. The metals stripped off during the collision of the cathode rods settle at the bottom of the cells where they are collected. A major problem with this cell type is that there is a high probability of break down since many small parts are involved.

6.2.1.2 Flow-Through Process

1) Mesh cathodes.

Mesh-flow-cathodes like other flow-through cathodes are different from force flow cathodes in that, unlike force flow cathodes, which are two-dimensional, these are three-dimensional. In flow-through processes cathodes are particulate or fibrous in structure, offering a very high real-to-apparent surface area ratio often reaching 10,000. Mesh cathodes are designed like a web of intertwining fibers submerged in a flowing electrolyte from which the metals plate onto. The metals are later extracted by using the impregnated cathodes as anodes in a conventional electroplating process. Due to its high cathode surface area, mesh cathodes are more efficient in treating solutions with low WADs and SADs concentrations. Technical problems associated with this process include the trapping of large particles between the merge and the unequal deposition of metals on the merge. The high cost of recovering the metals from the mesh makes the process not attractive economically.

2) Packed bed cells.

The cathodes here are composed of fine grain metallic particles of the same metal targeted for recovery. The metals recovered, plate on the surfaces of the grainy cathodes and are extracted by melting or scraping. Cells with these cathodes are efficient in treating solutions with very low WADs and SADs concentrations. Due to the very high cost of the process it is rarely applied.

3) Fluidized-bed cells.

The cathode here is similar as in the packed-bed cells, with the difference in the systems being, that in the fluidized-bed cell the particles are dispersed/suspended in a mobile electrolyte agitated to a circular motion by the introduction of the electrolyte.

An advantage of this method is that it can be continuous by bleeding the particles in a recycle stream. The complexity of the process and the cost involved has not made it attractive as a metal recovery option and consequently not for cyanide treatment.

Conclusion.

As a method for cyanide remediation the electrolytic process has major advantages over other chemical and biological processes. The process does not produce any toxic sludge requiring further treatment, it favours the recovery of metals and it is not affected by the presence of organic or metallic impurities (Sobral et al. 2002)

Essentially, electrowinning is an electroplating process whereby a direct current is applied and the metal ions plate out onto a cathode. The anodes and cathodes are usually made of an inert material. Cathodes are commonly made of polished stainless steel or carbon fibers, while the anodes are usually made of non-consumable materials such as platinized titanium, ruthenized titanium, lead, or graphite (Schulte, 2005).

6.3 Hydrolysis – Distillation

Introduction

The cyanide ion readily hydrolyzes in water producing gaseous hydrogen cyanide ($HCN_{(g)}$), which is given off (Eqn 6.3a) (Adams M. D., 1990),

$$CN^- + H_2O \rightarrow HCN\uparrow + OH^- \qquad \text{------eqn 6.3a}$$

Equation 6.3a can be divided into two parts; it is the sum of eqns 6.3b and 6.3c.

$$H_2O \Leftrightarrow OH^- + H^+ \qquad \text{----eqn 6.3b}$$

$$H^+ + CN^- \Leftrightarrow HCN \qquad \text{----eqn 6.3c}$$

In the case of metal complexes as iron-complex, the metals are precipitated as hydroxides of those metals (Equation 6.3.1). In such cases as with strong complexes of iron and other SADs, the dissociation of the complex will need for example the occurrence of photolysis by UV radiation.

$3OH^- + Fe^{3+} \rightarrow Fe(OH)_3\downarrow$ -----eqn 6.3.1

In alkaline environments with increased temperatures, free cyanide reacts with water to give formate and ammonia (eqn 6.3a).

$CN^- + 2H_2O \rightarrow HCOO^- + NH_3$ --------eqn 6.3a

Hydrogen cyanide undergoes complete hydrolysis in water and the rate of hydrolysis is temperature dependent accompanied by an increase in the redox potential (Oelsner et al. 2001). The product of hydrogen cyanide hydrolysis in water is pH dependent. At low pH i.e. in acidic environments ammonium formate (eqn 6.3b) is produced while at high pH formic acid (eqn 6.3c) is produced.

$HCN + 2H_2O \rightarrow HCOONH_4$ ------ eqn 6.3b

$HCN + 2H_2O \rightarrow NH_3 + HCOOH$ ------ eqn 6.3c

The aqueous hydrogen cyanide formed in eqn 6.3a can volatize as hydrocyanic gas ($HCN_{(g)}$), which has a lower vapour pressure than water and therefore goes into the gaseous phase much faster than water.

$$HCN_{(aq)} \rightarrow HCN_{(g)}$$

This method of treatment of cyanides makes use of distillation principles by exploiting the fact that at a temperature of 26°C which is close to normal room temperature, hydrocyanic gas has a vapour pressure of 100KPa which is higher than that of water (34KPa) at the same temperature.

In distillation, two liquids are separated if the difference in their partial pressures at a given temperature is large enough or a complete separation is accomplished in a single step if the difference in their boiling points is 100°C. The ability of hydrocyanic gas to get into the gaseous phase readily than water can be enhanced to separate it from water by increasing the temperature of the solution, reducing the external pressure and by increasing the surface area of the solution (through agitation). Increasing the surface of the solution is important since only the hydrocyanic liquid on the surface is able to get to the gaseous phase.

In a closed system, the vapour pressure above a solution is equal to the sum total of the partial vapour pressures of the liquids in the system. This means that, the vapour above the liquid will be enriched in the more volatile liquid and its concentration is equal to its partial pressure ratio in the total vapour pressure of the gas above the liquid. In closed systems the hydrocyanic gas can be captured for further treatment, but in open systems as in tailings ponds this escapes to the atmosphere especially in warm and arid environments (young & Jordan, 1995). The treatment of cyanide by hydrolysis and evaporation in tailings ponds must be strictly regulated to avoid poisoning. (The hydrolysis of hydrogen cyanide is further discussed in the chapter 9.4.)

6.4 Membranes Treatment

This is the separation of suspended and/or dissolved solids from a solution with the use of a semi-permeable membrane. It has been applied in the treatment of cyanide containing wastewaters. There are basically two types of membrane processes, the pressure-driven and the electrically driven processes (EPRI, 1997).

6.4.1 Pressure- Driven Process.

This process utilizes hydraulic pressure to force water molecules through a membrane. As the water is forced through the membrane, a concentrate of impurities (ions, organic matter, bacteria. e.t.c.) depending on the permeability of the membrane is retained in the feed water. The product of the process (the permeate) pure water is then harvested. Pressure-driven processes are the most commonly used systems.

The pressure-driven processes can be further categorized based on membrane permeability. In order of decreasing permeability these processes can be classified in to microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). MF and UF are used for removing organic molecules, large colloidal particles and most microorganisms. MF membranes are often used to control turbidity and for trapping colloidal suspensions. MF and UF are good for treating wastewaters but will not provide enough filtration for drinking water treatment. The treatment of water for drinking often requires the application of either RO or NF to meet standards. Not withstanding, the treatment of water for drinking requires the application of MF and UF for pretreatment of the water for removing coarser material before the application of NF or RO for final treatment. Drinking water treatment is mostly done with RO, but NF is also been used as it operates at lower pressures and has a high recovery rate (EPRI, 1997). Of special interest to this work will be the application of reverse osmosis for the separation of cyanide salts from water.

6.2.1 Electrically-Driven Process (Electrodialysis).

Also known as the electrodialysis process, these systems, unlike the pressure driven processes are driven by electrical current or by an electric potential. The filters/membranes employed in electrodialysis are semi-permeable to ions based on the charge of the ions, the electric potential applied and on their ability to reduce the ionic content of water (Osmonics, 1997). This occurs through the application of an electric potential across the system. This process has been employed successfully in the separation and subsequent extraction of cyanide compounds (Millman & Heller, 1982). In this process, ions are taken out of solutions and moved across alternating membranes. An improved version of this process is the electrodialysis reversal (EDR) process. Periodic reversal of the direct-current driving force prevents scaling and fouling of the membrane surface as in the electrodialysis processes (Osmonics, 1997), and this has increased the efficiency and the operating life of membranes. Ion exchange membranes are paramount in this process. The membrane is composed of alternating cation-selective and anion selective membranes in a membrane stack with flow channels between them (fig 6.4.2). The cathode and the anode are placed at both ends of the chamber such that they exert a pulling force on counter ions in the solution depleting the feed solution of these ions.

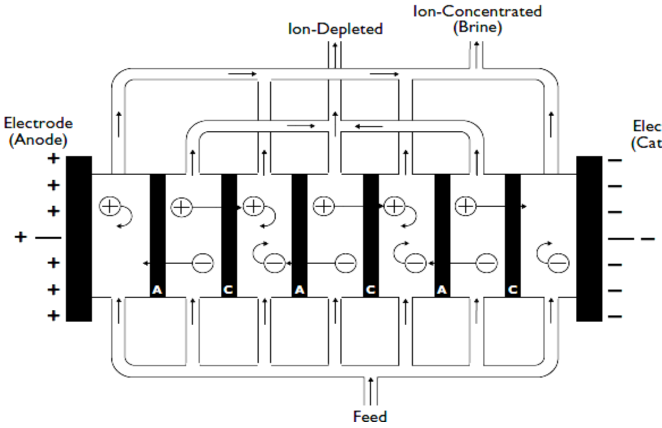


Figure 6.4.2: Electrodialysis Reversal (EDR) System (A=anion selective membrane, C=cation selective membrane)(Osmonics, 1997).

For a salt dissolved in a solution flowing between the membranes, the application of an electric potential (by introduction of a direct current) causes the positive ions (cations) to migrate to the cathode while the negative ions (anions) migrate to the anode. The presence of the alternating membranes ensures that the salt is removed from every compartment and collected in the intervening compartment.

Conclusion

Cyanides in solution can be separated by either electrodialysis or by reverse osmosis (Young & Jordan, 1995). In cyanide separation by electrodialysis the membrane used is permeable to the cyanide ion. The cyanide solution to be treated is placed in the halve cell containing the cathode. The negatively charged cyanide ions migrate through the membrane to the other halve of the cell to the anode. In reverse osmosis, hydraulic pressure is applied to a solution containing cyanide and water is forced out of the solution through a membrane impermeable to cyanide. Both methods have proven successful in the treatment of both free and complex cyanides

Chapter 7

Complexation Methods

7.1 Acidification - Volatilization - Recovery (AVR).

This process also known as the Mills-Crowe process was developed around 1930 at the Flin Flon operation in Canada. It is based on the observation that when the pH of a cyanide solution drops to below 9.3, there is formation of the hydrocyanic acid which volatizes and escapes as hydrogen cyanide gas ($HCN_{(g)}$) from the solution from a pH of 8.0 and below (Miller J. D., 2003). In most AVR processes, sulphuric acid is often employed. In the AVR process the escaping hydrocyanic gas is channeled through an alkaline medium where it is captured or stripped off from the flowing gas. This alkaline medium can be e.g. caustic (NaOH), lime ($Ca(OH)_2$). The chambers where the mixing of the cyanide solutions and the acids occur are sealed to prevent any escape of the hydrogen cyanide gas. Consider the reaction that occurs during hydrolysis of the cyanide ion in water (eqn 7.1a),

$$CN^- + H_2O \rightarrow HCN + OH^- \qquad \text{------- eqn 7.1a}$$

This reaction is at equilibrium when the pH is 9.3 (Young & Jordan, 1995). At pH values above 9.3 the reaction moves to the left maintaining cyanide ions in solution explaining why cyanidation occurs at pH values above 11. As the pH falls below 9.3 the reaction moves to the right encouraging formation of the hydrocyanic gas ($HCN_{(g)}$)**.** The lower the pH falls the higher the rate of formation and volatilization of hydrocyanic gas. At pH values of 2 and below hydrocyanic gas is evolved from weak acid dissociable (WAD) cyanide complexes (Young & Jordan, 1995) (Equation 7.1a).

$$M(CN)_x^{y-x} + xH^+ \Rightarrow x(HCN)_{(g)} + M^{y+} \qquad \text{------ eqn 7.1a}$$

$$Cu\,(CN)_3^{2-} + H_2SO_4 \Rightarrow CuCN_{(s)} + 2HCN_{(g)} + SO_4^{2-} \qquad \text{------ eqn 7.1b}$$

$$2HCN_{(g)} + Ca(OH)_2 \Rightarrow Ca(CN)_{2(aq)} + 2\,H_2O \qquad \text{------ eqn 7.1c}$$

$$Ca(CN)_2 + H_2SO_4 \Rightarrow CaSO_4 + 2HCN \qquad \text{------ eqn 7.1d}$$

In equation 7.1b, hydrogen cyanide is released following the acidification of a copper cyanide (WAD) solution. The released hydrogen cyanide is precipitated by reacting it with calcium hydroxide (eqn 7.1c) to give calcium cyanide. Further acidification of the calcium cyanide by addition of sulfuric acid will result in the release of hydrogen cyanide gas (eqn 7.1d). 67% of copper cyanide complex can be treated in this manner while 33% remains complexed (Davies et al. 1998).

SADs and thiocyanates can also be treated in a similar manner but the pH must be below zero. This is a great challenge as it entails a great consumption of acid. For this reason AVR processes are done at pH values between 1.5 and 2 resulting in only a slight alteration of SADs and thiocyanates. In cases where lime ($Ca(OH)_2$), will be used for the neutralization of the cyanide free rest solution (for discharge or recycling) after acidification to drive out cyanide, care should be taken to avoid using sulphuric acid for acidification to avoid formation of gypsum.

The liquid leaving the reaction chamber is stripped using a stream of air in a packed column. The cyanide-laden air passes through a second chamber flowing counter to a stream of alkaline solution (e.g. caustic solution with a pH of 11 (Barr et al. 2007)). When the alkaline solution is of caustic, the cyanide in the gas stream reacts with the caustic forming sodium cyanide (eqn 7.1e), which can be recycled to the leaching system.

$$HCN_{(g)} + NaOH_{(aq)} = NaCN_{(aq)} + H_2O \qquad \text{------ eqn 7.1e}$$

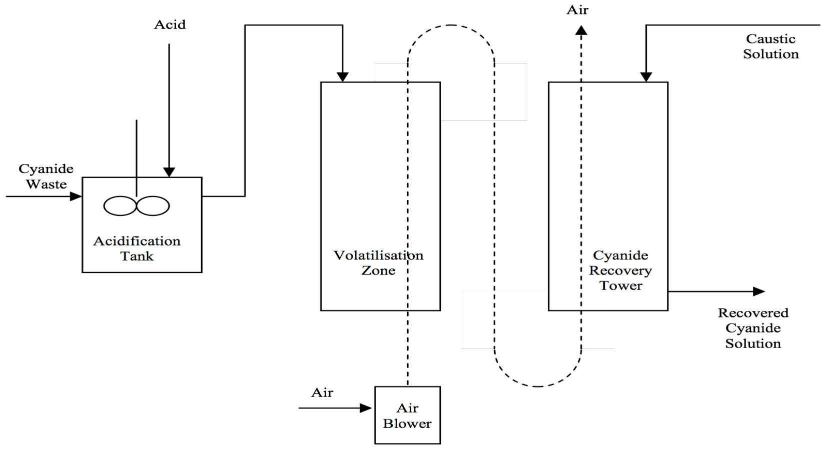


Figure 7.1: Flow diagram of an AVR circuit (Lee, 2005)

Cyanide recovery can be improved by increasing the number of stripping and adsorption (Fig 7.1) stages for cyanide or by resizing the columns (Miller J. D., 2003). Cyanide recovery percentages of 99.0% and above have been achieved.

The use of lime or soda, precipitates the metals in the cyanide free solution as hydroxides (Equation 7.1f).

$$M^{y+} + y(OH^{-}) \rightarrow M(OH)_y \qquad \text{-------eqn 7.1f}$$

In cases where lime is used there is the formation of gypsum (Equation 7.1g);

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O_{(s)} \qquad \text{-------eqn 7.1g}$$

Separation of metal hydroxides and gypsum is difficult when these are dissolved in water (Young & Jordan, 1995). This implies other acids such as nitric acid (HNO_3) or bases such as caustic (NaOH) can be used. Despite the fact that the usage of nitric acid and caustic is more expensive, the extra cost is made for during separation and treatment of the sludge. This technology is good as the recovered cyanide can be recycled in the leaching process and also the production of poisonous products (cyanates, thiocyanates, chloramines, ammonia etc) as it is the case with oxidation processes does not arise. It can be particularly good for remote locations so as to reduce the cost of constantly bringing in new cyanide for leaching (Miller J. D., 2003).

The system has a series of drawbacks/disadvantages including, that it demands a high initial investment for plant installation and energy for aeration, it can hardly achieve cyanide waste emission standards therefore the end products require further treatment before disposal. Because of the high cost of acids, the AVR process is best applied for small amounts of waste with very high cyanide concentration. Such wastes can be wastes from solvent extraction and ion exchange processes. If not the amount of acid needed will make the process uneconomical. Therefore, it can be best applied in conjunction with a pre-concentration stage, which may be by ion exchange or solvent extraction (Lee, 2005).

7.2 Flotation

This technology was developed in 1880 for application in the concentration of minerals from ores. Flotation is a separation process based on increasing the buoyancy or making suspended particles in a liquid buoyant by attaching fine gas bubbles to them. It is particularly effective for the separation of very tiny particles or light particles with a low settling velocity. Flotation methods have been classified based on the method of production of the bubbles.

- Dispersed air flotation.

The bubbles here are produced by mechanically dispersing air fed through a tube with an end equipped with rotating impellers or sparged diffusers. The bubbles produced by this method are generally too large to be effective for the floating of very fine particles The ineffectiveness owing to the large size of the bubbles formed by dispersing air in floating fine particles makes this method of flotation a rarity in industrial processes. It is very effective in treating scum/foam forming waste.

- Vacuum flotation.

Air bubbles are formed by dispersing air into the effluent to be treated. This continues until air saturation in the effluent is achieved. Once saturation is achieved a partial vacuum is applied. Due to the partial vacuum condition imposed on the system small bubbles form which attach to the particles to be floated causing them to float to the surface.

- Dissolved flotation.

In this method, air is dissolved in pressurized water and then the pressure is released. Air is added to water at the pump suction point. This air-water mixture is allowed to settle permitting the air to dissolve in the water. This air/solution mixture is then gradually released through a pressure-reducing valve into a zone of low pressure in the flotation chamber where bubbles with sizes 30 – 120 µm in diameter are formed.

7.2.1 Froth Flotation

This is the selective separation of particles based on the difference in their abilities for air bubbles to adhere on to them. This is particularly useful for separating minerals in mineral/water slurry. In situations where this desired quality/property difference is not large enough to permit envisaged separation rates, the mineral surfaces can be engineered or treated accordingly through chemical methods. The ability to chemically alter the surface properties of minerals has widened the application of froth flotation in mineral separation processes (Kawatra, 2002). The difference in wetability between minerals can be described in terms of hydrophobicity or hydrophilicity. Hydrophilicity increases as hydrophobicity decreases and vice versa.

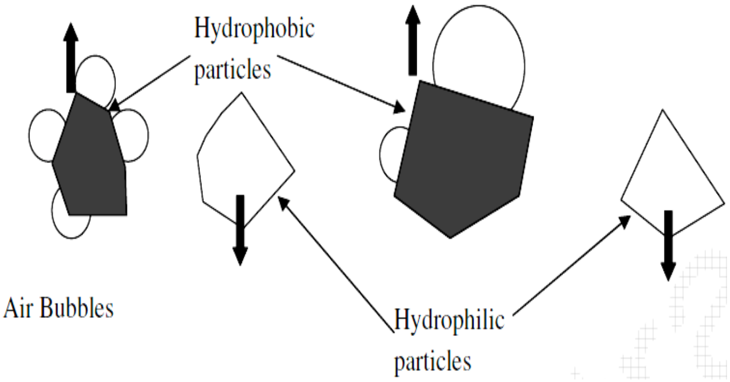


Figure 7.2.1: Selective attachment of air bubbles to hydrophobic particles. The buoyancy of the bubbles then carries these particles to the surface, leaving the hydrophilic particles behind (Kawatra, 2002).

When air bubbles are passed through a suspension containing different mineral particles, the tendency for the air bubbles to attach to specific mineral types increases based on the higher the degree of hydrophobicity of a particular mineral type. Minerals with greater degrees of hydrophobicity adsorb air bubbles faster than those with lower degrees of hydrophobicity (and consequently higher hydrophilicity) (Fig 7.2.1).

The now buoyant hydrophobic particles are floated to the surface while the hydrophilic particles remain in solution. The angle at which the bubbles are attached to the mineral/particle surfaces also determines the strength of adhesion between the particle and the air bubble (kawatra 2002).

7.2.2 Factors That Influence Froth Flotation

7.2.2.1 Reagent Type

In natural or real forms, mineral particles in suspensions hardly attain conditions proper for separation by froth flotation. Chemical treatment of these particles is required to upgrade certain mineral properties e.g. hydrophobicity/hydrophilicity or ionic charge e.t.c, to permit a froth flotation separation process. Different minerals have different characteristics and therefore the need to chemically treat or modify a particular mineral may not be necessary for another mineral. This means different reagents are required for different minerals or mineral combinations (Kawatra, 2002).

7.2.2.2 Collectors

These are substances or chemicals that are used to selectively attach minerals to particle surfaces. Collectors form a thin hydrophobic nonpolar hydrocarbon monolayer film on the particles and the collectors also increase the angle of adherence of the bubbles onto the mineral surfaces. The collectors can be nonionic, or ionic. When the collector is ionic it can either posses a cationic or an anionic end. What is important is that the ionic end has an opposite charge to the charge of the particle to be extracted (Bucsh et al. 1980). Nonionic collectors are simple hydrocarbon oils, while cationic and anionic collectors have both a polar end and a nonpolar end. The polar end is used to attach the collector to the particle while the nonpolar hydrophobic end is available for interaction and attachment to air bubbles. Attachment of the polar end to the mineral surface can either be through chemisorptions or by physical adsorption (chapter 5 of this work describes chemisorptions and physical adsorption in details). Flotation using ionic collectors can extract cyanide complexes from bulk solutions.

7.2.2.3 Frothers

These are chemicals that ensure that the air bubbles remain stable, separated and well dispersed in the solution, and when the air bubbles get to the surface they remain stable i.e. they do not collapse but form a froth layer that can be extracted. Alcohols are the most widely used froths e.g. methyl Isobutyl Carbinol or 4methyl-2-pentanol. There are many other frothers and trials are been done on new generation frothers.

7.2.2.4 Modifiers

These substances determine whether or not a collector attaches to a mineral surface. They can accelerate the rate of adsorption of a collector on a mineral surface (referred to as accelerators in this case) or may hinder a collector from attaching onto a mineral surface (referred to as depressants in this case). Cyanide is a powerful depressant. Modifiers are not specific in their role as a modifier may accelerate the rate of adsorption of a collector onto a mineral surface for a particular mineral/collector combination while in another mineral collector combination it will hinder the adherence of the same collector onto a mineral surface.

Examples of modifiers are substances that affect the pH of a solution. Most chemicals assume a positive surface charge under acidic conditions and likewise a negative surface charge under alkaline conditions. The pH at which a mineral switches from having a positive surface charge to a negative surface or vice versa varies from one mineral to another. Therefore by manipulating the pH of a solution, adsorption and consequently flotation of a particular mineral type can be achieved. Kawatra 2002, considered the case of pyrite, galena and chalcopyrite mineral species in suspension. In this experiment it was demonstrated that, in the presence of a reasonable concentration of the sulfhydryl collector Xanthate, the preference of adsorption of the collector begins with pyrite, then galena and finally chalcopyrite as the pH increases. This implies that pyrite becomes sufficiently hydrophobic at a lower pH than galena, which becomes hydrophobic at a much lower pH than that required by chalcopyrite. As hydroxide ions are being added to increase the pH of the solution, this generates a struggle between the sufhydryl ions and the hydroxide ions for adsorption onto the mineral surfaces (Fig 7.2.2.4a). Based on fig 7.2.2.4a it can be inferred that at a defined pH and Xanthate concentration as in zone A, none of the minerals can be floated. In zone B, chalcopyrite can be floated. In zone C both galena and chalcopyrite can be floated. At conditions of zone D all the minerals can be floated. This implies therefore that a separation of the three can be done by, starting with conditions of zone B, where only chalcopyrite can be extracted, then move to conditions of zone C to extract galena and finally to conditions of zone C to harvest pyrite.

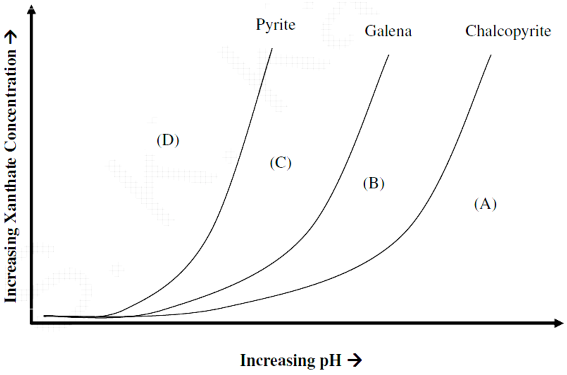


Figure 7.2.2.4a: Schematic of the pH response curves for sulfhydryl collector adsorption on different sulfide minerals. These curves mark the boundary where the given mineral becomes sufficiently hydrophobic to float. Both xanthates and dithiophosphates exhibit curves of this form, with different pH values and concentrations for each type of collector (Kawatra, 2002).

Cyanide is an important depressant during the flotation of sulphide minerals and in other froth flotation process (Huiatt, 1984). Due to its high reactivity, cyanide complexes with these metals preventing the metals from attaching to the collector e.g. Xanthate and hindering their ability to adsorb air bubbles and become buoyant (Kawatra, 2002). When in solution, copper ions activate sphalerite but adding cyanide can reverse this activation. This is also useful during the separation of lead and zinc. Huiatt 1984, also discusses the application of cyanide and cyanide complexes as depressants. Cyanide is also a very strong depressant for pyrite (Kawatra, 2002). Fig 7.2.2.4b shows the effect of cyanide on the flotation of some sulphide minerals as the pH varies.

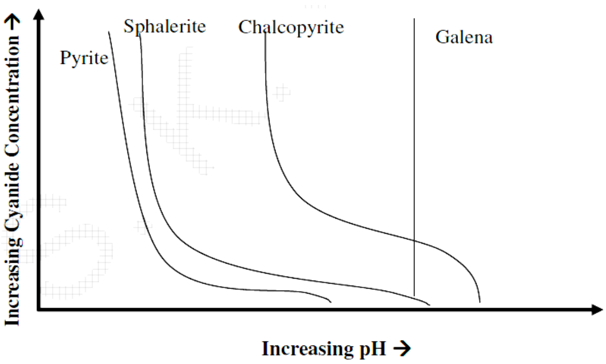


Figure 7.2.2.4b: Effect of cyanide depressant on flotation of minerals as a function of pH. It is interesting to note that flotation of galena (PbS) is unaffected by the presence of cyanide (Kawatra, 2002).

7.2.3 Flotation Of Cyanides

Bucsh et al 1980 demonstrated that cyanide-metal complexes can be extracted from solution by ion-precipitate flotation, if the cyanides are precipitated with an appropriate metal. Latskowska & Riga 2007 also demonstrated the flotation of free cyanides after coagulation and flocculation with appropriate reagents. In their experiment, Busch et. al 1980 stabilized or precipitated cyanide with iron salts forming iron cyanide complexes. Based on the ambient pH they ended with either ferric (Fe^{4+}) or ferrous (Fe^{3+}) complexes. After, using a quaternary amine tricaprylmethyl ammonium chloride a cationic surfactant they precipitated iron-cyanide complexes as a waxy solid. These were then treated and floated accordingly. The ionic ends of the quaternary amine bonded the collector to the cyanide complexes while the nonionic end attached to air bubbles providing buoyancy to float these species to the surface for collection.

$$(y\text{-}x)R_4NCl + M(CN)_x^{(y-x)} \rightarrow (R_4N)_{y-x}M(CN)_{6(s)} + (y\text{-}x)Cl^- \quad \text{-----eqn 7.2.3}$$

Where;

R_4NCl is the quaternary amine (collector).

$M(CN)_x$ is the metal cyanide complex, usually a SAD.

$(R_4N)_{y-x}M(CN)_{6(s)}$ is the resultant double salt.

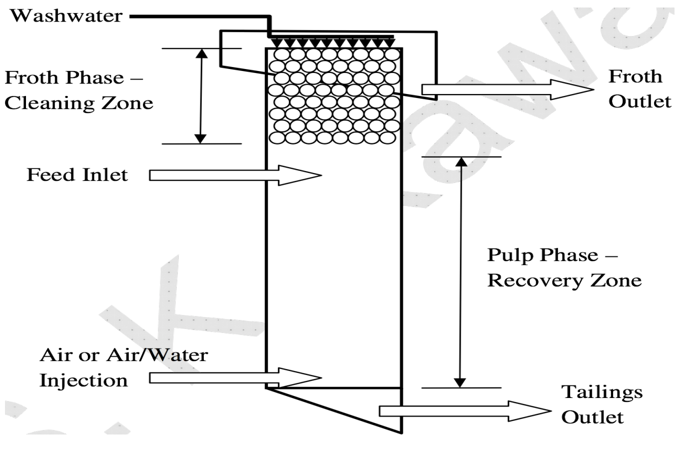


Figure 7.2.3: Schematic of a flotation column Flotation machine (Kawatra, 2002).

The double salts coalease, forming colloids or particles of larger sizes. Both ferrihexacyanide ion and ferrohexacyanide complexes were floated but the flotation of ferrous complexes was slower owing to the slow kinetics of reaction between ferrocyanide and the surfactant (Bucsh et al.1980).

While there is great potential for the treatment of cyanide waste through flotation there has been little work done on the flotation of the free cyanide. Emphasis has been on the flotation of SAD complexes formed naturally or through metal addition (Young & Jordan, 1995). Also the fate of thiocyanides in flotation has not been established but it can be assumed that with the right reagents (collectors, modifiers, and e.t.c.) these can also be treated. Flotation of WADs has only been partially. Flotation of cyanides is only possible after formation of insoluble cyanide complexes.

Flotation as a treatment method would not qualify for complete treatment of cyanide wastes as it can only partially treat WADs and the remediation of thiocyanates has not been established. Free cyanides have been treated by flotation (Latkowska & Figa, 2007), but the complete process has not been totally understood. This is only possible after the free cyanide was reacted with iron to form insoluble complexes. Therefore it can be used as a pretreatment method before the application of more aggressive cyanide treatment methods.

7.3 Metal Addition

Introduction

This is the addition of an appropriate metal salt into a cyanide solution with the aim of converting the cyanide species to either a form more susceptible to available remediation technologies or to a form considered less polluting or toxic.

This technique has been employed in the gold mining industry in the Merrill-Crowe process, where after the leaching of gold from the ore has occurred, the leachate is then treated with zinc salt resulting in a double benefit for the industry. Upon addition of zinc salt to the pregnant solution, gold ions are replaced by zinc ions in the aurocyanide complex resulting in the precipitation of pure gold and a residual zinc-cyanide complex solution. In effect, aurocyanide $[Au(CN)_2^-]$ a strong acid dissociable

(SAD) cyanide complex has been replaced by zinc-cyanide [$Zn(CN)_4^-$] a WAD which can be easily remediated (eqn 7.3a).

$$4Au(CN)_2^- + 2Zn° \rightarrow 4Au° + 2Zn(CN)_4^{2-} \qquad \text{------eqn 7.3a}$$

Other metals capable of precipitating gold from the cyanidation leachate include aluminum, copper and iron (Young & Jordan, 1995).

In other processes ferrous (Fe^{2+}) and Ferric (Fe^{3+}) cations have been added to cyanide solutions to yield strong iron cyanide complexes, $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ respectively. These reactions are very pH dependable. At pH values greater than 8.5 ($pH > 8.5$) ferrous cations (Fe^{+2}) react with cyanide to give ferrohexacyanide complex [$Fe(CN)_6^{-4}$], while at pH values between 5 and 8 (pH 5-8) ferric cations (Fe^{+3}) react with cyanide giving ferrihexacyanide [$Fe(CN)_6^{-3}$] (Latkowska & Figa, 2007). These compounds are considered very stable and non-polluting owing to their resistance to decomposition or dissociation. However, this is not the case when these compounds are exposed to ultraviolet light. When exposed to UV light, these compounds undergo photodecomposition (Also chapter 8.7). The ability of these compounds to decompose on exposure to UV light has let to the development of alternative solutions.

A primary alternative solution has been the precipitation of these ferrohexacyanide and ferrihexacyanide anions as insoluble double salts (Latkowska & Figa, 2007). Precipitation of ferrohexacyanide anions as a double salt can be achieved by the addition of a variety of metal ions including those of iron, copper, nickel and zinc (Young & Jordan, 1995). When ferric (Fe^{3+}) ions are added to ferrohexacyanide solution at a pH of 3 to 4, prussian blue is precipitated (eqn 7.3b).

$$3Fe(CN)_6^{4-} + 4Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_{3(s)} \qquad \text{-------eqn 7.3b.}$$

Ferrohexacyanide anion reacts with various metal ions at a pH of between 3 and 5 as follows, with cupric cation it reacts to yield $Cu_2Fe(CN)_6$, reacts with nickel cation to yield $Ni_2Fe(CN)_6$, and it reacts with zinc cation to yield $Zn_2Fe(CN)_6$. The reactions with metal cations can be represented as (eqn 7.3c),

$$Fe(CN)_6^{4-} + 2M^{2+} \rightarrow M_2[Fe(CN)_6]_{(s)} \qquad \text{-------- eqn 7.3c.}$$

Where M = a metal ion with a valence of +2.

In a similar manner ferrihexacyanide anions can be precipitated as a double salt. When ferrihexacyanide anions are reacted with ferrous cations at a pH of between 3 and 5 the result is a Prussian brown (eqn 7.3d).

$$2Fe(CN)_6^{3-} + 3Fe^{2+} \rightarrow Fe_3[Fe(CN)_6]_{2(s)} \qquad \text{----eqn 7.3d. (Prussian brown)}$$

When ferrihexacyanide anions are reacted with ferric cations the result is a Prussian green at a pH of between 3 and 4 (eqn 7.3e).

$$Fe(CN)_6^{3-} + Fe^{3+} \rightarrow Fe_2(CN)_{6(s)} \qquad \text{----eqn 7.3e. (Prussian green)}$$

Precipitation of free cyanide as a salt has also been achieved using cuprous (Cu^{1+}) and argentous (Ag^{1+}) yielding CuCN and AgCN respectively as single salts (Young & Jordan, 1995).

The SAD complexes, cemented metals and cyanide precipitates formed through metal addition are all very stable. Stringent pH control is critical if the stability of these compounds is to be maintained after completion of the processes. Metal addition as a method for remediating thiocyanides has not been established but thiocyanides are expected to be removed through substitution for cyanides.

7.4 Solvent Extraction

Introduction.

The solvent extraction process is a method of separating solids, liquids, or gasses either dissolved-in or in particulate form in a solvent. The solvent extraction method can be employed in the extraction of impurities in a chemical solution. In the solvent extraction process, a solvent or diluent is applied to a solution of many species to make a particular or group of extractants with solvating, chelating or ion exchange capabilities susceptible to dissolution. The extractant is either added together with the solvent or is added before the addition of the solvent. The role of the extractant is to go into a chemical reaction with the target species resulting in the formation of a new chemical. This new chemical formed, should ideally be 100% soluble in the added solvent and 0% soluble in the previous solvent in which it existed. A 100% solubility of the target substance is hardly achievable, but the new chemical should be more soluble in the newly added solvent. The force responsible for transferring the newly formed species between the two immiscible solvent liquid phases is referred to as the solvent extraction. Solvent extraction exploits the fact that some elements/species (solids, liquids or gases) are more soluble in one solvent than in another. Once a solvent is introduced into a system that a particular solute is less soluble in, the solute gradually migrates from its previous host solvent into the newly introduced solvent. For separation of the two diluents to be possible, they must be immiscible in each other and be of different densities. The extractant-solute complex or solute should remain dissolved-in and attached to the new diluents/solvent, which should have selectivity for the aqueous species being remediated. A combination of the diluents and the extractants (where applicable) is called the organic phase. When the organic phase and the aqueous phase are mixed together the organic phase with the assistance of the extractant strips the target/solute species from the aqueous phase. There are various groups of metal extractants including chelating agents, ion pair extractants, neutral or solvating extractants, organic acid extractants, and ligand substitution extractants (Kordosky et al. 2011). The classification of the extractants was based on their structure, extraction and stripping chemistry, and the metal species extracted.

Equation 7.4a describes a solvent extraction process:

$$(y\text{-}x)R_4NCl + M(CN)_x^{y-x} \rightarrow (R_4N)_{y-x}M(CN)_{6(s)} + (y\text{-}x)Cl^- \quad \text{------ eqn 7.4a}$$

Where:

R_4NCl, is the extractant.
$M(CN)_x^{y-x}$, dissolved solute, which in this case is a metal-cyanide complex.
$(R_4N)_{y-x}M(CN)_{6(s)}$, newly formed species.

A solvent extraction process aided by a chemical reaction, which may occur within the organic phase, the liquid phase, or at the interphase between them, is referred to as reactive extraction. Werner Halwachs first used the term ‘reactive extraction’ in 1981. Often than not, reactive extraction is accompanied by the formation of metal complexes which if coagulation occurs can result in a shut down of the process or system due to clogging. This sometimes dictates the application of modifiers. Modifiers inhibit coagulation and therefore clogging.

7.4.1 Principle Of Solvent Extraction

When a solute is dissolved in a liquid and a second solvent is introduced with a greater solubility for the solutes than the first solvent, a greater portion of the solute migrates to the added solvent by a force called the chemical potential. The physical-chemical force responsible for the transfer of the solute between the two immiscible liquid phases is referred to as solvent extraction. This movement of the extractant from the first solvent to the second solvent continues until equilibrium is reached. 100% equilibrium is not reachable, and therefore in chemical processes, 90-99% solute transfer is considered sufficient enough (Halwachs, 2011). The time required by such a system to attain equilibrium is a function of the product K_ta, where K_t = mass transfer coefficient and a = interface area/liquid volume. Figure 7.4.1a describes what happens when two immiscible liquids are mixed together. Initially, there will be mixing defined by the formation of micro droplets of each other mixed together. These droplets gradually segregate from each other and merge with their likes as soon as the mixture is allowed to settle, resulting in two different liquid layers with the denser one lying below.

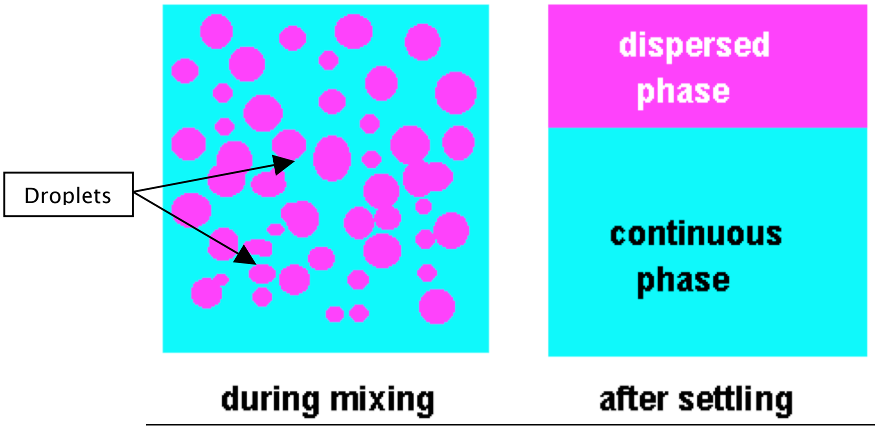


Figure 7.4.1a: Mixing and settling phases of a liquid two-phase system (Halwachs, 2011).

The equilibrium state of the systems is defined by a distribution coefficient (D) defined as,

$$D = \frac{\text{extractant in organic phase}}{\text{all species in aqueous phase}}$$

D is influenced by the initial concentration of the extractant in the solution and also by the concentration of the total chemical species in the liquid phase, while it is independent of phase flow conditions and is characteristic for a particular solute-solvent-aqueous system. D is an important parameter in the design of a solvent extraction system.

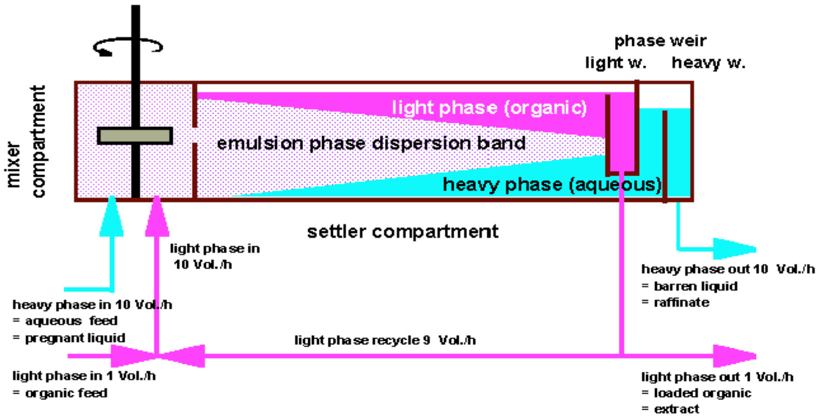


Figure 7.4.1: Conventional mixer-settler contactor (Halwachs, 2011)

The two systems are allowed to settle by gravity or centrifugal force. The time required for the two liquids to separate depends on a number of factors including the viscosity and the density of the mixture, interfacial tension between the two liquids and the size of the droplets of the dispersed phase (Fig 7.4.1a). While there exist a number of formats that the mixer-settler equipment for solvent extraction can take, a typical conventional mixer-settler looks like this (Fig 7.4.1).

In the mixer component, the ratio of organic feed to aqueous feed is 1:1. For a good separation, the ratio of aqueous feed to organic feed in the mixer chamber should be close to one. After the mixing has occurred, the mixture is left to settle to allow for the separation of the liquid and the organic phases. These are then collected separately as the loaded organic feed floats above the barren liquid feed. 90% of the loaded organic feed is recycled in the system and just 10 percent is retained. Note that despite the fact that 90% of the organic feed introduced to the system is recycled feed, the transfer of the target element to the organic feed from the aqueous feed is maintained because of the willingness of the target solute to move to the organic phase. Continuous recycling of the organic phase into the system or repeating the extraction process many times over ensures a very high degree of extraction of the target substance. The mixer-settler contactor is the most popular design tool for carrying out continuous solvent extraction processes in laboratories as it offers a continuous feeding, mixing and gravity settling/separation compartments. In the continuous mixer-settler contactor, the flow capacity of the system is exceeded when the upper boundary of the emulsion phase dispersion band crosses the bottom boundary of the light or organic phase or when its lower border drops below the upper layer of the heavy (aqueous) phase upper boundary. These imaginary boundaries are kept constant during the designing phase of the system. The settling compartment is constructed to be 10 fold larger than the mixing compartment. This allows for sufficient settling time and for separation to occur especially for systems with low coalescence rates, which might occur due to high viscosity and/or low density, and/or low interfacial tension (Halwachs, 2011). Repeated mixing and settling enhances separation and therefore it is common practice to see a battery of multiple mixing and settling chambers in a single unit. It is customary during the mixing of the aqueous and the organic phases to add some substances called modifiers that assist in maximizing the extraction process. After an appropriate time limit the aqueous phase (now a solution stripped of the species to be extracted) and the organic phase (now loaded with the species to be remediated) are separated, effecting the separation. The process is repeated using the loaded organic phase and an aqueous phase of smaller volume and appropriate chemistry is done to concentrate the species to be extracted. This second step results in a concentrated solution of the target species, while the organic phase is stripped and can be recycled and reused. Some processes are spontaneous while others need a longer period and so they are allowed to mix and settle for the components to separate out.

7.4.2 Solvent Extraction Of Cyanide

Solvent extraction of gold from diluted pregnant leach solutions has many advantages over other metallurgical methods such as adsorption onto activated carbon or ion exchange resins (Zhang et al. 2002). The high solubility of copper in cyanide has rendered recovery of gold from gold leach solutions with high amounts of dissolved copper extremely difficult in systems using the carbon in pulp (CIP) method (Davies et al. 1998). Soluble copper reacts with cyanide forming copper species [$Cu(CN)_3^{-2}$, $Cu(CN)_4^{-3}$] that compete with auro-cyanides [$Au(CN)^{-2}$] for active sites on activated carbon during adsorption or during ion exchange.

Davies et al 1998 used an extractant with a high loading capacity, composed of a mixture of a quaternary amine and a weak acid from Henkel, LIX 7820® of the LIX 7800® series. The quaternary amine in LIX 7820® is aliquat® 336 (tricapryl monomethyl ammonium chloride) in combination with 4-nonylphenol in a 1:2 molar ratio. Quaternary amines are well known extractants for anionic species including cyanide metal complexes (Davies et al. 1998). The general formula for aliquat 336® is $R3N^+\text{-}CH3X^-$ where R = mixture of C_8 and C_{10} hydrocarbon chains, and X^- = a small anion (Cl^-, OH^-, CO_3^{2-}, HSO_4^-, SO_4^{2-}). At pH values below 10.5, nonphenol occurs as an acid leaving the quaternary amine (Q^+) in equation 7.4.2a&b positively charged and requiring appropriate anions to attain neutrality. Anionic metal complexes including metal cyanide complexes are attracted to fill this need. Equation 7.4.2b describes the solvent extraction of a cyanide species in water.

$$Q^+(RO)^-_{(org)} + HOH \rightarrow Q^+_{(org)} + ROH_{(org)} + OH^-_{(aq)} \qquad \text{------ eqn 7.4.2a}$$

$$2Q^+_{(org)} + Cu(CN)_3^{2-}{}_{(aq)} \rightarrow (Q^+)_2Cu(CN)_3^{2-}{}_{(org)} \qquad \text{------ eqn 7.4.2b}$$

Where:

ROH is nonylphenol

Q^+ is the quaternary amine cation.

When the extractant (QRO) is dissolved in a solvent (water (H_2O)) and the pH is increased to values ≤10.5 by addition of an acid, the extractant splits given a positive end (quaternary amine cation) Q^+ and a negative end (RO^-). The positive end bonds with the anionic species i.e. cyanide metal complex in this case, while the negative end bonds with a positive hydrogen ion to give nonylphenol.

Once the quaternary amine cations have loaded the anions, a process to regenerate the quaternary amine cations and recover the anions (metal cyanide complexes in this case) is carried out. This involves contacting the loaded amine cations with a strip solution at a pH ≥ 13. The phenoxide ion (RO^-) at this pH recombines with the quaternary amine cation (Q^+) regenerating the extractant while the copper cyanide complex anion is released (Equation 7.4.2c) extracting the cyanide-complex in the process.

$$(Q^+)\ 2Cu(CN)_3{}^{2-}{}_{(org)} + 2ROH_{(org)} + 2OH^-{}_{(aq)} \rightarrow$$

$$2Q{+}RO^-{}_{(org)} + 2H_2O + Cu(CN)_3{}^{2-}{}_{(aq)} \qquad \text{------eqn 7.4.2c}$$

Chapter 8

Oxidation Methods

8.1 Catalytic Oxidation

Introduction

This is a chemical oxidation process whereby hydrocarbons (CHs) are being combined with oxygen at specific temperatures (often very high temperatures) yielding carbon dioxide (CO_2) and water (H_2O) (Emission control, 1995), or the breakdown of volatile organic compounds into harmless substances of water, carbon dioxide and sometimes hydrochloric acid. As the name suggests, this method of oxidation requires a catalyst. In general, the reaction takes place as follows (eqn 8.1a).

$$HC_s + O_2 \xrightarrow[500-900F]{Catalyst} H_2O + CO_2 \qquad \text{---eqn 8.1a}$$

In the absence of a catalyst, the temperatures required are extremely high as in the example below (eqn 8.1b). This is referred to as thermal oxidation. No catalyst is required and the temperature needed to provide activation energy for the reaction is between 1400°F and 1800°F as oppose to between 500°F and 900°F when a catalyst is used (Equation 8.1a).

$$HC_s + O_2 \xrightarrow[1400-1800F]{\text{Thermal } E_n \text{ no catalyst}} H_2O + CO_2 \qquad \text{--eqn 8.1b}$$

Many chemicals have been shown to exhibit catalytic activity. In many instances the gases are preheated to temperatures slightly above temperatures required for the reaction and then introduced to the reaction chamber containing the catalysts where the reactions occur on the surface of the catalyst. These catalytic reactions are often exothermic, and produce CO_2 and H_2O**.** The heat given-off by the exothermic reactions can be captured before the gases are released to provide energy for the preheating of other gases before introduction into the main reaction chamber.

8.1.2 Drawbacks Of Catalytic Oxidation

Three major problems are encountered in catalytic processes resulting in a decrease in performance or complete deactivation of the system/process in extreme situations. These problems accumulate gradually over a long period of time in a process called aging. These are:

1) Masking,

This is a situation where other chemicals referred to as contaminants from the exhaust make their way into the reaction chamber and settle on the surfaces of the catalyst reducing the amount of active surface available on the surfaces of the catalyst for the oxidation reaction. By determining the cause of the contamination or the source of the contaminant, appropriate measures can be taken to restore the performance of the catalyst. In some situations simple washing can be enough to regain full performance of the catalyst.

2) Chemical Poisoning,

In this situation, the active surfaces for reaction on the catalysts are attacked by alien chemicals. This results in an alteration of the chemical composition of the catalyst, thereby affecting its capacity to perform its function. Previously, this effect was thought to impart a permanent damage on the catalyst, but that is no longer the view as new generation high-tech catalysts are formulated intelligent enough to resist chemical poisoning.

3) Thermal Sintering.

This is any damage cause to the catalyst by heat. Such damages are not reversible as they result in a collapse of the washcoat (Emission control, 1995). Such damages occur as a result of a system failure and steps can always be taken to avoid such occurrences.

8.2 Chlorine Treatment Of Cyanides

Introduction

This is the destruction of cyanide by the addition of chlorine in an alkaline environment. It has been practiced ever since the development of the cyanidation process in 1889 making it once the most common method for cyanide destruction (Young & Jordan, 1995; Botz M. , 1999). Chlorination is no more the most widely used method for the treatment of cyanide wastes, due to the fact that it is not very successful in treating slurries. Alkaline chlorination is good for the treatment of slow flowing solutions with low to high initial levels of cyanide. Because of the high reactivity of chlorine, an electrochemical chlorination process was developed which produces chlorine in situ (in an electrolytic cell) for the process avoiding the transportation of chlorine to the process sites thereby avoiding the occurrence of accidents that may occur during the transportation of the gas (U.S. Department of Energy, 1998).

8.2.1 Reaction Chemistry

Generally speaking the reaction between chlorine or other chlorine compounds (e.g. hypochlorite, chlorine dioxide) and simple cyanides e.g. sodium cyanide or potassium cyanide is spontaneous and independent of pH (ASTI A. S., 2007). This reaction produces toxic cyanogen chloride that volatilizes at pH values below 8.0. To avoid the production of cyanogen chloride gas ($CNCl_{(g)}$), the pH is maintained between 8.5 and 9.0, a pH range within which cyanogen chloride decomposes to cyanate (ASTI A. S., 2007). At this pH range of 8.5 to 9.0 the complete oxidation of free cyanides occurs between 10 and 30 minutes. The rate of the reaction i.e. oxidation of free cyanides can be increased by raising the pH. When the pH range is increased to between 10 and 11 the time for complete oxidation is reduced to between 5 and 7 minutes (ASTI A. S., 2007). Figure 8.2.1 is the process flow diagram of the alkaline chlorination of cyanides.

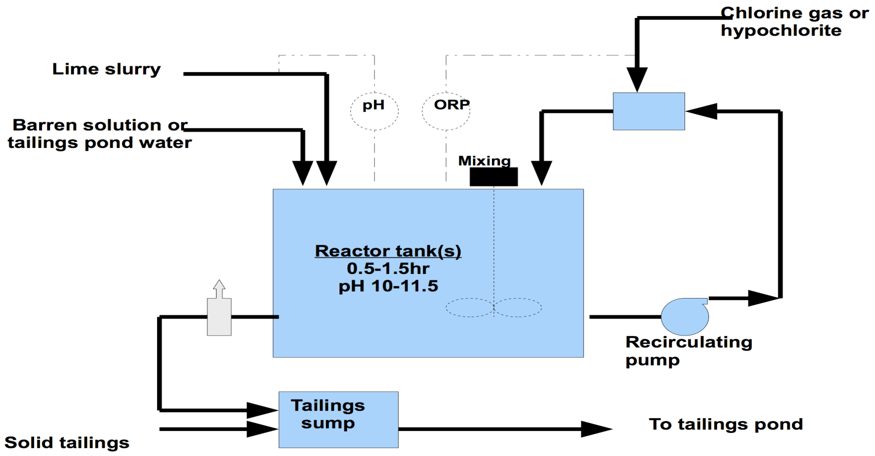


Figure 8.2.1: Flow diagram of alkaline chlorination of cyanides. (Adapted from the Schematic flow diagram of a typical alkaline chlorination system (Dzombac & Ghosh, 2006)).

The Oxidation of cyanides by chlorine occurs in a two steps reaction. First, there is the conversion of cyanide to cyanogen chloride (CNCL) (eqn 8.2.1a), also called chlorocyanogen or tear gas.

$$CL_{2(g)} + CN^{-} \rightarrow CNCL + CL^{-} \qquad \text{--------eqn 8.2.1a}$$

Secondly, there is the hydrolysis of cyanogen chloride to give cyanate (eqn 8.2.1b);

$$CNCL + H_2O \rightarrow CNO^{-} + CL^{-} + 2H^{+} \qquad \text{-------eqn 8.2.1b}$$

The hydrogen ions produced during the hydrolysis of cyanogen chloride (eqn 8.2.1b) neutralize the lime in the solution pushing the pH downwards and away from optimum conditions. Therefore a base (added as sodium hydroxide or calcium hydroxide) must always be added to compensate for the drop in pH. The chlorine introduced into the system does not only react with cyanides, but it also reacts with WADS (eqn 8.2.1d) and thiocyanides (eqn 8.2.1c) (Young & Jordan, 1995). The high pH in the reaction chamber favours the formation of sulphates and the metal-hydroxides formed precipitate (Young & Jordan, 1995). In both situations there is the consumption of lime accounting for the high lime demand of the process.

$$SCN^{-} + 4Cl_{2(g)} + 10(OH)^{-} \rightarrow OCN^{-} + SO_4^{2-} + 8Cl^{-} + 5H_2O \qquad \text{-------eqn 8.2.1c}$$

$M[(CN)_x]^{y-x} + xCl_{2(g)} + (2x+y)(OH)^- \rightarrow xOCN^- + 2xCl^- + M(OH)_y + xH_2O$ ----eqn 8.2.1d

In eqn 8.2.1d, x = Number of cyanide ions, y = valence of the metal (M) and M is a metal.

The chemical composition of the effluent produced from the alkaline chlorination of cyanides depends on the quantity of excess chlorine present in the reaction chamber (Botz M. , 1999). In the presence of slightly excess chlorine, the cyanates are hydrolyzed giving ammonia (eqn 8.2.1e),

$$OCN^- + 3H_2O \xrightarrow[\text{as catalyst}]{\text{Chlorine}} NH_4^+ + CHO_3^- + OH^- \qquad \text{---------eqn 8.2.1e}$$

In a situation of enough excess chlorine there is the further oxidation beyond breakpoint chlorination where ammonia is completely oxidized to give nitrogen gas (eqn 8.2.1f and g) (Botz M. , 1999).

$$3Cl_2 + 2NH_4^+ \xrightarrow{\text{excess chlorine}} N_2 + 6Cl^- + 8H^+ \qquad \text{----------eqn 8.2.1f}$$

$$2OCN^- + 3Cl_{2(g)} + 4OH^- \rightarrow N_{2(g)} + 2CO_{2(g)} + 6Cl^- + 2H_2O \qquad \text{------eqn 8.2.1g}$$

The presence of any ammonia in the cyanide waste to be treated by alkaline chlorination results in the formation of chloramines. Due to this reaction, i.e. the formation of chloramines, it is not economically advisable to chlorinate beyond the chlorination breakpoint to a free chlorine residual as chloramines can also destroy free cyanides in a slower oxidation process compared to oxidation by chlorine or hypochlorite. The presence of chloramines inhibits the completion of the reaction resulting in the possible appearance of insoluble metallic cyanides in the effluent (ASTI A. S., 2007). This situation can be avoided by avoiding the breakpoint phenomenon where there is excess chlorine than is required during the oxidation of free cyanides and WADs (ASTI A. S., 2007), and/or by establishing the proper oxidation-reduction potential for the reaction.

8.2.2 Hypochlorite Oxidation Of Cyanides

Following observations from the chlorine oxidation of cyanides where hypochlorite produced by the hydrolysis of chlorine (eqn 8.2.2a) oxidizes cyanides to cyanogenchloride (eqn 8.2.2b) that further hydrolyzes to cyanates (eqn 8.2.2c), a process for the destruction of cyanides using hypochlorite was also conceived (Young & Jordan, 1995). Sodium hypochlorite commonly used for the hypochlorite oxidation of cyanides as a strong alkaline oxidizing agent (Durney, 1984). When used, its alkalinity reduces the demand/addition of a base.

$Cl_{2(g)} + 2OH^- \rightarrow Cl^- + OCl^- + H_2O$ ------eqn 8.2.2a

$CN^- + OCl^- + H_2O \rightarrow CNCl_{(aq)} + 2OH^-$ ------eqn 8.2.2b

$CNCl_{(aq)} + 2OH^- \rightarrow OCN^- + Cl^- + H_2O$ -------eqn 8.2.2c

Hypochlorites also react with thiocyantes (eqn 8.2.2d) and metal-cyanide complexes (eqn8.2.2e) like chlorine to yield cyanates (Young & Jordan, 1995).

$SCN^- + 4OCl^- + 2OH^- \rightarrow OCN^- + SO_4^{-2} + 4Cl^- + H_2$ ------eqn 8.2.2d

$M(CN)_x^{y-x} + xOCl^- + yOH^- \rightarrow xOCN^- + xCl^- + M(OH)_y$ ------eqn 8.2.2e

When hypochlorite is in excess in solution it reacts with cyanates to give nitrogen and carbon dioxide (eqn 8.2.2f).

$2OCN^- + 3OCl^- + H_2O \rightarrow N_{2(g)} + 2CO_{2(g)} + 3Cl^- + 2OH^-$ ------eqn 8.2.2f

Justification for the preferential usage of hypochlorite rather than chlorine for cyanide treatment does not rest on the difference of chlorine demand but rather on the lime consumption in the two processes. Looking at eqns 8.2.2(g, h, I, and J), the consumption of chlorine for the chlorine process and for the hypochlorite process is the same, but caustic is required for the oxidation of cyanides by chlorine (eqn h) but zero amount of caustic is required for the oxidation of cyanides by hypochlorite (eqn i). In eqn 8.2.2g one molecule of chlorine is required for the production of one hypochlorite molecule as well as one molecule of hypochlorite is required for the production of one molecule of sodium hypochlorite eqn 8.2.2h.

$Cl_2 + H_2O \rightarrow HOCl + HCl$ ------eqn 8.2.3.g

Or sodium hypochlorite, which is made from chlorine gas, water, and caustic:

$HOCL + NaOH \rightarrow NaOCI + H_20$ ------eqn 8.2.2h

Therefore, using chlorine for oxidation of sodium cyanide gives, eqn 8.2.2I:

$CI_2 + 2NaOH + NaCN \rightarrow NaCNO + 2NaCI + H_2O$ --eqn 8.2.2I

or when hypochlorite is used for the oxidation of sodium cyanide eqn 8.2.2J:

$5NaOCI + H_2O + 2NaCN \rightarrow 2\ NaHCO_3 + N_2 + 5NaCl$ ------eqn 8.2.2J

Addition of lime to raise the pH above 8.5 is because at lower pH values toxic cyanogen chloride is produced instead of the less toxic cyanate. The extra quantity in the reactants in both eqn 8.2.2I and eqn 8.2.2J is the added caustic soda (NaOH) in eqn 8.2.2I. This is because hypochlorite can function as a base for neutralizing the acid formed, thereby eliminating the caustic demand for the process and it also hydrolysis the cyanides to cyanates (Young & Jordan, 1995; ASTI A. S., 2007). Hypochlorite has 50% neutralizing capacity of lime. This makes the use of hypochlorite economically attractive than chlorine application especially when dealing with small waste amounts.

Advantages/Disadvantages of Alkaline Chlorination

I. **Advantages**;

1) The process does not need the application of a catalyst.

II. **Disadvantages**;

1) The process is very expensive due to a very high consumption of chlorine. This increases the cost of reagents and makes the process expensive. This high

consumption results from the fact that thiocyanates are the cyanide species most susceptible to chlorination and therefore are first attacked before any other cyanide species (Huiatt, 1984) whereas in the sulfurdioxide process they are the last to be attacked.

2) The formation of toxic chlorine derivatives such as cyanogen chloride makes the process not very attractive. Cyanogen chloride is heavier than air and can accumulate in a low-lying area where it may cause throat and eye irritation (Moran R. E., 2000). The cyanogen chlorides along with any residual chlorine can be toxic to aquatic inhabitants (Huiatt, 1984).
3) Difficult for application for slurry treatment.
4) Cannot handle strong acid dissociable cyanide complexes. e.g. cyanide complexes with iron, cobalt, silver and gold.
5) The presence of any organic matter increases chlorine consumption.
6) The cyanide is not recovered and therefore cannot be recycled.

Despite the wide spread use of the various chlorine oxidation processes, the degree of care exercised over chlorine concentrations and to avoid the formation of toxic and biologically persistent organochlorine compounds, there is still the generation of toxic by-products often requiring further/additional treatment (Invgvorsen et al. 1991).

8.3 Hydrogen Peroxide Process

Introduction

This is the oxidation of cyanide (CN^-) to cyanate (OCN^-) by hydrogen peroxide. Hydrogen peroxide is a stronger oxidant than oxygen but weaker than ozone. It is preferred as an oxidant for the treatment of cyanide wastes because it is cheap, water soluble, and easy to handle and store (Young & Jordan, 1995). This method has long been applied in treating cyanide wastes (Mehmet et al. 2005). The process was applied mainly for treatment of cyanide waste batch solutions since it was difficult to treat slurries with this method (Logsdon et al. 1999). Initial attempts at using hydrogen peroxide for treatment of cyanide slurries showed that the consumption of peroxide was far above estimates from the reaction stoichiometry (EPA C. , 2002; Botz M. , 1999; EPA:US, 1994). The continuous flow system for peroxide oxidation of cyanide also known as the Degussa process was designed by DEGUSSA AG in Germany and the first industrial scale trial was done at a gold mine owned by Ok Tedi Mining Limited in Papua New Guinea from November 1983 until March of 1984 (Knorre & Griffiths, 1984). Salts of transition metals e.g. copper, vanadium, tungsten or silver can be used as catalysts for the process (Khodadadi et al. 2005), at concentrations of 5-50 mg/L.

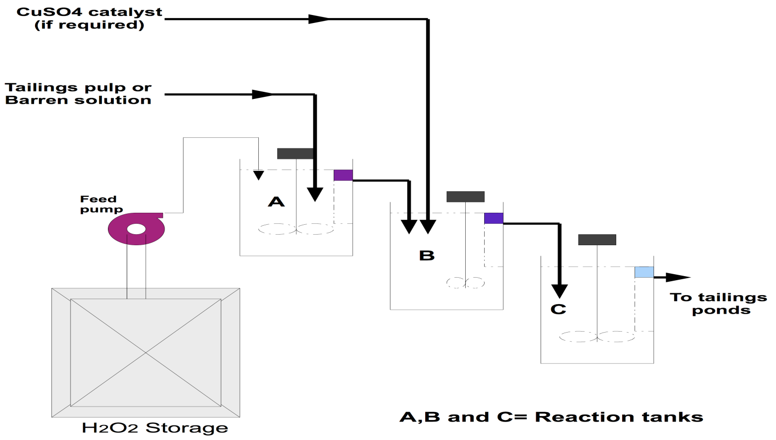


Figure 8.3: Hydrogen peroxide cyanide treatment flow diagram. Adapted from (Dzombac & Ghosh, 2006).

The advantages of the process include the facts that there is no production of environmentally harmful by-products (meaning salts produced are soluble and therefore can't persist in the environment giving rise to other pollution problems (Iordache et al. 2003)), there is no addition of other chemicals/substances which might result in salting-up of the process effluent thereby polluting open water ways and the remainder of any excess peroxide readily decomposes into harmless substances, water and oxygen (Knorre & Griffiths, 1984; Griffiths et al. 1987). The oxidation of cyanide by hydrogen peroxide is a single step reaction producing a cyanate which subsequently hydrolyses to give a carbonate and ammonium ions. Using hydrogen peroxide for the treatment of cyanide wastes is good when the initial cyanide concentration is low. This process oxidizes free cyanides and WAD cyanides to cyanates. The metals released from the WAD cyanides are precipitated as metal hydroxides while stable iron-cyanide complexes are removed as insoluble copper-iron-cyanide complexes. The decision on whether to use hydrogen peroxide for cyanide waste treatment depends on the reaction time, the temperature, the desired end products, the types and concentrations of the various cyanide compounds in the waste and the economics of the system (Khodadadi et al. 2005). Disadvantages of the hydrogen peroxide treatment of cyanides include, the formation of ammonia which is harmful to marine inhabitants especially fish, and the high cost of purchasing and handling hydrogen peroxide (EPA:US, 1994).

8.3.1 Peroxide Oxidation Chemistry

Hydrogen peroxide is added as a liquid to tailings slurry in a reaction chamber where it oxidizes free cyanides and weak acid dissociable cyanide complexes to cyanates. This reaction can be violent and explosive even resulting in fires if any combustible material (wood, old cloths, rags e.t.c.) is present. It is always recommended that specially designed tanks and handling equipment should be used (EPA:US, 1994). The reaction goes are follows eqn 8.3.1a,

$$CN^- + H_2O_2 \rightarrow OCN^- + H_2O \qquad \text{------eqn 8.3.1a}$$

The cyanate formed hydrolyses to a carbonate and ammonia in the presence of excess peroxide in solution (eqn8.3.1b).

$$OCN^- + 2H_2O \xrightarrow{\text{Excess peroxide}} CO_3^{2-} + NH_4^+ \qquad \text{----eqn 8.3.1b}$$

Critical to the rate of the reaction at ambient temperatures is the rate of dissociation of the metal-cyanide complexes, which also depends on the pH of the solution and the amount of excess hydrogen peroxide given that there is enough copper sulphate ($CuSO_4.5H_2O$) in solution to catalyse the reaction. Addition of a catalyst may not be necessary in cases when one of the metal catalysts is present in enough quantity in the effluent, as often is the case with dissolved copper salts in mine tailings (Mehmet et al. 2005; Mudder et al. 2001). Introducing a copper solution of 10mg/l concentration increases the rate of the reaction 2 to 3 folds. The presence of 20% excess hydrogen peroxide increases the rate of the reaction by 30%. There have been reports of an increase in the rate of the cyanide oxidation by increasing the temperature in the system but this can be misleading (Khodadadi et al. 2005). Care must be taken here given that the boiling point of free cyanide is relatively low (25.75°C), increasing the temperature might result rather to lose of free cyanides to the atmosphere than for the free cyanides being oxidized to cyanates. Khodadadi et al. 2005, concluded that the concentration of hydrogen peroxide in solution, the pH of the solution and the temperature of the solution are the most important rate determining factors. The pH of the solution is controlled by the application of lime.

The peroxide oxidation of weak acid dissociable (WAD) cyanide complexes is represented by the equation eqn 8.3.1c,

$$Me(CN)_4^{2-} + 4H_2O_2 + 2HO^- \rightarrow Me(OH)_2 + 4OCN^- + 4H_2O \quad \text{------eqn 8.3.1c}$$

Where Me = Cu, Ni, Zn, Cd e.t.c.

Examples of WADs include; $Cd(CN)_4^{2-}$, $Zn(CN)_4^{2-}$, $Cu(CN)_4^-$, $Cu(CN)_4^{2-}$, and $Cu(CN)_4^{3-}$

The presence of some heavy divalent metal ions e.g. copper ions assist in the precipitation of very stable cyanide complexes which can not be oxidized by hydrogen peroxide. The stable cyanide complexes precipitated as double salts due to the presence of an appropriate divalent ion include; $Au(CN)_2^-$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and $Co(CN)_6^{4-}$ (Griffiths et al. 1987). The precipitation of iron-cyanides follows the following reaction since ferrocyanide is not oxidized to ferricyanide in the process (eqn 8.3.1d).

$$2Cu^{2+} + Fe(CN)_6^{4-} \rightarrow Cu_2Fe(CN)_6 \quad \text{------eqn 8.3.1d}$$

Because this method does not treat SADs it is sometimes referred to as a selective detoxification process (Griffiths et al. 1987). Depending on the pH in the reaction chamber, the cyanates further slowly hydrolyze giving either carbon dioxide and ammonium (eqn 8.3.1e) or a carbonate and ammonia (eqn 8.3.1f).

$$CNO^- + 2H^+ + H_2O \rightarrow CO_2 + NH_4^+ \quad \text{------ eqn 8.3.1.e}$$

$$CNO^- + OH^- + H_2O \rightarrow CO_3^{2-} + NH_3 \quad \text{------- eqn 8.3.1f}$$

The amount of hydrogen peroxide consumed during the oxidation of cyanides is higher than expected. This is attributed to the oxidation of other metal-cyanide complexes present in the solution not considered in the stoichiometric estimations. This will be typical for mine wastes owing to the large variety of cyanide species present in solution. Even when other metal-cyanide complexes are factored in, it is always hard to estimate their concentrations due to the spatial and temporal variations of mineral/metal species within a mine. The oxidation of sulphites (eqn 8.3.1g), thiocyanates (8.3.1h), and also metal ions in low oxidation states (8.3.1i) can help explain the more than expected consumption of hydrogen peroxide (Griffiths et al. 1987).

Peroxide oxidation of sulphites (eqn 8.3.1g).

$$S^{2-} + H_2O_2 \rightarrow S + 2OH^- \qquad \text{------ eqn 8.3.1g}$$

Peroxide oxidation of thiocyanides (eqn 8.3.1h).

$$SCN^- + H_2O_2 \rightarrow S + OCN^- + H_2O \qquad \text{------ eqn 8.3.1h}$$

Peroxide oxidation of ions in lower oxidation states (eqn 8.3.1i).

$$2Cu^+ + H_2O_2 \rightarrow 2Cu^{2+} + 2(OH)^- \qquad \text{------ eqn 8.3.1i}$$

As a result of such uncertainties, a continuous flow system was designed only with the assistance of a parallel laboratory size process from where the various system parameters are monitored for adjustment in the main reaction chamber (Knorre & Griffiths, 1984). This parallel system makes it possible for any adjustments in response to changing conditions in the reaction chamber to be made in good enough time as not to permit any malfunctioning of the process. Any hydrogen peroxide remaining after oxidation of free cyanides and WADs degrades through hydrolysis.

8.3.2 Role Of pH In Peroxide Oxidation Of Cyanides

There is a great deal of literature on the impact of pH on the rate of oxidation of cyanides by hydrogen peroxide. Investigations have been done for varying pH ranges but often falling between pH 8 and 11. (Mehmet et al, 2005; khodadadi et al 2005).

8.4 Ozone Treatment Of Cyanides

Introduction

A German chemist C.F. Schonbein discovered ozone in 1840. It is a powerful oxidizing agent (Oxomax, 2005; Gogate & Pandit, 2004), only next to OH radicals (Baratharaj, 2009). Ozone is very unstable in water, and depending on the water quality (pH and natural organic matter) the half-life of ozone ranges from a few seconds to hours (Gunten, 2003). Ozone reacts with most species containing multiple bonds (such as C=C, C=N, N=N, C≡N e.t.c.), but will also react with single bonded species C-C, C-O, O-H at lower rates because there is simply no easy chemical pathway for the oxidation of single bonded species to occur faster (Gogate & Pandit, 2004). With cyanide, the reaction is radical and in a chain series, '*In general, electron-donating groups enhance the oxidation by ozone whereas electron-withdrawing groups reduce the reaction rates. Furthermore, the kinetics of direct ozone reactions depend strongly on the speciation (acid-base, metal complexation)'* (Gunten, 2003).

Ozone is a poisonous pale blue gas with a sharp, cold, irritating odour and heavier than air. At concentrations above 0.01ppm in the air, it is detectable by most humans (Rakovsky et al. 2009). Exposure to between 0.1 and 1.0 ppm concentration of ozone can result in headaches, itching eyes and irritations in the respiratory tract (Rakovsky et al. 2009). Onsite production of ozone is advisable as ozone is thermodynamically unstable, very reactive and spontaneously reverts to oxygen making transportation of ozone very difficult (Salama, 2000). Ozone is 5 times more oxidizing than oxygen and about twice more oxidizing than chlorine making it more reactive with other elements and compounds (Australia Environment, 2003; Oxomax, 2005). It has an oxidation potential of -2.07V only after fluorine (-3.06), hydroxyl radicals (-2.80), and atomic oxygen (-2.42), which is greater than that of hypochlorite (-1.49V) or chlorine (-1.36V) (Salama, 2000). Ozone remains a very powerful oxidant because it can act on its own or will decompose in water to give hydroxyl radicals that are the strongest oxidants in water (Gunten, 2003). It is capable of oxidizing all metals (except Pt, Au, and Ir), all non-metals to their highest oxidation states and organic and inorganic compounds under mild conditions (Rakovsky et al. 2009). Its high reactivity compared to other oxidants (e.g. 20 t0 50 times more than chlorine (Oxomax, 2005)) and high kill rate of microorganisms (Fungi, Bacteria & Viruses (Rakovsky et al. 2009)) make it the preferred biocide in water treatment. Due to the aforementioned characteristics only small quantities of ozone are needed to perform the same as larger amounts of other oxidants and ozone treatment requires reduced retention time and storage facilities (Oxomax, 2005).

8.4.1 Chemistry Of The Ozonation Process

Cyanide oxidation to cyanate by ozone occurs at a pH of 9 to 10 (Baker, 1970, 1985). It is a spontaneous reaction with the rate of reaction only limited by the transfer of the gas to the liquid phase (Carrillo-Pedroza & Soria-Aguilar, 2001). It is believed to occur following one of two major pathways, the simple pathway (eqn 8.4.1a) or the catalytic pathway (eqn 8.4.1b).

$$\mathrm{CN^- + O_{3(aq)} \xrightarrow{\text{without catalyst}} OCN^- + O_{2(aq)}}$$ ----------eqn 8.4.1a

$$\mathrm{3CN^- + O_{3(aq)} \xrightarrow{\text{With catalyst}} 3OCN^-{}_{(aq)}}$$ ----------- eqn 8.4.1b

Looking at the simple reaction path it can be deduced that the reaction rate is linear with one mole of ozone consumed by one mole of cyanide. Therefore the reaction rate is limited by the rate of addition of ozone or simply by the ozone concentration, '*On* *the other hand, cyanide decay linearly with time which means that cyanide oxidation rate is constant, that is to say, that follows a zero order reaction where the cyanide destruction velocity increasing proportionally with the ozone addition rate, the oxidation of cyanide is a first order reaction with respect to ozone and zero order with respect to cyanide'* (Carrillo-Pedroza & Soria-Aguilar, 2001). An advantage of the simple pathway is that oxygen is released which can further oxidize cyanide (Young & Jordan, 1995). The catalytic pathway is more efficient and has been observed at high addition rates, although very rarely (Young & Jordan, 1995).

$$2OCN^- + 3O_{3(aq)} + H_2O \rightarrow 2HCO_3^- + N_{2(g)} + 3O_{2(aq)} \quad \text{------ eqn 8.4.1c}$$

Oxidation rate, g/l per min=[190.53+/-15] [ozone addition rate, g/min] (Carrillo-Pedroza & Soria-Aguilar, 2001).

The cyanate formed from equations 8.4.1a and 8.4.1b, hydrolyses in the presence of excess ozone yielding bicarbonate and nitrogen (eqn 8.4.1c). The addition of ozone is encouraged by the fact that ozone does not oxidize the cyanate to nitrite or nitrate as neither nitrification nor denitrification are needed (Young & Jordan, 1995). Further addition of ozone, converts cyanates to nitrogen gas and carbonate (eqn 8.4.1d).

$$2OCN^- + O_{3(aq)} + H_2O \rightarrow 2HCO_3^- + N_{2(g)} \quad \text{--------(eqn 8.4.1d)}$$

Ozone oxidation of cyanides is faster than ozone oxidation of cyanates resulting in the presence of cyanates at the end of the reaction (Carrillo-Pedroza & Soria-Aguilar, 2001).

Ozonation is effective against free cyanides, WADs and thiocyanates but not against SADs (Huiatt, 1984). Hydroxide readily decomposes ozone resulting in a slow down of ozone oxidation of cyanide species at pH levels above 11. This makes it hard for the operator, because maintaining a pH above 11 is necessary to avoid generation and volatilization of the poisonous hydrocyanic gas for safety purposes. Notwithstanding, the oxidation of cyanides to cyanates by ozone is done at pH between 10 and 12 where the reaction rate is good and relatively constant (USEPA U. S., 2000). For Ozonation carried out following the simple oxidation path (eqn 8.4.1a), the average retention time for complete oxidation of cyanide to cyanate is between 10 to 30 minutes. The hydrolysis of cyanate to bicarbonate and nitrogen is a much slower process.

The oxidation of cyanides to cyanates by ozone can be catalyzed by nickel or copper. These can sometimes be in good enough quantity in the solution as it is the case with most mine wastes solution or it can be added. Unfortunately, both nickel and copper have negative affects on the oxidation of cyanates (USEPA U. S., 2000). SADs are only partially being oxidized by ozone but in combination with ultra-violet light (uv-oxidation) SADs can be completely oxidized (USEPA U. S., 2000).

8.5 INCO Process

Introduction

This is a method for the selective oxidation of cyanides in industrial waste effluents (Inco EPA 1993) to cyanates using a mixture of sulphur dioxide and air in the presence of a catalyst at a controlled pH (Scott, 1984). The process treats all forms of cyanides (Free cyanides, WADs and SADs). Free cyanides and WADs are oxidized to cyanates and the metals involved in the WADs complexes are precipitated as hydroxides. As for the SADs e.g ferric cyanide complexes, these are reduced to the ferrous state and precipitated as insoluble double salts of the respective metals e.g. copper, zinc etc (Terry et al. 2001).

The Inco Process was invented at the International Nickel Corporation (INCO) Laboratories in the early 1980’s (Robbins at al. 2001). Commercialization of the process began in the late 1970s, and it was patented in 1984 in Canada. A major advantage of the Inco process is that, the oxidation of cyanide occurs before thiocyanide oxidation making the process economical compared to other methods for the treatment of effluents derived from the cyanidation of sulphidic minerals (Scott, 1984). Scott 1984 further warned that despite this being an advantage, it turns out to be a disadvantage if the removal of thiocyanides becomes necessary.

There are two versions of this process. There is one as described above which was developed by INCO and there is a second version, which was developed at Heath Steel Mines Ltd. and patented by Noranda Incorporated. Both processes are similar in methodology but vary in operating procedure. Despite their similarity in end results, the INCO process is the most widely used in tailings treatment prior to disposal (USEPA U. E., 1993; Terry et al. 2001).

8.5.1 Differences Between The Two SO_2 Processes

In the sulphur dioxide process of INCO, both free and complexed cyanides are oxidized to cyanate in the pH range 7 to 10 (Scott, 1984). WAD cyanides are converted to cyanates and the residual metal ions are precipitated as their respective hydroxides. Any iron cyanide complexes present are converted from the ferric to the ferrous forms and precipitated as insoluble double salts. These ferrous forms are sparingly soluble at pH values below 9.5. The process uses sulphur dioxide as a gas, sulfite as a salt or as a solution in combination with air as an oxidant. To obtain optimum pH for the reaction lime is needed for pH regulation and soluble copper is used as a catalyst (Scott, 1984; Lemos et al. 2006). In the sulphur dioxide process designed by Noranda Incorporated, only pure sulphur dioxide is used. The main difference is that the Noranda process is best suited for sites with high concentration of antimony and arsenic (EPA:US, 1994).

8.5.2 Inco-Process Chemistry.

This process can be divided into four main steps although all occur simultaneously.

1) Oxidation of cyanides:

There is first the oxidation of free cyanides and WAD cyanide complexes to cyanates releasing the metals. The quantity of SO_2 added depends on the total cyanide in the barren bleed and also on the pH demand. This reaction requires copper to serve as a catalyst (Equation 8.5.2a).

Oxidation of free cyanides:

$CN^{-} + SO_2 + O_2 + H_2O \xrightarrow{\text{copper as catalyst}} OCN + H_2SO_4$ ------eqn 8.5.2a

Oxidation of WADs:

$Me(CN)_4^{2-} + 4SO_2 + 4O_2 + 4H_2O \xrightarrow{Cu^{2+}\text{(catalyst)}} 4OCN^{-} + 4H_2SO_4 + Me^{2+}$..eqn 8.5.2b

Where $Me^{2+} = Zn^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}$

The Inco process is done at a pH of between 8 and 9. As a consequence of the formation of sulphuric acid in both equation 8.5.2a and eqn 8.5.2b there is a drop in the pH within the system from the initial pH for reaction. There is a need to reverse the pH shift to the desired value and this is done by addition of an alkaline solution. The metal ions liberated at this oxidation stage precipitate as hydroxide salts while iron-cyanide complexes are precipitated as insoluble double salt.

2) Neutralization:

This is the addition of lime to neutralize the acid formed in the reaction chamber consequently pushing the pH to a desired level.

$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O$ ------ eqn 8.5.3c

3) Precipitation of metal hydroxides;

$Me^{2+} + Ca(OH)_2 \rightarrow Me(OH)_{2(precipitated)} + Ca^{2+}$ ------ eqn 8.5.2d

$2Me^{2+} + Fe(CN)_6^{2} \rightarrow MeFe(CN)_{6(precipitate)}$ ------ eqn 8.5.2e

4) Copper catalyst in solution;

SO_2 / CN_{WAD} = 46,2 g/g (Saarela & Toivo, 2004))

In this process copper plays two important roles. It catalyses the oxidation reaction and also assists in the precipitation of the ferrocyanide. Copper sulphate ($CuSO_4$) solution is best suited for these roles. The free cyanide in the solution quickly complexes with the copper in $CuSO_4$ giving Copper(I) cyanide complex (Cu(CN)), which is believed to be the catalyst for the oxidation of CN^- to CNO by SO_2 and O_2 (Huiatt, 1984).

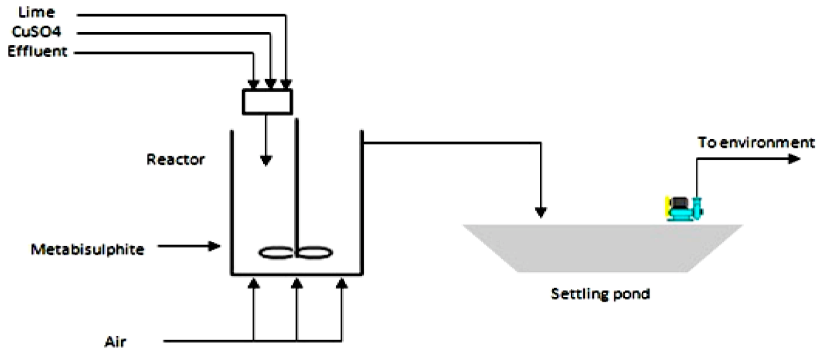


Figure 8.5.2: Inco process flow diagram (http://www.goldmetallurgy.com/)

The INCO process has proven resilient to a variety of effluents. This can be credited to the flexibility of the process. Based on the spatial and temporal variations in effluent characteristics, reaction variables can be adjusted as need arises to accommodate these variations. Gold mill effluents so far pose the greatest challenge in terms of effluent variability. Added to the free cyanides contained in gold mill effluents, variable amounts of thiocyanate, and mixtures of copper, nickel, iron, and zinc cyano-complexes are present. The Inco process is also efficient for the removal of metals such as Cu, Fe, Ni and Zn. The aforementioned metals are removed obtaining residual concentrations of less than 1mg/litre with occasional higher concentrations for Cu and Zn due to their slow rates of hydrolysis. Experimental results show that for a tailings effluent containing 40 to 2,000mg/l of CN_{total}, residual CN_{total} in the effluent of the process can be less than 0.5mg/litre and are about 1mg/litre (Huiatt, 1984).

With sufficient copper to catalyse the oxidation process, the rate-limiting factor for the Inco Process is the rate of oxygen transfer to the solution. The amount of copper needed for catalysis can be estimated/calculated from the stoichiometry of the reaction. Aerating and agitating the solution in the reaction chamber is paramount if optimum oxidation rate is desired. Critical to obtaining optimum oxidation rates is the relationship between air volume and tank volume.

The Inco process can treat cyanide compounds from a single source or a mixture of cyano-compounds from different sources. This implies, barren solutions can be combined with tailings and treated together. In this situation the following factors will have to be considered; plant operation, equipment or space available, reagents available, effluent composition, solids composition and process control strategy. '*In general, conceptual engineering by Inco is possible from estimates of these variables, but detailed engineering should be undertaken only after empirical response studies for a particular effluent. Likewise, process control strategy is quite effluent specific. Numerous options are available and should be evaluated during laboratory trials'* (Huiatt, 1984).

8.5.3 Factors That Affect The Inco Process

i) Role of pH

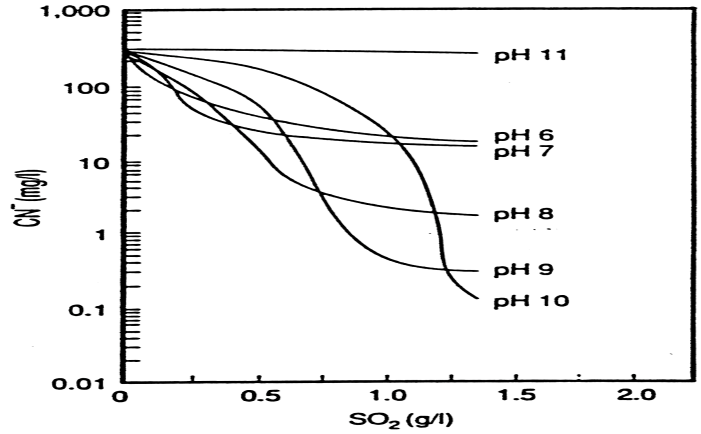


Figure 8.5.3a: pH effect on oxidation rate (Mudder et al. 2001).

An observation of fig 8.5.3a shows that the oxidation of cyanides is best when the pH is 10.

ii) Effect of copper

The removal kinetics and the efficiency of the process are highest when the concentration of dissolved copper in the reaction chamber is 50mg/l as can be seen on figure 8.5.3b.

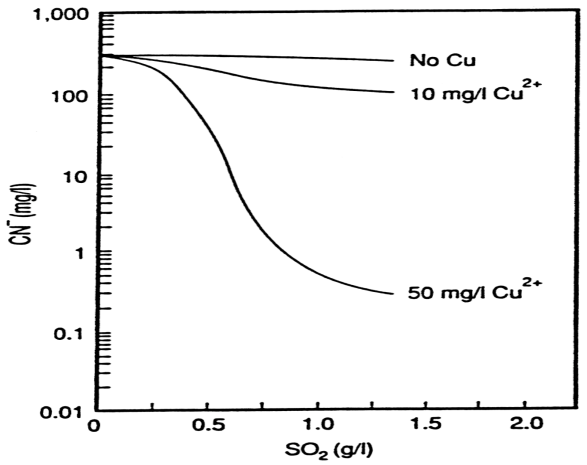


Figure 8.5.3b: Effect of copper concentration on the oxidation rate (Mudder et al. 2001).

This implies that in situations where the concentration of dissolved copper (X_{Cu}) in the effluent is enough (i.e. where $X_{Cu} \geq 50$mg/l), there will not be a need for the addition of extra copper.

iii) Source of sulphur dioxide;

Selecting a source for sulphur dioxide depends on the location of the treatment plant, the cost of the reagents, and the process control strategies. The location of the treatment plant is critical in the treatment of mine effluents. This is because most mines are situated in remote areas and this normally poses enormous transportation challenges. While elemental sulphur remains the cheapest source for sulphur dioxide generation, the cost of a sulphur roaster for the generation of sulphur dioxide may make production of sulphur dioxide expensive and unattractive for small-scale treatment plants. However, depending on the accessibility of the treatment site, the cost of transporting sulphur dioxide by rail or road can be very low.

There is hardly any tonnage price discrepancy between liquid sulphur dioxide and solid sulphites such as sodium sulphite (Na_2SO_3) or sodium metabisulphite ($Na_2O_2S_5$). Application of the sulphite has added advantages, as these sulphites possess an acid neutralising quality even though not as much as for lime. Notwithstanding, the use of the sulphites reduces by approximately 50% the amount of lime needed for acid neutralization. Other added advantages for the application of sulphites (especially sodium sulphite) are that they are very soluble in water (250g/l) and are safer to handle. The application of ammonium bisulphite (NH_4HSO_3) as a sulphur dioxide source is done only after a well thought through impact assessment of the generated ammonia on the process effluents has been carried out.

Advantages/Disadvantages Of Inco Process

Below is a tabulated summary of the advantages and the disadvantages of the Inco process.

Table 8.5.3: Advantages and disadvantages of Inco Process (Mudderet al. 2001).

Advantages	
1	The process has been proven in numerous full-scale applications to yield low effluent cyanide and metal concentrations.
2	The process is effective in treating slurries as well as solutions.
3	The process is suitable for batch or continuous treatment.
4	All forms of cyanide including stable iron cyanide complexes are taken out of solution.
5	Capital and operating cost are comparable with other chemical treatment processes.

Disadvantages	
1	During the treatment of waste with high amounts of cyanides, the reagent costs and the cost of electricity can be very high.
2	Cyanide is not recovered
3	There is often a very high levels of sulphates in the treated solutions.
4	Additional treatment may be necessary for the removal of iron cyanide, thiocyanate, cyanate, ammonia, nitrate and/or metals for solutions to be discharged to the environment.

8.6 Photolytic Degradation

Introduction.

Photolytic reactions are characterized by a free radical mechanism initiated by the interaction of photons of a particular energy level with the molecules of chemical species with or without a catalyst (Gogate & Pandit, 2004). This interaction results in a transfer of energy from the electromagnetic radiation to the molecules, enhancing reduction/oxidation reactions by supplying energy to catalyze the electron transfer processes involved (Young & Jordan, 1995). Photo degradation is best understood when light is treated as bundles of particles with specific and discrete energies (Qasim, 1997). As it is clearly stated in Qasim 1997 that, *'the reason spectroscopic techniques can ascertain the structure of compounds is because different structures absorb energies at specific frequencies or wavelengths. In other words, absorbed energy is quantized by having discrete energy levels and is specific to the particular structure. The intensity (a measure of molar absorptivity of absorbed light) is proportional to the amplitude of the wave and is also specific to the wavelength at which absorption takes place, further, this intensity is a measure for determining whether the electronic, vibrational, or rotational transition is allowed'*. In photo initiated chemical reactions, chemicals absorb electromagnetic radiation thereby gaining energy to promote electron(s) from their ground state valence band to the excited state conductance band making it/them susceptible to attack from chemicals available in the environment. This process creates a hole, h^+, in the valence band and an excited electron, e^-, in the conductance band (Young & Jordan, 1995). This is only possible when the UV radiation possesses energy equal to or greater than the band gap of the chemical or in a situation where a catalyst is used, greater than the band gap of the semiconductor.

In photo-reduction the compound that absorbs the light energy accepts the excited electrons from another species to fill its valence vacancy, while in photo-oxidation processes the energy-absorbing compound donates electrons to another species to fill their electron vacancy/demand.

There are two basic requirements that must be fulfilled for a photo-initiated chemical reaction to occur (Oelsner et al. 2001)

1) The molecule (chemical species) must absorb light energy (photons)

2) Radiation energy must match energy difference of ground and excited state i.e. the amount of energy in the photons should be enough to break the chemical bond.

After the absorption of light photons from ultraviolet, visible light or from both, the outer electrons of molecules become stimulated/excited and begin to vibrate. The strength of the vibration, which depends on the amount of energy absorbed from light photons may result in the dissociation of the molecule. This can occur within a time frame of 10-15 seconds.

8.6.1 Cyanide Photolysis/Photo-Catalysis

Direct photochemical degradation or photolysis of cyanide is possible for WADs, SADs and for free cyanides. Cyanide photolysis has been reported as being partly responsible for the reduction of cyanide amounts in tailings ponds (Botz & Mudder, 2000; Davies et al. 1998; Simovic & Snodgrass, 1999). This is especially possible for ferric and ferrous cyanide complexes. The following reaction mechanisms have been proposed for the photo-oxidation of iron cyanide complexes (Eqns 8.6.1a; 8.6.1b and 8.6.1c),

$$Fe(CN)_6^{3-} + H_2O \xrightarrow[\text{UV radiation}]{\downarrow\ \downarrow\ \downarrow} \left[Fe(CN)_5H_2O\right]^{2-} + CN^- \quad \text{------ eqn 8.6.1a}$$

$$\left[Fe(CN)_5H_2O\right]^{2-} + 2H_2O \xrightarrow[\text{UV radiation}]{\downarrow\ \downarrow\ \downarrow} Fe(OH)_{3(S)} + 5CN^- + 3H^+ \text{----eqn 8.6.1b}$$

$$Fe(CN)_6^{3-} + 6H_2O \xrightarrow[\text{UV radiation}]{\downarrow\ \downarrow\ \downarrow} \left[Fe(H_2O)_6\right]^{3+} + 6CN^- \quad \text{-----eqn 8.6.1.c}$$

These reaction pathways have also been seen for cyanide-cobalt [$(Co(CN)_6)^{3-}$] complex which is the strongest cyanide complex. The above reactions occur at wavelengths approximately 420nm (Young & Jordan, 1995). In these reactions, there is the liberation of free cyanides that is thought to explain why in cyanide spills in rivers there is massive fish kill during the day than in the night. The potential for iron-cyanide complexes to breakdown through photolysis calls to question the addition of ferric and ferrous cations to cyanide waste to form strong/stable cyanide complexes as a remediation method because the photo-degradation of ferric and ferrous cyanides reverses in the dark (ICMI, 2011).

Experiments conducted by Oelsner et al 2001, showed that the concentration of total cyanides reduced by about 90% after exposing a 2000ml solution of iron-cyanide complex for 14 days to a UV radiation with a wavelength of 253nm or visible light induced photolytic degradation of cyanide complexes. Further tests showed that there was no significant photolytic degradation in both cases after three days. This amount was corrected as the loss of cyanide through heating which was estimated to have contributed 30-35% of reduction in total cyanide, was not subtracted when calculating the total lose of cyanide due to photolysis in the experiments.

The photolytic degradation of iron-cyanide complexes is visually apparent as the colour of the solution changes from colourless to intense yellow-brown indicating the hydration of the Fe(III) following the collapse of the cyano-complex. The pH of the medium also rose by 0.3 to 0.4 points indicating the hydrolysis of the cyanide ion that generates hydroxyl ions (OH^-) causing the pH to rise.

8.6.2 Homo/Heterogeneous Photolysis Of Cyanides

Since many of the previously discussed chemical oxidation methods cannot remediate SADs, there have been attempts to combine these processes so as to obtain a noble method. Free cyanides are not remediated in photolysis while SADs are not remediated by most oxidation methods. Most common amongst these attempts has been the combination of photolysis with ozonation, peroxide oxidation, and chlorination, for the simple reasons that photolysis does not require the introduction of a chemical and so no side reactions of the chemicals are expected, photolysis will decrease the consumption of the reagents and finally that photolysis cracks the strong cyanide complexes releasing free cyanide which can be attacked by the oxidizing agents.

Homogenous photolysis of cyanides is not attractive as there is consumption of the photosensitizers and these need to be added in excess to ensure that the process goes to completion, i.e. the complete oxidation of the cyanides. This makes these processes expensive. Added to the cost of reagents there is also the generation of effluents containing excess reagents that will require further treatment thereby increasing the cost. This may seem simple when discussing only about peroxide and ozone as these can be left to decompose to water and oxygen over a period of time in a holding pond. However such a simple solution is not available for other chemicals (photosensitizers). A solution to this is the use of catalytic photosensitisers, which can be recycled (Young & Jordan, 1995). There are two main ways of applying the catalysts; they can either be in the same state as the chemical to be treated in which case it is called homogenous photocalysis or that the catalyst and the chemical to be treated are in two different states in which called it will be called heterogenous photocatalysis. The terms homogenous or heterogenous only indicate whether the photocatalyst and the chemical to be treated are in the same physical state or not.

8.6.2.1 Cyanide Oxidation Through Homogenous Photolysis With Ozone

A combination of the ozonation and the photolytic processes treats free cyanides, WADs and SADs. The UV light can be supplied artificially or from a natural source (Sunlight). Once ozone in solution absorbs UV radiation it dissociates giving oxygen and hydroxyl radicals (Equation 8.6.2.1a). Increasing the UV intensity, the ozone concentration (flow rate) and temperature of the solution increases the rate of cyanide degradation (Young & Jordan, 1995).

In this process there is the oxidation of cyanides by ozone (eqns 8.4.1b) but this process is dominated by the oxidation of cyanide by the hydroxyl radicals (eqn 8.6.2.1b) formed in the process which are stronger oxidizers than ozone.

$$H_2O + O_{3(aq)} \xrightarrow[\text{UV radiation}]{\downarrow\ \downarrow\ \downarrow} 2OH + O_{2(aq)} \qquad \text{------ eqn 8.6.2.1a}$$

$$CN^- + 2OH \xrightarrow[\text{UV radiation}]{\downarrow\ \downarrow\ \downarrow} OCN^- + H_2O \qquad \text{------ eqn 8.6.2.1b}$$

Because the hydroxyl radicals formed in eqn 8.6.2.1a do not posses any charge they have a higher affinity for electrons than ozone and so will attack any chemicals including thiocyanates, WADs and SADs oxidizing them in the process. The cyanates formed are then hydrolyzed according to the following reaction path, eqn 8.6.2.1c:

$$OCN^- + 3H_2O \rightarrow NH_4^+ + HCO^{3-} + OH^- \quad \text{------ eqn 8.6.2.1c}$$

Otherwise the cyanate is degraded by photolytic ozonation to give bicarbonate, and one of nitrogen gas (eqn 8.6.2.1d), nitrite (eqn 8.6.2.1e) or nitrate (eqn 8.6.2.1f)

$$OCN^- + 3OH^+ \xrightarrow[\text{UV raduiation}]{\downarrow\ \downarrow\ \downarrow} HCO_3^- + \frac{1}{2}N_{2(g)} + H_2O. \quad \text{------ eqn 8.6.2.1d}$$

$$OCN^- + 6OH^+ \xrightarrow[\text{UV raduiation}]{\downarrow\ \downarrow\ \downarrow} HCO_3^- + NO_2^- + H^+ + 2H_2O \quad \text{------ eqn 8.6.2.1e}$$

$$OCN^- + 8OH^+ \xrightarrow[\text{UV raduiation}]{\downarrow\ \downarrow\ \downarrow} HCO_3^- + NO_3^- + H^+ + 3H_2O \quad \text{------ eqn 8.6.2.1f}$$

The consumption of ozone is 5 times higher when nitrate is produced. This high reagent consumption makes photo-ozonation very expensive and not attractive as a remediation method.

8.6.2.2 **Cyanide Oxidation Through Homogenous Photolysis Of Hydrogen Peroxide**

Free cyanides, WADs, SADs and thiocyanates can be oxidized by photolysis of hydrogen peroxide (eqn 8.6.2.2a).

$$H_2O_2 \xrightarrow[\text{UV raduiation}]{\downarrow\ \downarrow\ \downarrow} 2HO^- \quad \text{------ eqn 8.6.2.2a}$$

The reaction path of the homogenous photolytic peroxide action on cyanides does not follow the normal peroxide cyanide oxidation reaction pathways for cyanides because eqn 8.6.2.2a occurs very rapidly.

As it can be seen in eqn 8.6.2.2a, the peroxide molecule degrades to hydroxyl radicals on absorption of UV light of a particular wavelength or energy. The hydroxyl radicals then attack cyanide oxidizing it in the process to yield cyanate, which hydrolyzes depending on the amount of excess peroxide present in the solution. For example it might hydrolyze yielding ammonium and bicarbonate ions (eqn 8.6.2.2b).

$$OCN^- + 3H_2O \rightarrow NH_4^+ + HCO_3^- + OH^- \quad \text{------ eqn 8.6.2.2b}$$

Increasing the UV intensity, or the peroxide concentration or the solution temperature increases the rate of reaction.

8.6.3 Heterogeneous Photocatalysis

'*Heterogeneous photocatalysis is based on the use of a source of UV radiation to stimulate a semiconductor material on whose surface the oxidation is carried out*' (Aguado et al. 2002). In heterogeneous photocatalysis, a substance out of phase with the reacting substance (often in liquid phase) is sort that on absorption of light energy promotes electrons from its valence band, across the band gap, to the conductivity band exposing them to attack from neighboring chemical species. These substances referred to as semiconductors promote these electrons creating an electron (e^-) and a hole (h^+) called together electron-hole pair. Owing to their charges both the electron and the hole can initiate redox reactions on the surface of the semiconductor if the reacting species are adsorbed on these surfaces. For the reaction to be continuous, the semiconductor surfaces must be free, implying that products of oxidation or reduction processes occurring on the surface of these semiconductors must immediately move away or be transported away from the semiconductor-surfaces allowing for other reactants to be adsorbed on the surfaces to be able to participate in the reaction(s), and also that these products must not engage in reverse reactions after leaving the semiconductor surface.

$$\text{Conductor} \rightarrow (e^- h^+)\ (x)$$

Three reaction paths have been proposed for the oxidation of cyanides in heterogeneous photocatalysis.

1) The first reaction path is believed to occur through the production of powerful oxidizing hydroxyl (OH^-) radicals which go further to oxidize any cyanides present in the solution (eqn 8.6.3a). Production of the hydroxyl radicals occurs through the reduction of water adsorbed on the semiconductor surfaces (eqn 8.6.3a) or the reduction of adsorbed hydroxide by the holes (h^+) in the valence band (eqn 8.6.3b).

$H_2O + h^+ \rightarrow OH^- + H^+$ ------ eqn 8.6.3a

$OH^- + h^+ \rightarrow OH^-$ ------ eqn 8.6.3b

2) In the second proposed reaction path, dissolved oxygen reacts with the excited electrons (eqn 8.6.3c) in the conduction band through a superoxide(O^-_2) as intermediate.

   $O_{2(aq)} + e^- \rightarrow O_2^-$ ------ eqn 8.6.3c

   $2O_2^- + 2H^+ \rightarrow 2OH^- + O_{2(aq)}$ ------ eqn 8.6.3d

The hydroxyl radicals produced in both reaction stages (eqn 8.6.3b and eqn 8.6.3d) above then react with cyanides as follows (eqn 8.6.3e),

$CN^- + 2OH^- \rightarrow OCN^- + H_2O$ ------ eqn 8.6.3e

The resulting cyanate hydrolysis as follows (eqn 8.6.3f),

$OCN^- + 3H_2O \rightarrow NH_4^+ + HCO_3^- + OH^-$ ----- eqn 8.6.3f

Or the cyanate gets involved in reactions with the hydroxyl radical similar with eqns (8.6.2.1 d, e or f) resulting in the formation of nitrogen gas, nitrite and/or nitrate. The first and second cyanide oxidation paths are effective in treating thiocyanates, WADs and SADs. Any ammonia produced during cyanate hydrolysis is being oxidized and therefore there is no fear of the production of poisonous ammonia gas.

3) In the third reaction path, cyanide is being reduced by the holes (h^+) in the valence band producing cyanyl radicals, CN^-.

$CN^- + h^+ \rightarrow CN°$

The cyanyl radicals produced are then attacked and oxidized by the hydroxyl radicals produced in eqns 8.6.3 a, b and d, and the hydrolysis of the cyanates is according to eqn 8.6.3 e.

Conditions For Optimal Photochemical Reaction

1) Purity of starting material.

This is crucial for all chemical reactions but especially for photochemical reactions. This is because the presence of colour or light absorbing impurities can greatly interfere with the process. Interference can result in the absorption of specific wavelengths necessary for the reaction or a reflection away from the substance of required wavelengths. This is so because the rate of the reaction greatly depends on the availability of light of a specific wavelength.

2) UV spectra of substrates.

The UV/VIS spectra of the substrate should be known. By noting the UV/VIS spectra of the photosensitive substrate, all other UV/VIS spectra not used in the activation of a specific substrate can be filtered out. By doing this, other chemicals that are photo active at different wavelengths (spectra) are not activated to compete for electron donation or acceptance with the target substance.

3) Choice of solvent.

Photochemical reactions can occur in the solid, liquid or gaseous but most are done in the liquid phase. This means that chemicals are dissolved in a solvent, making the characteristics of selected solvents very important for the reactions. Given their importance solvents are required to have the following characteristics,

1) The solvent must dissolve all the reactants.
2) The solvent must be transparent at the irradiation wavelength for the reaction.
3) The solvent must be free of impurities.

In most situations these reactions do not occur in a single process. There is often the production of intermediates. Therefore, the solvents should also be capable of dissolving the intermediates formed (König n.d.).

Chapter 9

Biodegradation Process

9.1 Introduction

This is the breakdown or transformation of cyanide and/or its complexes biologically into simpler less toxic products. It is nature's way of dealing with organic matter, converting them to harmless products (Kiruthika & Shrinithia, 2008). This process exploits the diversity in metabolic modes and adaptability of microorganisms to degrade cyanides. Biodegrdation is based on the facts that microbes can use cyanide as a source for nitrogen and carbon for the synthesis of amino acids and that metal-complexed cyanides can be oxidized by microbes to carbonate and ammonia (Adams et al. 2001). Over time these natural phenomena have been reinforced by biostimulation and biouagmentation procedures. Cyanide biodegradation is achieved through a combination of hydrolytic, oxidation, reduction and substitution processes and finally any released metals are sorbed onto a biofilm. Biodegradation is used already in treating cyanidation wastes in many mines including Homestake Gold Mine in Lead, South Dakota (Logsdon et al. 1999), and there is continuing research to optimize the process. Unfortunately, most of the cyanide present in polluted environments or in wastes is in the form of metal (such as Fe, Cu, Ni, and Zn) complexes that are highly stable and not readily biologically available and therefore are more resistant to biological degradation compared to free cyanide (Kwon et al. 2002). Biodegradation is particularly attractive for the treatment of wastes with high organic and cyanide content as microbial action can be employed in degrading both (Fallon, et al. 1991). All presently used physical/chemical methods for the treatment of cyanide wastes require further treatment to comply with emission standards making biodegradation a viable option as it readily satisfies statutory limits for direct discharge (Rodrigo, et al. 2005). Biodegradation is less expensive than the chemical degradation methods and faster than natural attenuation (Noah et al. 1999). In biodegradation, there is often a need to improve the availability of vital nutrients (Carbon, phosphorous, carbon and other trace elements) to compensate for their non-availability or limited supply in an environment. This is referred to as biostimulation. Despite the high initial investment involved in biological treatment methods, chemical/physical treatment methods for cyanide are more expensive (Lien, et al. 1991). Depending on the biodegradation route involved, the process can be a one step process where the cyanide compounds are broken directly into harmless substances or it may be a series of processes.

In plants cyanide is generated as a byproduct of the oxidation of 1-aminocyclopropane-1-carboxylic acid the direct precursor of the plant hormone, ethylene (Goudey et al. 1989). Many microorganisms have developed metabolic cyanide detoxification pathways some of which have been employed in industrial processes (Dumestre et al. 1997; Altringer et al. 1992; van Zyl et al. 2011). Bacteria degradation of cyanide looks very promising not only because these bacteria can synthesize cyanide degrading/detoxifying enzymes but also that they can assimilate the byproducts (Ruby & Kunz 2005). Notwithstanding, there is sufficient evidence that high concentrations of products of cyanide assimilation can themselves reduce the rate of cyanide assimilation as it was the case with increased ammonia concentration (Suh et al. 1994). This is due to the fact that in the presence of alternative sources of vital nutrients, cyanide nolonger exist as the sole source and the other sources are preferred.

Most often in cyanide wastes, the cyanide ion is held in complexes with bonds of varying strengths. In situations where the cyanide ion is tightly held in chemical bonds, there is first a need to detach the cyanide ion from the complexes before its destruction. The release of metal ions previously held in complexes with the cyanides into solution poses enormous and new challenges as different metal ions are of different toxicity levels to different bacteria/enzymes. In (Suh et al. 1994) the rate of cyanide assimilation was halved when the concentration of ammonium chloride (NH_4Cl) in the medium exceeded 1mM. At such high concentrations of ammonium, cyanide no longer exists as the limiting nitrogen source and excess ammonium in the medium suppressed the rate of degradation of cyanide by the microorganisms. Isolation of the cyanide ions from cyanides can be achieved through bacterial processes. Examples of such bacteria capable of doing that include bacillus subtilis (Ebbs, 2004) and other nitrilases have been found to be effective. In Ebbs 2004, bacillus subtilis was used for the hydrolysis of a nitrile (acrilonitrile) to release cyanide, as the bacteria catalyzed the hydrolysis of the nitrile, there was not a parallel mechanism to consume the cyanide resulting in an increase in cyanide concentration in the system, which lead to an autolysis of the bacteria. Therefore, even when photolysis is applied in parallel to biodegradation, the rate of cyanide consumption should be equal to the rate of release of cyanide from the complexes.

Bacteria have been found to use cyanide as sole nitrogen source (Yogesh 2008) but not so many organisms can use cyanide as sole carbon source (Luque-Almagro et al. 2005). There are many postulations as to why cyanide can't act as a convenient source of carbon or why cyanide is a poor carbon source. These include:

1) That the oxidation state of +2 of carbon in cyanide makes it a very poor source of carbon.
2) That at concentrations where cyanide can act as sole carbon source for microorganisms it will be very toxic (Kunz et al. 1992).

Cyanide is used by certain microbes as their sole sources of nitrogen in their cellular metabolism for the synthesis of amino acids (Altringer et al. 1992). The oxidation state of +3 of nitrogen in cyanide makes it a good source of nitrogen for organisms even in dilute concentrations. '*Microorganisms are known to possess various enzymes capable of converting cyanide into compounds which may serve as carbon and nitrogen substrates. Such enzymes include formamide hydro-lease (EC 4.2.1.66), L-3-cyanoalanine syntheses (EC 4.4.1.9) hyposulfite sulfurtransferase (EC 2.8.1.1), and oxygenases'* (Invgvorsen et al. 1991). Bacteria that can use cyanide as sole nitrogen source include Pseudomonas fluorescens NCIMB 11764 (Wang et al. 1996). There have also been reports of the potential of nitrogen-fixing cyano bacteria for the degradation of cyanides (Ganzer & Maier 1988). Most noted amongst the bacteria used for cyanide degradation are the pseudomonas, Achromobacter, Flavobacterium, Nocardia, Bdellovibrio, Mycobacterium and the tried and true nitrifiers, Nitrosomonas, and Nitrobacter (Carroll, 2009). A number of industries have developed cyanide detoxification products including Novo industries, which developed a cyanidase preparation, from a strain of Alcaligenes denitrificans that converts cyanide into formate and ammonia (Dumestre, et al. 1997). These biodegradation processes can degrade both simple and complex cyanides. The cyanides are converted to bicarbonate and ammonia, while the released metals are either absorbed by the biofilm or are precipitated (Ackil, 2003). Despite the ability of microorganisms/enzymes to detoxify cyanide, the process can be inhibited as a result of blockage of the active sites of enzymes thereby limiting substrate uptake (Zaher, et al. 2006). Critical to constructing a microbial/enzymatic degradation system is the ability of these organisms/substances to progressively adapt to petit increases in cyanide concentrations (Suh et al. 1994). A major draw back of biodegradation like other natural attenuation processes (volatilization, adsorption, photolysis etc) is that the kinetics of BDMs is not fast enough as required for industrial purposes (Rodrigo et al. 2005).

In nature over 10,000 cyanogenic plants are known (Oelsner et al. 2001) bacteria, archaea, algae and fungi that can produce and/or degrade cyanide (Huertas et al. 2006; Miller & Conn 1980; Brandl et al. 2008; Igeno et al. 2007). The first report of cyanide degradation by a fungus (Marasmius oreades) was reported by von Losecke in 1871 (Knowles 1976) and since then many other fungal degradation of cyanide has been reported. Bacteria can treat wastes with cyanide concentrations up to 350mg/l while cell-free enzymes can treat concentrations >1000mg/l (Adams et al. 2001). The advantages of using free cell enzymes include (Adams et al. 2001);

1) They can withstand and degrade higher cyanide concentrations.
2) There is not the need to add vital nutrients to support life as with microbes.
3) Enzymes are not easily affected by toxic metals present in the waste.
1) Enzymes have the potential for increased kinetics.

For maximum assimilation of cyanide-metal compounds to be achieved, the pH for maximum growth of the bacteria in use should correspond with the pH of instability of the compound. Such that at the pH were the compound is unstable or begins to dissociate the potential for bacteria assimilation of its component ions is maximum (Sartaj, 2008). This has many advantages as it was noticed during the biodegradation of acrylonitrile by bacillus subtilis (Ebbs, 2004). The absence of a cyanide degrading bacteria resulted in the subtilis' cell lysis/rupture as a result of increased cyanide concentration in the system (Suh et al. 1994). This further strengthens the need for a system to take care of the waste produced in the degradation processes to be designed in. For an organism to be considered suitable for application in cyanide-biodegradation processes there are basic characteristics it should possess, including (Luque-Almagro et al. 2005; Kiruthika & Shrinithia, 2008):

1. Its metabolism should be cyanide insensitive (Oelsner et al. 2001). An alternative respiratory pathway insensitive to cyanide inhibition exists in some plants, bacteria, filamentous fungi and certain yeasts (Jeppsson et al. 1995). In this way the iron in cytochrome oxidase is not attacked by cyanide. Organisms can either achieve this by having an alternative oxidase described in plants or the cytochrome bd (which is cyanide insensitive) in bacteria (Larson et al. 2005).
2. A system for specific metal acquisition. The formation of very stable metal-cyanide complexes results in an almost unavailability of essential growth metals to organisms. The formation of siderophores permits for iron supply for bacteria (Huertas M.-J. et al. 2006).
3. A cyanide assimilatory pathway. A cyanotrophic organism must have a system permitting it to convert poisonous cyanide into a less or non-poisonous substance.

'The success of biodegradation depends upon the presence of microbes with the physiological and metabolic capabilities to degrade the pollutants in the contaminated environment [2]. The biological treatment relies upon on the acclimation and enhancement of indigenous microorganisms such as bacteria, but most of the time the environmental conditions, mainly the chemical composition, must be previously modified. The addition of nutrients to a contaminated site in order to enhance the activity of indigenous microorganisms is called biostimulation. By contrast, the inoculation with specialized microflora is called bioaugmentation' (Igeno et al. 2007).

Many organisms possess multiple cyanide degradation pathway but may choose a particular path over another based on external factors including the following (Ebbs, 2004),

a. Availability of oxygen or oxygen concentration.
b. Ph of the environment.
c. Cyanide concentration.
d. Cyanide bioavailability and solubility in soil water systems.

Four enzymatic paths have been identified based on (Raybuck S. A., 1992):

a. Cofactor requirement.
b. The viability of the cell for cyanide treatment.
c. Availability of the cyanide form used.
d. The product of the enzymatic reaction.

The four degradation paths are,

1) Substitution/addition paths.
2) Hydrolytic paths.
3) Oxidation paths.
4) Reduction paths.

Cyanide is toxic to almost every organism because of its ability to bond irreversibly with metalloproteins, such as the cytochromes involved in all known respiratory processes (Huertas M. J., et al., 2006; Kiruthika & Shrinithya, 2008) (refer to chapter 3 for cyanide toxicity).

For biodegradation to be possible the cyanide must be biologically available. This means that cyanides tightly held in strong complexes are not available and therefore must be freed through processes such as dissolution by acidification and photodegradation. Recent findings by Luque-Almagro et. al 2005, show that Pseudomonas pseudoalcaligenes CECT5344 does not only grow on waste waters containing heavy metals but that they can degrade both free and complexed cyanides in solutions with as much as 30mM free cyanide at elevated pH levels as 11.5. There is now a question on the necessity to shatter the metal complexes before biodegradation Baxter and Cumming 2006 in Carroll 2009. Because cyanides are a bad source of carbon, microorganisms will exhaust all other sources of carbon and energy before turning to cyanide. This implies that in cyanide biodegradation systems all other carbon sources must be eliminated, imposing cyanide as the sole source for carbon and nitrogen (Oelsner et al. 2001). Oelsner et. al 2001, also achieved the biodegrardation of iron-cyanide complexes using Pseudomonas putida DSM ATCC 12 735 17 514 and Pseudomonas fluorescence DSM 50 090.

Microbial detoxification of cyanides offers great opportunities for the high tech industries as non-living and dead microbial biomass, through biosorption can be used to harness the collection of particularly rare earth minerals (Gold, silver, and platinium) from process effluents. Algae like Anabaene and Chlorella have demonstrated high potential in the selective recovery of lead, cadmium, copper and zinc. The presence of reactive or active groups (carboxyl, amine, amidazole, phosphate, sulfhydryl, sulfate, hydroxyl e.t.c.) on dead cells surfaces causes these dead cells to function as ion exchangers in appropriate pH environments. (Kiruthika & Shrinithya, 2008).

Ammonia is the main toxic compound in effluents from biodegradation units. Modern cyanide biodegradation systems are equipped with ammonia detoxification units that are divided into two parts. Effluents from biodegradation units are first channeled to an oxic chamber where autotrophic nitrifying bacteria convert ammonia in the effluent to nitrites and nitrates. Effluent from the oxic chamber containing the nitrites and nitrates is sent to an anoxic chamber where denitrifying bacteria convert the nitrites and the nitrates to nitrogen (Park et al. 2008).

9.2 Oxidative Pathway

This pathway is very seldom reported or used. Many of the enzymes (oxidoreductases) believed to catalyze these processes are metalloenzymes. These metalogenes are themselves very susceptible to cyanide poisoning. By-products of the oxidative pathway are ammonia and carbon dioxide. Monoxygenase catalyzes the conversion of cyanides to cyanates in a first step (eqn 9.2a) which (cyanates) are later hydrolyzed to ammonia and carbon dioxide in a second step (eqn 9.2b) catalyzed by dioxygenase an enzyme similar to cyanase (EC 3.5.5.3) (Kunz et al. 1992).

$$\mathrm{HCN} + \mathrm{O_2} + \mathrm{H^+} + \mathrm{NAD(P)H} \xrightarrow[\text{enzyme and catalyst}]{\text{monoxygenase}} \mathrm{HOCN} + \mathrm{NAD(P)^+} + \mathrm{H_2O} \quad \text{-eqn 9.2a}$$

$$\mathrm{HCN} + \mathrm{O_2} + 2\mathrm{H^+} + \mathrm{NAD(P)H} \xrightarrow[\text{enzyme and catalyst}]{\text{dioxygenase}} \mathrm{CO_2} + \mathrm{NH_3} + \mathrm{NAD(P)^+} \quad \text{--eqn 9.2b}$$

Bacteria capable of degrading both free cyanides and complexed metal-cyanides (MCN^{2-}) have been reported (Knowles 1976; Kunz et al. 1992). These include pseudomonas flourescens NCIMB 11764 and the E. coli strain BCN6. Kunz et al 1992 did further research on this pathway and found out that carbon dioxide and ammonia were not the only by-products of the oxidative biodegradation of cyanides. They confirmed the presence of other by-products formamide and formate. Following this discovery they concluded that organisms utilize many pathways during cyanide degradation with one pathway being dominant. From this it can be concluded that with every other factor being constant an organism will utilize a pathway most favored by other factors such as availability of oxygen, carbon dioxide, other carbon source, pH, e.t.c. To confirm this they attempted to degrade cyanides with washed cell of pseudomonas flourescens under anaerobic conditions and this failed. This confirmed their thought that cyanide transformation by pseudomonas flourescens NCIMB 11764 is an inducible process and also oxygen dependent (Kunz et al. 1992).

9.3 Reductive Pathway

This pathway has not been well studied. '*Anaerobic conditions for the reduction of cyanide waste are not as common*' (Raybuck, 1992). Notwithstanding there are a number of organisms that can degrade cyanide following this route including klebsiella oxytoca (Kao, 2003) to ammonia and methane (eqn 9.3).

$$\mathrm{HCN} \xrightarrow[2H^+]{2e^-} \mathrm{CH_2} \underset{\substack{\text{Hydration of this}\\ \text{compound gives}\\ \downarrow \\ \mathrm{CH_2{=}O}}}{\text{-----------}} \mathrm{NH} \xrightarrow[2H^+]{2e^-} \mathrm{CH_3\text{-}NH_2} \xrightarrow[2H^+]{2e^-} \mathrm{CH_4} + \mathrm{NH_3}$$

eqn 9.3

In methanogenic conditions, degradation of cyanide has been reported for methanogens of the Methanothrix genus. The production of formate as byproduct has lead to speculations that hydrolysis of cyanides by methanogens might be the dominant mode of cyanide degradation (Fallon et al. 1991). The use of isotopic carbon $C^{14}N$ has not confirmed degradation through reduction and suggestions have been made of the possibility of hydrolytic processes being responsible (Raybuck A. S., 1992).

9.4 Hydrolytic Pathway

This treatment method has many advantages as compared to the other methods. In this method there is direct cleavage of the carbon-nitrogen triple bond eliminating the possibility of further reactivity (Raybuck S. A., 1992). Cyanide loss during the cyanidation process has also been attributed partly to hydrolytic decomposition (Adams M. D., 1990; Wantanabae et al. 1998). This method can either occur through hydrolysis, catalyzed by cyanidase with formic acid and ammonia being byproducts or through hydration catalyzed by cyanide hydratase with formamide as byproduct. The hydrolytic pathway is proving to be the most promising as it shows good activity at high cyanide concentrations (Dumestre et al. 1997). Products from both hydrolysis and hydration are very less toxic and can serve as food substrate for growth of other organisms. The hydrolytic pathway requires no additional cofactors with the only requirement being the presence of a functional enzyme (Raybuck S. A., 1992; Dumestre et al. 1997). This can be an anaerobic or an aerobic process. Fallon et al. 1991 suggested that the emission of methane during anaerobic biodegradation of cyanide could be due to cyanide hydrolysis despite that organisms capable of that were not found. Hydrolytic degradation of cyanide has also been found in some fungi e.g. Fusarium solani Strem-phyliumloti and Gloeocercospora sorghi (Dumestre et al. 1997).

The hydrolytic degradation of cyanides can occur either in a single step or in two separate steps. In the two-step process, there is first the hydration of cyanide to formamide (fig 9.4a).

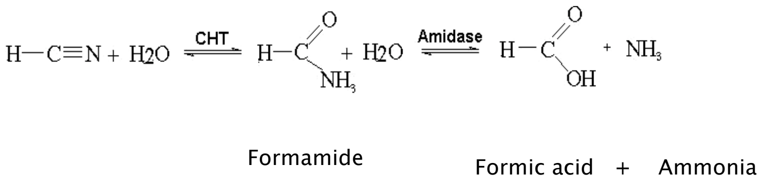


Figure 9.4a: Cyanide hydrolysis by cyanide hydratase (CHT) with formamide as the product and a further hydrolysis of formamide catalyzed by an amidase giving formic acid and ammonia as products.

The first step is catalyzed by the enzyme cyanide hydratase. In the second step, the formamide is hydrolyzed to formic acid (formate) and ammonia (fig 9.4a). The second step is catalyzed by the enzyme amidase. Both enzymes i.e. cyanide hydratase and amidase are all cyanide hydratases.

The conversion/hydrolysis of formamide is catalysed by formamidase (an amidase) and it is often at 25% the rate of assimilation of cyanide by cyanide-hydratase (Dumestre et al. 1997)

In the single step process, cyanide is converted directly to formic acid and ammonia without formation of the intermediate formamide. This process is catalyzed by the enzyme cyanide dihydratase a cyanide hydratase (fig 9.4b).

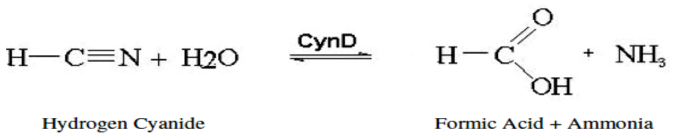


Figure 9.4b: Cyanide hydrolysis by cyanide dehydratase (CynD) to formic acid and ammonia.

This method of cyanide degradation is widely used by plants to degrade any cyanide used to combat diseases. Once a plant is attacked by a disease, there is first the hydrolysis of cyanogenic glycosides releasing cyanide which wades off the attack and then the cyanide must be degraded before it kills the plant itself. Examples of such plants include Gloeocercospora sorghi and Hel-minthosporium turcicum (Raybuck A. S., 1992). During anaerobic hydrolytic cyanide degradation, formate can occur as a bi-product when there is incomplete metabolism of the formate formed especially as the rate of formate assimilation is slower than the rate of cyanide assimilation.

This process of cyanide hydration has been found in Alcaligenes xylosoxidans subsp. Denitrificans (Raybuck S. A., 1992). Formate and ammonia were the products when cyanide was treated with washed cells. The resultant cyanate and organic nitriles are not hydrolysed. At high concentrations of cyanide the cells are destroyed.

Giving that the first step i.e. the step resulting in the formation of formamide is the rate determining step, it is only logical to conclude that the first step would occur such as to prevent accumulation of a detectable formamide pool (Fallon R. D., 1992).

A major advantage of the hydrolytic pathways is that these do not rely on the use of cyanide metabolizing enzymes. This makes them better for degrading cyanide concentrations higher than living cells can tolerate, as cyanide is a toxin to respiratory systems. A major handicap of hydrolitic pathways is that they have not proven efficient for waste of metal-cyanide complexes.

9.5 Substitution/Addition Pathway

This degradation path exploits the thiophilic (affinity for sulfur) and the neucleophilic (higher reactivity with reaction sites of lower electron density) character of the cyanide ion (Raybuck S. A., 1992). These reactions require either a sulfur transferase converting cyanide to thiocyanates or a pyridoxal phosphate enzyme. Sulfurtransferases (EC 2.8.1.1–5) catalyze the transfer of sulfane sulfur from a donor molecule to a thiophilic acceptor. These enzymes are widely distributed in plants, animals, and bacteria, and have been implicated in a wide range of biological processes. (Aphey et al. 2003)

Examples of sulfurtransferases include Rhodanase (a protein) and 3-mecaptopyruvate sulfurtransferase. Rhodanase is highly concentrated in the mitochondria of the mammalian liver where it detoxifies cyanide. In this method an enzymes combines with a substrate and produces an intermediate (enzyme/substrate complex) that further reacts to yield the product.

i. Rhodanase.

Rhodanase has been found in animals, plants, fungi and other micro-organisms. Bacteria sources include Escherichia coli, Bacillus Megaterium (Castric & Conn, 1971), Pseudornonas aeruginosa, Thiobacillus denitrificans, Rhodospirillurn palustris, Klebsiella pneumoniae, and Azotobacter vine- landii (Raybuck A. S., 1992)). The reaction path for this sulfuration process is catalyzed by the enzyme Rhodanase (EnzS) (eqn 9.5a)

$$CN^{-} + S_2O_3^{-2} \leftrightarrow SCN^{-} + SO_3^{-2} \qquad \text{------ eqn 9.5a}$$

This has been found to occur in two steps. The resultant thiocyanate is less toxic (Raybuck S. A., 1992).

b. First there is the formation of an enzyme persulfide intermediate ($EnzSS^{-}$). This occurs as the thiosulphate ($S_2O_3^{-2}$) donates a sulphur to a cysteine sulfhydryl of the protein to form the enzyme per-sulfide intermediate ($EnzSS^{-}$) (eqn 9.5b).

$$S_2O_3^{2-} + EnzS^{-} \leftrightarrow EnzSS^{-} + SO_3^{2-} \qquad \text{------eqn 9.5b}$$

This stage, i.e. the formation of the persulphide is the rate-limiting step for these reactions.

c. In the second step, cyanide attacks the enzyme-persulfide intermediate forming a thiosulfide with one of the sulphurs and the enzyme molecule is released.

$$CN^{-} + EnzSS^{-} \leftrightarrow EnzS^{-} + SCN^{-} \qquad \text{------ eqn 9.5c}$$

It should be noted that this stage is diffusion limited. Thiocyanate (SCN^{-}) is an oxidation product of the cyanide anion (CN^{-}), produced in the presence of a sulfur donor.

ii. 3-Mercaptopyruvate sulfurtransferase.

The co-substrate mercaptopyruvate arises from the transamination of cysteine. The enzyme has been found in animal, fungal and bacteria species (E. Coli and vinelandi (Jarabak & Westley, 1980)). Mercaptopyruvate is the single sulfur donor but there are many sulfur acceptors (Thiophiles) including cyanide. The complication of dealing with many sulfur acceptors, combined with the rapid formation of cyanohydrins between cyanide and mercaptopyruvate, results in a deviation from standard Michaeliis-Menten kinectics (Jarabak & Westley, 1980; Raybuck S. A., 1992). Equation 9.5c1 is called the Michaeliis-Menten equation for enzymatic catalysis.

$$V = \frac{V_{max}[S]}{K_m + [S]} \qquad \text{-----------eqn 9.5c1}$$

Where:

ν = Reaction rate.

[S] = Substrate concentration for which V_{max} is attained.

V_{max}=Maximum rate achieved by the system.

K_m= Michaelis constant which is the substrate concentration at which the rate of the reaction is half of V_{max}.

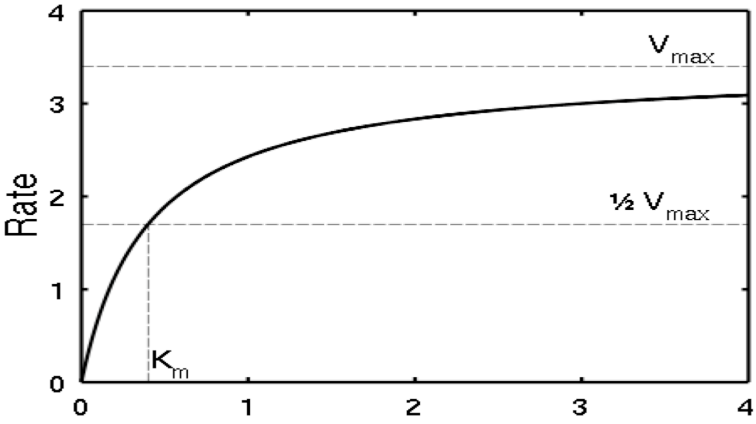


Figure 9.5.a: Michaelis-Menten saturation curve of an enzyme reaction (wikipedia 2012).

In this degradation pathway the formation of an intermediate is not a prerequisite for enzyme action, the substrates cyanide and 3-Mercaptopyruvate sulfurtransferase are simply bound in a ternary complex (Raybuck A. S., 1992).

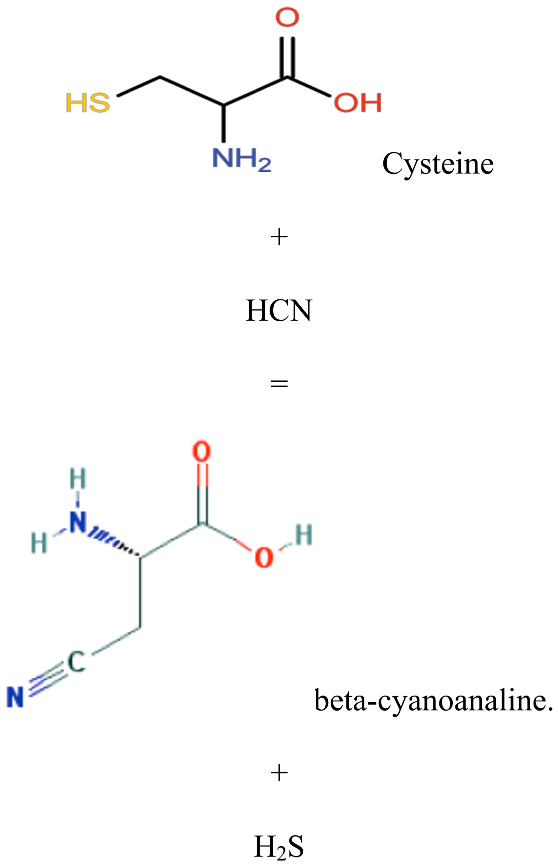
3-mercaptopyruvate + cyanide ↔ pyruvate + thiocyanate.

Examples of pyridoxal phosphate enzymes include β-cyanoalanine synthase and γ-cyano-α-aminobutaric acid synthase.

iii. β-cyanoalanine synthase.

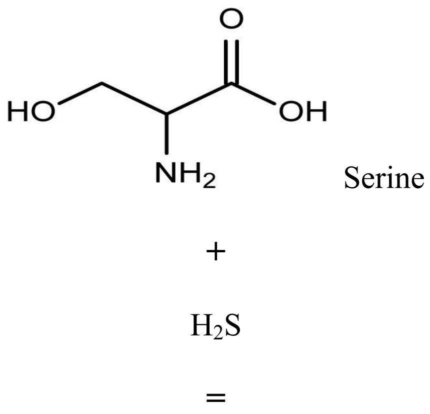
This enzyme catalysis the substitution of a three-carbon amino acid with cyanide resulting in an intermediate (β-cyanoalanine) that is later hydrolyzed to asparagin. The enzyme has been found in many organisms including Escherichia coli, Bacillus megaterium and Chromatium violaceum, and additionally in algae and higher plants (Castric & Strobel, 1969; Raybuck S. A., 1992; Yoshikawa, et al., 2000). This enzyme has also been found in non-cyanogenic plants (Mizutani et al. 1987). The occurrence of this enzyme also in non-cyanogenic plants implies that cyanide production and metabolism is not limited to cyanogenic plants. β-cyanoalanine synthase was noticed to be present in C. violaceum by Brysk et al 1969 when they incubated C. violaceum with serine or succinate and $KC^{14}N$ (Rodgers, 1982). In their first study, Brysk et al 1969 reported the formation of β-cyanoalanine and minute amounts of asparagine. In a follow-up publication in 1970, Brysk and Ressler reported the formation of β-cyanoalanine and y-cyano-α-aminobutyric acid when washed cells of C. violaceum were incubated with cyanide and one of serine, threonine or glutamate. Contrasting the findings of previous studies by Brysk and Co. with that of Rodgers in 1982 which claimed that only β-cyanoalanine could be identified amongst other products after incubating washed cells of C. violaceum NCIB 9131 with cyanide and one of glutamate, O-acetyl-l-serine or serine, it can be concluded that the product of incubating C. violaceum with cyanide and one of glutamate, O-acetyl-l-serine or serine depends on a number of factors including the '*use of different strains of C. violaceum and the use of cells harvested at different stages in the growth cycle*' (Rodgers, 1982).

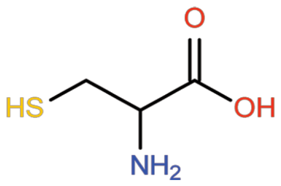
The enzyme can be formed from cysteine or from O-acetyl-serine but the rate of enzyme production from cysteine is 17 to 18 times greater than when serine is used (Knowles, 1976). Detection of β-cyanoalanine-synthase in many bacteria systems is probably as a result of an ancillary reaction of cysteine synthase upon exposure of the organism to cyanide (Raybuck A. S., 1992). Below is a demonstration of the conversion of cystein to beta-cyanoalanine.



Conversion of cysteine to betacyanoalanine by cyanide

In a second step the β-cyanoalanine is then hydrolyzed to asparagine or aspartate in a reaction catalyzed by β-cyanoalanine hydrolase or by asparaginase (Ebbs, 2004; Irwin & Zschoche, 1970). When serine is used, two possible reaction paths for the formation of cyanoalanine are thought to exist. The serine is either converted to cysteine or the serine is directly acted upon (Blumenthal et al. 1963). Below is a demonstration of the conversion of serine to cysteine.





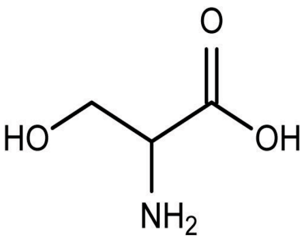
Cysteine

+

H_2O

Conversion of serine to cysteine

Looking at the diagrams above, it is realized that one of the OH groups of serine is exchanged for an HS from the hydrogen sulphide to give cysteine. In the second reaction path, the serine reacts directly with hydrogen cyanide yielding β-cyanoalanine.

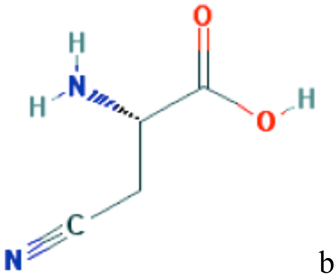


Serine

+

HCN

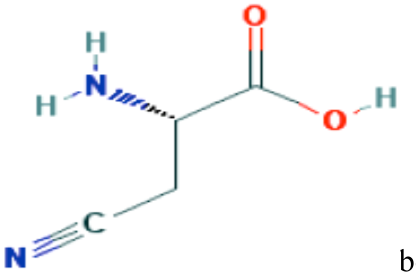
=



beta-cyanoanaline

Direct reaction of serine and cyanide to give beta-cyanoalanine

In the direct conversion of serine to beta-cyanoanaline through its reaction with HCN, a hydroxyl group (OH^-) in serine is replaced with a cyanide ion (CN^-) to give beta-cyanoalanine. The beta-cyanoalanine from both scenarios is hydrolyzed to give asparagine or aspartate. See below, for the direct degradation of cyanide/HCN by serine through serine conversion to cyanoanaline without cysteine formation and hydrolysis of cyanoalanine to asparagine.

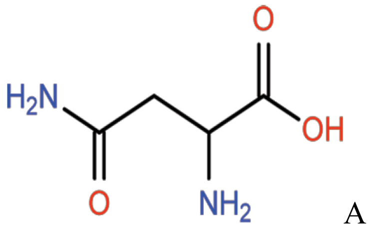


beta-cyanoanaline

+

H_2O

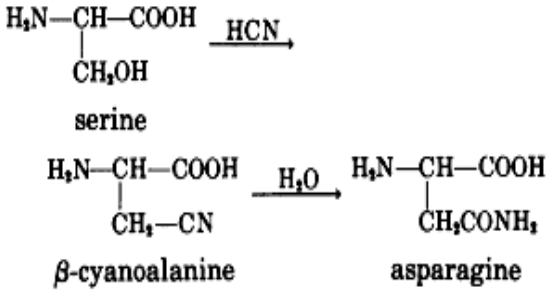
=



Asparagine

Hydrolysis of beta-cyano-alanine to asparagine

Another perspective of the direct conversion of serine to asparagin,



Direct degradation of cyanide by serine without a cysteine as intermediate. (Knowles, 1976)

Whatever the substrate cysteine or serine, the end product is asparagine through hydrolysis of β-cyanoalanine. It should also be noted that the conversion of cysteine to β-cyanoalanine is 50 fold greater than the conversion of serine (Knowles, 1976). O-acetyl serine (OAS) of serine can also be used as a substrate for cyanide degradation by cyanoalanine synthase (Cipollone et al. 2008) and conversion is 17 to 20 fold greater than when serine is used.

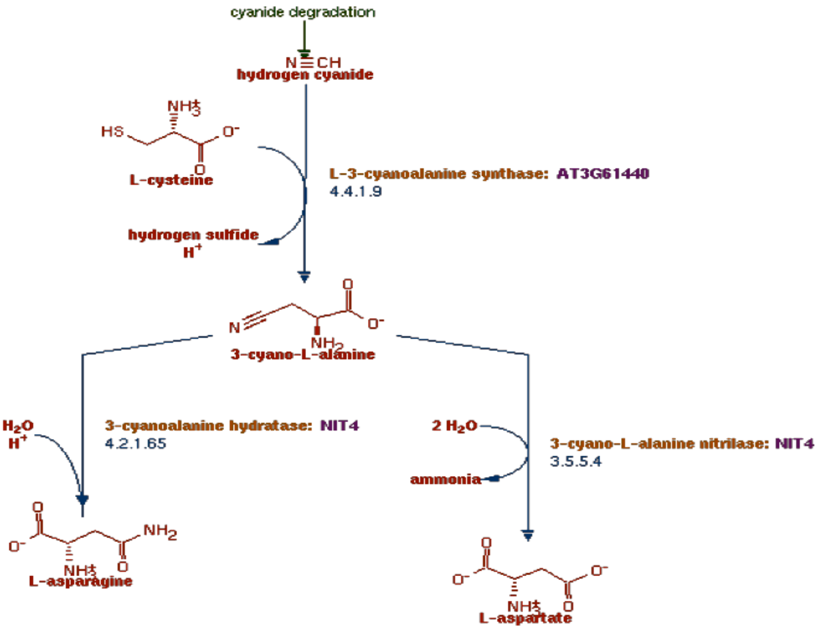


Figure 9.5b: Enzymatic (beta-cyanoalanine synthase) biodegradation of cyanide (Biocyc, 2011).

Formation of cyanoalanine is catalyzed by the enzymes cyanoalanine synthase. The hydrolysis of cyanoalanine to asparagine is catalyzed by the enzyme 3-cyanoalanine L-hydratase (fig 9.5b). The asparagine formed can be further hydrolyzed to yield L-aspatate (fig 9.5c) or there can be a direct double hydrolysis of cyanoalanine to give L-aspartate. The direct double hydrolysis of cyanoalanine to L-aspartate is catalyzed by the enzyme cyanoalanine nitrilase (fig 9.5b).

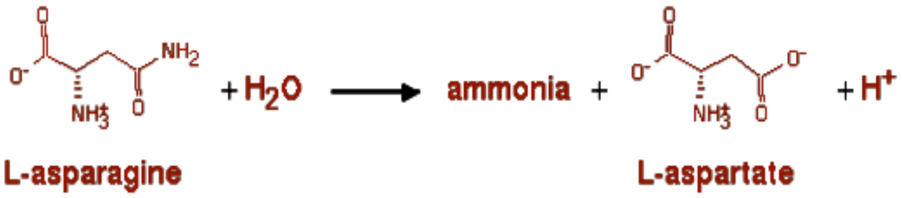


Figure 9.5c: Hydrolysis of asparagines to aspartate (Biocyc, 2011)

Factors That Affect Biodegradation Process

Bacteria are very sensitive to pH values. At a pH of 9 and above bacterial cyanide degradation is very slow. Despite the effect of pH, it is suggested that under extreme alkaline conditions a reduction in cyanide degradability is likely due to the unavailability of cyanide as it is strongly bonded to the complex than to a reduction in enzyme/bacterial activity (Dumestre et al. 1997).

The cyanide concentration is also a problem. At some elevated cyanide concentrations bacteria activity are impeded and in some extreme cases the bacteria are killed. In anaerobic processes, the rate of cyanide assimilation is positively correlated to temperature, pH and trace metal concentration (Fallon et al. 1991).

9.6 Aerobic Processes

Under aerobic conditions hydrogen cyanide is converted to hydrogen cyanate (eqn 9.6a). Aerobic cyanide biodegradation processes can deal with cyanide concentrations of up to 200ppm conveniently although treatment of more cyanide concentrated wastes has been reported. This conversion requires an enzyme to catalyze the formation of hydrogen cyanate. Soon after the hydrogen cyanate is formed it hydrolyses to give ammonia and carbon dioxide (eqn 9.6b).

$$2HCN + O_2 + (\text{enzyme}) = 2HCNO \qquad \text{------ eqn 9.6a}$$

$$HCNO + H_2O = NH_3 + CO_2 \qquad \text{------ eqn 9.6b}$$

The oxidation of cyanides to cyanates in a single step under aerobic conditions requires the participation of a mineral, bacteria or photo catalyst. This direct oxidation process occurs following equation 9.3c.

$$2CN + O_2 + \text{catalyst} = 2CNO \qquad \text{------ eqn 9.3c}$$

These aerobic oxidation processes have received more attention than the anaerobic process over the past 30 years (Fallon R. D., 1992)

9.7 Anaerobic Processes

This is the degradation of cyanide (free and complex cyanides) in the absence of air or oxygen. Scarcity of literature on the anaerobic degradation of cyanide is because of two reasons; 1) the toxicity of cyanides to anaerobic organisms e.g. methanogens and the difficulty of acclimatization of the sludge, and 2) the anaerobic degradation of cyanides has not been conclusively proven or is poorly understood (Guzen et al. 2000). Anaerobic degradation of cyanides occurs in highly reducing/reduced environments. Such environments can be found in certain portions of tailings dams. Inhibition of anaerobes is particularly easy because they have a lot of metallo-enzymes that are easily targeted for inhibition by cyanide (Cipollone et al. 2008). The presence of HS or H_2S is a precondition for anaerobic degradation to occur. Whether HS or H_2S is dominant is a function of the pH of the environment. When the soil has a high pH above 7, HS^- is dominant while at pH values below 7, $H_2S_{(aq)}$ is dominant. Equations 9.7 a and b illustrate the anaerobic degradation of these sulfur species:

$$CN^- + H_2S = CNS^- + H_2 \quad \text{------ eqn 9.7a}$$

$$HCN + HS^- = CNS^- + H_2 \quad \text{------ eqn 9.7b}$$

The microorganisms capable of anaerobic degradation of cyanide are very sensible to minor cyanide concentrations. Concentrations as low as less than 1mgCN/Liter can be lethal to methanogenic bacteria (Cuzin & Labat, 1992; Fallon et al. 1991). Despite the extreme toxicity of cyanide to methanogens, the probability of the cyanide concentration reaching toxic levels is very reduced. This is because methanogens can feed on formate that is a product of hydrolytic degradation of cyanide thereby thermodynamically favouring this process (Fallon et al. 1991) in a system. Notwithstanding, the anaerobic processes have not received much attention also because they can not reduce cyanide concentrations to desired levels fit for disposal to the environment and also due to the generation of ammonia which is an undesirable by-product. Compared to the 2mgCN/liter concentration threshold for anaerobic bacteria degradation systems, aerobic systems have a threshold of 200mgCN/liter and higher (Smith & Mudder 1991).

9.8 Effect Of Metal/Heavy-Metal Ions On Bacterial Activity

Heavy metal ions are metal ions with a density above 5 g/cm3 (Nies, 1999). '*The first microorganisms affected by the heavy metal ions released into the environment are bacteria. The bioavailability of metals to bacteria depends on the form of the metal occurrence (free ion, organic complex, inorganic complex) and physical and chemical properties of the environment*' (Szymanska & Domka, 2003). Some heavy metals are essential for plant metabolism but these become toxic when in high concentration (Nies, 1999). Many studies have been carried out on this topic but conclusive results are hard to make. This is so because differentiating the influence on microbial activity of other environmental factors such as organic matter and temperature from those of heavy metal ions is difficult. In addition, biological processes in polluted habitats can be affected by factors induced by the presence of metals e.g. changes in pH or availability of nutrients (Monserrat & Erland, 1996). The behavior of a heavy metal ion in the soil is controlled by factors such as solubility–precipitation and sorption–desorption reactions, which are essential parameters when evaluating the toxicity of heavy metal ions to organisms. Lighthart et al. 1983 in (Saeki et al. 2002) predicted the inhibition of microbial respiration when free copper ion concentration reached a value of 0.01 to 0.1 mM in soil. Studies have shown that free metal ions have a greater effect on microbial activity than those tied in metal complexes (Saeki et al. 2002). Given that the amount of a given metal (e.g. Fe, Cu, Cr, Mo, Zn) necessary for correct metabolism or the amount of a specific metal (e.g. Pb, Hg, Cd) toxic to an organism is idiosyncratic, measurements/calculations should be made for specific ions and on specific microorganisms (Szymanska & Domka, 2003). Szymanska & Domka, 2003, stated that the effect of metal ions in pure cultures is different from the effects in natural environments. Microorganisms are also affected by the products of reduction/oxidation reactions of these metals in the environment. The time needed to develop resistance to a particular metal ion varies from organism to organism. Monserrat & Erland, 1996 observed that a time period of 2years averagely is needed for bacteria to develop resistance to lead. Three different hypotheses have been proposed to explain the effect of time on heavy metal toxicity and microbial community intolerance (Monserrat & Erland, 1996).

a. Tolerance may result from the unavailability of added metals as they turn to be adsorbed/bonded to organic matter.

b. The bacterial community may have become more tolerant over time to increased metal ion concentrations.

c. Addition of metal ions would kill less tolerant organisms leaving only the tolerant population that becomes more tolerant over time.

Advantages Of Biodegradation

1) Ionic cyanide, WAD cyanide, ferrocyanides, thiocyanides, thiocyanates and metal cyanide comlexes can be treated by this method.

2) There are different microbes with optimum cyanide degradation rates from approximately 4˚ to 30˚C.

3) Can be used at various stages in the cyanide contamination source, spent heap, e.t.c

4) Biodegradation can treat wastes with high cyanide concentrations >350mg/l and at pH of 7.5 to >11.5.

5) Process versatility means that it can be adapted to existing mine infrastructure.

6) Nutrients typically cost <$0.05/1000 gallons.

7) Process wastes (e.g. nitrates) are treated and metals e.g. selenium, arsenic, mercury are removed.

Chapter 10

Results and Discussions

10.1 Results

This section focuses on illustrating the efficiency of industrially applicable methods for the treatment of cyanide wastes and especially on methods relevant to the mining industry. By this criterion, results of laboratory experiments and field trials for the chemical treatment methods, photolysis and biological treatment methods are the focus, while a few other selected methods will also be discussed. At the end of this section tables summarizing the applicability/functionality of all the methods will be made.

To demonstrate the efficiency of the various methods for cyanide treatment many laboratory and field experiments have been done. Unfortunately, the absence of a reliable technique for calculating the amount of the different cyanide species in a waste sample makes the situation even worse (Environment Australia, 2002; Huiatt, 1984). Collecting and preserving a sample is problematic. To avoid the loss of cyanide through evaporation samples are stored in alkaline media at pH values 11 and slightly above using sodium hydroxide. At this pH, there is the possibility for the disintegration of metal cyanides resulting in the formation of their corresponding metal hydroxides (Pohlandt et al. 1983).

There are four available methods for calculating the amounts of different cyanide species in a sample; the total cyanide method, the cyanide amenable to chlorine method, the weak-acid-dissociable cyanides method and the free cyanide method (Huiatt 1983).

In the total cyanide method, a sample of cyanide waste containing free cyanides, WADs, SADs (except gold, cobalt and platinum complexes) and other inorganic complex cyanides is acidified. With the aid of an appropriate catalyst to assist the disintegration of the complexes, the cyanide released is captured in an alkaline solution and measured to determine the amount of free cyanide. A major problem with this method is the possibility of interference by sulfide and thiocyanates. Because sulphide distils with hydrogen cyanide it can therefore interfere with the results. This sulphide can also be generated through the decomposition of thiocyanate and/or of thiocyanate complexes

In a second method, which analyzes a sample for cyanide amenable to chlorination, a sample is taken and divided into two portions. One is analyzed for total cyanide as above and the second portion is treated with sodium hypochlorite in an alkaline medium for one hour and then also analyzed for total cyanide. The assumption is that the sodium hypochlorite would oxidize all cyanides amenable to chlorine including thiocyanate. The difference in the total cyanide values between the unchlorinated sample and the chlorinated sample is equal to the amount of cyanide amenable to chlorine in the original sample. Although mining companies using chlorination for the treatment of cyanides prefer this method its efficiency is not better as that of calculating for total cyanides since it is based on the total cyanide method prone to other interferences.

The third method analyzes a sample for weak acid dissociable cyanides. In this case which is similar to the first method when analyzing for total cyanides different reagents zinc acetate and acetic acid-sodium acetate are used and the pH is kept at approximately 4.5 which is much higher than in the first procedure to analyze for total cyanides. So far cyanide liberation from ferro, ferric and cobalt complexes has not been reported and interference from thiocyanate does not happen. There have been reports of the possibility of 2% liberation of cyanide from ferrocyanides by Conn 1981 in (Huiatt 1983). This method measures the amounts of cyanide ion, hydrogen cyanide, and complexes of cadmium, copper, nickel, silver and zinc.

The fourth and last method measures the amount of hydrogen cyanide in a system. Here the pH is kept at almost neutral i.e. approximately 8 and the liberated HCN is captured by either sparging or solvent extraction. Most international bodies do not accept this method because it is very liable to interferences from especially ionizable metal cyanide complexes such as zinc cyanide and other species in the solution including thiocyanates, sulfides, oxidizing agents, nitrates, urea, and other inorganic compounds which can interfere with the results depending on the procedure used.

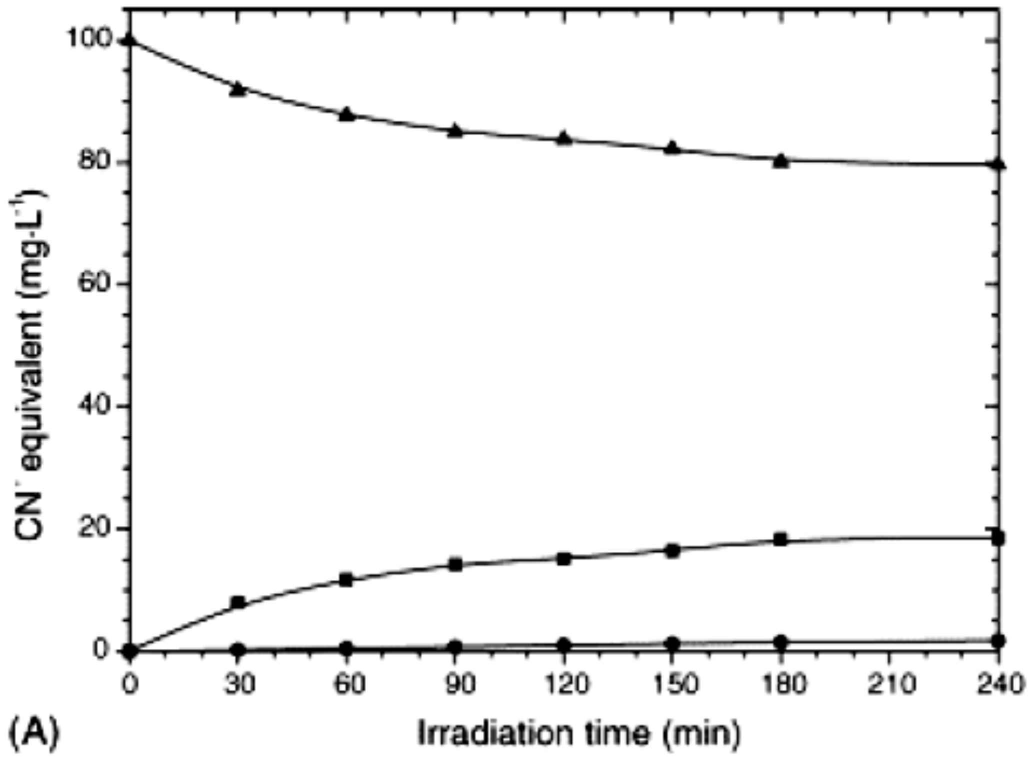
With no reliable method for calculating the exact quantity of different cyanide species in a sample, it is clear that the criterion for describing the toxicity of cyanide wastes based on a calculation of the total amount of cyanide in the sample using the first method above is unreliable, vague and only understood in the context in which it is intended for. While the phrase total cyanide includes all the cyanide species (i.e. free cyanides, WADs and SADs), this takes another definition when discussing the toxicity of effluents from cyanide treatment processes. In this case, the term is used to mean only the amount of free cyanides (CN^- and HCN) released from a sample after satisfactorily acidifying the sample. This is problematic as it involves the application of hash techniques to separate the cyanide ions from strong metal complexes for measurement (Environment Australia, 2002). Often than not, many cyanide ions tightly bonded in extremely strong cyanometal- complexes are not liberated for calculation and therefore are considered not available.

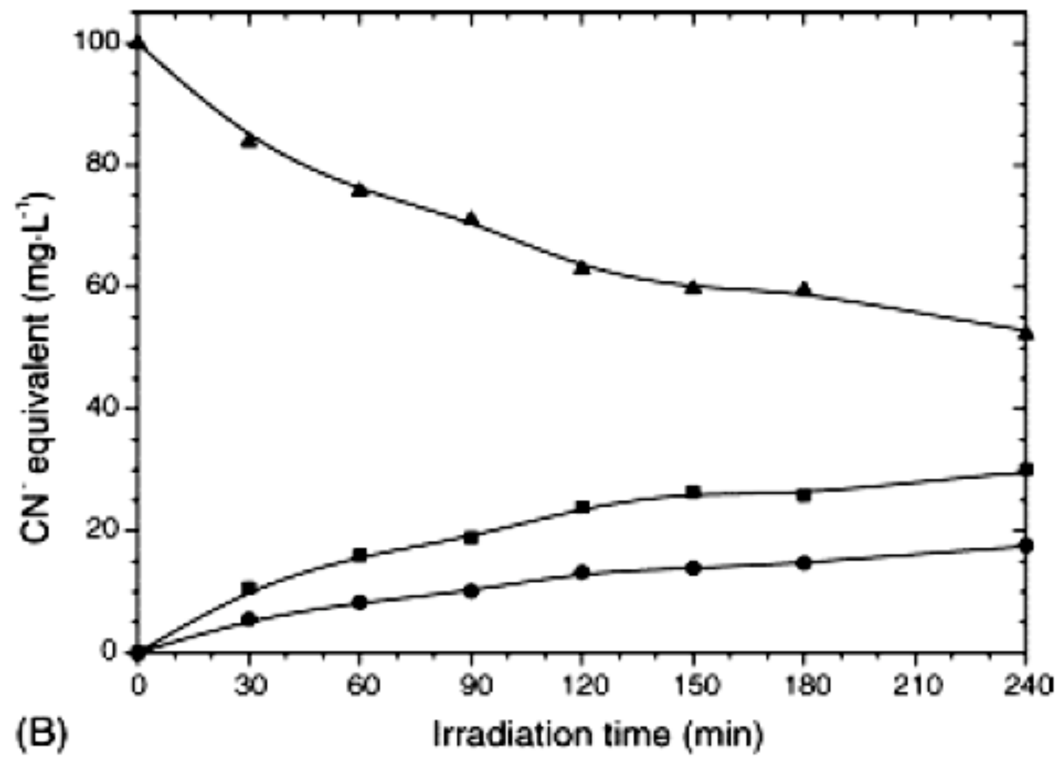
Knowing that most WADs are soluble in aqueous systems, that SADs will disintegrate on exposure to UV light, and that the stability of cyanides is influenced by fluctuations of many external factors (temperature, pH, redox condition etc), it is fair to conclude that this criterion does not succinctly define the eco-toxicity of cyanide species. Therefore, care should always be exercised when expressing the amount of total cyanides in process effluents. A more efficient system might or might not meet a discharge requirement simply because the total cyanide concentration in the influent was falsely estimated resulting in a false bias.

10.1.1 Oxidation methods

10.1.1.1 **Photolytic Degradation.**

The photolytic/photocatalytic degradation of cyanides (Free cyanides, WADs and SADs) has been extensively studied (chapter 8.6) with UV light of wavelength mostly between 420nm and 400nm. The photocatalytic degradation of iron-cyano-complexes was tested by Grieken et al using homogeneous and heterogeneous processes with Degussa P25 TiO_2 and silica supported TiO_2 catalysts (Grieken et al. 2005). In one of many experiments conducted, Grieken et al tested the influence of pH variations on the photocatalytic degradation of hexacyanoferrate(III) complexes and found that the production of free cyanide increased as the pH was increased corresponding to the degradation of the cyanide complex, while the formation of cyanate depended on the initial pH as it fell slowly with increase in pH (fig 10.1.1.1a).


CN⁻ equivalent (mg·L⁻¹)
100
80
60
40
20
0
0
30
60
90
120
150
180
210
240
Irradiation time (min)
(A)


CN⁻ equivalent (mg·L⁻¹)
100
80
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210
240
Irradiation time (min)
(B)

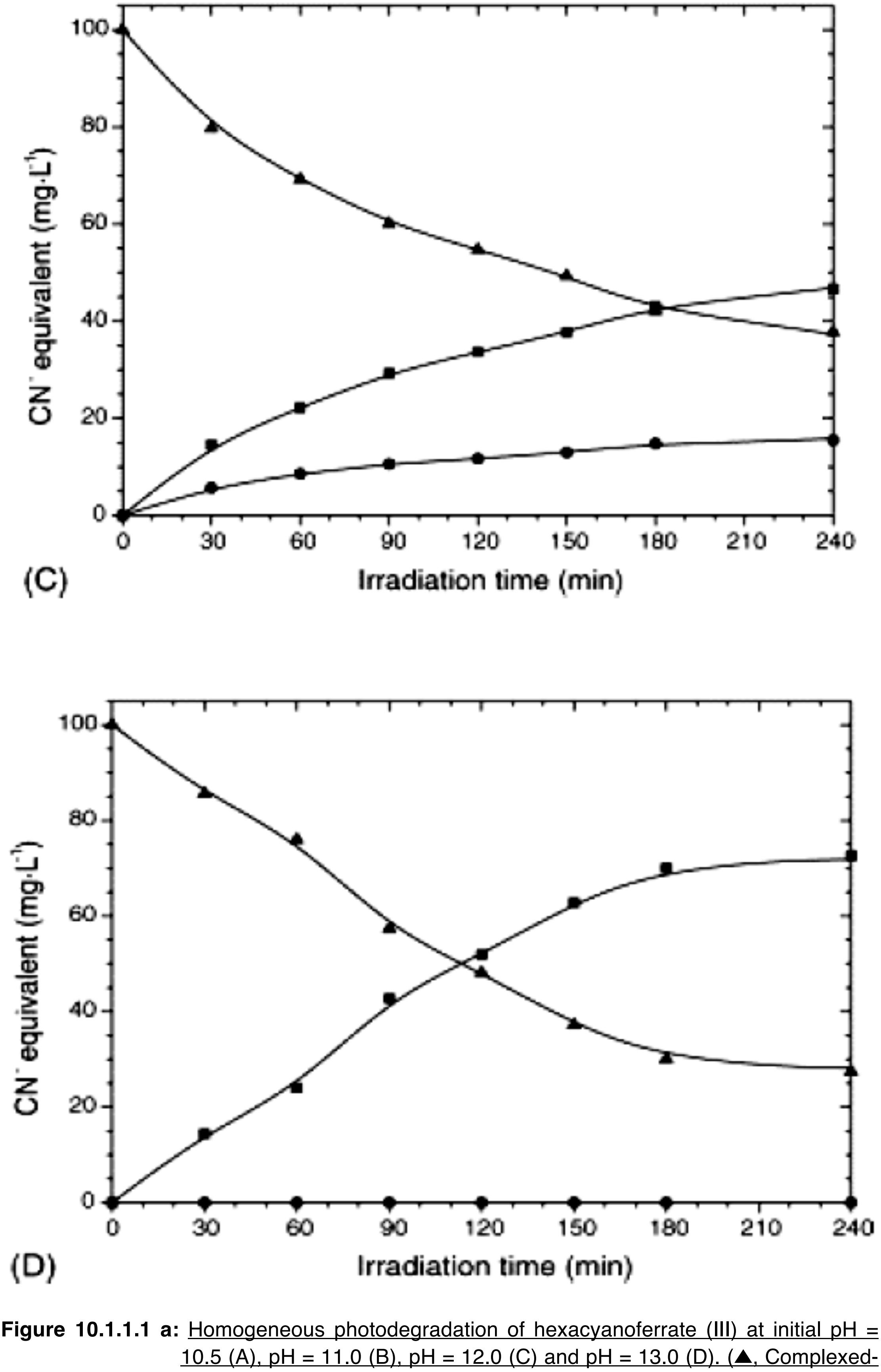


Figure 10.1.1.1 a: Homogeneous photodegradation of hexacyanoferrate (III) at initial pH = 10.5 (A), pH = 11.0 (B), pH = 12.0 (C) and pH = 13.0 (D). (▲, Complexed-cyanide; ■, Free Cyanide; ●, Cyanate) (Grieken et al. 2005).

In a similar experiment using hexacyanoferrate(II), no cyanate was formed (fig 10.1.1.1b). However, in both cases the final oxidation state of iron was +3 as there was the reddish colour change attributed to the deposition of $Fe(OH)_3$.

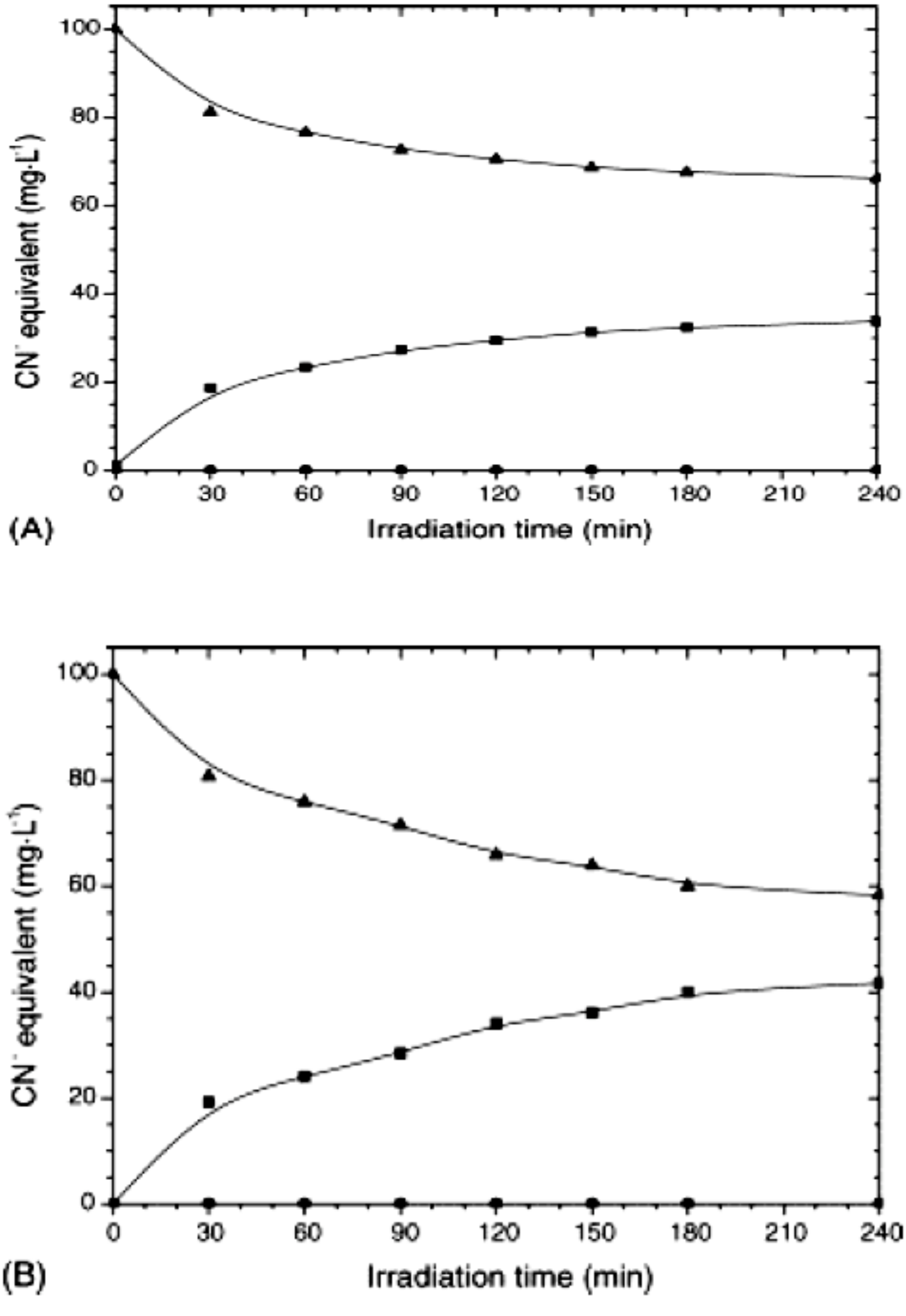
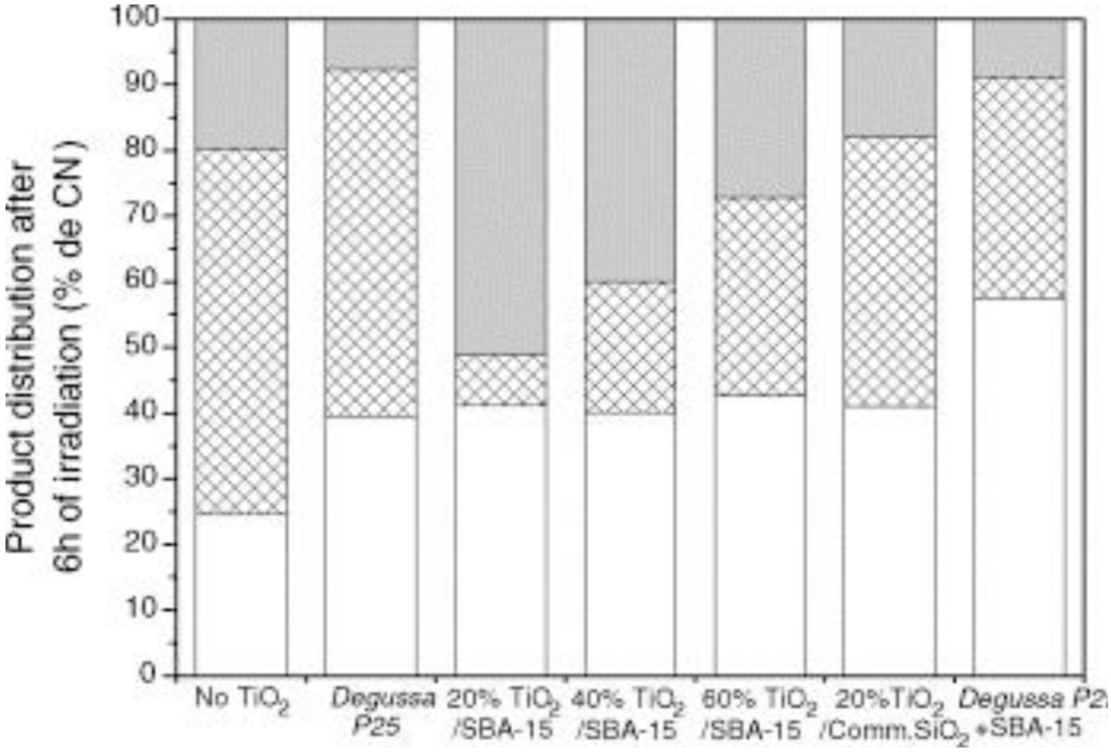


Figure 10.1.1.1b: Homogeneous photodegradation of hexacyanoferrate (II) at initial pH = 11.0(A) and pH = 12.0 (B). (▲, Complexed-cyanide; ■, Free Cyanide; ●, Cyanate) (Grieken et al. 2005).

Figure 10.1.1.1c shows the distribution of cyanides after irradiation with no catalysts and in the presence of catalysts. Grieken et al showed that without the use of catalysts the degradation of ferrocyanides was approximately 25%, which matches with the results found, by others including Oelsner et al 2001.



Key

▒	Cyanate
▩	Free cyanide
□	Complexed cyanide

Figure 10.1.1.1c: Comparison of products distribution obtained upon UV-irradiation of hexacyanoferrate (III) solutions in the presence of different catalysts. (Complexed-cyanide, P Free Cyanide, Cyanate)(Grieken et al. 2005).

Further work to verify the influences of the amount of catalyst (TiO_2), the amount of oxygen and the flow rate were done (Osathaphan et al. 2008). Osathaphan et al, 2008, showed that after a minimum required amount (0.1g/l) of the catalyst was present in the solution, further addition of the catalyst did not influence the rate of cyanide degradation (fig 10.1.1.1d).

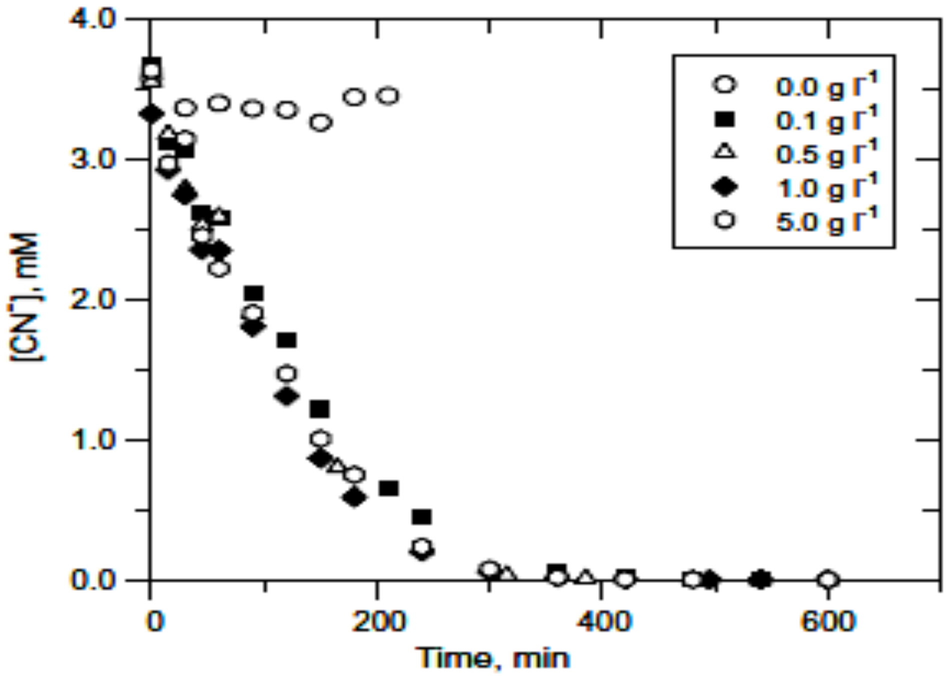
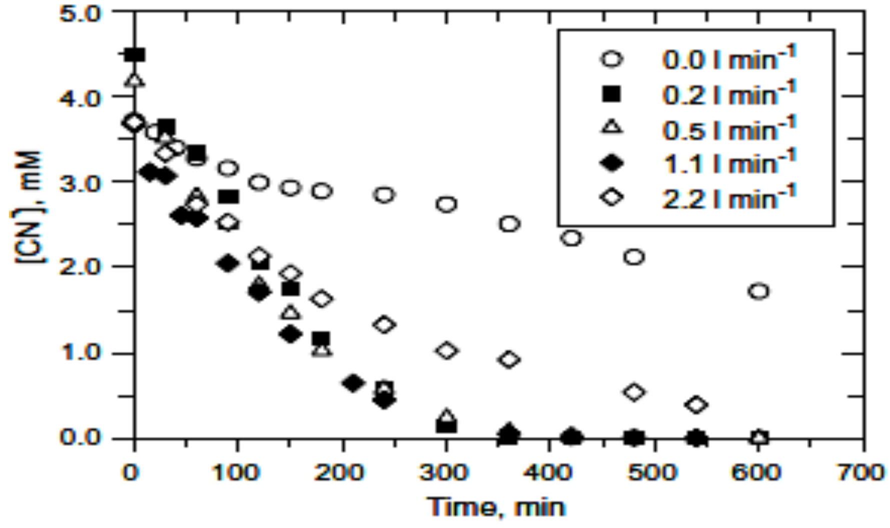
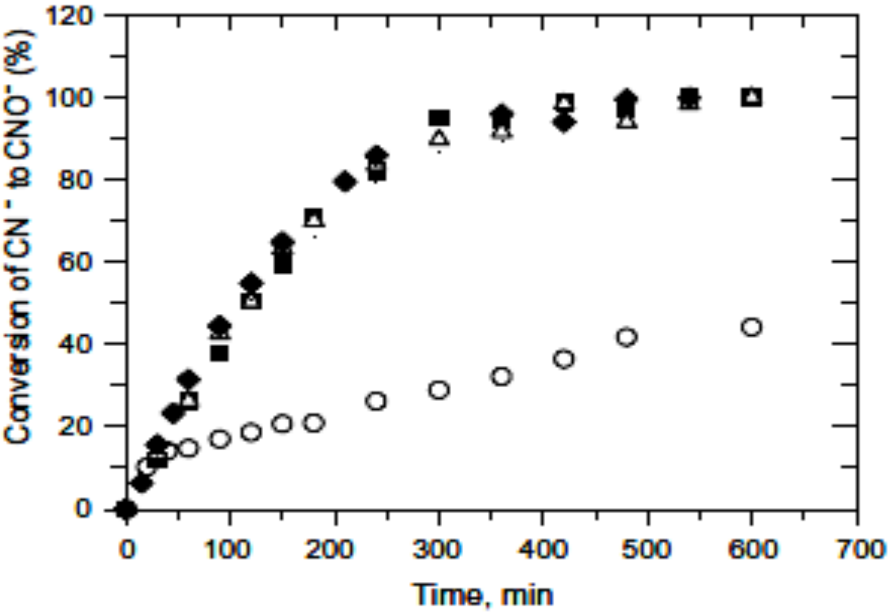


Figure 10.1.1.1d: Photocatalytic oxidation of cyanide as a function of time at different amounts of Degussa P25 TiO2. (Experimental conditions: pH 13.0; air-flow rate = 1.1 l/min) (Osathaphan et al. 2008).

The rate of addition of the catalyst also showed the same result as they showed that increasing the rate of addition of the catalyst only influenced the rate of degradation until a certain amount after which any rate increase did not have any influence on the rate of conversion of cyanide (fig 10.1.1.1e(a)). Figure 10.1.1.1e(b) also demonstrates that the degradation only occurred over a certain amount of time and that further irradiation did not result in more degradation.



(a)



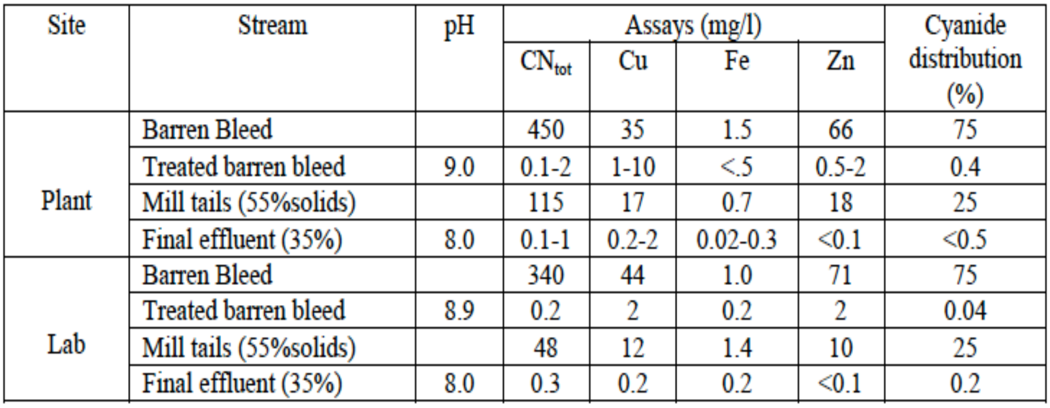
(b)

Fig. 10.1.1 1e: Photocatalytic oxidation of cyanide (A) and percentage of cyanide conversion to cyanate (B) as a function of time with different flow rates. (Experimental conditions: pH 13.0; [TiO2] = 0.1 g/l)(Osathaphan et al. 2008).

10.1.1.2 **Inco or SO2/air Process**

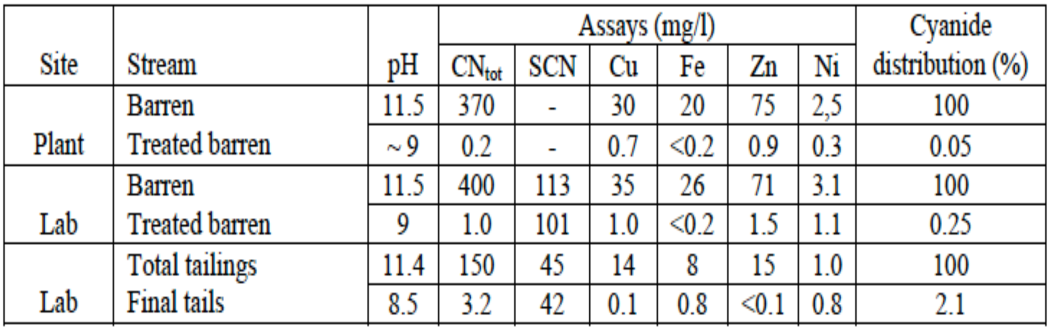
Devuyst has published many reports on the engineering and economic efficiencies of the Inco process. One of such publications shows results from both laboratory and field tests of the Inco process for three different sites, Scottie Gold mines, McBean gold mines and Campbell Red lake Mines Ltd (Devuyst et al. 1984). In all three instances there was correlation of the field results and the laboratory results for the reduction of total cyanide and amounts of metals, and there was evidence in the McBean gold mill results that the process almost completely did not treat thiocyanides (Tables 10.1.1.2 a, b and c).

Table 10.1.1.2a: Scottie Gold Mines results(Devuyst et al. 1984).



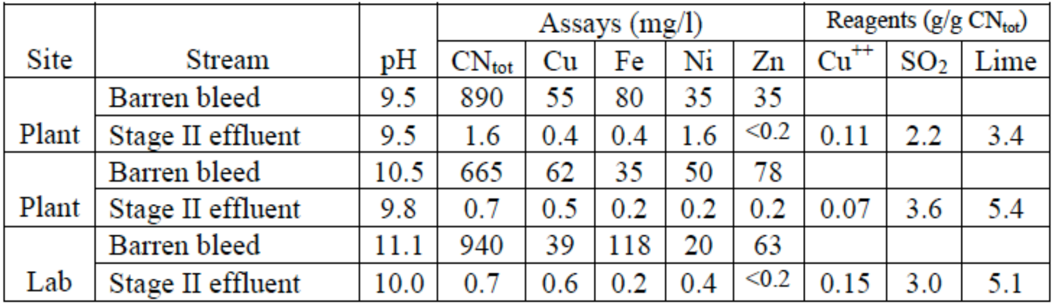
Site	Stream	pH	Assays (mg/l)				Cyanide distribution (%)
			CN_{tot}	Cu	Fe	Zn	
Plant	Barren Bleed		450	35	1.5	66	75
	Treated barren bleed	9.0	0.1-2	1-10	<.5	0.5-2	0.4
	Mill tails (55%solids)		115	17	0.7	18	25
	Final effluent (35%)	8.0	0.1-1	0.2-2	0.02-0.3	<0.1	<0.5
Lab	Barren Bleed		340	44	1.0	71	75
	Treated barren bleed	8.9	0.2	2	0.2	2	0.04
	Mill tails (55%solids)		48	12	1.4	10	25
	Final effluent (35%)	8.0	0.3	0.2	0.2	<0.1	0.2

Table 10.1.1.2b: McBean mill results(Devuyst et al. 1984).



Site	Stream	pH	Assays (mg/l)						Cyanide distribution (%)
			CN_{tot}	SCN	Cu	Fe	Zn	Ni	
Plant	Barren	11.5	370	-	30	20	75	2,5	100
	Treated barren	~9	0.2	-	0.7	<0.2	0.9	0.3	0.05
Lab	Barren	11.5	400	113	35	26	71	3.1	100
	Treated barren	9	1.0	101	1.0	<0.2	1.5	1.1	0.25
Lab	Total tailings	11.4	150	45	14	8	15	1.0	100
	Final tails	8.5	3.2	42	0.1	0.8	<0.1	0.8	2.1

Table 10.1.1.2c: Campbell Red lake pilot plant studies(Devuyst et al. 1984).



Site	Stream	pH	Assays (mg/l)					Reagents (g/g CN_{tot})		
			CN_{tot}	Cu	Fe	Ni	Zn	Cu^{++}	SO_2	Lime
Plant	Barren bleed	9.5	890	55	80	35	35			
	Stage II effluent	9.5	1.6	0.4	0.4	1.6	<0.2	0.11	2.2	3.4
Plant	Barren bleed	10.5	665	62	35	50	78			
	Stage II effluent	9.8	0.7	0.5	0.2	0.2	0.2	0.07	3.6	5.4
Lab	Barren bleed	11.1	940	39	118	20	63			
	Stage II effluent	10.0	0.7	0.6	0.2	0.4	<0.2	0.15	3.0	5.1

The results from the tests showed that the removal of total cyanide was in excess of 99%. Metals such as Ni, Cu, Zn and Fe are removed to less than 1mg/l, although there are often higher residual values for Zn and Cu. A possible reason for this being that their hydrolysis is much slower than for the other metals. Devuyst et al also found that the oxidation of thiocyanides was limited to between 10 – 20%, and that the reduction in total cyanide concentration was inversely proportional to the amount of nickel present. They found that for effluents with a low nickel concentration and a total cyanide concentration of 40-2000mg/l, the total cyanide concentration could be reduced to less than 0.5mg/l. Such a great reduction in CN_{tot} concentration could not be reached when there was a higher nickel concentration in solution. They could only get it down about 1mg/l. These results are in line with other experimental results of the American Environmental Protection Agency (EPA: U S, 1994), Devuyst et al., 1989a, 1989b and 1991 in Mudder et al. 2001 and Koksal et al 2003 e.t.c.

10.1.1.3 Alkaline Chlorination

Despite being one of the oldest methods for treating cyanide wastes, there is not so much interest in it precisely because of the dominance of the Inco process. This method is presently being applied for the treatment of wastewaters from the electroplating industry that are mainly of WADs and free cyanides and a small portion of SADs. This is because WADs and free cyanides are amenable by chlorination, while SADs are not (Griffiths et al. 1987) and also because chlorination is not ideal for slurries. Table 10.1.1.3a shows results of some experiment conducted to treat cyanide wastewaters from the Giant Yellowknife mine and Mosquito Greek mine (EPA, 1994).

Table 10.1.1.3a: Degradation of cyanides within the Giant YellowKnife and he Mosquito Greek mine(EPA, 1994).

Source of sample	CN_{tot} (mg/l)	WADs (mg/l)	Concentration after treatment. (mg/l)	Efficiency
Giant Yellowknife mine	7.8	-	0.05	99.34%
Mosquito Greek mine	310	-	25	91.93%
Mosquito Greek mine	-	226	0.5	99.78%

When the effluent from the chlorination of cyanides at the Giant Yellowknife mine was left in the pond for fifteen days the concentration of the total cyanide dropped to 0.02mg/l. This reduction was attributed to the role of natural degradation processes. The treatment of cyanides with chlorine is done in two phases with the first phase being conversion of the cyanides to cyanates within 15minutes (Cushnie, 1994) and the hydrolysis of the cyanates to ammonia and carbonate that occurs within 1 to 2 hours(EPA, 1994). The use of cyanide wastes from the plating industry to qualify the efficiency of the chlorination process cannot clearly demonstrate its efficiency against SADs as the quantity of SADs present is generally limited in those wastes.

10.1.1.4 **Peroxide Oxidation.**

When OK Tedi Gold Mine in Papua New Guinea decided to use hydrogen peroxide oxidation for the treatment of its cyanide wastes, engineers at Degussa AG, Germany were assigned the task of designing the treatment plant. Six months after operation of their process plant the following results were obtained (table 10.1.1.4a) (Griffiths et al. 1987). Some amounts of iron cyano-complexes are removed from the waste like in the chlorination process due to the precipitation of SADs especially ferrous and ferric cyano-complexes by divalent metal cations as double salts.

Table 10.1.1.4a: Results from Ok Tedi mine site(Knorre & Griffiths, 1985).

	Before H_2O_2 treatment	After H_2O_2 treatment
Tailings flow M^3/h (nominal)	1100	1100
Solids content % (nominal)	45	45
pH	10.5 - 11.0	10.2 - 10.8
Free cyanide mg/l	50 - 100	Undetectable
Easily liberatable cyanide (mg/l)	90 - 200	< 0.5
Total cyanide (mg/l)	110 - 300	1 - 10
Dissolved Cu (mg/l)	50 - 100	< 0.5
Zn (mg/l)	10 - 30	< 0.1
Fe (mg/l)	1 - 3	1 - 3

Khodadadi et al 2005 showed that the rate of conversion of cyanide to cyanate can be increased 2-3 folds by applying 10mg/l Copper as a catalyst and an excess of 20% hydrogen peroxide increases the rate by 30%. Using concentrations of 6.65mg/l, 3.32mg/l and 2.99mg/l solutions of hydrogen peroxide, Khodadadi et al 2005 investigated the effect of different peroxide concentrations (Fig 10.1.1.4a) and retention times on the oxidation of cyanides (Fig 10.1.1.4b).

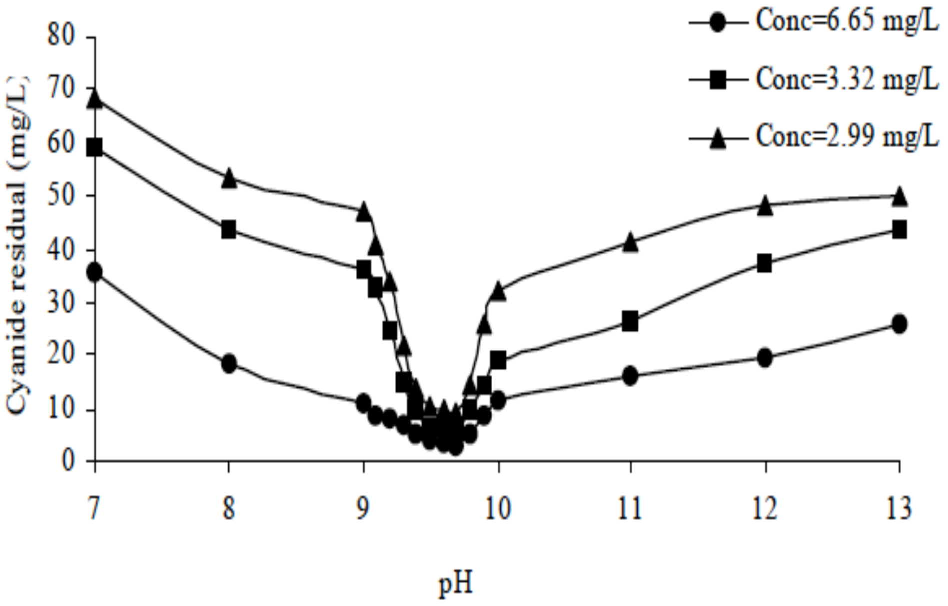


Figure 10.1.1.4a: The effect of hydrogen peroxide concentration on cyanide removal with the presence of 30 mg/L copper sulfate on cyanide removal (Khodadadi et al 2005).

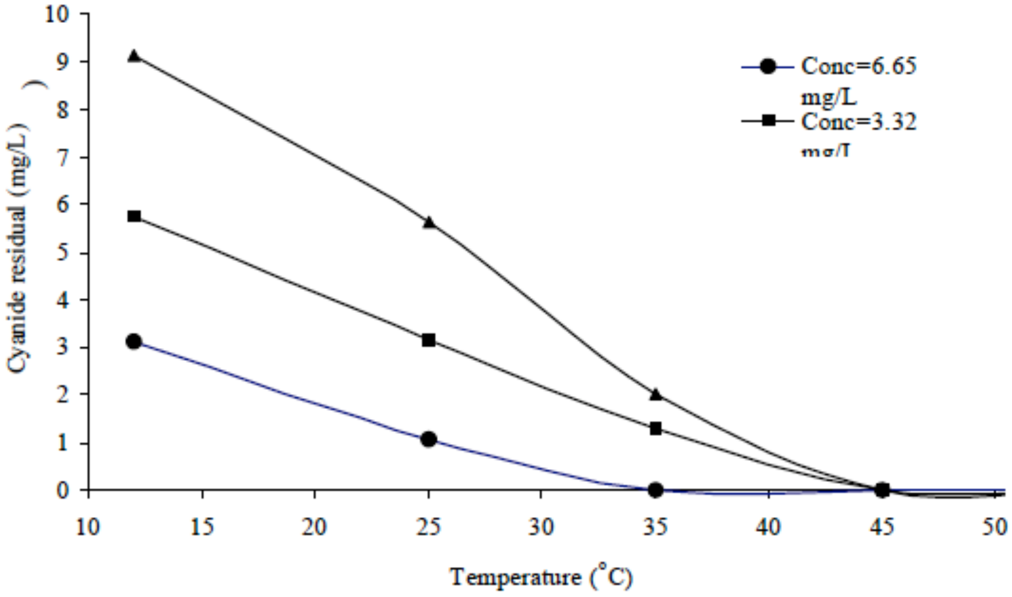


Figure 10.1.1.4b: The effect of temperature on cyanide removal using •6.65, ▪3.32 and ▲2.99g/L of hydrogen peroxide (Khodadadi et al 2005).

Figure 10.1.1.4a demonstrates that the removal of cyanides was optimum at a pH of approximately 9.7. While increasing the temperature increased the rate of the reaction, they concluded that at temperatures above 12°C most of cyanide lose was due to formation of HCN which evaporated due to its low point of 25.75°C. At temperatures above 12°C the rate of release of oxygen by hydrogen peroxide increases and this may increase so high that it exceeds the rate of oxidation of the cyanides resulting in an increase of the residual cyanide content in solution.

10.1.1.5 **Ozonation of Cyanides**

Experiments to decipher the stoichiometry of the reaction between ozone and cyanide revealed that ozone reacts faster with the cyanide ion (CN^-) than with hydrogen cyanide (HCN) (Gurol et al. 1984). With constant amounts of ozone and total cyanides in solution, an increase of the pH will yield a higher concentration of cyanide ions that was matchad by an increase in the cyanide conversion rate. Experiments on free cyanide with a flow rate of 0.5l/min and ozone with a flow of 19mg/min were conducted to check the residuals of total cyanide, cyanate and ozone for three different pH values 11.2, 7.0, and 2.5 over time (fig 10.1.1.5a).

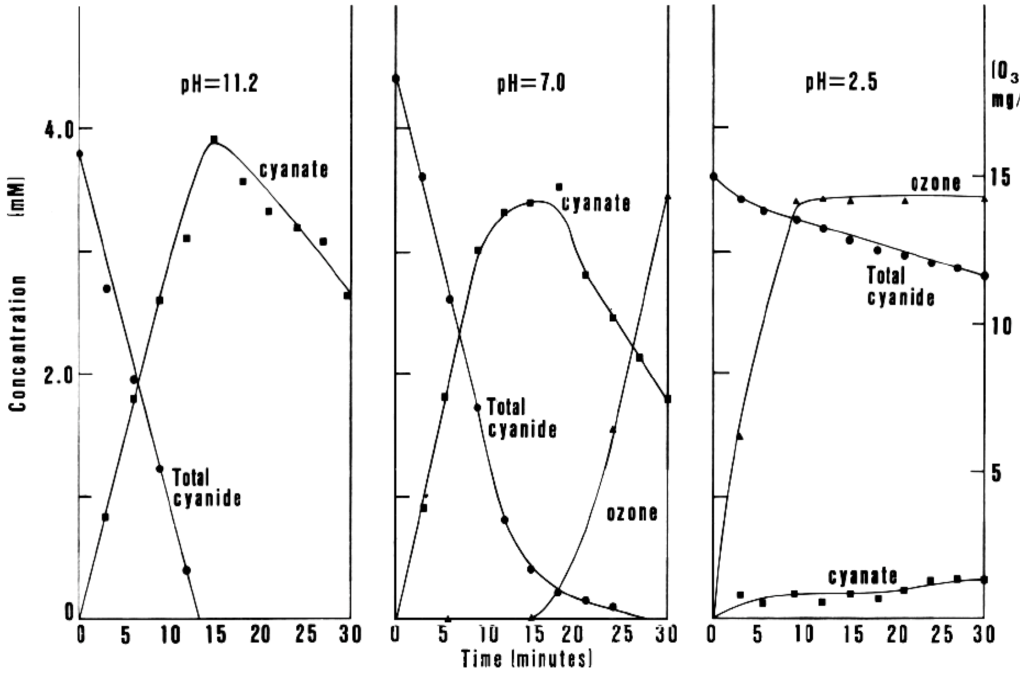


Figure 10.1.1.5a: Profiles of total cyanide, cyanate and ozone residual in the bubble reactor for pH 11.2, 7.0 and 2.5 (Gurol et al.1984).

At pH 11.2 the rate of disappearance of cyanide was equal to the rate of formation of cyanate until all the cyanide was consumed at which point the cyanate reacted with ozone in a much slower reaction leading to a drop in the cyanate concentration. During the course of this process there was no appearance of residual ozone as it was being immediately consumed in oxidation and decomposition reactions. At a pH of 7.0 there is the presence of HCN that undergoes a slower oxidation. The rate of conversion of cyanide was the same as in the first process until when the total cyanide ion was consumed. This resulted in cyanate decomposition while there was still some cyanide in solution and resulted also in the presence of residual ozone in solution. At a pH of 2.5 the volatilization of cyanide was responsible for more lose of cyanide than oxidation resulting in the early appearance of ozone in solution. Gurol et al 1984 experimented in details with Wads and iron cyano-complexes.

The results obtained by Gurol et al 1984 when the pH was 11.2 where similar to findings by Carillo & Soria 2001. In their work Carillo et al 2001 found that in the presence of free cyanide ions there is no accumulation of ozone in the solution. Many reports from experimental trials found that when there is cyanide in the solution the value of pH, ORP (oxidation reduction potential) and dissolved ozone stay relatively constant (Nava et al. 2003; Gurol et al. 1984). These values start fluctuating after completion of cyanide oxidation. The redox potential and dissolved ozone get a small increase while the pH drops slightly (fig 10.1.1.5b).

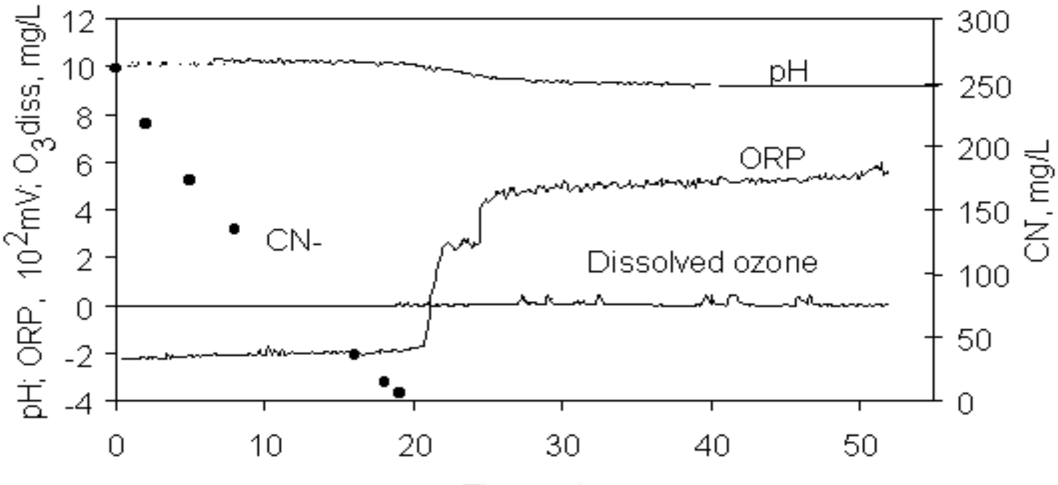


Figure 10.1.1.5b: Cyanide ozonation, T=27°C, Fg=4l/min, Vsg=2.92cm/s, Vsl=1.4l/min, VaO_3g=0.068g/min (Carillo-Pedroza & Soria-Aguilar, 2001).

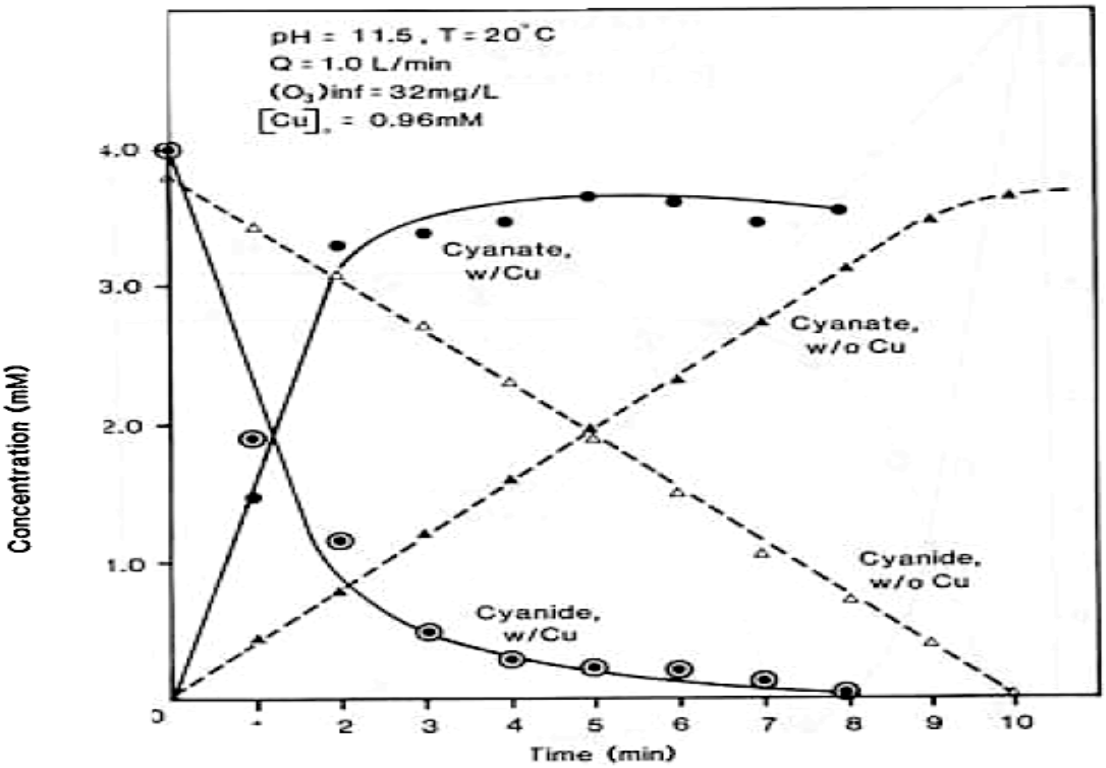


Figure 10.1.1.5c: Oxidation of Cyanide to Cyanate by Ozone (Gurol et al. 1984).

Figure 10.1.1.5c shows the influence of copper as catalyst in the oxidation of cyanide to cyanate by ozone. It can be seen that in the presence of copper as a catalyst the rate of oxidation is increased.

10.1.1.6 Biological degradation of cyanides

Test results from the biological degradation/oxidation of cyanides show that microorganisms can degrade cyanides with a limited concentration and this amount depends on the organism's resistance to cyanide toxicity. Generally the maximum concentration of cyanide which microorganisms are believed to treat is approximated to be slightly above 350mg/l. Dead cells and enzymes can treat cyanide with concentration above 1000mg/l as they are less prone to cyanide toxicity. In both situations as mentioned above the total amount of cyanide is reduced to below 0.1mg/l within 4 to 5 hours. Adams et al 2001 showed using a biological cyanide degradation (BCND^{TM}) process developed by Applied Biosciences that for different organisms maximum cyanide assimilation occurred within ≈4˚C and <30˚C, and within a pH range of 7.5 to <11.5. Simulating field conditions in a laboratory, Adams et al 2001 degraded cyanide of ≈70mg/l cyanide concentration to 0.01mg/l that was the prescribed discharge limit in approximately 34 days (figure 10.1.1.6a).

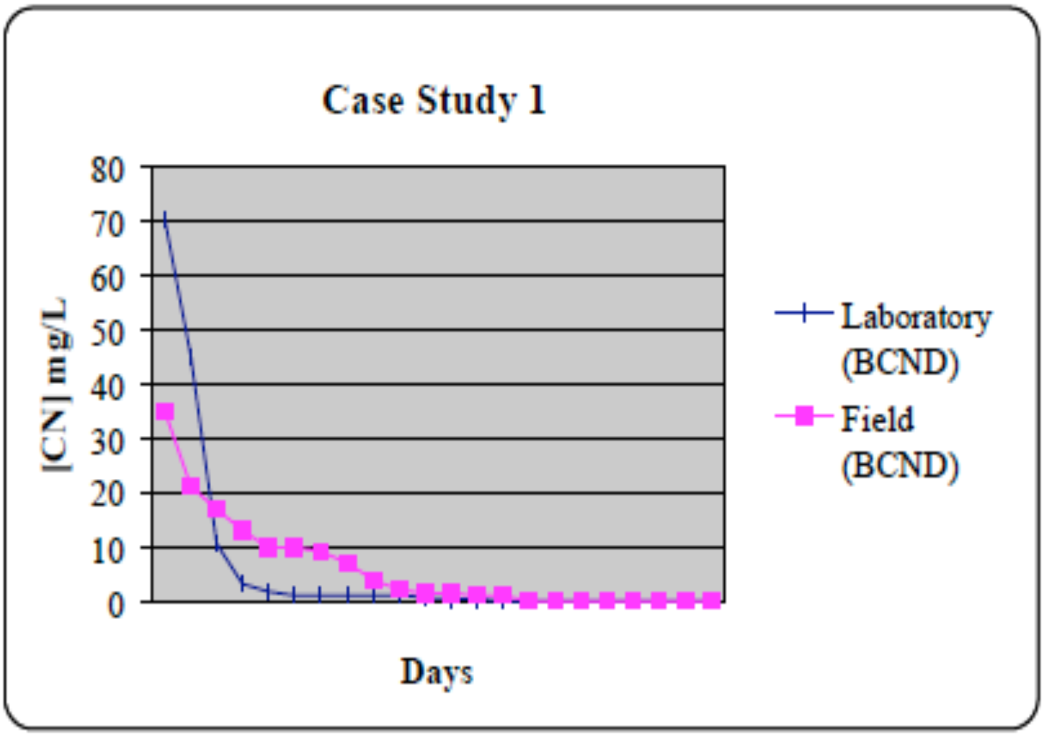


Figure 10.1.1.6a: Case Study 1 laboratory and field cyanide biodegradation results in process and wastewaters (Adams et al. 2001)

Adams et al 2001, compared the effectiveness of the biodegradation process and other water rinsing process of hydrogen peroxide and iron sulfate found that biodegradation was not only faster but it was cheaper (figure 10.1.1.6b).

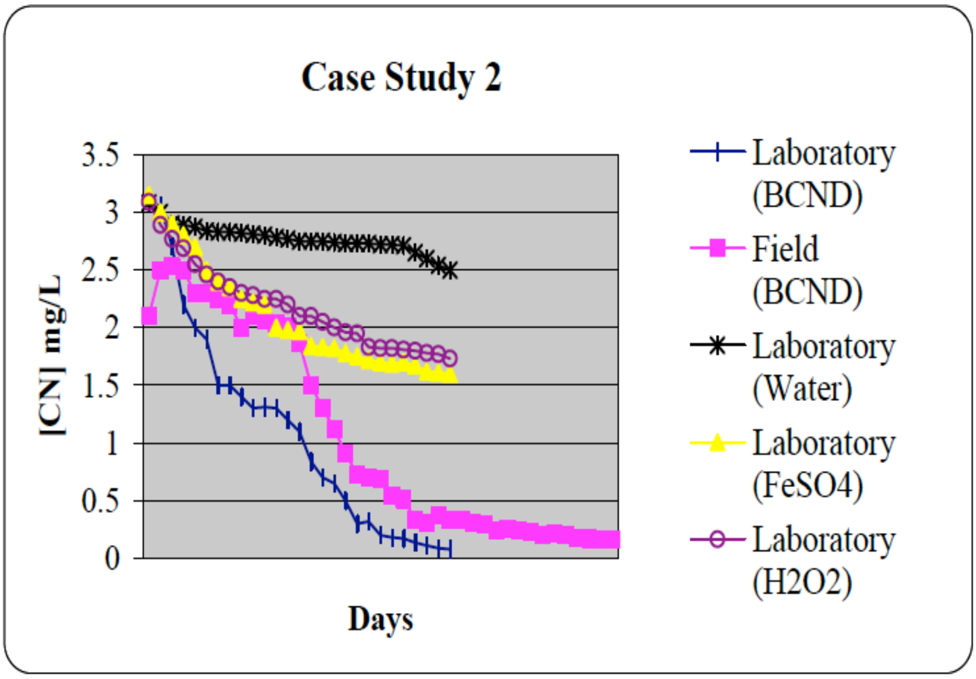


Figure 10.1.1.6b: Case Study 2 laboratory and field cyanide biodegradation of waters and spent heaps (Adams et al. 2001).

Unlike in microbial cyanide degradation where the cyanide degradation rate increased with temperature increase, Adams et al noticed that the rate of enzymatic cyanide degradation dropped as the temperature increased (Figure 10.1.1.6c) probably due to denaturing of the protein.

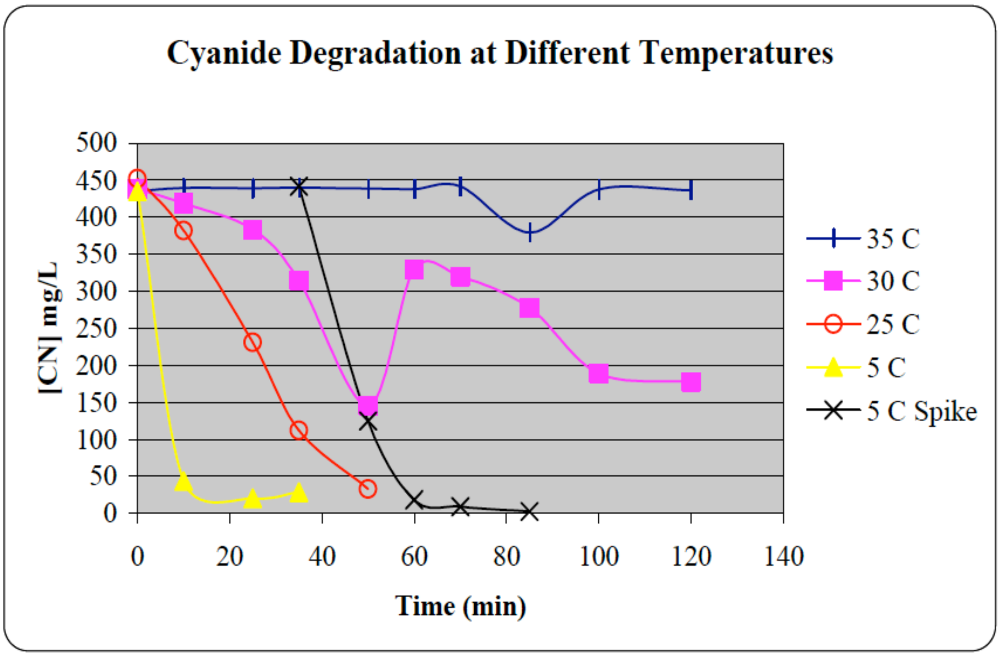


Figure 10.1.1.6c: Enzymatic cyanide degradation as a function of temperature (Adams et al. 2001).

10.1.2 Adsorption of Cyanides

10.1.2.1 **Adsorption**

This method has not been very attractive to main cyanide waste producers because it has not been successful for the adsorption of free cyanides as it is for WADs (Cu, Ni, Zn, Hg cyanide complexes etc) and SADs in particular of gold and silver cyanide complexes where it is used for the extraction of these metals. Both naturally occurring and artificially produced free or metal impregnated adsorbents have been used. Using a 100mg/l concentration of CN^- at a pH of 10.5 – 11 with varying concentrations of adsorbents Deveci et al 2006 found that the removal rate of CN^- increased when the pure activated carbon (Figure 10.1.2.1a) was used and when it impregnated with metal ions of copper and silver (Figure 10.1.2.1b).

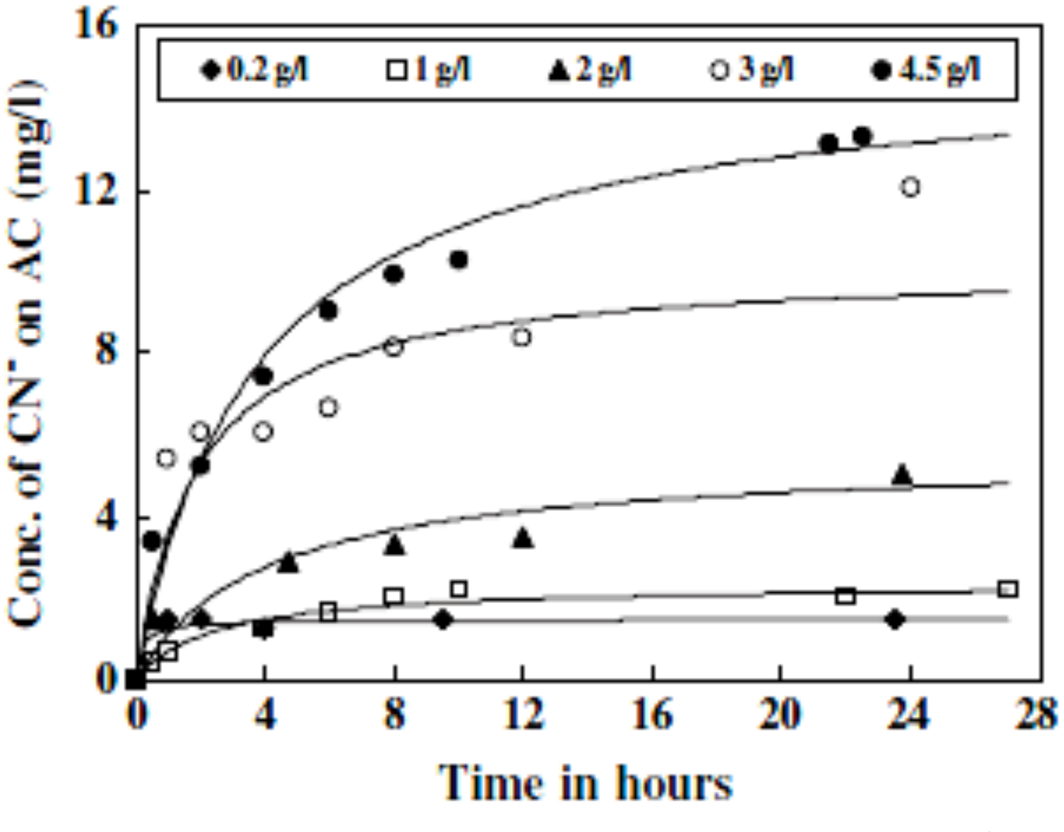


Figure. 10.1.2.1a: Removal of cyanide from solution using plain activated carbon (AC) at the adsorbent dosages of 0.2–4.5 g/l ([CN–]0: 100 mg/l, pH 10.5–11) (Deveci, 2006).

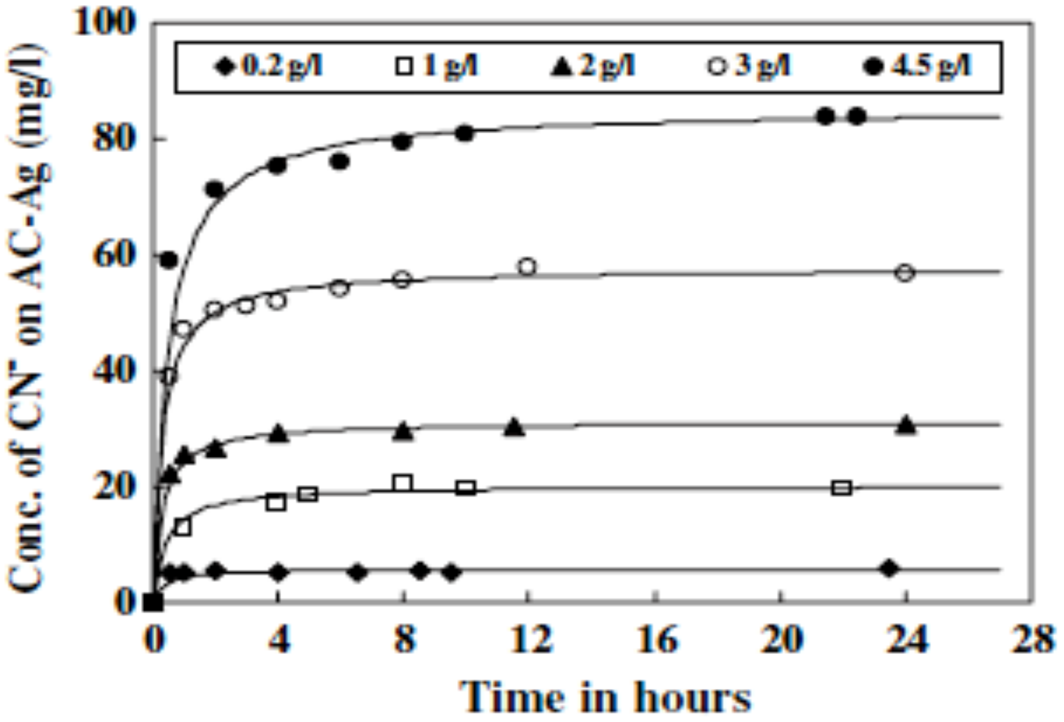


Figure 10.1.2.1b: Removal of cyanide from solution using silver-impregnated activated carbon (AC–Ag) at the adsorbent dosages of 0.2–4.5 g/l ([CN$^-$]0: 100 mg/l, pH 10.5–11) (Deveci, 2006).

Figure 10.1.2.1c shows the removal rate of CN$^-$ when pure activated carbon was used for adsorption and when it was impregnated with metals ions of copper and silver.

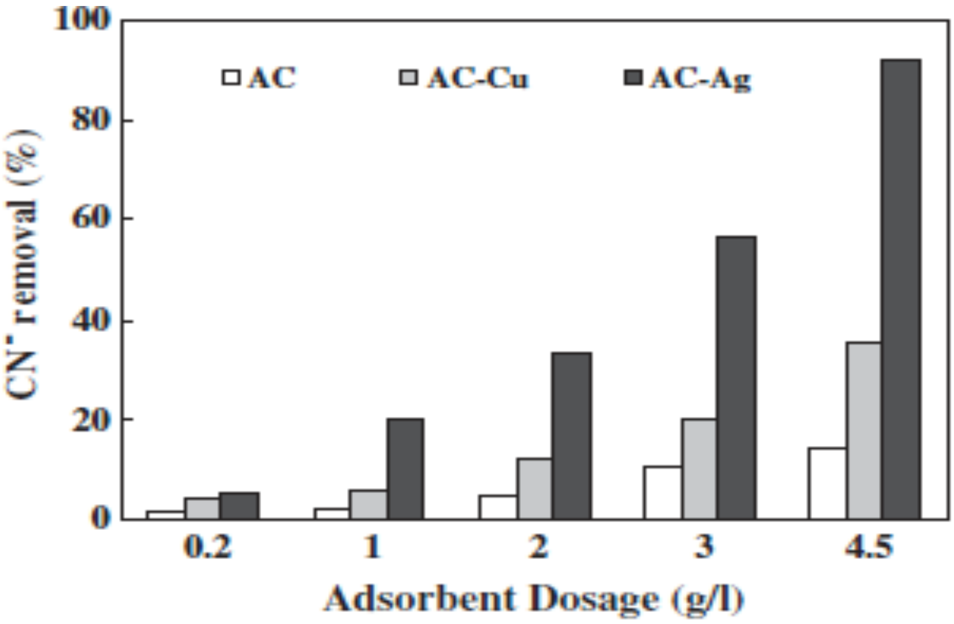


Figure 10.1.2.1c: Comparative performance of plain (AC), copper- (AC–Cu) and silver-impregnated (AC–Ag) activated carbons for the removal of cyanide at different adsorbent dosages (0.2–4.5 g/l) over an equilibrium period of 22 h ([CN–]0: 100 mg/l, pH 10.5–11) (Deveci, 2006).

10.1.3 Physical Methods

These processes include dilution, electrowinning, hydrolysis, and membrane treatments. Dilution as a method for treating cyanide waste is generally not accepted.

10.1.3.1 Electrowinning

The winning of metals and the subsequent oxidation or recirculation of the freed cyanide ions has been used for the treatment of cyanide wastes. Experimenting with copper cyanide solutions, success rates of 60% have been achieved for copper winning Lu et al 2002a in Lemos et al 2006. For different cyanide complexes the amount of energy needed for the dissociation varies depending on the strength of the complex. This method is very efficient for treating concentrated solutions, because evolution of hydrogen dominates in dilutes solutions and this has the potential of masking reactions responsible for the deposition of metals at the cathode.

Tables 10.1.3.1a, b, c and d summarize the efficiencies of the various processes for cyanide degradation. The efficiency is graded as follows: xxxx is ≥ 90% efficiency, xxx is efficiency between 60% and 90%, xx is efficiency between 10% and 60%, and x is efficiency below 10 % and O implies the process does not treat that substance. It must be emphasized that the percentages given in the tables are just approximations from various experimental and field trials as the efficiency of the various processes is greatly influenced by several internal and external factors that may result in fluctuations of the efficiency. Where a process can treat solutions it is denoted yes and where not it is noted as no. No, does not necessarily imply that a process can not apply in that case but it can be that it may be very expensive or not very suitable in that circumstance. When the effluents from a process need further treatment to meet discharge limits it is denoted yes and when not it is denoted no. The abbreviation ‘ppt’ is used to denote a situation where a species is simply precipitated out of solution. How much further treatment an effluent from a degradation process needs before the effluent meets discharge standard varies. Some process effluents require just a bit of treatment to qualify for discharge while others need a lot.

Table 10.1.3.1a: Characteristics of Chemical treatment, photolysis and biodegradation methods for treatment of cyanide wastes

Treatment Method	**Free Cyanide**	**WADs**		**SADs**		**SCN^-**	**Solution**	**Slurry**	**Need further treatment**
		Cd/Zn	**Cu/Ni**	**Fe**	**Others**				
Catalytic Oxidation	xxx	x	x	o	o	o			Yes
Chlorination	xxxx	xxxx	xxxx	o	o	xxxx	Yes	No	Yes
Hydrogen peroxide	xxxx	xxxx	xxxx	o(ppt)	o	o	Yes	No	Yes
Ozonation	xxxx	xxxx	xxxx	o	o	xxxx	Yes	no	Yes
Sulfur Dioxide Oxidation	xxxx	xxxx	xxxx	o(ppt)	xxx	xx	Yes	Yes	yes
Direct Photolytic Degradation	o	xx	xx	xxxx	xxx	x	Yes	No	Yes
Biodegradation	xxx	xxx	xxx	xxx	xxx	xxx	Yes	No	Yes

Key

🟥	≥ 90%	🟦	60%≥ X ≥10%	🟫	no effect
🟩	90%≥ X ≥60%	🟨	X < 10%		

Table 10.1.3.1b: Characteristics of Adsorption methods for treatment of cyanide wastes

Treatment Method	Free Cyanide	WADs		SADs		SCN^-	Solution	Slurry	Need further treatment
		Cd/Zn	Cu/Ni	Fe	Others				
Mineral Adsorption (Estimation)	🟦 xx	🟦 xx	🟩 xxx	🟩 xxx	🟩 xxx	🟨 x	Yes	Yes	yes
Untreated AC	🟫 o	🟦 xx	🟦 xx	🟦 xx	🟦 xx	🟨 x	Yes	No	yes
Cu-treated AC	🟫 o	🟩 xxx	🟩 xxx	🟩 xxx	🟩 xxx	🟦 xx	Yes	no	yes
Treated Resin	🟫 o	🟥 xxxx	🟥 xxxx	🟥 xxxx	🟥 xxxx	🟦 xx	Yes	Yes	yes

Key

🟥	≥ 90%	🟦	60%≥ X ≥10%	🟫	no effect
🟩	90%≥ X ≥60%	🟨	X < 10%		

Table 10.1.3.1c: Characteristics of Physical methods for treatment of cyanide wastes

Treatment Method	Free Cyanide	WADs		SADs		SCN^-	Solution	Slurry	Need further treatment
		Cd/Zn	Cu/Ni	Fe	Others				
Electrodialysis	xxxx	xxxx	xxxx	xxxx	xxxx	xxxx	Yes	No	No
Electrowinning	o	xxxx	xxxx	xxxx	xxxx	o	Yes	No	Yes
Hydrolysis/ Distillation	xx	o	o	o	o	o	Yes	Yes	Yes

Key

🟥	≥ 90%	🟦	60%≥ X ≥10%	🟫	no effect
🟩	90%≥ X ≥60%	🟨	X < 10%		

Table 10.1.3.1d: Characteristics of complexation methods for treatment of cyanide wastes

Treatment Method	**Free Cyanide**	**WADs**		**SADs**		**SCN^-**	**Solution**	**Slurry**	**Need further treatment**
		Cd/Zn	**Cu/Ni**	**Fe**	**Others**				
AVR	xxxx	xxx	xxx	xx	xx	xx	yes	No	yes
Metal Addition	xxx	o	o	xxxx	xxxx	o	Yes	No	Yes
Flotation	o	x	x	xxx	xxx	o	Yes	Yes	yes
Solvent Extraction	x	x	x	x	x	x	Yes	No	yes

Key

🟥	≥ 90%	🟦	60%≥ X ≥10%	🟫	no effect
🟩	90%≥ X ≥60%	🟨	X < 10%		

10.2 Discussion

This thesis has investigated the environmental and cost effectiveness of various cyanide treatment methods. Despite the availability of numerous treatment methods, a decision on the best available method for treatment is hard to make as every method has its limitations depending on the quantity and quality of the different cyanide species comprising the waste, volume of the waste, nature (slurry or solution) of the waste, other metals and pollutants present, and in some cases the prevailing environmental conditions (temperature and precipitation) etc. Based on the influences of internalities and externalities on treatment methods it is wise that the choice of best treatment method for a cyanide waste should be made on a case-by-case basis. Not withstanding, biodegradation has an edge over the other treatment methods with respect to cost. Except in the cold climates where the cost of raising the temperature within the system to permit microbial/enzyme activity is exorbitant, biodegradation is more environmentally friendly and cheaper.

In this section the efficiency of the various methods will be analyzed in groups i.e. the adsorption methods, the physical methods, the complexation methods, the oxidation methods and biodegradation method. Emphasis will be on how these various groups treat free cyanides, WADs, SADs, and thiocyanate, and how the various groups are suited for the treatment of solutions, slurries, different waste volumes and their costs. Cyanide waste treatment methods are basically divided into two main groups, separation and destruction methods. These two groups are further divided into sub sections based on how the separation or destruction is achieved.

10.2.1 Separation Methods

The separation of cyanide species can be achieved by using physical methods, adsorptive methods or complexation methods. The main purpose of the separation methods is to capture the cyanide species without destroying the carbon nitrogen triple bond for reuse or recycling. Concentrating and recovering the cyanide purifies the waste before discharge to the environment (Young & Jordan, 1995).

The physical separation method includes the application of membranes, hydrolysis, dilution, and electrowinning. The adsorptive method is divided into two, the ion exchange and adsorption processes. The complexation method is divided into the flotation method, metal addition, solvent extraction and the acidification-volatilization-recovery method.

These methods are similar in that, every one of these methods involves the application of either a physical or an electric/electrostatic force, or both. These methods do not produce any toxic wastes. The main limitation of the separation technologies is their inability to handle large volumes of waste, especially dilute effluents due to the prohibitive cost associated with them. While the physical methods generally do not involve the introduction of other chemicals, the adsorption and complexation methods might, but these will be involved only in physical bonding (involving ionic or weak Van der Waals forces). Generally speaking, and with the exception of a few discrepancies, the separation methods can treat free cyanides, thiocyanates, WADs and SADs. In all instances, except for electrodialysis and reverse osmosis, there is a need to further treat the effluents from the different separation methods.

10.2.1.1 **Adsorption Methods**

These methods include the processes of adsorbing cyanides on natural mineral surfaces, on activated mineral surfaces and on chemically activated mineral or artificially produced highly porous substances (Resins) in ion exchange processes. While these methods generally treat all forms of cyanides, their efficiency is highly correlated to the number of available adsorption cites on their surfaces. This implies that surfaces with a higher number of adsorption sites have efficiencies higher than those surfaces with a limited number. By this claim, chemically activated surfaces are more efficient than physically activated surfaces that are also more efficient than surfaces that are neither physically nor chemically activated. These processes are generally inefficient (can treat only a small amount of cyanides) as they can handle only a limited number of cyanides and are not suited for large volume wastes because of the cost involved. Untreated activated carbons and untreated resins do not adsorb free cyanides while natural mineral surfaces can adsorb a high amount of the free cyanides. All the processes are not good for the treatment of thiocyanates and the cost of regenerating the surfaces is very high making the processes costly. An advantage of these processes is that they do not produce other toxins and therefore they can be good for the pretreatment of wastes before biodegradation.

10.2.1.2 **Complexation Methods**

The complexation methods (AVR, metal addition, flotation and solvent extraction) are generally used to reduce cyanides from a more stable form to a less stable (AVR and metal addition) or to extract very stable cyanide complexes from a mixture before they dissolve or disintegrate (flotation and solvent extraction). In some instances metal addition can be used to produce a very stable form of cyanide to curb mobility of the cyanide ion as a method of treatment. This is often the case when ferric and ferrous cations are reacted with WADs and SADs to produce double salts, which are more stable. The metal addition process is important for the gold mining industry where gold is precipitated as a stable complex (SAD) with cyanide but on addition of zinc ions the cyanide leaves the SAD (gold cyanide complex) to complex with zinc forming a WAD. The disadvantage with complexation methods is that there is always the need for the application of a chemical or a metal. AVR requires reduction of pH that is acid consuming, cementation requires addition of a metal, flotation often requires the application of frothers, surfactants and modifiers and solvent extraction requires the application of an extractant of solvating, chelating or ion-exchange potentials. All these added substances make the processes expensive and not appropriate for large volumes of wastes. The effluents from these methods are less toxic and therefore these methods are applied for pretreatment and treatment of small volumes of wastes. Flotation and solvent extraction treat SADs better than WADs while cementation and AVR are better for treating free cyanides and WADs.

10.2.1.3 **Physical Methods**

These processes include dilution, membrane technology, electrowinning and hydrolysis/distillation. Dilution as a process is not acceptable because the total amount of cyanide released is not affected. In hydrolysis and distillation cyanides are often left in natural waters with pH values approximated 7.0 to disintegrate releasing cyanide ions that hydrolyze to HCN and volatize given the low vapor pressure of

HCN. This process generally does not treat thiocyanates, WADs and SADs. Electrowinning is good for treating WADs and SADs while membrane technology treats solutions of free and complex cyanides. These processes do not require the use of chemicals but membrane and electrowinning technologies are energy consuming and therefore are expensive when treating large volumes of waste.

10.2.2 Destruction Methods

Destruction of cyanides can be achieved through oxidation, which can be biological or chemical/physical methods. The physical oxidation methods are the photolytic and catalytic oxidation. In these cases there is the transfer of electromagnetic and heat energy energies respectively to catalyze electron transfer processes. These do not involve the participation of additional chemicals. The chemical oxidation methods involve the addition of chemicals such as in chlorine oxidation, sulphur dioxide oxidation, ozone oxidation and hydrogen peroxide oxidation. Added to this list of destruction methods is the biological method. Oxidation processes for cyanide degradation are cyanide degradation processes that result in the alteration/destruction of the carbon-nitrogen triple bond. Generally, the chemical oxidation methods are not very effective in treating SADs.

10.2.2.1 Oxidation methods

These processes can be divided into three groups, the physical, the chemical and the biological processes. Cyanide photolysis can be direct or indirect. In direct photolysis, the remediated compound receives the energy while indirect photolysis requires the application of a catalyst that receives the energy and then induces the breakdown of the cyanide compound. Free cyanides are not treated by direct photolysis, only some WADs and SADs especially the iron cyanide complexes. The problem with photolytic disintegration is that the process is reversible in the absence of light.

The chemical oxidation methods are the most widespread. But these, except for the Inco process (SO2/air process) and hydrogen peroxide processes which precipitate stable iron-cyanide complexes as insoluble ferricyanide salts generally these are not good for treating SADs and slurries. When applicable the chemical consumption is exorbitant. Worst still, the cost of the chemicals makes them expensive and these generally produce other toxic non-cyanide compounds making these methods not environmentally friendly. A major advantage of these processes that made them preferable for the mining industry is that the reactions involved in these processes are almost spontaneous thereby permitting the rapid treatment of large volumes of cyanide mining wastes within short periods of time.

Biological treatment on the other hand treats all forms of cyanides (free cyanide, WADs and SADs). The concentration of cyanide in the waste that can be treated biologically depends on whether microorganisms or cell free extracts (enzymes) are used and whether the process is aerobic or anaerobic. Free cell extracts can handle wastes with higher concentrations of cyanide than systems employing microorganisms. Both chemical and bio-oxidation processes are accompanied by metal leaching. When the concentration of heavy metals especially nickel is very high in the waste this can pose enormous problems for biodegradation processes by inhibiting the ability of microbes to degrade cyanides.

The cost of chemicals and the expertise required for handling and using these chemicals becomes a great challenge as compared to biodegradation where the costs of producing bacteria colonies and running the processes are comparatively very low. The effluents from biodegradation plants are non-toxic.

Summary

The adsorption, complexation and physical methods are generally referred to as cyanide recovery technologies. While there have been powerful arguments in favor of cyanide recovery and recycling technologies, proponents of these arguments acknowledge that the cost of the recovery technologies is high but they rely on the sales of recovered metals to make up for the extra cost. Unfortunately these recovery technologies hardly meet discharge specifications and therefore there is always the need for cyanide destruction technologies. The chemical detoxification processes are not only expensive but they also produce very toxic effluents. This is however not the case with biodegradation. Biodegradation processes are cheap and yet can recover metals that can be sold to generate extra income. A major challenge for using biological detoxification is its susceptibility to temperature variations and external carbon loading. Because biodegradation uses organisms and/or enzymes that require a minimum temperature within the system to be active or atleast operate minimally, this can be challenging in cold climates during the winter season as it might require expensive external heating to sustain the system. Making cyanide the limiting source for carbon availability in biodegradation systems is vital if microbes are expected to degrade cyanide for their carbon need. These must be well handled, as biodegradation facilities are very prone to external carbon loading that reduce the role of cyanide as the limiting carbon source.

Current social and political climates favor biological as oppose to chemical/physical treatment methods for cyanide (Meyers et al.1991). The race between biological treatment and chemical treatment for which of them is more environmentally friendly and economically beneficial has narrowed down to the later, as biodegradation is clearly more environmentally friendly. This is so because not only is biological treatment cheaper but also it is showing great potential in the area of metal leaching (Kiruthika & Shrinithya, 2008). The application of different bacteria cultures at different stages in biological treatment processes has meant that unlike the chemical treatment processes which only treat the cyanides while generating toxic wastes like ammonia and nitrates, and the cyanide recovery methods which are generally limited in their ability to handle large volumes of diluted waste solutions, biodegradation treats large volumes of waste (diluted and concentrated) and can deal with cyanides, thiocyanates, and cyanates, while ammonia and nitrates are biologically treated in separate nitrification and denitrification units (Carroll, 2009).

May and Alexander 2001, observed that stimulating naturally existing indigenous organisms in cyanide polluted environments for cyanide degradation can be less expensive and faster than natural attenuation, implying that there is an abundance of bacteria species for biodegradation. There is also evidence that biological treatment of cyanide waste presents benefits both environmentally and financially (Huertas M.-J. , et al., 2006; May & Alexander, 2001). However, biological treatment that is the foundation of natural attenuation is becoming less costly with advances in biotechnology and can be just as effective (Carroll, 2009). Despite a higher initial cost for biodegradation, its lower operating cost makes it a financial windfall for users in the long term (Carroll, 2009).

Although extensive research has been done so far on the biodegradation of Cyanides, a one solution bioreactor with a fixed bacteria feed is a difficult option as there are many factors which determine the appropriateness of a bacteria to degrade a cyanide compound. Sobolewski 2000, reports that in a particular mine, bacteria species vary temporally and spatially. Different leached heaps were very unique from each other, implying that cyanide degraders are adapted to ambient conditions (temperature, pH, redox condition, cyanide concentration, etc). Therefore, the chemical composition of the waste limits the abundance and variability of microorganisms capable of surviving and/or degrading cyanide in that environment. The presence of a cyanide degrading microorganism in a cyanide polluted environment is not an indication of cyanide degradation, as factors such as an increased cyanide concentration level or the presence of toxins (e.g. mercury, Arsenic) can suppress an organism's ability to degrade cyanide compounds (Sobolewski, 2000). The Selection of a treatment method for a particular waste is not an easy process as many factors including the nature of the waste and the desired outcome are considered (glossary 1x, 2x, 3x, and 4x).

The cost of cyanide biodegradation is influenced by a number of externalities, the most important of which are ambient temperature and influx of organic material. During the winter months in cold climates biodegradation is hard to carry out and plants that rely on it for cyanide waste treatment must have large holding facilities where tailings can be held for treatment in the summer months (Martel & Bocking, 2003).

10.2.3 Implications Of This Research

This research addresses currently pressing issues as depletion of global mineral reserves, mining of low grade ore deposits, re-mining and/or restoration of abandoned mine sites, mining economics, public view of pollution associated with mining (especially mining with cyanide) and legislation guiding the handling and treatment of mine wastes.

Without doubt, the discovery and development of new mineral deposits has not matched increasing demand for minerals and especially for the rare-earth minerals. To dampen down this demand stress, there is pressure to develop low-grade mineral deposits that in the case of gold mining results in excess application of cyanide to scavenge for any iota of gold in the ore body. This excess use of cyanide results in a greater quantity of cyanide in the effluent. The depletion of mineral deposits has also resulted in an increase in the price of minerals and this has created other opportunities for miners. Miners can re-mine old mine wastes profitably and the cost of restoration of polluted current/abandoned mine sites can be greatly reduced through income generated by the sales of minerals harvested on these sites. This can be achieved if mine waste treatment is carried out in conjunction with metal leaching. This research has the potential of greatly changing the economics of mining projects in developing countries in particular. The problem of pollution from mining is extreme in the developing countries, but this can now be seen as a missed opportunity if the trend continues.

For developing countries like Cameroon that are just beginning to mine their mineral deposits, the economics of these mining projects can be enhanced by looking at mine wastes as secondary mines with the potential of creating jobs and generating extra income while preserving the environment. This can be achieved easily through biodegradation techniques that degrade any pollutants and extract potential polluting metals present in the mining tailings.

10.2.3.1 **Mining in Cameroon**

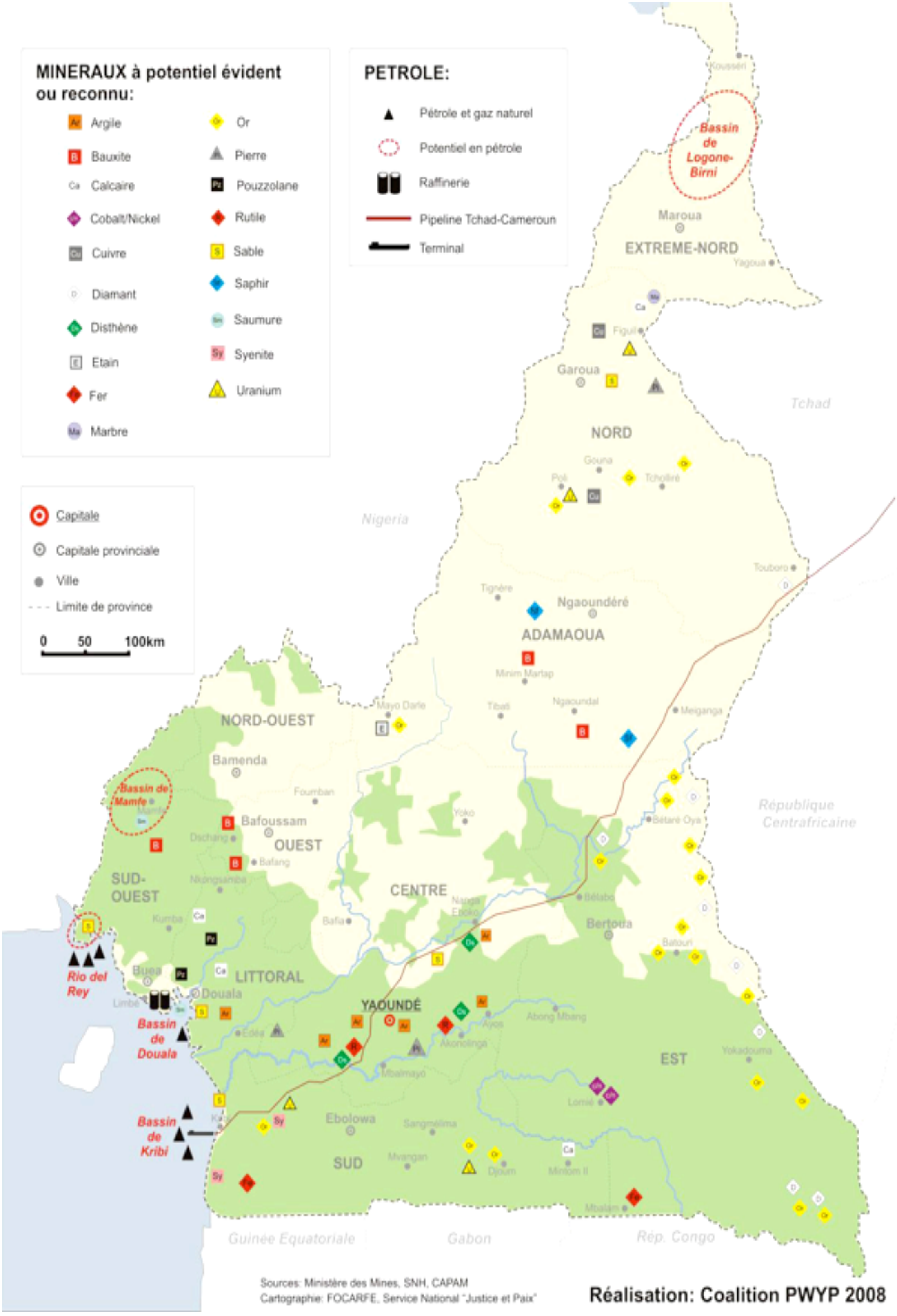
Cameroon is projected to become a mining giant in the next decade following the discovery of several ore deposits including amongst others large deposits of cobalt, nickel, iron, bauxite, gold, diamond, etc (fig 10.2.3.1). These projects are in their infancy stages and therefore projected gangue/tailings characterization is not very informative qualitatively (types of pollutants) and quantitatively (the amounts of each pollutant). An 'Environmental And Social Assessment Waste Management Plan' for the Nkamouna cobalt/nickel mining project (Table 10.2.3.1) prepared for Geovic Cameroon PLC by the environmental consultancy group Knight Piesol and Co neither includes the types nor quantities of metals expected in the waste. It rather presents the pollutants under broad topics such as flocculants, sulfur, and corrosion inhibitors, e.t.c. It can be speculated that sulfur will occur combined with other elements or metals, such as with iron in pyrite as indicated in the chart. These can pose pollution problems if not well handled.

Table 10.2.3.1: Chemicals used at the Nkamouna Project site (Geovic Cameroon, 2011)

Chemicals	Use	Toxicity	Recommended disposal	Comment
Sulfur	Mineral Processing	Non Toxic	Suitable waste disposal facility	Flammable
Flocculant	Mineral Processing	No Known Effects on Ingestion	Landfill	
Dense Soda Ash	Mineral Processing	Low	Landfill	
Pyrite	Mineral Processing	Low	Landfill	
Sodium Hydroxide	Mineral Processing		Suitable waste disposal facility	
Sodium Hydrosulphide	Mineral Processing	High Toxic	Suitable waste disposal facility	
Diesel	Fuel	Harmful or toxic on ingestion	Mixed with absorbing minerals, use suitable waste disposal facility	Flammable
Corrosion Inhibitor	Water Treatment			
Antiscalent	Water Treatment			
Biocide	Water Treatment			

As earlier noted, minerals do hardly exits alone as they often exist in combination with other metals (minerals). Though the associated minerals may not be in large quantity they can make a large difference in the economics of mining projects especially if these metals fall within the class of rear earth highly demanded metals (gold, silver, platinum, coltan, cobalt).

Mineral Deposits In Cameroon



Sources: Ministère des Mines, SNH, CAPAM
Cartographie: FOCARFE, Service National "Justice et Paix"

Réalisation: Coalition PWYP 2008

Figure 10.2.3.1: Map of mineral deposits in Cameroon (Min. Cam 2012). (Argile = Clay, Bauxite = Bauxite, Calcaire = Limestone, Cobalt/Nickel = Cobalt/Nickel, Cuivre = Copper, Diamant = Diamond, Disthene = Disthene, Etain = Tin, Fer = Iron, Marbre = Marble, Or = Gold, Pierre =

Stones, Pouzzolane = pozzolan, Rutile = Rutile, Sable = Sand, Saphire = Saphir, Saumure = Salt water or brine, Syenites = Syenites, Uranium = Uranium).

Recommendations

Given that the chemical methods that are the most widely used for treating cyanide wastes are expensive and produce effluents containing other toxins, it is clear that a combination of methods should be the way forward. Methods for the capture and reuse of cyanides should be used at pretreatment stages for cyanide wastes treatment processes. This should be in combination with methods that harvest metals from these wastes. In this way the final residue will be low in cyanide and metal concentrations making it fit for fast and easy biodegradation. Therefore the following recommendations:

- The process of cyanide treatment should begin during the usage of cyanide. This can be achieved by optimizing the usage of cyanide in processes to reduce the quantity of cyanide in effluents. For heap leaching and other mining processes this should begin during ore beneficiation. This will reduce the amount of cyanide lost to cyanicides, as this determines the concentration and variety of cyanide species in the effluent. The second treatment stage should be the degradation of any left over cyanides biologically as this treats most of the toxic effluents (Ammonia, nitrates, nitrites e.t.c.) generated in the earlier stage of treatment.
- There should be more research on the bioaugmentation of microbes and microbial biomass for the selective extraction of metals from wastes and for the biodegradation of cyanides.
- There should be legislation to encourage the development and use of biodegradation methods for cyanide treatment.

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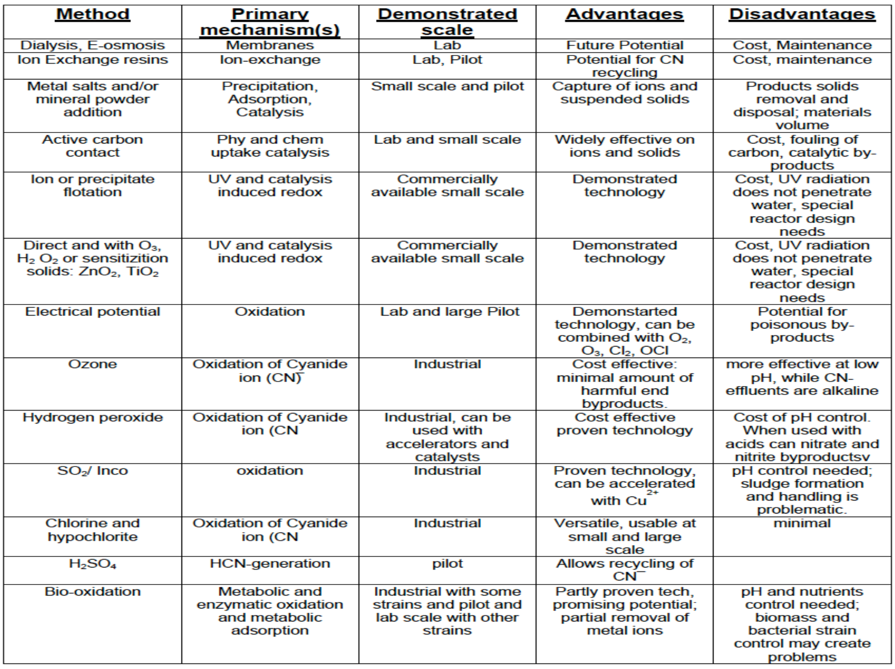
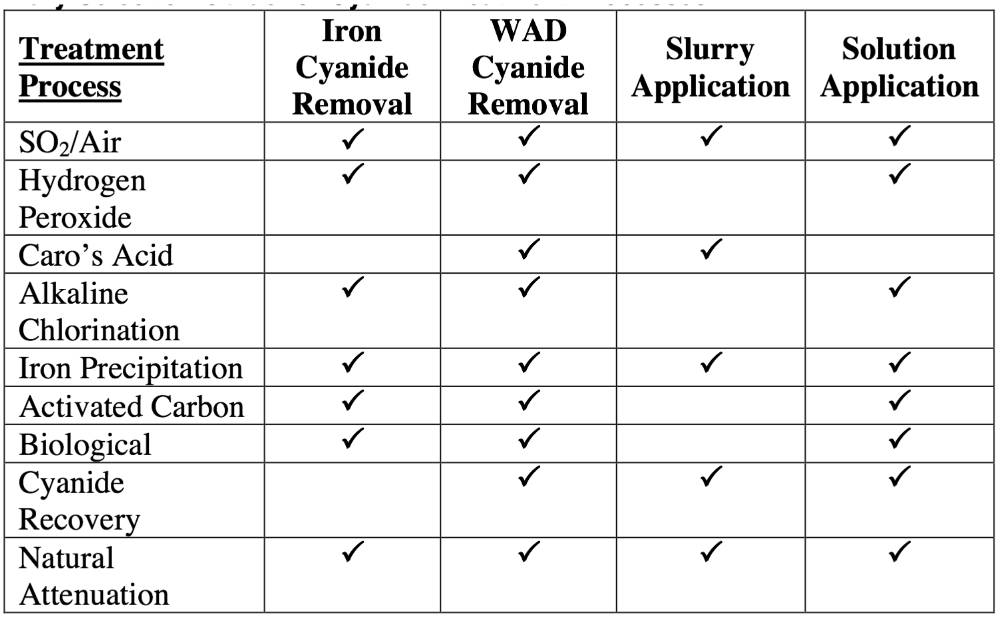
Glossary

Table 1x; Cyanide Abatement and destruction technologies for CN containing effluents (Yarar, 2001)



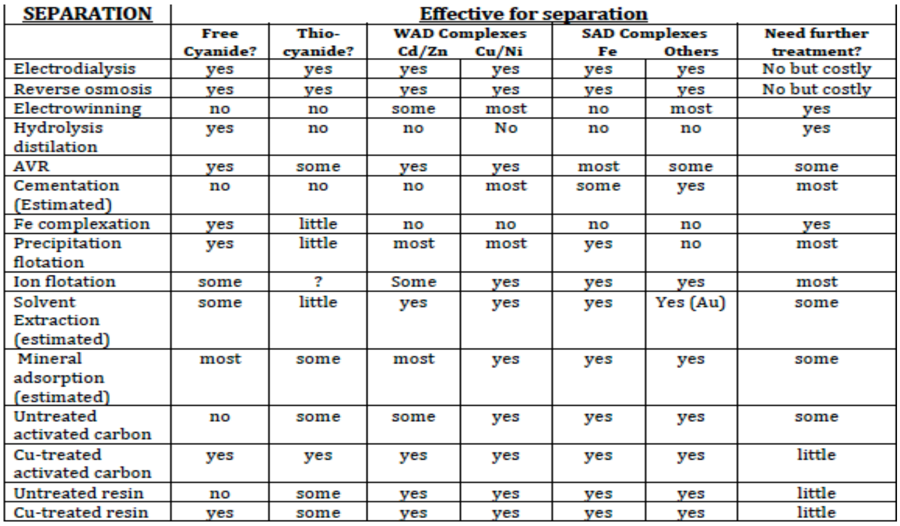
Method	**Primary mechanism(s)**	**Demonstrated scale**	**Advantages**	**Disadvantages**
Dialysis, E-osmosis	Membranes	Lab	Future Potential	Cost, Maintenance
Ion Exchange resins	Ion-exchange	Lab, Pilot	Potential for CN recycling	Cost, maintenance
Metal salts and/or mineral powder addition	Precipitation, Adsorption, Catalysis	Small scale and pilot	Capture of ions and suspended solids	Products solids removal and disposal; materials volume
Active carbon contact	Phy and chem uptake catalysis	Lab and small scale	Widely effective on ions and solids	Cost, fouling of carbon, catalytic by-products
Ion or precipitate flotation	UV and catalysis induced redox	Commercially available small scale	Demonstrated technology	Cost, UV radiation does not penetrate water, special reactor design needs
Direct and with O_3, H_2 O_2 or sensitizition solids: ZnO_2, TiO_2	UV and catalysis induced redox	Commercially available small scale	Demonstrated technology	Cost, UV radiation does not penetrate water, special reactor design needs
Electrical potential	Oxidation	Lab and large Pilot	Demonstarted technology, can be combined with O_2, O_3, Cl_2, OCl	Potential for poisonous by-products
Ozone	Oxidation of Cyanide ion (CN^-)	Industrial	Cost effective: minimal amount of harmful end byproducts.	more effective at low pH, while CN- effluents are alkaline
Hydrogen peroxide	Oxidation of Cyanide ion (CN	Industrial, can be used with accelerators and catalysts	Cost effective proven technology	Cost of pH control. When used with acids can nitrate and nitrite byproductsv
SO_2/ Inco	oxidation	Industrial	Proven technology, can be accelerated with Cu^{2+}	pH control needed; sludge formation and handling is problematic.
Chlorine and hypochlorite	Oxidation of Cyanide ion (CN	Industrial	Versatile, usable at small and large scale	minimal
H_2SO_4	HCN-generation	pilot	Allows recycling of CN^-	
Bio-oxidation	Metabolic and enzymatic oxidation and metabolic adsorption	Industrial with some strains and pilot and lab scale with other strains	Partly proven tech, promising potential; partial removal of metal ions	pH and nutrients control needed; biomass and bacterial strain control may create problems

Table 2x; Preliminary Selection Guide for Cyanide Treatment Processes (Botz M. , 1999)



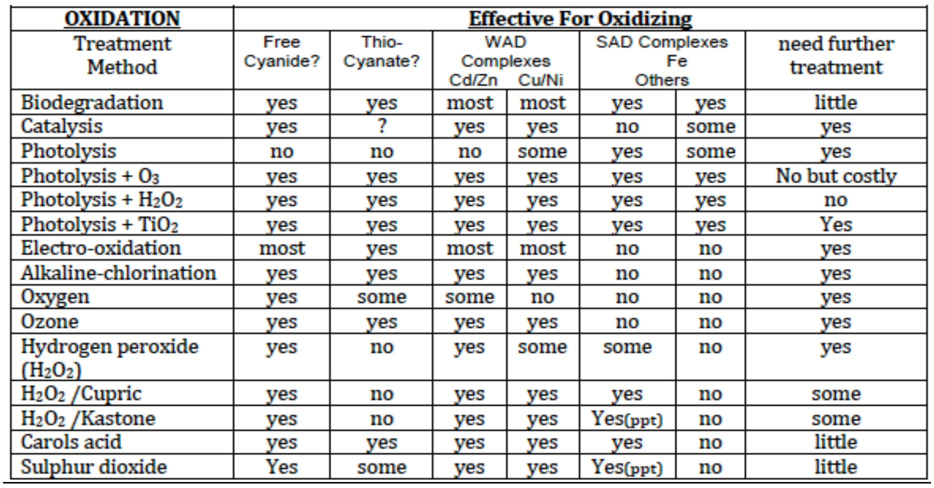
Treatment Process	**Iron Cyanide Removal**	**WAD Cyanide Removal**	**Slurry Application**	**Solution Application**
SO_2/Air	✓	✓	✓	✓
Hydrogen Peroxide	✓	✓		✓
Caro's Acid		✓	✓	
Alkaline Chlorination	✓	✓		✓
Iron Precipitation	✓	✓	✓	✓
Activated Carbon	✓	✓		✓
Biological	✓	✓		✓
Cyanide Recovery		✓	✓	✓
Natural Attenuation	✓	✓	✓	✓

Table 3x; Effectiveness of separation processes for cyanide remediation (Young & Jordan, 1995)



SEPARATION	Effective for separation						
	Free Cyanide?	Thio-cyanide?	WAD Complexes		SAD Complexes		Need further treatment?
			Cd/Zn	Cu/Ni	Fe	Others	
Electrodialysis	yes	yes	yes	yes	yes	yes	No but costly
Reverse osmosis	yes	yes	yes	yes	yes	yes	No but costly
Electrowinning	no	no	some	most	no	most	yes
Hydrolysis distilation	yes	no	no	No	no	no	yes
AVR	yes	some	yes	yes	most	some	some
Cementation (Estimated)	no	no	no	most	some	yes	most
Fe complexation	yes	little	no	no	no	no	yes
Precipitation flotation	yes	little	most	most	yes	no	most
Ion flotation	some	?	Some	yes	yes	yes	most
Solvent Extraction (estimated)	some	little	yes	yes	yes	Yes (Au)	some
Mineral adsorption (estimated)	most	some	most	yes	yes	yes	some
Untreated activated carbon	no	some	some	yes	yes	yes	some
Cu-treated activated carbon	yes	yes	yes	yes	yes	yes	little
Untreated resin	no	some	yes	yes	yes	yes	little
Cu-treated resin	yes	some	yes	yes	yes	yes	little

Table 4x; Effectiveness of separation processes for cyanide remediation (Young & Jordan, 1995)



OXIDATION	Effective For Oxidizing						
Treatment Method	Free Cyanide?	Thio-Cyanate?	WAD Complexes		SAD Complexes		need further treatment
			Cd/Zn	Cu/Ni	Fe	Others	
Biodegradation	yes	yes	most	most	yes	yes	little
Catalysis	yes	?	yes	yes	no	some	yes
Photolysis	no	no	no	some	yes	some	yes
Photolysis + O_3	yes	yes	yes	yes	yes	yes	No but costly
Photolysis + H_2O_2	yes	yes	yes	yes	yes	yes	no
Photolysis + TiO_2	yes	yes	yes	yes	yes	yes	Yes
Electro-oxidation	most	yes	most	most	no	no	yes
Alkaline-chlorination	yes	yes	yes	yes	no	no	yes
Oxygen	yes	some	some	no	no	no	yes
Ozone	yes	yes	yes	yes	no	no	yes
Hydrogen peroxide (H_2O_2)	yes	no	yes	some	some	no	yes
H_2O_2 /Cupric	yes	no	yes	yes	yes	no	some
H_2O_2 /Kastone	yes	no	yes	yes	Yes(ppt)	no	some
Carols acid	yes	yes	yes	yes	yes	no	little
Sulphur dioxide	Yes	some	yes	yes	Yes(ppt)	no	little