MICROBIAL OXIDATION OF ARSENITE IN GOLD MINE EFFLUENT

BY

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DECLARATION

The Registrar
University of Durban-Westville

Dear Sir

I, Anusha Ramdial, registration number 8932786; hereby declare that the thesis entitled 'MICROBIAL OXIDATION OF ARSENITE IN GOLD MINE EFFLUENT' is the result of my own investigation and research and that it has not been submitted in part or in full for any other degree or to any other university.

A Ramd

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22/04/2000

Date

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NOMENCLATURE

a	activity
A	constant in Debye and Huckel correlation
B	constant in Debye and Huckel correlation
c	concentration (mol/dm^3)
E	electrode potential (V)
F	Faraday constant (96 500 C)
H_f	Heat of formation (kcal)
I	ionic strength (mol/dm^3)
K	equilibrium constant
n	no. of electrons e^- (equivalents/mol)
N	number of measurements
ppm	parts per million (units used are equivalent to mg/dm^3)
R	universal gas constant (8.314 J/mol.^{0}K)
s	standard deviation (small sample)
T	temperature (^{0}C)
Z	ionic charge

Greek letters

γ	activity coefficient
μ	chemical potential (cal)
v	stoichiometric coefficients
σ	standard deviation (large sample)
∂	ion-size parameter ($\overset{0}{A}$)

Superscripts

$^\circ$	standard state

Subscripts

$_0$	equilibrium state
i	chemical species

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CHAPTER 1

SYNOPSIS

The problem of arsenic pollution is encountered in many industrial sectors, but it is particularly severe in the mining sector. This is because mines have been forced to shift their attention towards processing refractory gold ores due to dwindling supplies of simple gold ores. The mining of refractory gold ores containing arsenic e.g. arsenopyrite has thus worsened the problem of arsenic pollution in the gold mining industry.

The initial focus of this research project was to investigate the bacterial oxidation of arsenite in gold mine effluent by a mixed bacterial culture. The bacterial culture consisted of *Thiobacillus thiooxidans, Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*. This culture has been used successfully in the MINBAC™ process for the pre-oxidation of refractory gold ores. Furthermore, this culture is known to be tolerant of high concentrations of arsenic, therefore it was deemed suitable for use in this investigation.

However, as a prelude to the bacterial oxidation, the chemical oxidation of arsenite by ferric ion in gold mine effluent was investigated. It was known from literature that the chemical oxidation of arsenite by ferric ion did not occur. This investigation into the chemical oxidation was therefore just to confirm what was already known from literature.

The investigation into the chemical oxidation of arsenite by ferric ion in gold mine effluent showed that the oxidation of arsenite did occur, contrary to what was expected. This therefore warranted further investigation, so the focus of this project shifted somewhat to incorporate a study of the chemical phenomenon observed. All experiments conducted using the mine effluent indicated that the chemical oxidation did occur. Conversions of up to almost 80 % of arsenite were recorded.

Since the mine effluent consists not only of arsenic and iron species, it was possible that a contribution by one of the other chemical species present in the reaction mixture resulted in the oxidation of arsenite occurring. The oxidation of arsenite in a synthetic solution consisting of arsenic and iron species only was therefore investigated. This investigation showed that the chemical oxidation of arsenite by ferric ion did occur in the synthetic solution.

The ferric to ferrous ion ratio affects the redox potential of the reaction mixture. The effect of different redox potentials on the chemical oxidation of arsenite by ferric ion in a synthetic solution was therefore investigated. It was found that the chemical oxidation did occur at ratios of 4 Fe(III) : 1 Fe(II) and 5 Fe(III) : 1 Fe(II). No oxidation was reported when a ratio of 3 Fe(III) : 1 Fe(II) was used. This indicates that the threshold value of the iron ratio lies somewhere between 3 and 4 and below this threshold value, the oxidation of arsenite does not occur.

The effect of a stainless steel surface on the oxidation of arsenite in gold mine effluent was also investigated. It was found that instead of the arsenite being oxidised to arsenate, the arsenate was reduced to arsenite.

The final part of the investigation involved the oxidation of arsenite in a synthetic solution by a mixed bacterial culture comprising *Thiobacillus thiooxidans, Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*. It was found that the oxidation of arsenite to arsenate did occur. Conversions of arsenite of almost 80 % were achieved. The oxidation of arsenite was found to be zero order in arsenite, as was found by other researchers, in both the bacterial and chemical oxidation processes.

CHAPTER 2

INTRODUCTION

Nowadays, all members of the industrial sector find themselves in the (unenviable) position where, in whatever they do, they have to take into account the impact of their operations on the environment.

All industries now have to take responsibility for their actions in terms of how their operations impact on the environment. This is especially relevant to the mining sector, which is notorious for its mismanagement of the environment. There have been some shocking incidents of pollution related to mining activities resulting in many casualties. Not very long ago, an incident of arsenic poisoning was reported where members of a rural community unwittingly drank water which was laced with very high amount of arsenic. The source of arsenic was apparently an industrial operation upstream of the water source used by these people.

The gold mining industry has long found itself faced with the problem of how to deal with all the waste water produced by its operations. However, with an increasing number of gold mines having to process refractory gold ores, the problem has just gotten bigger. During the processing of arsenical refractory gold ores, the arsenic is solubilised. This results in high concentrations of arsenic downstream of the operation. Arsenic is highly toxic to all living organisms so it is imperative that the arsenic in the mine effluent be removed so that there is no pollution of the environment.

Not only has the arsenic to be removed from the effluent, but it also then has to be disposed of. The problem with arsenic removal is finding a method which gives a stable compound of arsenic since many forms of arsenic, previously thought to be stable, have proved to be highly unstable. These supposedly stable compounds have been found to decompose to arsenite, one of the most toxic forms of arsenic when simply exposed to atmospheric carbon dioxide.

Hence, one of the main concerns when selecting a method of arsenic removal is to consider what the product of that process is. Generally, compounds of arsenate are more stable than compounds of arsenite and it is widely accepted that arsenite is more toxic than arsenate. Arsenic is present in mine effluent in two valence forms viz. arsenite and arsenate. It is therefore necessary to oxidise arsenite to arsenate and then remove the arsenate from the mine effluent. In so doing, a relatively stable form of arsenic would have been produced and would then have to be disposed of.

This project investigated the oxidation of arsenite by both chemical and bacterial methods. Ferric ion was used to chemically oxidise arsenite to arsenate whilst a mixed bacterial culture was used for the bacterial oxidation of arsenite.

CHAPTER 3

LITERATURE SURVEY

3.1 ARSENIC

3.1.1 Arsenic in nature

Arsenic occurs naturally in the form of enargite (Cu_3AsS_4), arsenopyrite ($FeAsS$), smaltite ($CoAsS_2$), realgar (As_2S_2) and orpiment (As_2S_3). These minerals are slightly soluble at a neutral pH, but they can be transformed into more soluble arsenic compounds through chemical processing e.g. when they are processed so that the elements found within them may be recovered, such as the recovery of gold occluded with arsenopyrite[1].

Arsenic is found in the biosphere in many different forms. The concentration of arsenic in sea water is about 2 μg/kg whilst the concentrations in fresh water vary (around a few μg/kg). The concentration of arsenic in groundwater sometimes exceeds 21 mg/kg. The average concentration of arsenic in the earths crust is 2 mg/kg and in normal soils it ranges from 1–40 mg/kg (Morita and Edmonds, 1992).

Arsenic is found in terrestrial plants and freshwater fish at levels of 0.05–0.2 mg/kg. Due to biotransformation and accumulation, marine animals and algae contain high concentrations of arsenic. Arsenic is found in the inorganic form in water and the earths crust (in the +3 and +5 valence states), whilst it is found in the organic form in marine animals and algae.

Arsenic is released into the atmosphere through the burning of fossil fuels and the smelting of non-ferrous ores. Other natural sources of arsenic are volcanism and the oceans (when arsenic is released by bubble bursting).

3.1.2 Chemistry of arsenic

There are three important valence states of arsenic viz. -3 in arsine (AsH_3), +3 in arsenic trioxide, (As_2O_3), and +5 in arsenic pentoxide (As_2O_5). The trivalent form of arsenic, arsenic trioxide, exists as arsenious acid ($HAsO_2$) when dissolved, and the pentavalent form as arsenic acid (H_3AsO_4). Hydrogen arsenide (As_2H_2), with an oxidation state of –1 has been prepared. Not many definite compounds of arsenic having even oxidation states exist. The oxide, As_2O_4 is apparently a compound of the +3 and +5 oxides. The mono sulphide AsS is a well known mineral.

Arsine

The free energy of arsine gas, AsH_3 (g), is found to be 42.0 kcal; using the entropy of arsine as 52 kcal and a value of 41.0 kcal for the heat of formation. The potentials of the arsine-arsenic couples are:

$$AsH_3 \Leftrightarrow As + 3H^+ + 3e^- \qquad E^0 = 0.60V \qquad \textbf{(3.1.2-1)}$$

$$3OH^- + AsH_3 \Leftrightarrow As + 3H_2O + 3e^- \quad E^0_B = 1.43V \qquad \textbf{(3.1.2-2)}$$

This indicates that arsine is a powerful reducing agent and should be readily oxidised by moderately strong oxidising agents. However, the oxidation by the hydrogen ion is not rapid.

Grube and Klebe reported that a metallic–arsenic cathode may be reduced to arsine, especially in alkaline solutions. Arsenious acid is reduced to arsine efficiently at a mercury cathode. The reduction of arsenic trichloride by stannous chloride apparently yields the solid arsenide, As_2H_2, which is unstable with respect to decomposition into the elements.

From this value it is evident that the concentration of AsO^+ is not large except in strongly acidic solution. The free energy of AsO^+ is –39.16 kcal.

The arsenious acid – arsenic acid couple

Liebhafsky calculated a value for the equilibrium constant for the oxidation of arsenious acid by tri-iodide as:

$$\frac{(H_3AsO_4)(H^+)^2(I^-)^3}{(I_3^-)(H_3AsO_3)} = 1.6X10^{-1} \qquad \textbf{(3.1.2-9)}$$

The free energy of the reaction is 1085 cal and the free energy of arsenic acid, H_3AsO_4 (aq), -183.8 kcal. The approximate values for the three dissociation constants are $K_1 = 4.8 \times 10^{-3}$, $K_2 = 1 \times 10^{-7}$,and $K_3 = 1 \times 10^{-13}$. From the free energies, the following are obtained:

$$H_3AsO_4(aq) \Leftrightarrow H^+ + H_2AsO^- \quad K = 2.5 \times 10^-_4 \qquad \textbf{(3.1.2-10)}$$

$$H_2AsO_4 \Leftrightarrow H^+ + HAsO_4^{2-} \quad K= 5.6 \times 10^{-8} \qquad \textbf{(3.1.2-11)}$$

$$HAsO_4^{2-} \Leftrightarrow H^+ + AsO_4^{3-} \quad K = 3 \times 10^{-13} \qquad \textbf{(3.1.2-12)}$$

The potentials of the couples are calculated to be:

$$2H_2O + HAsO_2 \Leftrightarrow H_3AsO_4 + 2H^+ + 2e^- \quad E^0 = -0.559V \qquad \textbf{(3.1.2-13)}$$

$$4OH^- + AsO_2^- \Leftrightarrow AsO_4^{3-} + 2H_20 + 2e^- \quad E^0_B = 0.67V \qquad \textbf{(3.1.2-14)}$$

The couple is capable of attaining a rapid reversible equilibrium. The mechanism of the oxidation of arsenite by iodine appears to be that of a direct oxygen shift through the medium of hypoiodous acid:

$$H_3AsO_3 + HIO \Leftrightarrow H_3AsO_4 + H^+ + I^- \qquad \textbf{(3.1.2-15)}$$

Arsenic sulphides

The more important sulphides of arsenic are arsenious sulphide, As_2S_3; and arsenic sulphide, As_2S_5; and their acid ions, thioarsenite, AsS_2^- and thioarsenite AsS_4^{3-}. Using the heat of formation of As_2S_3, the free energy is estimated to be –32.5 kcal. For the precipitation of the sulphide, the free energy of formation is calculated to be:

$$3H_2S + 2HAsO_2(aq) \Leftrightarrow 4H_2O + As_2S_3 \quad \Delta H_f^0 = -45.5\text{ kcal} \qquad \textbf{(3.1.2-16)}$$

For the solution of $As_2S_3^{2-}$ in sulphide, an approximate value of the free energy of formation is:

$$As_2S_3 + S^{2-} \Leftrightarrow 2AsS^{2-} \quad \Delta H_f^0 = -10\text{ kcal} \qquad \textbf{(3.1.2-17)}$$

Using this, the standard electrode potential of As may be calculated:

$$As + 2S^{2-} \Leftrightarrow AsS_2^- + 3e^- \quad E^0 = 0.8V \qquad \textbf{(3.1.2-18)}$$

The sulphide with a valence of +3 is oxidised to thioarsenate by polysulphide. From the potential of S_2^{2-} it can be stated that:

$$2S^{2-} + AsS_2^{2-} \Leftrightarrow AsS_4^{3-} + 2e^- \quad E^0_B > O.6V \qquad \textbf{(3.1.2-19)}$$

Arsenic trichloride

The free energy of formation for the hydrolysis reaction may be calculated using the free energy of the trichloride, $AsCl_3$:

$$AsCl_3(l) + 2H_2O \Leftrightarrow HAsO_2 + 3H^+ + 3Cl^- \, \Delta H_f^0 = -6.42\text{ kcal} \qquad \textbf{(3.1.2-20)}$$

3.1.3 Toxicity of arsenic

Arsenic compounds are notorious as poisons. The toxicity of arsenic depends on its chemical form. Arsine (AsH_3), an inorganic form of arsenic is highly toxic and arsenite is more toxic than arsenate. The toxicity of organic arsenic compounds varies. Organic compounds of natural origin appear to be non-toxic or of low toxicity; whilst some synthetic compounds, especially those of arsenite, are extremely toxic. Generally, compounds of arsenite are much more toxic than those of arsenate[2].

3.2 SOURCE OF ARSENIC POLLUTION IN THE GOLD MINING INDUSTRY

Arsenic is found in significant amounts in many ores and concentrates which are processed by the mineral industry. Arsenopyrite is by far the most common and widespread mineral form of arsenic[13]. Arsenic is an unwanted impurity, thus it ends up in the process effluent. It is estimated that the mineral industry produces 300 000 tons of arsenic per year in the form of liquid and solid waste[5].

The world-wide trend in gold mining in recent years has been towards recovering gold from refractory ores. It is estimated that up to one third of the worlds total production of gold is now from refractory deposits[3]. Gold deposits are said to be refractory in nature when the gold is locked in various host minerals, unlike the simple ores. The processing of refractory arsenical ores leads to an unacceptably high level of arsenic in the mine effluent.

Concentrates of gold bearing ores are traditionally roasted to break down the sulphides and release the gold. The gold is subsequently recovered in the cyanide leaching step. However, the dissemination of fine grained or submicroscopic gold within the sulphide minerals arsenopyrite (FeAsS) or pyrite (FeS_2) renders the gold inaccessible to cyanide leaching. Even fine grinding of the refractory ore does not result in the liberation of gold. Therefore, the sulphide mineral has to be broken down to liberate the gold or be made porous[4] so that the cyanide solution reaches the gold contained in the ore. Generally, the sulphide minerals are removed by oxidative means so that the gold may be eventually liberated.

The refractory ore is thus treated so that the gold may be exposed and subjected to the leaching step. But, this treatment also affects the arsenic in arsenopyrite. The arsenic is converted to arsenic oxide, some of which is solubilised during the leaching process. Furthermore, the solubility of arsenic is much greater because the cyanide treatment is done in a basic medium. Hence concentrations of arsenic ranging from 1000 ppm to 4000 ppm downstream of the cyanide leaching step have been reported.

In South Africa, the maximum discharge level of arsenic to rivers and water courses is 0.5mg/l[8]. It is anticipated that this value might be further reduced in order to put South Africa in line with international standards, e.g. in Brazil, the maximum discharge level is 0.3 mg/l. The threshold limiting value for arsenic trioxide is 0.5 mg/m^3. This type of legislation as a result of increasing environmental awareness is in line with the international trend of trying to reduce and redress man's prolonged negative impact on the environment. This trend therefore compels those industries which produce arsenic-containing effluents to make sure that the methods they use to remove arsenic from effluents comply with these standards.

3.3 METHODS OF ARSENIC REMOVAL

Methods such as direct precipitation, adsorption and flocculation have been used to remove arsenic from effluents.

Direct precipitation of arsenic involves the precipitation of arsenic by the addition of a soluble chemical. The traditional method of treating effluents containing arsenic by the addition of lime to produce calcium arsenate and calcium arsenite is an example of this. This method does reduce the arsenic concentration to acceptable levels but it has been found that the long-term stability of these compounds is questionable[5]. Arsenic may be precipitated by the addition of iron oxide to produce ferrous arsenate and ferric arsenate. Arsenic has also been precipitated as magnesium arsenate, barium arsenate and copper arsenate.

Robins and Tozawa[7] reported that the most cost effective method of arsenic removal is direct precipitation by the lime addition method. The drawback of the lime addition method is that the calcium arsenate precipitate is unstable when exposed to atmospheric carbon dioxide[7]. The unstable arsenic then redissolves causing contamination of the water. The long-term stability of iron arsenate and sodium arsenate has also been questioned. According to Haines[8], basic ferric arsenate is stable under practical dumping conditions. Basic ferric arsenate forms when the molar ratio of iron to arsenic is greater than 4:1. These compounds have solubilities that are a hundred to a thousand times lower than simple ferric arsenates[8], which are formed at a ferric ion to arsenate ratio of 1:1.

Adsorption involves the removal of arsenic from solution by adsorption onto a solid phase, which acts as an active surface. This includes ion exchange of arsenic on resins and adsorption of arsenic onto activated carbon or preformed hydrous ferric oxide[6].

Flocculation relies on the insolubility of metallic arsenites or arsenates. In this method the arsenic is trapped in a gelatinous precipitate, usually of iron or aluminium hydroxide. This results in a strong chemisorption of arsenic ions on the metallic hydroxides.

All the aforementioned methods, transform arsenic in solution from a dissolved form to a solid form. This solid can then be separated from the liquid phase by some physical separation method e.g. filtration, flotation or decantation. This solid form, generally a precipitate, then has to be dealt with. Most often, this precipitate is stored over a long period of time in much the same manner as one would do with nuclear waste. This is because there are few, if any, uses for it. Hence, any process that is used for the removal of arsenic from contaminated water has to meet two requirements viz.

- The precipitate containing arsenic must be sufficiently stable and insoluble so that it may be stored over a long period
- The supernatant stream must comply with receiving water quality standards.

3.3.1 Effect of arsenic valence state

Tozawa and Nishimura[9] reported that arsenate was completely removed by coprecipitation with ferric hydroxide over a wide range of pH. At a molar ratio of 2Fe(III) : 1As(V), the concentration of arsenate was reduced to less than 0.5 ppm over a pH range of 3 to 6. Thus, it follows that to remove arsenic species from aqueous solutions, all the arsenic species should be in the pentavalent form to ensure that the concentration of arsenic is reduced to the desired level. This entails that all the arsenite be oxidised to arsenate before precipitation is attempted.

3.3.2 Stability of precipitates

It is generally accepted that arsenate is the thermodynamically stable form of inorganic arsenic[2,10]. Arsenate ions are more easily precipitated than arsenite ions in solution. Also, metal arsenates are generally less soluble than metal arsenites[5].

Thus, on taking all the aforementioned factors into account, it appears that the logical approach to the removal of arsenic from effluents would be to first oxidise arsenite to arsenate and then precipitate it as basic ferric arsenate.

3.4 CHEMICAL OXIDATION OF ARSENITE

The oxidation of arsenite to arsenate may be achieved by simple aeration. Arsenite is oxidised by dissolved oxygen. However, the oxidation rate is extremely slow therefore this method is impractical. Furthermore, Tozawa and Nishimura[9] reported that arsenite is oxidised by oxygen only when cupric ions are present at a pH of 11.2. If arsenite were to be oxidised by oxygen at a pH lower than this, then a catalyst will most probably be required. Robins[5] reported that air and oxygen at ambient temperature was not able to oxidise arsenite except in very alkaline solutions when the reaction was catalysed by copper.

Arsenite has been oxidised using chlorine, sodium hypochlorite and hydrogen peroxide. These methods are effective but if they have to be used on an industrial scale then the process cost becomes prohibitive. Also, according to legislation, the concentration of chlorine cannot exceed 10μg/L thus ruling out any method utilising chlorine. The oxidation of arsenite by hydrogen peroxide in ammoniacal solutions having a pH of 9.3 does occur[9]. However, the oxidation rate decreases with decreasing pH because hydronium ions are liberated during the oxidation reaction. When buffering agents are added to the solution, the reaction does occur.

Tozawa and Nishimura[9] also reported that arsenite is rapidly and completely oxidised by ozone over a pH range of 1 to 11. Barrett et al[11] reported that arsenite may be oxidised using ferric ion.

3.4.1 Chemical oxidation of arsenite by ferric ion

Barrett et al[11] reported that the chemical oxidation of arsenite by ferric iron should occur. This chemical reaction should occur at a temperature of 45^0C, a pH of 1.3 and redox potentials in sulphate media being 670 and 470 mV for Fe(III)/Fe(II) and As(V)/As(III) respectively.

They studied the oxidation of arsenic by using a synthetic solution. Arsenopyrite was added to a solution of ferric sulphate which had a pH of 1.3. The pH of the solution was adjusted using sulphuric acid. The reaction mixture was monitored over several weeks, and they found that the reaction did not occur. This indicates that although the reaction is thermodynamically favoured, there is a kinetic restriction. This result is consistent with the non-complementary nature of the reaction in which two moles of Fe(III) react with one mole of As(III). Thus, they concluded that in order for the reaction to occur, a catalyst is necessary.

3.5 BACTERIAL OXIDATION OF ARSENITE

The use of micro-organisms in the leaching of minerals offers an alternate route to conventional processes employed. Biological leaching of refractory gold ores has even led to increased gold recoveries upon cyanidation of the bioleached residues. A potentially viable alternative to the chemical oxidation of arsenite is the bacterial oxidation of arsenite using a mixed bacterial culture already used in the gold mining industry for the pre-oxidation of refractory gold ores.

A commercial bacterial oxidation process, MINBAC™, was jointly developed by MINTEK, Anglo American Corporation of South Africa Limited and Vaal Reefs Exploration and Mining Company Limited for the pre-oxidation of refractory gold ores. The process uses bacteria as a catalyst to promote sulphide oxidation by oxygen at low temperatures and ambient pressure. The process is autocatalytic i.e. while it is necessary to seed the process with suitable bacteria initially, the bacteria are thereafter produced by the process reactions. The bacteria used in the MINBAC™ process is a mixed bacterial culture of iron and sulphur oxidising bacteria comprising *Thiobacillus ferrooxidans, Thiobacillus thiooxidans* and *Leptospirrulum ferrooxidans.* The operating temperature for optimum bacterial oxidation by this mixed bacterial culture is from 35 to 45 ^{0}C.

Wakao et al[13] reported on the microbial oxidation of arsenite in acid mine water from a sulphur-pyrite mine. The water from the mine flowed into a river which ran through the mine area. The water from the mine contained high concentrations of dissolved inorganic arsenic. Arsenic was present in the mine waters in both the three and five valence states. However, as the distance of the sampling points on the river moved further away from the mine drift, the ratio of the arsenite to arsenate in the water changed. The amount of arsenite decreased and the amount of arsenate increased. This oxidation of arsenite in the acid mine water was attributed to microbial factors. This was verified by them isolating arsenite-oxidising bacteria from the mine water. The bacteria which was isolated was found to be resistant to up to 500 ppm of arsenic. Their study also showed that *Thiobacillus ferrooxidans* and *Thiobacilllus thiooxidans* are individually unable to catalyse the oxidation of arsenite

Robins[5] reported that *Thiobacillus ferrooxidans* was used to oxidise ferrous to ferric ion in solutions containing up to 10 ppm of arsenic. The oxidised solution was then neutralised and iron was precipitated. The arsenic levels were reduced to approximately 0.2 ppm. It has also been reported by Erlich[31] that *Thiobacillus ferrooxidans* was used in the oxidation of arsenopyrite where the concentrations of arsenic in solution was up to 1200 ppm.

Spencer at al[14] showed that a moderately thermophilic bacterial culture was able to oxidise arsenite to arsenate. The culture that was used occurs naturally in soil and was isolated in Western Australia. It comprised three morphologically distinct bacteria. It follows from this that naturally occurring bacterial cultures could be used to oxidise arsenite.

Braddock et al[15] have shown that *Thiobacillus ferrooxidans* is unable to catalyse the oxidation of arsenite. Barrett et al[11] found that a moderately thermophilic mixed bacterial culture was also unable to catalyse the oxidation of arsenite. However, when the mixed culture was grown on arsenopyrite concentrate then it was able to catalyse the oxidation of arsenite. The occurrence of the oxidation was attributed to the presence of the sulphide mineral arsenopyrite. The oxidation of As(III) by Fe(III) occured when cells were present in a mixture to which 1% (by weight) of pyrite had been added. Thus they concluded that the oxidation of As(III) occurs on the pyrite surface.

It is possible that due to the deposition of precipitates on the pyrite surface, the oxidation does not go to completion in the absence of cells because of deterioration of the pyrite surface. However, when cells are present during the oxidation they continuously regenerate fresh catalytic surfaces. Furthermore, in order to ensure that there is a high concentration of Fe(III), there should be large numbers of cells present in the medium to catalyse the oxidation of Fe(II) to Fe(III). It is also known, from Espejo et al[16] and Pinches et al[7], that bacteria attached to solids exhibit a higher degree of oxidative activity than those freely suspended, so this could be another possible explanation for the bacterial oxidation.

Dempsey et al[12] used bacterial oxidation to enhance the recovery of gold from refractory ores. They used a mixed bacterial culture, consisting mostly of *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* to catalyse the oxidation of sulphide minerals by oxygen. They found that large bacterial population densities, which could be greater than 10^9 bacteria/ml, are required to sustain acceptable pyrite oxidation rates. The bioreactors are inoculated with a 20 % by volume active slurry culture to bacteria-free slurry in order to initiate the bacterial oxidation. The reactors that were used were flat-bottomed mechanically agitated, rubber-lined mild steel tanks. They were aerated with compressed air, supplemented with carbon dioxide in order to sustain bacterial growth. The inlet concentration of carbon dioxide was set at 2700 ppm. The temperatures of the reactors were maintained at 35 to 40 ^{0}C.

Pooley[4] and Wakao et al[13] showed that mixed bacterial cultures produce better results than pure bacterial cultures. *Thiobacillus ferrooxidans, Thiobacillus thiooxidans* and *Leptospirrulum ferrooxidans* occur naturally in mining situations as was found by many researchers eg. Braddock et al[15] isolated *Thiobacillus ferrooxidans* from Eva Creek in Alaska, a place which is heavily affected by placer gold mining and is known to contain large amounts of arsenic. Also, Wakao et al[13] found *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* in the waters discharged from the Matsuo sulphur-pyrite mine. Pooley[4] found that enriched cultures obtained from the same site as the mineral to be treated or from a locality containing minerals of a similar chemistry are most likely to serve as the culture for that bacterial process.

3.5.1. Mechanism of bacterial oxidation

Barrett et al[11] proposed two pathways for the bacterial oxidation of arsenopyrite. The first pathway involves the direct oxidation of arsenic in arsenopyrite by the bacteria to As(III). Eligwe[35] reported that during direct oxidative attack, the bacteria attach themselves to the surface of the mineral which is in a solution containing adequate nutrients for bacterial survival. Following the attachment of the bacteria to the mineral surface, dissolution of the mineral occurs. The mineral is thus oxidised.

It is possible that a second, parallel, minor pathway exists; involving oxidation of As(III) by Fe(III). However, the importance of this pathway depends on the concentration of Fe(III). The overall oxidation of arsenopyrite increases as the concentration of Fe(III) increases and this can be attributed to the increasing contribution by the second pathway. The subsequent oxidation of As(III) to As(V) involves reaction with Fe(III) on the pyrite surface to overcome kinetic restrictions on the reaction rate. During the oxidation of As(III), Fe(III) is reduced to Fe(II). The bacteria once again oxidise the Fe(II) to Fe(III) and so the process continues in this cyclic manner.

It is believed that bacterial oxidation by direct and indirect means can occur simultaneously.

3.5.2 The chemistry of sulphide mineral oxidation by bacteria

The oxidation of arsenopyrite may be written as follows:

$$FeAsS + \frac{13}{4}O_2 + \frac{3}{2}H_2O \Leftrightarrow H_3AsO_4 + FeSO_4 \qquad \textbf{(3.5.2-1)}$$

The ferrous sulphate is then oxidised to the ferric form by the bacteria.

$$4FeSO_4 + 2H_2SO_4 + O_2 \Leftrightarrow 2Fe_2(SO_4)_3 + 2H_2O \qquad \textbf{(3.5.2-2)}$$

The ferrous sulphate then reacts further with the mineral and arsenic in solution according to the equation:

$$2FeAsS + 2Fe_2(SO_4)_3 + \frac{5}{2}O_2 + 3H_2O \Leftrightarrow 2H_3AsO_4 + 6FeSO_4 + 2S \qquad \textbf{(3.5.2-3)}$$

During the oxidation of arsenite by ferric ion, the ferric sulphate is once again reduced to ferrous sulphate. This ferrous sulphate will then be oxidised by the bacteria to ferric sulphate and in this way the ferric ion is continuously regenerated in a cyclic reaction so that there is no shortage of oxidising agent for the oxidation of arsenite.

Further reaction between arsenic acid and ferric sulphate results in the formation of ferric arsenate.

$$2H_3AsO_4 + Fe_2(SO_4)_3 \Leftrightarrow 2FeAsO_4 + 3H_2SO_4 \qquad \textbf{(3.5.2-4)}$$

According to the reaction described by the last equation, ferric arsenate may precipitate, but it will stay in solution if the pH at which the reaction occurs is below 1.8.

The oxidation of arsenopyrite in the presence of *Thiobacillus ferrooxidans* proceeds at a rate which is much faster than if the bacteria were not present[4].

Torma[18] reported that the oxidation of arsenopyrite occurs as a result of electrochemical reactions.

It is important that optimum conditions for bacterial activity are maintained. In the case of bacterial oxidation of a sulphide mineral, it is necessary to maintain the redox potential of the leach solution close to or above the oxidation potential of the sulphide mineral being oxidised. This requires that the concentration of ferric ion in solution be higher than ferrous ion in solution.

The bacterial oxidation of ferrous ion involves the movement of both hydrogen ions and electrons. It is therefore evident that pH will have a definite effect on the metabolism of the bacteria. The optimum pH for bacterial leaching is 1.8 or less. At this pH, ferric ion and other dissolved metals are readily kept in solution. In most bacterial leaches, there is a nett production of sulphuric acid, therefore any form of control to maintain the pH is not required. It is normal during a leach for the pH to drop from 2.0 to less than 1.0.

3.6 BACTERIAL CULTURE USED

A mixed bacterial culture of iron and sulphur oxidising bacteria comprising *Thiobacillus ferrooxidans, Thiobacillus thiooxidans* and *Leptospirrulum ferrooxidans* was used for the experimental work. This is the same mixed bacterial culture which was used in the MINBAC™ process. These are aerobic bacteria which rely on the oxidation of reduced iron and sulphur compounds for their existence.

Thiobacillus ferrooxidans have the ability to oxidise reduced sulphur compounds and ferrous ion to ferric ion. *Thiobacillus thiooxidans* can oxidise reduced sulphur compounds. *Leptospirrulum ferrooxidans* can oxidise ferrous ion to ferric ion.

They are mesophilic chemolithoautotrophic bacteria which derive all their necessary requirements for growth from inorganic compounds. Their energy source is iron and their source of carbon is carbon dioxide. They are active over a pH range of 1 to 5, having an optimum pH for growth of 2. The optimum temperature for growth of mesophiles is 35^0C.

Thiobacillus ferrooxidans is a rod shaped, acidophilic, motile, non-spore forming gram-negative bacterium which occurs singly or sometimes in pairs. It is 1.6-2.0 µm in length and 0.5 µm in width. It is morphologically and physiologically identical to *Thiobacillus thiooxidans.* It is necessary that the solid substrates which it utilises be rendered soluble before bacterial oxidation can occur. At the same time, minerals which the bacteria require for growth and metabolism must be readily available.

Various researchers have studied the oxidation of ferrous ion by *Thiobacillus ferrooxidans.* The mechanism which they proposed uses oxygen as the final electron acceptor. They found that bacterial activity was inhibited by copper, nickel, chromium and mercury ions. It was also found that some inorganic compounds inhibit the action of *Thiobacillus ferrooxidans*[35].

Leptospirillum ferrooxidans is an acidophilic mesophile. They are spiral in appearance (simply put, they look like curved rods). They are actively motile, in comparison with *Thiobacillus ferrooxidans* which may be classified as being sluggishly motile.

3.7 BACTERIAL GROWTH

Bacterial cultures may be grown in two different ways, either batch-wise or continuously. Continuous growth requires a much more complicated set-up than batch growth and would be most suitable in the case of an investigation into a continuous oxidation process. It was decided that for this study, the bacteria would be grown batch-wise for the case of simplicity as well as the fact that the oxidation of arsenite was to be attempted on a batch basis. Depending on the outcome of this work, the subject could be investigated further on a continuous basis.

3.7.1 Batch growth

For batch culture experiments, Braddock et al[15] inoculated 5 to 10 ml of exponentially growing *Thiobacillus ferrooxidans* cells into 500 ml Erlenmeyer flasks containing the growth medium. The flasks were placed on a rotary shaker and maintained at 22.5 °C. The inoculums that Macdonald et al[17] used for batch growth of *Thiobacillus ferrooxidans* were near the end of the log phase or at the start of the maximum stationary phase. The cell population of the inoculums were approximately 1x 10^8 cells/ml. A reciprocating water bath shaker was used for batch growth.

Growth cycle phases for batch cultivation

The batch growth process is dependent on the starting conditions of both cells and medium. There are four distinct growth phases in batch culture.

Lag phase

There is no increase in the number of cells whilst the cells adapt to the new environment. The length of the lag phase depends on:

- The growth stage of the inoculum i.e. the age of the inoculum
- Size of the transferred inoculum

- Changes in the nutrient composition, if any, experienced by the cells

In order to minimise the lag time, the inoculum should meet the following criteria:

- Inoculating culture should be as active as possible and the inoculation should be carried out in the exponential growth phase
- A reasonably large inoculum should be used – it should be 5-10 % of the new medium volume

Exponential growth phase

At the end of the lag phase, the population of micro-organisms is well adjusted to the new environment and cells can then multiply rapidly. The cell mass (number of living cells) doubles regularly with time.

Stationary growth phase

During this period, the population reaches its maximum size.

Death phase

There is a decline in cell numbers. The death of a population usually follows an exponential decay. The death phase begins when the population cannot sustain itself due to nutrient depletion and build up of toxins.

3.7.2 Nutritional requirements for bacterial growth

Bacteria have specific nutrition requirements for growth. On average, the non-metals carbon, oxygen, hydrogen, nitrogen, phosphorus and sulphur; and the metals potassium and magnesium, comprise 98% of the dry weight of bacteria[32]. They are termed macronutrients since their required concentrations in the growth media are greater than $1x10^{-4}$ $mol.l^{-1}$. Other elemental nutrients are termed micronutrients or trace elements and are usually required at concentrations less than $1x10^{-4}$ mol.l^{-1}. The total weight of all microorganisms comprises 80–90 % water. The main constituents of cellular material are carbon, oxygen, hydrogen and nitrogen. They account for 90-95% of the cell dry weight.

Carbon is a constituent of organic cellular material. It is also the energy source for the bacteria. Autotrophs obtain cell carbon from carbon dioxide via carbon fixation. Chemolithotrophs derive their enegy from oxidation-reduction reactions and use inorganic electron donors. Nearly all chemolithotrophs require oxygen as an electron acceptor.

Nitrogen comprises 8-14% of the dry weight of bacteria. Nitrogen is required because it is a constituent of proteins, nucleic acids and coenzymes. Hydrogen is a constituent of all organic compounds in the cell, as well as being found in the cell water. It is derived from the carbon source. Oxygen is found in all the organic cell components and in the cell water. Molecular oxygen is required as a terminal electron acceptor in aerobic metabolism. Sulphate is used by most bacteria to meet their demand for sulphur. Sulphur is a constituent of proteins and some coenzymes. Bacteria usually use inorganic phosphate as the source of phosphorus. Phosphorus is a constituent of nucleic acids, phospholipids, nucleotides and certain coenzymes. The principal inorganic cation in the cell is potassium. It is a cofactor of some enzymes, is required in carbohydrate metabolism and is involved in many transport processes. Magnesium is required as a cofactor for enzymes and because it is a constituent of cell walls and membranes

The specific nutritional requirements of the mixed bacterial culture that was to be used in this study are as follows:

- The bacteria require a source of nitrogen, phosphate and trace amounts of calcium, magnesium and potassium.

- They obtain their energy for growth from the oxidation of ferrous ion, soluble and insoluble sulphides, sulphur and soluble sulphur compounds so these compounds need to be present in the growth medium.
- They need air since they utilise oxygen and carbon dioxide from air for organic synthesis.

The solubility of oxygen and carbon dioxide is low in the highly acidic medium in which the reaction is carried out, therefore one has to strive to attain the maximum rate of mass transfer of these gases so as to not limit bacterial growth. It has been found that increasing the carbon dioxide content of air stimulates the growth of *Thiobacillus ferrooxidans* when ferrous ion is used as the substrate[18]. However, it was found that it could not tolerate concentrations of dissolved oxygen greater than 8 ppm[35].

3.7.3 Factors affecting bacterial growth

Optimum growth of bacterial cultures are dependent on various factors. The bacteria have to be grown in the correct medium, which contains all the necessary nutrients as well at the correct temperature. If the temperature is too low then growth will be very slow or will not occur at all. On the other hand, excessive temperature is also undesirable. The rate of bacterial growth increases with increasing temperature, up to a point. Beyond this temperature, cells die off and there is denaturation of the cells.

The bacteria are also sensitive to pH. Most microorganisms can tolerate a wide range of pH in the external environment. However, it is imperative that the intracellular pH is maintained within narrow limits. If the pH of the cell is not maintained at the required level, then this could affect cell respiration and hence cell growth and eventually the cell will die.

3.8 ANALYTICAL METHODS

It was anticipated that the concentrations of various chemical species would have to be monitored during experimental work. These are total iron, ferrous ion, ferric ion, total arsenic, arsenate and arsenite.

3.8.1 Determination of arsenic concentrations

Various methods have been used for arsenic speciation. These include atomic absorption spectrometry, high precision liquid chromatography, polarography, gel permeation chromatography and inductively coupled plasma-mass spectrometry.

Sharma[19] used differential pulse polarography to simultaneously determine the concentrations of As(III) and total arsenic in industrial waste water. A polarographic analyser together with a drop timer and an X-Y recorder is used for polarographic measurements. The working electrode is a dropping mercury electrode, a micro-saturated calomel electrode is used as the reference electrode and platinum wire is used as the auxiliary electrode. However, this method is only suitable for very low concentrations of arsenic.

Esteban et al[20] used differential pulse anodic stripping voltammetry on a rotating gold electrode and differential pulse cathodic stripping voltammetry onto a hanging mercury drop electrode to determine the concentrations of As(III) and total arsenic respectively. However, this method is also for very low concentrations of arsenic.

Hambsch et al[21] used atomic absorption spectrometry to determine the concentration of As(III) in groundwater samples. The As(III) is first extracted

from the water samples using silver diethyldithiocarbamate. It is then analysed using graphite furnace atomic absorption spectrometry.
Hering et al[6] used hydride generation flame atomic absorption spectrometry to determine arsenite concentration. An atomic absorption spectrometer, equipped with an electrodeless discharge lamp and coupled to an hydride generation system is used. Hydride generation is achieved by using sodium borohydride ($NaBH_4$). The same method is used to determine total arsenic concentration by first reducing any As(V) with potassium iodide.

The silver diethyldithiocarbamate method is a spectrochemical method that can be used to determine As(III) concentration. It requires the use of a spectrophotometer and an arsenic determination apparatus. The arsenic determination apparatus is specially designed for this method and consists of a conical flask with a bubbler attachment. The As(III) is reduced to arsine gas (AsH_3) using zinc metal in an acidic solution. The generated arsine passes through a scrubber packed with lead acetate wool to absorb any hydrogen sulphide gas and is then absorbed in a bubbler containing a solution of silver diethyldithiocarbamate in pyridine. The red complex that is formed can then be analysed using a spectrophotometer. Peaks occur at a wavelength of 538 nm.

Ion exclusion chromatography is a method that has been used by Mintek[22] to measure the concentrations of As(III) and As(V) in solutions containing iron and sulphuric acid. The iron is removed by ion exchange prior to the speciation of arsenic. The eluent used is phosphoric acid and the arsenic species are detected spectrophotometrically at 195 nm. As(III) and As(V) are eluted at different times and hence form different peaks on the chromatogram, thus enabling their speciation. This method requires the use of an ion chromatograph and a UV-vis spectrophotometer. In addition, a Dionex HPICE As-1 ion exclusion column, designed specifically for arsenic speciation, is required. This column is manufactured by the Dionex

Corporation and sold exclusively to those clients in possession of a Dionex system.

Johnson et al[23] used the molybdenum blue method to determine the concentration of As(V) and total arsenic in natural waters. Arsenate forms a blue molybdoarsenate complex with molybdenum and it is this property of arsenate that lends itself to spectrochemical analysis. In order to determine total arsenic, As(III) is oxidised to As(V) using potassium iodate prior to analysis. This ensures that all the arsenic in the sample is in the five oxidation state and the sample can then be analysed for total arsenic. The absorbance of the resulting blue complex is measured at a wavelength of 865 nm using a UV-spectrophotometer.

Brown et al[24] used a similar method, except that they used solvent extraction to remove the alcohol extractable molybdate complex that arsenate forms and analysed the extract for As(V). Since As(III) does not form this complex, the remaining aqueous phase will retain all the As(III). However, this method does not ensure that dissolved As(III) is completely isoamyl alcohol insoluble or that the As(V) derived compound is completely isoamyl alcohol soluble.

3.8.2 Determination of iron concentration

Various colourimetric methods may be used to measure ferric iron concentration. Steiner and Lazaroff[25] used a spectrophotometric method for direct continuous determinatioln of the concentration of ferric ions in an autotrophic iron oxidation. A recording spectrophotometer is used for the determination of ferrous and ferric ion concentration by scanning the UV-absorbing region of the spectrum between 220 and 304 nm. Ferric ion absorbs strongly in the 295-304 nm region and ferrous ion absorbs strongly in the 220-

250 nm region. Sulphuric acid is used to dilute samples and no colour reagent is added.

Bastian et al[26] used a method which involved the formation of a ferric sulphate complex by adding sulphuric acid to a perchloric acid solution containing Fe(III). This method is temperature sensitive - the absorbance increases with increasing temperature. The absorbance is read in the 305-320 nm range.

Muir and Andersen[27] used the phenanthroline method to determine the concentrations of Fe(II) and Fe(III) in copper process metallurgical solutions. This spectrochemical method has also been used by the American Public Health Association[28] to determine the concentration of iron in water. Ferrous ion reacts with phenanthroline to form an orange-red complex $[(C_{12}H_8N_2)_3Fe]^{2+}$. The colour intensity is independent of the acidity in the pH range 2-9 and is stable for long periods. Ferric ion may be reduced to ferrous ion with hydroxylamine hydrochloride or with hydroquinone and then treated with phenanthroline in the pH range of 3.2 to 3.3. All the iron is therefore in the ferrous form and hence the total iron concentration may be determined.

Three molecules of phenanthroline chelate each atom of ferrous ion to form an orange-red complex. The ferrous ion-phenanthroline complex forms on a gram for gram basis i.e. 1 g of phenanthroline forms a complex with 1 g of ferrous ion. The resulting solution is independent of pH from 3 to 9 and is stable for at least 6 months. A pH between 2.9 and 3.5 ensures rapid colour development in the presence of an excess of phenanthroline. The absorbance of the resulting coloured complex is measured at a wavelength of 510 nm using a spectrophotometer.

The presence of the following ions interfere with results obtained via the phenanthroline method: silver, bismuth copper, nickel and cobalt interfere seriously, as does perchlorate. There is interference from phosphates, chromium and zinc in concentrations exceeding 10 times that of iron, copper and cobalt in excess of 5 mg/l, nickel in excess of 2 mg/l and molybdate. Other ions interfere to a lesser extent but not sensibly if their concentrations do not exceed that of iron. This method is suitable for iron concentrations from 0.02 to 4 ppm.

3.9 ELECTROCHEMISTRY

3.9.1 Oxidation–reduction (redox) reactions

Oxidation is defined as the loss of electrons and reduction as the gain of electrons. Electrons are transferred during an oxidation-reduction (redox) reaction. During a redox reaction, one reactant is oxidised while the other is reduced. The reactant which is oxidised is also the reducing agent (reductant) whilst the reactant which is reduced is also the oxidising agent (oxidant). A redox reaction consists of two half reactions, which when added gives the complete reaction. The following reaction is an example of a redox reaction:

$$Fe^{3+} + e^{-} \Leftrightarrow Fe^{2+} \qquad E^{0} = 0.771 \text{ V} \qquad \textbf{(3.9.1-1)}$$

$$2I^{-} \Leftrightarrow I_{2} + 2e^{-} \qquad E^{0} = -0.536 \text{ V} \qquad \textbf{(3.9.1-2)}$$

To obtain the overall cell reaction, multiply equation (3.9.1-1) by two (in order to balance the number of electrons transferred) and then add the two equations. It is important to note that when the half reaction is multiplied by any factor, it is only the stoichiometric coefficients that change and not the electrode potentials.

Thus the overall reaction is given by equation (3.9.1-4):

$$2Fe^{3+} + 2e^{-} \Leftrightarrow 2Fe^{2+} \qquad E^{0} = 0.771 \text{ V} \qquad \textbf{(3.9.1-3)}$$

$$2I^- \Leftrightarrow I_2 + 2e^- \qquad E^0 = -0.536\ V$$

$$2Fe^{3+} + 2I^- \Leftrightarrow 2Fe^{2+} + I_2 \qquad E^0_{cell} = 0.235\ V \qquad \textbf{(3.9.1-4)}$$

3.9.2 Standard electrode potentials

The standard electrode potential is defined as the potential difference set up when a solution of unit activity with respect to the ion concerned, M^{z+} has a rod of metal, M immersed in it. The standard electrode potential, E^0 is measured at a temperature of 25°C and the reference standard is the standard hydrogen electrode for which the E^0 value is arbitrarily taken as zero.

Tabulated values of standard electrode potentials are found in many chemistry books. The values used in this study were obtained from Latimer[29]. The half reactions in this table are written as oxidation reactions. The most positive couple is thus the strongest reducing agent i.e. undergoes oxidation and the most negative couple is thus the strongest oxidising agent i.e. undergoes reduction.

The magnitude of the electrode potential is a property of the metal concerned. It is also dependent on the temperature and the activity (or approximately, the concentration) of the ion.

3.9.3 The Nernst equation

Tabulated values of electrode potentials for redox couples at standard conditions are readily available. However, data for non-standard conditions is not readily available. The Nernst equation may be used to calculate electrode potentials under non-standard conditions.

The Nernst equation relates the electrode potential of an electrochemical reaction to the activities of the chemical species involved in the reaction and the standard electrode potential, E^0.

For the reaction:

$$\alpha A + \beta B \Leftrightarrow \varphi C + \delta D \qquad (3.9.3\text{-}1)$$

the potential may be calculated using the Nernst equation

$$E = E^{o} - \frac{RT}{nF}\ln\frac{(a_C)^{\varphi}(a_D)^{\delta}}{(a_A)^{\alpha}(a_B)^{\beta}} \qquad (3.9.3\text{-}2)$$

where: E^0 is the standard electrode potential (V)

R is the universal gas constant = 8.314 J/K.mol

T is the absolute temperature (K)

n is the number of electrons in the balanced half-reaction (equivalents/mole)

F is the Faraday constant = 96 500 C

a_i is the activity of species i

$\alpha, \beta, \varphi, \delta$ are stoichiometric coefficients

The term $\frac{(a_C)^{\varphi}(a_D)^{\delta}}{(a_A)^{\alpha}(a_B)^{\beta}}$ is called the reaction quotient, Q, and is the ratio of the activities of the products and reactants, each raised to the power of their stoichiometric coefficients in the balanced half reaction. It is important to remember that the reaction quotient represents all the reactants and products of the nett ionic half-reaction and not just the substance changing its oxidation state. In order to get an approximation of the electrode potential, the concentrations of the ions may be used. However, the exact form of the equation is written in terms of activities and not concentrations.

The Nernst equation is valid for a single redox couple. If the Nernst equation is to be used to calculate the redox potential of a ferric/ferrous sulphate solution, then it must be assumed that a single redox couple dominates the redox reaction. In this case, the assumption that the ferric-ferrous couple dominates the redox reaction will be made. Inherent in this assumption is the fact that any other redox reactions that occur exert a negligible influence on the overall exchange current density.

3.9.4 Calculation of activities

The correlation of Debye and Huckel may be used to calculate the activity coefficient for an ionic species in solution:

$$-\log \gamma_i = \frac{A z_i^2 \sqrt{I}}{1 + \partial_i B \sqrt{I}} \qquad \textbf{(3.9.4-1)}$$

where: γ_i is the activity coefficient of species i

z_i is the ionic charge of species i

∂_i is the ion-size parameter of species i ($\overset{0}{A}$)

A,B are constants characteristic of the solvent (water) at the given temperature and pressure

I is the ionic strength

Ionic strength is defined as

$$I = \frac{1}{2}\sum c_i z_i^2 \qquad \textbf{(3.9.4-2)}$$

where: c_i is the concentration of species i

z_i is the ionic charge of species i

Values for ∂_i and values for the Debye-Huckel constants A and B were taken from Langes Handbook of Chemistry[30].

The Debye-Huckel correlation for activity coefficients gives relatively good predictions at low ionic strengths (0.01M). If ionic strengths are higher, then the equation has to be modified.

The activity is related to the concentration by:

$$a = \gamma_i c_i \qquad \textbf{(3.9.4-3)}$$

3.9.5 Limitations to the use of electrode potentials

Electrode potentials are instrumental in the understanding of electrochemical processes. However, certain properties of chemical systems limit the accuracy with which electrode potentials can be measured. This in turn affects the use of electrode potentials in predicting chemical behaviour. These limiting effects are generally difficult to quantify but it is important to be aware of the limitations associated with the use of electrode potentials and the chemical properties responsible for them.

Very often, calculated values of electrode potentials are different from measured values. These differences are sometimes too large to be ascribed to experimental errors.

In order to describe the potential of an electrode properly using the Nernst equation, the electrode reaction must be reversible. In other words, the oxidation and reduction reactions must be the exact opposite of each other and each reaction must occur rapidly. Many half-reactions do not behave in this manner and are therefore not properly described by the Nernst equation. There is therefore a large difference between the measured redox potential and the redox potential calculated using the Nernst equation.

Generally, chemical cells are constructed such that electrolyte solutions of different compositions are in contact with each other (i.e. no salt bridge). When these liquid junctions exist, a potential develops at the interface. This is caused by differences in rates of diffusion of ions between the solutions. This potential gradient is called a liquid-junction potential and its magnitude depends on the relative mobilities of the ions and the magnitude of the concentration gradient. In can sometimes be as large as 30 mV. It is usually impossible to eliminate liquid junctions in a cell, therefore the effect of the junction potential is minimised by using a high concentration of electrolyte in the salt bridge.

It is important to always bear in mind that electrode potentials represent thermodynamic properties of redox substances. Thus they may be used to predict whether a reaction may occur but they cannot offer any direct information about the rate of reaction.

3.10 POTENTIAL-pH DIAGRAMS

Potential-pH diagrams were originally intended for the theoretical prediction of oxidation-reduction catalysts (a method devised by Michaelis) and to determine the conditions under which oxidation and reduction reactions are possible in aqueous solutions.

Oxidation-reduction reactions are one of the most useful reactions employed in analytical chemistry. It is therefore important that there is a way in which these reactions may be predicted so that the conditions under which a specific reaction may or may not occur may be known. pH is one of the most influential factors with respect to the occurrence of redox reactions. It influences the majority of oxidation-reduction systems. Oxidation-reduction potentials make it possible to predict reactions for each pH. Potential-pH diagrams present both of these properties in a very useful form. A comparison of various diagrams should enable one to predict the likelihood of an oxidation-reduction reaction occurring.

However, it must be stressed that these diagrams give an indication of the possibility of the reaction occurring from a thermodynamic point of view. No kinetic factors are considered and at some stage in a study, these factors have to be introduced. But, a knowledge of the equilibrium potential for each pH is still a good enough first approximation to determine the possibility of a specific reaction occurring.

These diagrams are based on the formulation of equilibria of all the possible reactions in a given system as a function of two independent variables. The other possible variables are considered to be parameters. The two independent variables are chosen such that the equilibrium formulae are linear or almost linear. In the case of chemical systems involving a gaseous phase, the independent variables are logarithm of the oxygen partial pressure, and the reciprocal of the absolute temperature, 1/T. In the case of electrochemical systems involving aqueous solutions, the independent variables are the equilibrium electrode potential and the pH of the solution. This method results in the equilibrium conditions of all possible reactions being represented on a plane diagram by straight lines.

Potential-pH diagrams provide an indication of the chemical configuration of the system being studied, on a thermodynamic basis. Since these diagrams are established at standard conditions, i.e. temperature of 25^0C, certain corrections have to be made if the information from these diagrams is going to be used under other non-standard conditions.

3.10.1 Method of establishing potential-pH equilibrium diagrams

Conventions for writing reactions

The reactions are written in a manner that does not necessarily imply that the reaction takes place in a definite direction e.g. from left to right.

Chemical reactions

A chemical reaction is a reaction in which only neutral molecules and positively or negatively charged ions participate, with the exclusion of electrons. The reactions can be written in the general form

$$v_1'M_1'+v_2'M_2'+\dots\dots \Leftrightarrow v_1''M_1''+v_2''M_2''+\dots \qquad \textbf{(3.10.1-1)}$$

where v_i are the stoichiometric coefficients and are positive numbers

Mi are chemical substances

Equation (1) may be written as

$$\sum vM = 0 \qquad \textbf{(3.10.1-2)}$$

where the stoichiometric coefficients of the products of the reaction are taken to be positive and those of the reactants as negative.

Electrochemical reactions

An electrochemical reaction is defined as a reaction involving negative electrons e^- as well as molecules and ions. Oxidation reactions involve the liberation of electrons whilst reduction reactions involve the absorption of electrons.

These reactions may be written in the general form

$$v_1'M_1'+v_2'M_2'+\dots\dots+ne^- \Leftrightarrow v_1''M_1''+v_2''M_2''+\dots \qquad \textbf{(3.10.1-3)}$$

or as

$$\sum vM + ne^- = 0 \qquad \textbf{(3.10.1-4)}$$

Method of writing the reaction

For every chemical reaction involving, among others, gases and/or dissolved substances there exists an equilibrium constant which has a specific value at a given temperature and total pressure. This constant is a function of the partial pressures (or fugacities) of the gaseous reacting substances and of the concentrations (or activities) of the dissolved reacting substances.

For every electrochemical reaction involving gases and/or dissolved substances there also exists an equilibrium constant. The value of this constant is a function not only of the partial pressures (or fugacities) of the gaseous reactants and of the concentrations (or activities) of the dissolved reactants but also of the difference in electric potential.

Therefore, in order to establish equilibrium diagrams as a function of pH and electrode potential, the influence of pH on the electrode potential of the various reactions taking place has to be investigated.

The general form of a reaction involving the conversion of an oxidised substance A into a reduced substance B will be written:

$$\alpha \mathrm{A} + c\mathrm{H_2O} + ne^- \Leftrightarrow \beta\, \mathrm{B} + m\mathrm{H}^+ \qquad \textbf{(3.10.1-5)}$$

By applying the general equilibrium formulae to reactions written in this way, equilibrium relations in terms of pH and electrode potentials will be obtained. The pH measures the effect of the H^+ ions and the electrode potential measures the effect of the charges.

3.10.2. Electrode potential equilibrium potential of an electrochemical reaction

In order to measure an electric potential during an electrochemical reaction, the potential of the solution relative to a reversible reference electrode on which the state of thermodynamic equilibrium of the electrochemical reference reaction is obtained, is measured. The difference in measured potential between an electrode and a reversible reference electrode is called the potential of the electrode or the electrode potential, E; and this electrode potential is the equilibrium potential of the reaction occurring on the electrode.

For any given electrochemical reaction, taking place under fixed physico-chemical conditions, there exists a fixed value of the electrode potential at which the equilibrium state of the reaction is obtained. When the potential of the reactant is equal to the equilibrium state electrode potential, a reaction in either the oxidation or reduction direction cannot occur. If the electrode potential has any other value, then a state of thermodynamic equilibrium will not be reached. It is therefore possible, from an energetic point of view, for the reaction to occur. If the electrode potential is greater than the equilibrium potential of the reaction then it is possible for the reaction to take place in the oxidation direction. If the electrode potential is below the equilibrium potential then it is possible for the reaction to take place in the reduction direction.

The equilibrium potential of an electrochemical reaction is equal to the reduction affinity per unit charge. In other words, it is the affinity of the chemical reaction obtained by combining, in the reduction direction, the electrochemical reaction being studied with the electrochemical reference reaction.

3.10.3 Construction of potential-pH equilibrium diagrams

A list of all the substances that have to be considered must be drawn up and their standard chemical potentials, μ° must be found from literature. Then, the various reactions in which these substances can take part must be written in pairs. The only substances that can be introduced besides those already under consideration are water, the H^+ ion and the free electric charge e^-. The reaction equations have the general form:

$$\alpha \mathrm{A} + c\mathrm{H_2O} + ne^- \Leftrightarrow \beta \mathrm{B} + m\mathrm{H}^+ \qquad \textbf{(3.10.3-1)}$$

The reactions are grouped according to the physical state of the substances A and B. Also, the oxidation numbers of the element under consideration is indicated for each reaction. The reactions are grouped as:

- homogenous reactions (two dissolved forms)
- heterogenous reactions involving two condensed substances (generally two solid forms)
- heterogenous reactions involving one condensed substance (generally solid) and one dissolved substance

When the system considered includes substances in the gaseous state, all or some of the following reactions are also considered:

- heterogenous reactions involving two gaseous substances (not considered when there is only one substance in the gaseous state)
- heterogenous reactions involving one gaseous substance and one dissolved substance
- heterogenous reactions involving one gaseous substance and one condensed substance (generally solid)

Equilibrium conditions for the reactions

For each of the reactions, evaluate the equilibrium condition by applying the equilibrium conditions.

For chemical reactions:

$$\sum \nu \ \log(M) = \log K, \text{ where } \log K = \frac{\sum \nu\mu}{1363} \qquad (3.10.3\text{-}2)$$

For electrochemical reactions:

$$E_o = E_o^0 + \frac{0.0591}{n} \sum \nu \ \log(M), \text{ where } E_o^0 = \frac{\sum \nu\mu}{23060n} \qquad (3.10.3\text{-}3)$$

The equations are written in a manner such that they make the influence of pH explicit (the influence of pH is implicit in the term $\sum \nu \ \log(M)$).

For chemical reactions of the form:

$$\alpha A + cH_2O \Leftrightarrow \beta B + mH^+ \qquad (3.10.3\text{-}4)$$

where A is the acid form and B the alkaline form, the condition for equilibrium is

$$\log \frac{B^\beta}{A^\alpha} = \log K + m \text{ pH} \qquad (3.10.3\text{-}5)$$

In the most common case when $\alpha = \beta = 1$, (3.10.3-5) becomes

$$\log \frac{B}{A} = \log K + m \text{ pH} \qquad (3.10.3\text{-}6)$$

Equation (3.10.3-6) makes it clear that the ratio of the fugacity or activity of the alkaline form to the fugacity or activity of the acid form increases linearly with pH.

For electrochemical reactions of the form:

$$\alpha A + cH_2O + ne^- \Leftrightarrow \beta B + mH^+$$

in which A is the oxidised form and B is the reduced form, the condition for equilibrium is

$$E_o = E_o^0 - \frac{0.0591m}{n} \text{pH} + \frac{0.0591}{n} \log \frac{A^\alpha}{B^\beta} \qquad (3.10.3\text{-}7)$$

In the most common case when $\alpha = \beta = 1$, (3.10.3-7) becomes

$$E_o = E_o^0 - \frac{0.0591m}{n}\,\mathrm{pH} + \frac{0.0591}{n}\log\frac{A}{B} \qquad (3.10.3\text{-}8)$$

From equation (3.10.3-8), it is evident that the fugacity or activity of the oxidised form A occurs in the numerator of the term $\log\frac{A}{B}$. Therefore, the equilibrium tension E_o increases when the percentage of the oxidised form increases.

If the concentration of A is equal to the concentration of B then substituting this in (3.10.3-6) or (3.10.3-8) results in an equation which expresses the conditions of pH and electrode potential for which the activities or the fugacities of these two forms are equal. This is valid if the forms A and B of the element in question are either both in the dissolved state or both in the gaseous state.

Thus for a chemical reaction

$$\mathrm{pH} = \frac{1}{m}\log K \qquad (3.10.3\text{-}9)$$

and for an electrochemical reaction

$$E_o = E_o^0 - \frac{0.0591m}{n}\,\mathrm{pH} \qquad (3.10.3\text{-}10)$$

The potential-pH diagram may now be drawn for the substance under consideration. The potential and pH are considered to be independent variables and the concentrations and pressures of substances A and B as parameters.

However, before proceeding with the construction of the diagram, lines representing the oxidation and reduction equilibria of water must be drawn.

The reduction equilibrium of water may be shown as

$$H_2 \Leftrightarrow 2H^+ + 2e^- \quad \textbf{(3.10.3-11)}$$

and its oxidation equilibrium as

$$2H_2O \Leftrightarrow O_2 + 4H^+ + 4e^- \quad \textbf{(3.10.3-12)}$$

At a hydrogen or oxygen pressure of 1 atm., the equilibrium of water can be expressed as:

$$\mathbf{E_{oa} = 0.000 - 0.0591\ pH} \quad \textbf{(3.10.3-13)}$$

$$\mathbf{E_{ob} = 1.228 - 0.0591\ pH} \quad \textbf{(3.10.3-14)}$$

Using equations (3.10.3-13) and (3.10.3-14), lines representing the oxidation and reduction equilibria are constructed.

By drawing lines which give the conditions under which the concentrations or activities of two dissolved substances are equal, the domains of relative predominance of the dissolved forms are established. Furthermore, by drawing lines which express the equilibrium conditions for two solid substances, the domains of relative stability of the solid substances may be ascertained. When these two diagrams are superimposed, the conditions of potential and pH under which a given solid substance and a given dissolved substance can be simultaneously stable may be determined.

These diagrams are valid only for solutions in which the metal or metalloid under consideration exists in the forms that have been considered in establishing the diagram. If the solution contains any other substances which are capable of forming soluble complexes with the metal or metalloid or insoluble salts, then the diagram has to be modified. This is so that a representation of the stability conditions of the 'foreign' substance is included on the diagram. The diagrams thus established will therefore not be of a binary form but of a ternary form.

3.10.4 Predictions using potential-pH diagrams

The potential-pH diagram shows the variation of a standard reduction potential with pH. However, it must be remembered that the cell potential only predicts the thermodynamic feasibility of a redox reaction. It gives no indication of the kinetics i.e. whether the reaction will occur at a measurable rate. Various factors influence whether the reaction is favoured kinetically or not. If a reaction is thermodynamically favoured but is found not to occur, then it could be attributed to one of the following factors:

- Reactions generally occur faster at higher temperatures so if a thermodynamically feasible reaction does not occur in the cold, it might occur if it is heated.
- The activation energy is likely to be high if covalent bonds have to be broken during some stage of the reaction. This could explain why reactions involving the breaking of covalent bonds occur so slowly.
- The reaction may be kinetically hindered due to the purely mechanical effect of an insoluble layer covering the reactant surface. If the insoluble layer is somehow removed, then the reaction could occur very quickly.
- A catalyst is essential for many redox reactions.
- Sometimes, a reaction is kinetically hindered and in order for it to occur, the redox potential needs to be greater than that calculated for the two half reactions. Redox reactions involving gaseous H_2 and O_2 are kinetically hindered to a considerable extent. The reaction becomes measurable only once the cell potential is more positive than a certain value. This value is estimated to be 0.6 V.

CHAPTER 4: EXPERIMENTAL WORK

The experimental work was divided into four parts viz.

- Chemical oxidation of arsenite by ferric ion in gold mine effluent
- Chemical oxidation of arsenite by ferric ion, in the presence of a surface, in gold mine effluent
- Chemical oxidation of arsenite by ferric ion in a synthetic solution
- Bacterial oxidation of arsenite in a synthetic solution

The chemical oxidation experimentation would serve to confirm what was already known from literature i.e. the chemical oxidation of arsenite by ferric ion does not occur. The chemical oxidation in the presence of a surface would enable one to find out if the stainless steel provided a pathway for electron transfer. The bacterial study would comprise two parts. Firstly, it would have to be found out if in fact the bacterial oxidation did occur and of so, what are the optimum conditions under which the bacterial oxidation would occur.

However; prior to commencing with experimentation, suitable analytical methods for determining various arsenic and iron concentrations had to be found. In Section 3.8, various methods of doing so were mentioned. Some of these methods were tested to try to find the most suitable one for use in this study. In the end, the choice of analytical method was based not only on this but also on whether the necessary equipment and accessories were readily available and that the chosen method was reliable.

4.1 ANALYTICAL METHODS: TESTING AND DEVELOPING

It was decided that two of the required three arsenic concentrations would be determined analytically and the third calculated by difference. The same methodology would apply to the iron concentrations.

4.1.1 Determination of arsenic concentration

Initially, polarography and the silver-diethyldithiocarbamate method were going to be used to determine the concentrations of total arsenic and As(III) respectively. Since a polarograph was not available, it was decided that one would be built. The necessary circuit diagram was obtained and an attempt was made to put the circuitry together. Once this was accomplished, the instrument would have to be tested and calibrated, a process which would take a fairly long time. Furthermore, it was found that there could be difficulties regarding the dropping mercury electrode. The electrode would have to be made using a capillary tube, connected to a mercury reservoir. There was no way of ensuring that the mercury would come through the tube at regular intervals, as was required. Also, mercury can only be purchased under licence and is quite costly. The mercury can be recycled i.e. used more than once, but this requires that it be purified after each use. There would, however, be the problem of disposing of the mercury which is highly toxic. After all these factors were carefully considered, a decision was taken against using polarography.

The possibility of using ion-exclusion chromatography was then pursued. A chromatograph for this purpose could not be found on the campus of the University of Durban-Westville, so attempts were made to locate one outside campus. An instrument was located at the Natal Technikon and a used Dionex HPICE As-1 column was obtained. However, attempts to condition the column proved unsuccessful and it was subsequently found that the column had been fouled and could not be used anymore. It was impossible to purchase a new column since the agents only sell these columns to clients who have purchased the entire Dionex system.

Next, the silver-diethyldithiocarbamate method was attempted. It was found that it was extremely difficult to reproduce results obtained via this method. There was excessive variation in results of analyses done in triplicate, notwithstanding the fact that all the aliquots were treated in an identical manner. This could have been due to any of the following reasons:

- The coloured complex formed is unstable and therefore has to be analysed as soon as possible.
- The complex is also light sensitive and must therefore be protected from direct light at all times. Inconsistencies may arise due to the complex being unwittingly exposed to light.
- Lead acetate wool is packed into the neck of the bubbler so that it will remove any hydrogen sulphide gas. The wool is prepared by soaking wads of cotton wool in lead acetate, so there is no way of ensuring that the same amount of lead acetate has been absorbed by each wad. This results in varying amounts of lead acetate being present during each analysis.

The possibility of using this method was therefore abandoned.

The molybdenum blue method was then investigated. It was successfully used to determine the concentrations of both As(V) and total arsenic. In the total arsenic determination, any As(III) in the solution is oxidised to As(V) using potassium iodate. A colourimetric reagent is then added and the resulting solution is then left to stand for four hours. After the blue coloration has developed completely, the absorbance of the solution is read at 865 nm against a blank. The blank which is used is a solution which has been treated in exactly the same way as the samples, except that no arsenic has been added.

The molybdenum blue method to determine arsenic concentrations was chosen for this study because:

- It gave accurate results
- The results were fairly easy to reproduce
- a spectrophotometer was available for use i.e. there was no problem in obtaining a suitable instrument

A detailed description of the method is given in Appendix A-1. Calibration curves for total arsenic and As(V) were developed using this method and are shown in Appendix A-5.

4.1.2 Determination of iron concentration

The phenanthroline method for the determination of ferrous and total iron, as detailed by the American Public Health Association[28] and Vogel[33] was attempted.

This method worked, but only for low concentrations of iron (0.02 - 4 ppm). Since the method worked, an attempt was made to extend it to higher concentrations of iron. This could be achieved by using either a larger volume of phenanthroline or a more concentrated solution of phenanthroline. This is because the coloured complex which forms is a complex of ferrous ion and phenanthroline, so for higher concentrations of iron, larger quantities of phenanthroline are required. This method was successfully extended to include concentrations of iron up to 900 ppm by using a larger volume of a more concentrated solution of phenanthroline with a smaller volume of sample.

The concentration of total iron was determined by first adding hydroxylamine hydrochloride to the solution to reduce all the ferric ion to ferrous ion and then treating it in the same way as was done for the ferrous ion determination.

The absorbance of the solution was read at 510 nm against a blank which had been treated in exactly the same manner as the samples, except that no Fe had been added.

It was decided that the phenanthroline method be used to determine the iron concentrations because:

- it gave accurate results
- the results were fairly easy to reproduce
- Since this was also a spectrochemical method, the same spectrophotometer which was being used for the arsenic analyses could be used for these analyses.

A detailed description of this method is given in Appendix A-3. Calibration curves for total ion and ferric ion were developed and are shown in Appendix A-5.

All analyses were done in triplicate and the two closest readings were used. The mean of these two readings was used and the standard deviation with respect to these readings were calculated (Refer to Appendix F).

4.2 EXPERIMENTAL APPARATUS – CHEMICAL OXIDATION

Refer to figure 4.2-1

The experimental apparatus consisted of a glass reactor immersed in a water bath so that the temperature of the reaction mixture could be controlled. The entire reactor was not immersed in the water, but at all times during experimentation, at least $^{7}/_{8}$ of the volume of liquid in the reactor was surrounded by the hot water of the water bath. This arrangement was found to accomplish isothermal conditions as was required. Gas was introduced through an inlet at the bottom of the reactor. Air was pumped using a diaphragm pump through a humidifier and then through a rotameter before finally entering the reactor. The air was dispersed through a sintered glass disc having a porosity of 1.

The reactor had a glass lid which had openings through which probes to measure temperature, pH and redox potential were inserted. There was also an exhaust line through which any gases could exit the reactor. The gases passed through a condensor, which was cooled with water, and then into a fume cupboard. A condensor was placed on the exhaust line to try to minimise liquid losses during experimentation. The reactor and condensor were held in the required position by clamps.

There was a sampling port on the side of the reactor with a septum held in place by a screw-on cap. This made it possible for samples to be removed as required using a syringe and needle.

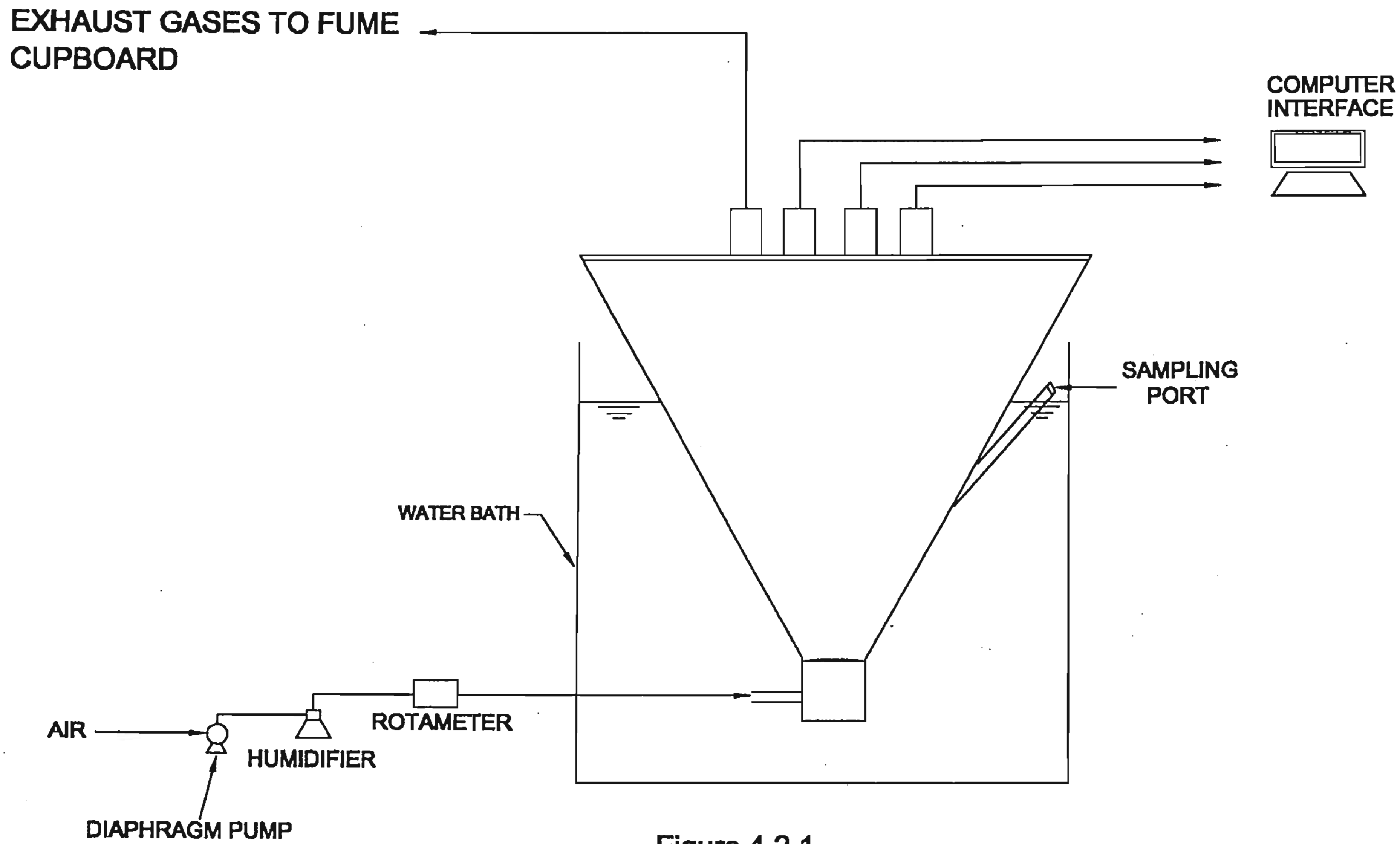


Figure 4.2.1

Schematic diagram of Chemical Oxidation apparatus

4.3 EXPERIMENTAL APPARATUS – BACTERIAL OXIDATION

Refer to figure 4.3-1

The experimental apparatus used for bacterial oxidation experimentation was essentially the same as that used for chemical oxidation. However, the following changes were made:

- Carbon dioxide had to be introduced to the reaction mixture. Carbon dioxide from a gas cylinder passed through a rotameter and then into the reactor via the gas inlet.
- The concentration of dissolved oxygen had to be monitored, so an additional probe had to be inserted. Therefore, an additional opening in the reactor lid was required.

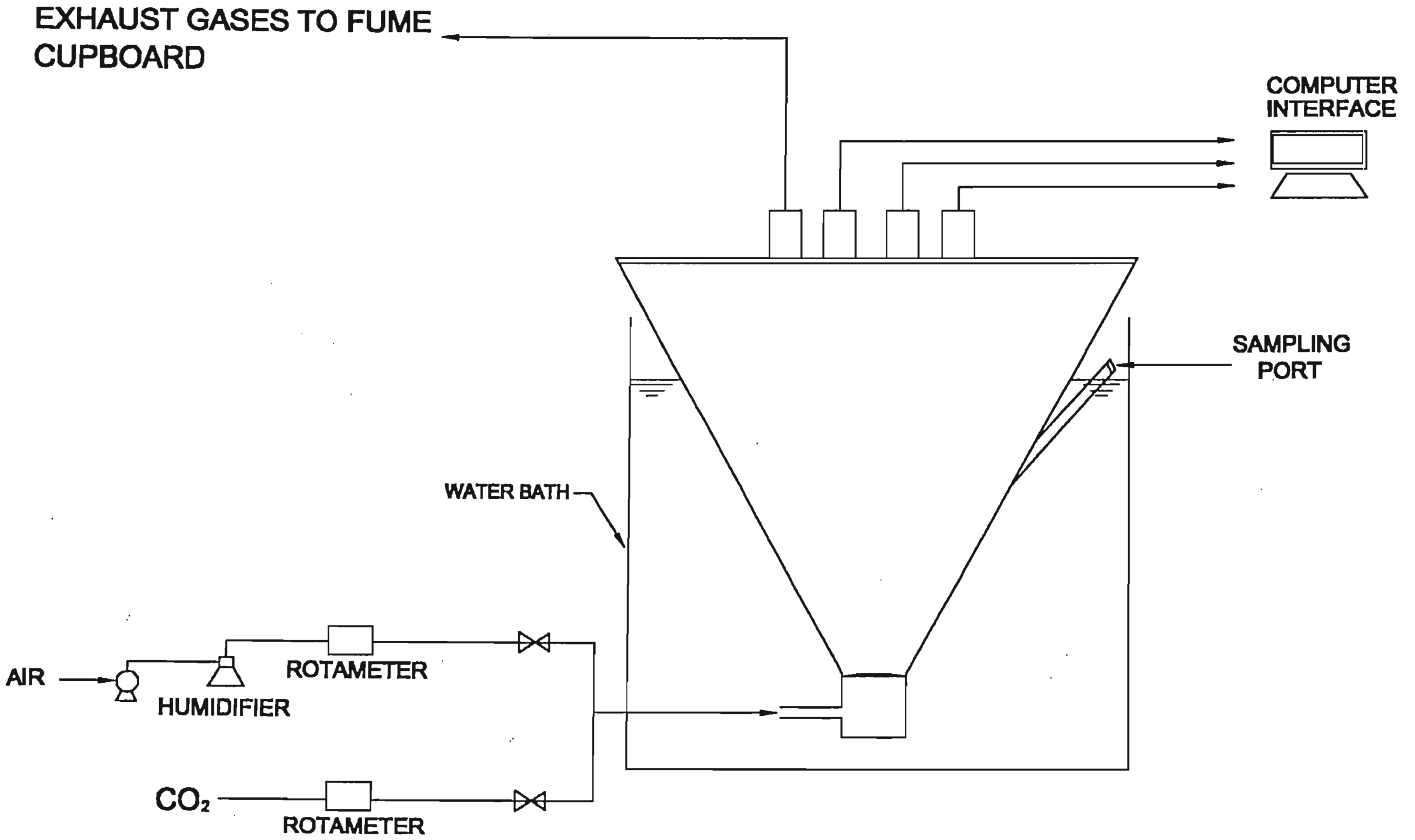


Figure 4.3.1

Schematic diagram of Bacterial Oxidation apparatus

4.4 EXPERIMENTAL PROCEDURE: CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN MINE EFFLUENT

- The concentration of total arsenite, arsenate and arsenite were determined.
- The mass of ferric ion to be added was calculated.
- The reactor was filled with a known volume of mine effluent. A typical analysis of mine effluent from this mine is shown in Table 4.4-1 overleaf
- Air was supplied to the reactor at a rate of 1 vvm (volume gas per volume liquid per minute)
- Fe^{3+} was added in the form of $FeCl_3.6H_2O$ or $Fe_2(SO_4)_3.6H_2O$ such that the ratio of Fe(III):As(III) was in excess of 2:1 (Refer to Appendix B-1 for the composition of the reaction solutions)
- The reaction mixture was allowed to heat up until it attained a temperature of 45^0C
- The pH of the reaction mixture was then adjusted to 1.3 using concentrated H_2SO_4
- Samples for analysis were removed every 12 hours, over a period of 72 hrs. The temperature, pH and redox potential were automatically recorded every 30 minutes using a computer interface
- All analyses (for arsenic and iron concentrations) were done in triplicate and the mean of the two closest results was used

Component	PC Shaft	No. 1 Dam	No.2 Dam	CIS Tails
Ca (mg/l)	97	173	171	-
Mg (mg/l)	25	388	408	-
Cu (mg/l)	0.5	0.5	0.5	1.6
As (mg/l)	0.23	2.30	2.71	745
Na (mg/l)	149	67	74	-
SO_4 (mg/l)	154	284	367	5451
Cl (mg/l)	169	87	91	-
Co (mg/l)	0.5	0.5	0.5	1.5
Zn (mg/l)	0.5	0.5	0.5	8.9
Ni (mg/l)	0.5	0.5	0.5	4.4
Pb (mg/l)	0.5	0.5	0.5	0.05
Fe (mg/l)	0.5	0.5	0.5	104.1

TABLE 4.4-1: Chemical composition of mine effluent from New Consort Mines

4.5 EXPERIMENTAL PROCEDURE: CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN A SYNTHETIC SOLUTION

The experimental procedure was identical to that used for chemical oxidation (Refer to Section 4.4). The difference in this case was that the solution to be used for the experiment was made up by using only arsenic and iron species Refer to Appendix B-2 for the composition of the reaction solutions.

4.6 EXPERIMENTAL PROCEDURE: CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION, IN THE PRESENCE OF A STAINLESS STEEL SURFACE, IN MINE EFFLUENT

The experimental procedure was identical to that of chemical oxidation (as in Section 4.4). Refer to Appendix B-3 for the composition of the reaction solutions. The only difference was that a piece of 316 stainless stain mesh was inserted in the reactor such that it was flush against the wall of the reactor.

The mass of the stainless steel mesh was recorded before it was inserted into the reactor, before the experiment was started. When the experiment was stopped, the stainless steel mesh was cleaned and the mass was once again recorded. The masses are given in Appendix B-3.

4.7 EXPERIMENTAL PROCEDURE: BACTERIAL OXIDATION OF ARSENITE IN A SYNTHETIC SOLUTION

4.7.1 Bacterial growth

A mixed bacterial culture, comprising *Thiobacillus thiooxidans, Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans* was used for the investigation into the bacterial oxidation of arsenite. The mixed bacterial culture was grown in a 9K medium as described by Silverman and Lundgren.

The 9K medium comprised the following in respective proportions per litre of nutrient: ammonium sulphate 3g, potassium chloride 0.1g, magnesium sulphate 0.5g, calcium nitrate 0.01g and potassium hydrogen phosphate 0.5g. The medium is supplemented with the bacteria's energy source, ferrous sulphate 44.8g/l and acidified to a pH of 1.8 using concentrated sulphuric acid. The optimum temperature for growth of this mixed bacterial culture is in the range of 35 to 40 °C.

The bacteria were grown in batch culture in an orbital shaking incubator at a temperature of 37°C. Cell growth was monitored by doing a cell count daily. When the cell count reached $1x10^8$ cells/ml, the bacteria were harvested and used as part of the inoculum for the bacterial oxidation reaction.

4.7.2 Preparation of inoculum

- The bacterial culture was grown until the culture had a cell count of $1x10^8$ cells/ml.
- The cells were harvested by centrifuging at 7000 rpm for 10 minutes.
- The resulting cells were then re-suspended in fresh medium.

4.7.3. Preparation of reaction mixture

- A synthetic solution containing arsenite, arsenate, ferrous ion and ferric ion was prepared. Refer to Appendix B-4 for the composition of the reaction solutions.
- The ratio of As(III) : Fe(III) that was used was 1:3
- The ratio of Fe(III) : Fe(II) was 3:1

4.7.4 Experimentation

- The reactor was filled with the synthetic solution.
- Air was supplied to the reactor at a rate of 1vvm. The carbon dioxide supply was supplemented with pure carbon dioxide from a gas cyclinder such that the ratio of oxygen : carbon dioxide was 20:1 (on a mass basis)
- The synthetic solution was allowed to attain temperature of 37^0C.
- The pH of the solution was then adjusted to 1.8 using concentrated H_2SO_4.
- The inoculum was then added and once the reaction mixture attained a temperature of 37^0 C, the pH of the solution was once again checked to ensure that it was 1.8
- The temperature, pH, redox potential and dissolved oxygen concentration were automatically recorded via a computer interface every 30 minutes.
- A sample was removed from the reactor every 24 hours.
- The sample was centrifuged at 2000 rpm for 5 minutes.
- 10 ml of the supernatant was then removed and diluted to 100 ml. This sample was then analysed for arsenic and iron species.
- All analyses (for arsenic and iron concentrations) were done in triplicate and the mean of the two closest results was used

CHAPTER 5

REACTOR DESIGN

5.1 CHEMICAL OXIDATION

A reactor for an isothermal batch process was designed. Essential features of the reactor that had to be kept in mind were:

- The reaction had to be carried out at 45^{0}C, so the temperature in the reactor had to be controlled
- There had to be adequate mixing of air with the liquid reaction mixture
- The reaction medium was highly acidic, having a pH of 1.3

A reactor, which was essentially a bubble column, was used (Refer to Figure 5.1-1). It consisted of a conical glass vessel with an inlet at the bottom for the supply of gas. A sintered glass disc having a porosity of 1 was attached to the 'neck' of the reactor, and this distributed the gas. The gas bubbles then passed through the reaction mixture and any remaining gas exited through the gas exhaust line. A glass vessel was used because of the highly acidic environment in which experimentation was conducted.

The problem of bubble coalescence is frequently encountered in bubble columns. The bubbles tend to aggregate and eventually form slugs. This decreases the area available for mass transfer, thus slowing down any chemical reaction which may be occurring. The use of a conical vessel encourages the outward movement of bubbles. This will discourage the bubbles from drifting towards each other and coalescing.

The reactor was immersed in a constant temperature water bath. Heat transfer between the hot water and the reaction mixture ensured that the temperature of the reaction mixture was maintained at the desired set point of 45^{0}C.

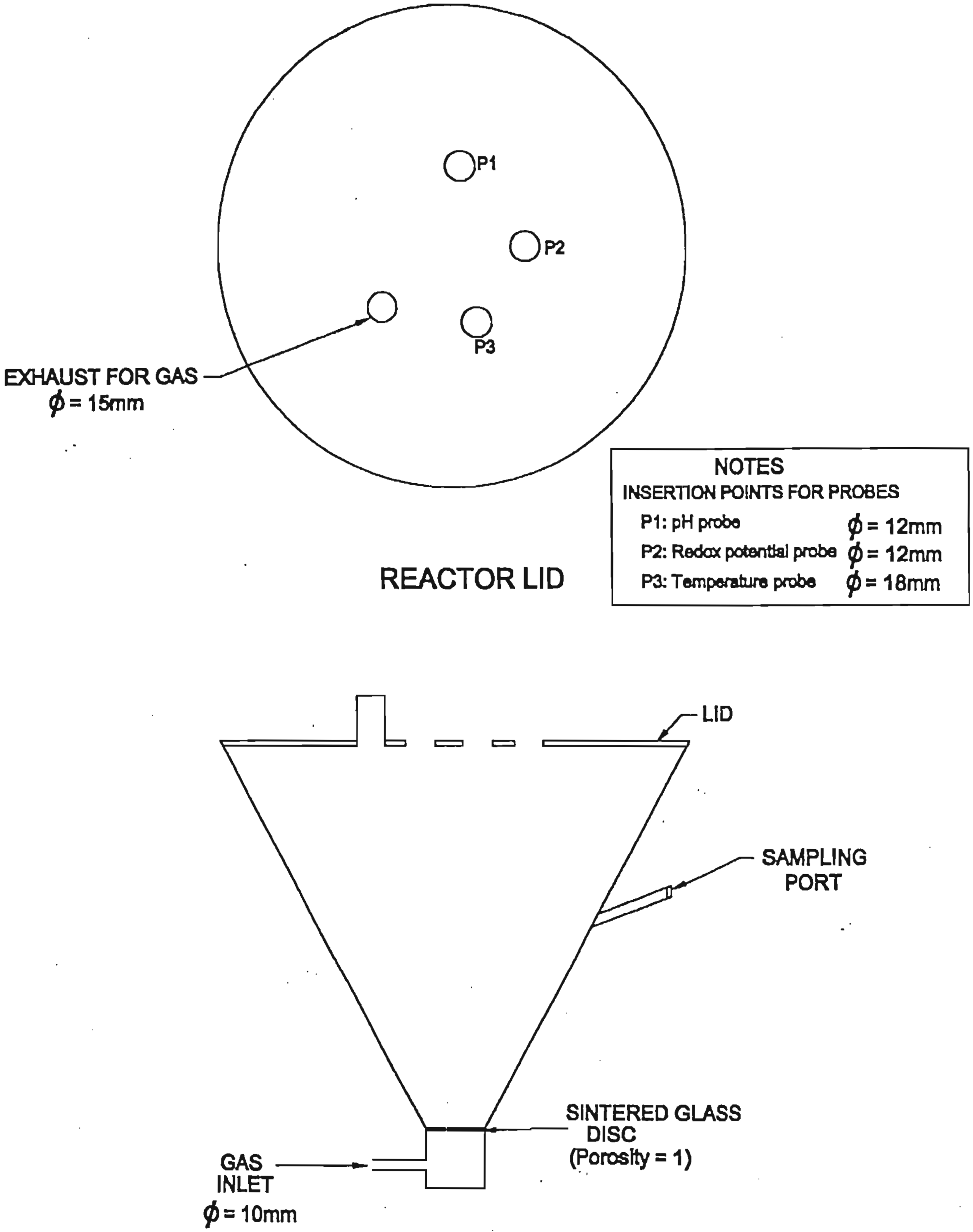


Figure 5.1.1
REACTOR FOR CHEMICAL OXIDATION

There was a sampling port on the side of the reactor through which samples were periodically withdrawn using a syringe and needle. The opening of the sampling port was secured by a septum, held in place by a screw on cap.

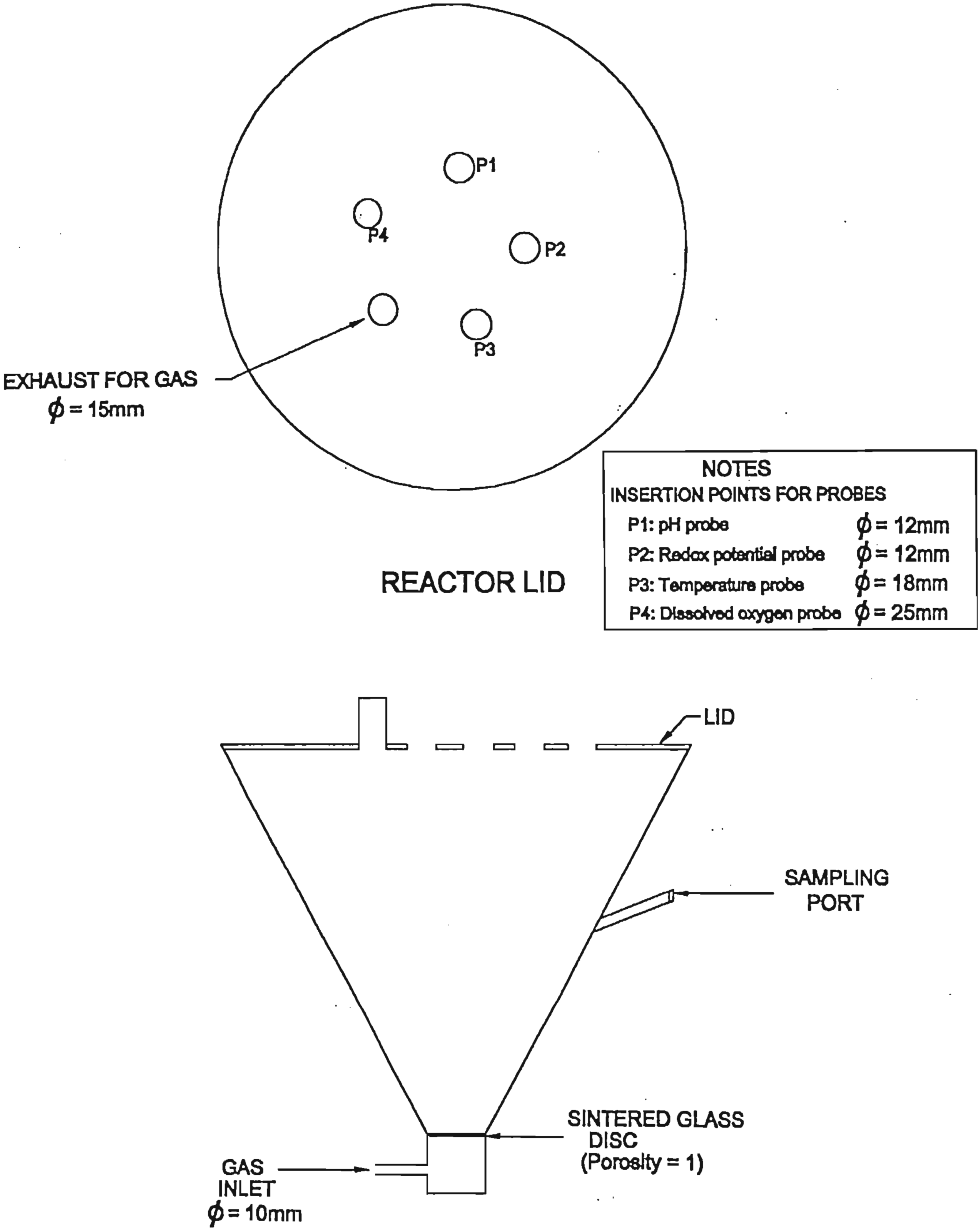
A snugly fitting glass lid closed the reactor. The lid had openings through which probes for temperature, pH and redox potential were inserted. O-rings were used at these insertion points for the probes so that liquid loss through these openings could be prevented. The lid also had an exhaust line through which any gas could exit. A condensor was inserted on the exhaust gas line in an attempt to minimise excessive loss of reaction liquid, as was encountered during initial experimental runs.

5.2 BACTERIAL OXIDATION

The reactor used for the bacterial oxidation experiments was almost identical to that used for chemical oxidation, since many of the requirements were similar (Refer to Figure 5.2-1). Essential features of the reactor that had to be met were:

- Good temperature control since the bacterial culture thrive within a specific temperature range
- Good gas-liquid contact
- The reaction medium is highly acidic, having a pH of 1.8

The temperature of the reaction mixture would have to be maintained within the range of 35 – 40 ^{0}C since the bacteria are sensitive to temperature changes. The reactor would therefore be immersed in a water bath. The reactor was made of glass since the reaction medium was highly acidic because the bacteria grow within a pH range of 1.8 to 2.



NOTES
INSERTION POINTS FOR PROBES
P1: pH probe ϕ = 12mm
P2: Redox potential probe ϕ = 12mm
P3: Temperature probe ϕ = 18mm
P4: Dissolved oxygen probe ϕ = 25mm

Figure 5.2.1
REACTOR FOR BACTERIAL OXIDATION

The reactor was closed by a closely fitting glass lid. The lid had openings through which probes to measure temperature, pH, redox potential and dissolved oxygen concentration could be inserted. O-rings were used at these insertion points for the probes so that there would be no liquid loss through these openings. There was also an opening on the lid through which exhaust gases could pass. A condenser was placed on this line so that fluid loss would be minimised.

In designing a reactor for the bacterial oxidation, the basic requirements for a microbiological process had to be met viz:

- Adequate supply of energy
- Supply of carbon
- Supply of oxygen (for aerobic process)
- Availability of nitrogen and nutrients.

Aerobic bacteria grow in the presence of free oxygen. The mixed culture used is an aerobic culture comprising *T. ferrooxidans, T. thiooxidans* and *L. ferrooxidans*. The source of carbon for this culture is carbon dioxide from air. To ensure that bacterial growth was not limited by carbon dioxide, the supply of air to the reactor was supplemented with pure carbon dioxide. Air, supplemented with pure carbon dioxide entered through an inlet at the bottom of the reactor and was distibuted by a sintered glass disc at the 'neck' of the reactor.

The bacteria obtain their essential nutrients from the growth medium in which they are suspended, prior to being inoculated into the reactor. They obtain energy by oxidising ferrous ion to ferric ion. The growth medium is supplemented with ferrous sulphate. This provides the source of ferrous ion for the bacterial energy requirement. The necessary nutrients were provided by suspending the bacteria in fresh medium and then inoculating this into the reactor containing the reaction mixture (comprising iron and arsenic).

Micro-organisms in their natural state contain a large amount of water. Hence, the difference between the density of water and the density of the micro-organisms is very small. Thus very little hydrodynamic drag is required to maintain the bacteria in suspension. If the fluid in which the micro-organisms are present are in a mild state of motion, then they will be suspended. Therefore, a microbiological process requires an essentially well mixed reactor in which motion is induced either through mechanical stirring or by the evolution of gas or by bubbling air through the medium.

It was decided not to use mechanical stirring because shear forces resulting from this could affect the bacteria suspended in the fluid. It seemed that mixing as a result of the gases entering the reactor would provide sufficient agitation of the reactants. The gases would also provide the necessary state of motion to suspend the bacteria in the mixture. At the same time, this mixing would not be too vigorous so as to be harmful to the suspended micro-organisms.

CHAPTER 6

EXPERIMENTAL RESULTS AND DISCUSSION

6.1 CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN GOLD MINE EFFLUENT

The investigation into the chemical oxidation of arsenite by ferric ion in gold mine effluent was intended to serve as a prelude to the bacterial oxidation of arsenite. It was expected that the chemical oxidation of arsenite would not occur. Thus, carrying out this investigation would serve only to confirm what was known from literature and lay a foundation for the investigation of the bacterial oxidation of arsenite in gold mine effluent.

However, the first experiment conducted, ChemOx 1, indicated that arsenite was in fact being oxidised to arsenate (Refer to Table 6.1-1). The table gives the temperature, pH and redox potentials recorded every twelve hours. The concentrations of arsenate, arsenite, ferric and ferrous ion; as obtained from the chemical analyses performed are also given. The standard deviation, with respect to the arsenate concentration was calculated (refer to Appendix F) and is shown in the table. More detailed results are shown in Appendix C-1.

Initially, a molar ratio of 5Fe(III): 1As(III) was going to be used. However, the amount of ferric ion added exceeded this ratio. Excess ferric ion was added to the mine effluent in an attempt to increase the redox potential. This is because the measured redox potential of the solution at the start of the experiment appeared to be rather low (358.40 mV). If the redox potential was too low, then it was feared that the reaction may not occur.

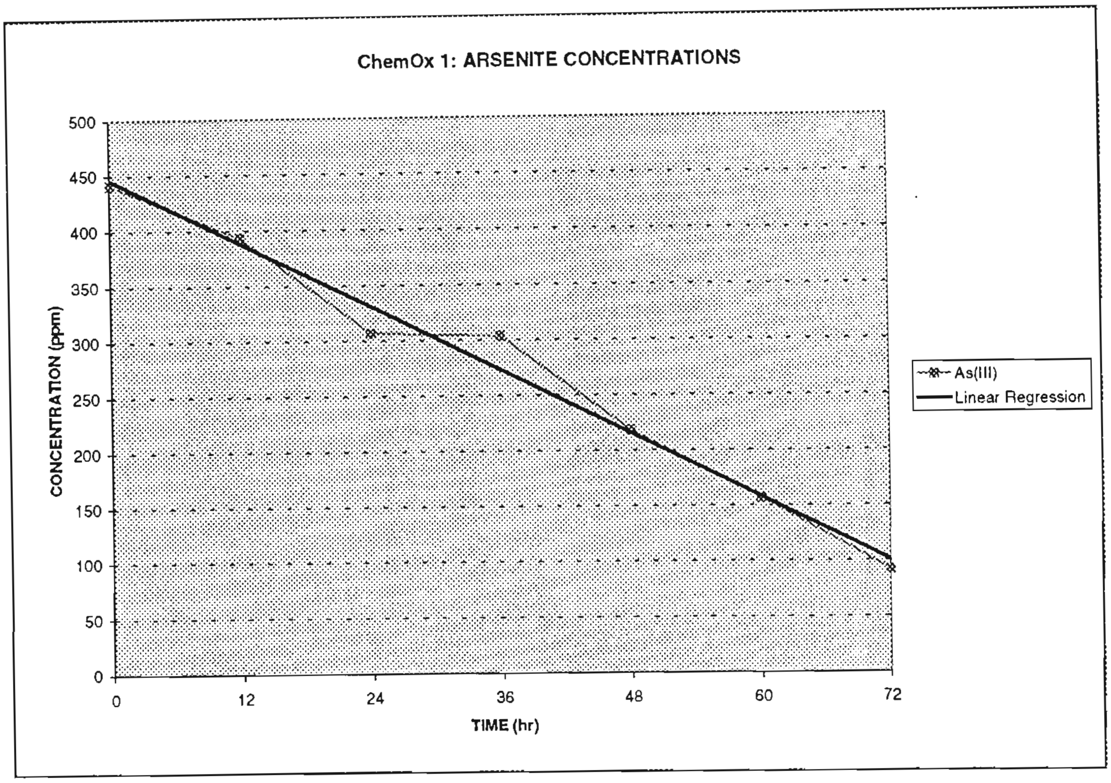
TIME (hr)	TEMP (°C)	pH	Red.Pot (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	45.40	1.29	358.40	1030	18.86	441	0	429	2242
12	44.60	1.26	359.10	1078	30.64	393	10.95	391	2280
24	45.0	1.27	359.30	1165	35.36	306	30.58	440	2232
36	44.90	1.27	358.80	1168	16.50	303	31.34	470	2202
48	44.90	1.27	359.40	1253	33.0	218	50.59	457	2215
60	44.70	1.24	360.60	1315	16.50	156	64.56	550	2122
72	45.20	1.23	362.10	1380	33.0	91	79.29	483	2189

TABLE 6.1-1: Results – ChemOx 1

Increasing the concentration of ferric ion ought to have resulted in an increase in the redox potential of the solution. However, this was not the case and this was attributed to the fact that there could have been interactions between the excess iron added and other ions present in the mine effluent. If the excess iron formed complexes with other ions present in the solution, then the redox potential would not change, as was observed.

An arsenite conversion of 79.29 % was obtained over a period of 72 hours. There is a sudden jump in conversion from 10.95 % at a time of 12 hr to 30.58 % at 24 hr. After this period, the increase in conversion is relatively steady. A possible explanation for this could be found if the temperatures are examined. Between time 0 hr and 12 hr, there was a slight decrease in the temperature. At time 12 hr, the temperature had fallen to below 45 ^{0} C and the conversion achieved during this period was 10.95 %. However, once the temperature started increasing and once again reached 45 ^{0} C, the conversion also shot up. The reason for the very slight increase in conversion in the next 12 hours i.e. from 24 hr to 36 hr is not apparent.

If arsenite concentration was plotted against time, as in graph 6.1-1, then the resulting graph (after performing a regression on the data), would be a straight line. This would indicate that the rate of arsenite oxidation is zero order in As(III) as was reported by Barrett et al.



GRAPH 6.1-1: ChemOx 1 Change in arsenite concentration with time

The redox potential of the reaction mixture stayed almost constant. The pH of the reaction mixture dropped from an initial value of 1.29 to 1.23, which is not significant. The concentrations of the iron species fluctuated slightly but do not appear to show any trend as such. One would have expected the concentration of ferric ion to be decreasing and the ferrous ion to be showing a corresponding increase according to the chemical reaction in which arsenite is oxidised to arsenate by ferric ion which is itself reduced to ferrous ion.

The results of this first experiment warranted further investigation since a chemical reaction was observed when none was expected. During this experiment, the temperature, pH and redox potential were manually recorded at 12 hourly intervals and a 10ml sample was removed from the reactor for analysis every 12 hours. Since a reaction was occurring, the reaction mixture had to be monitored more closely. The experimental set up was therefore modified so that the instruments which measured temperature, pH and redox potential were linked to a computer. Data was thus automatically recorded via this computer interface every 30 minutes.

The chemical oxidation was then investigated further using this modified set up. A molar ratio of 5Fe(III) : 1As (III) was used. The results of two more experiments (ChemOx 2 and ChemOx 3) are shown in Tables 6.1-2 and 6.1-3 respectively. Detailed results are given in Appendix C.

TIME (hr)	TEMP (^{0}C)	pH	Red.Pot. (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	43.68	1.27	572.76	1127	14.14	588	0	74.94	1275
12	45.87	1.23	569.07	1117	37.71	598	-1.70	81.45	1269
24	45.82	1.19	569.38	1170	56.57	544	7.37	79.28	1271
36	45.42	1.18	571.23	1248	63.64	466	20.70	76.87	1273
48	45.15	1.10	570.30	1208	11.79	506	13.90	78.31	1272
60	44.16	1.11	570.61	1242	21.21	473	19.57	81.69	1268
72	46.56	0.94	570.61	1507	18.86	208	64.67	85.30	1265

TABLE 6.1-2: Results - ChemOx 2

A slight decrease in arsenate concentration at t = 12 hr was observed during ChemOx 2. However; an examination of the standard deviations for t = 0 hr and t = 12 hr reveals that these values are quite high (a very high value of 37.73 % for 12 hr) therefore it is highly probable that there was an error with one of the concentrations. It is highly unlikely that the arsenate concentration decreased as this would indicate a reduction rather than an oxidation reaction. The rest of the experiment indicated an oxidation reaction, hence it was obviously not the case. It was therefore assumed that the drop in concentration was due to an experimental error and since the difference was not substantial (only 10 ppm), it was ignored.

There is a sudden jump in conversion from 19.57 % at 60 hr to 64.67 % at 72 hr. The reason for this is not known and since the kinetics of the reaction were not studied, no conclusion regarding this could be drawn. The ferrous ion concentration increased slightly during the course of the experiment.

Conversions of arsenite of 64.67 % and 47.53 % for ChemOx 2 and ChemOx 3 respectively, were recorded. Thus it was consistently found that the oxidation of arsenite to arsenate in the gold mine effluent was in fact occurring.

TIME (hr)	TEMP (°C)	pH	Red.Pot (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	45.91	1.27	554.92	745	11.79	116	0	62	387
12	45.45	1.32	561.69	762	7.07	99	14.40	57	392
24	45.84	1.32	554.61	763	9.43	97	15.84	57	392
36	45.66	1.29	558.61	795	2.36	66	43.21	76	373
48	45.45	1.26	553.38	797	0	64	44.65	81	368
60	45.35	1.24	554.30	782	2.36	79	31.69	58	391
72	45.58	1.26	558.92	800	0	60	47.53	57	392

TABLE 6.1-3: Results - ChemOx 3

In all chemical oxidation experiments, the pH dropped as the reaction progressed. There was a significant drop in pH during ChemOx 2, while the change observed during the other two experiments was much smaller. There was no appreciable change in the redox potential. A difference of 2 to 4 mV was observed in all chemical oxidation experiments. The standard deviations for ChemOx 1 and ChemOx 2 were higher than one would have expected. However, for ChemOx 3 for which an arsenite conversion of almost 48 % was recorded, the standard deviation was within acceptable limits.

According to the work of Barrett et al[11], the oxidation of arsenite should occur at a temperature of 45^0 C and pH of 1.3. They attempted the reaction at 70^0 C. The logic behind using this elevated temperature was most probably to speed up the reaction (if it did occur). However, they found that the reaction did not occur, even at a temperature much higher than the prescribed one of 45^0 C.

They concluded that although thermodynamically favoured, the oxidation reaction was kinetically restricted. This was in keeping with the non-complementary nature of the reaction, where 2 moles of Fe(III) react with 1 mole of As(III), according to the following reaction:

$$FeAsS + 11Fe \rightarrow 12Fe + As + S \qquad \textbf{(6.1-1)}$$

Thus they believed that a catalyst was required in order for the reaction to occur.

This investigation was carried out at a temperature of 45^0 C and pH of 1.3, in keeping with the requirements described by Barrett et al[11]. Fe(III) was added to the mine effluent so that the molar ratio of Fe(III):As(III) was in excess of 2:1. A ratio of 5:1 was used, which is 2,5 times the minimum ratio. This would compensate for any of the Fe(III) that could have been lost through complex formation with other ions in the mine effluent and through incomplete dissolution of the Fe(III). Barrett et al[11] did not indicate the ratio that was used in their experiments.

This investigation showed that the chemical oxidation of arsenite by ferric ion in gold mine effluent did occur. It was therefore necessary to establish why the reaction occurred when it should'nt have. A closer examination of the conditions under which this investigation was conducted and the conditions under which Barrett et al[11] conducted their investigation was required. Upon comparing the reaction conditions, two differences were found.

The first factor was the temperature. Barrett et al[11] carried out their investigation at 70^0 C whilst this investigation was done at 45^0 C. If the reaction was attempted at 70^0C, then the only thing that could happen is that the oxidation of arsenite would occur faster (assuming that the oxidation was occurring) and thus the conversion of arsenite would increase.

The second factor was the composition of the reaction mixture. The reaction mixture of Barrett et al[11] consisted of water, to which they added arsenopyrite, ferric sulphate and sulphuric acid; i.e. they used a synthetic solution which contained these chemical species only.

The mine effluent used in this investigation was obtained from New Consort Gold Mines. A chemical analysis of this effluent is shown in Table 4.4-1. From the analysis, it is evident that mine effluent from this mine contains significant amounts of calcium, magnesium, sodium, chlorine and sulphate. It also contains, in smaller amounts; cadmium, copper, cobalt, zinc, nickel, lead and iron. The occurrence of the oxidation of arsenite in the mine effluent could therefore be attributed to the presence of one (or more) of these chemical species. It must therefore be noted that the investigation reported by Barrett et al[11] was done under different conditions with respect to this series of experiments and hence does not provide an appropriate basis for comparison.

In order to ascertain if one (or more) of the other chemical species in the mine effluent somehow contributed to the oxidation of arsenite, the chemical oxidation of arsenite by ferric ion in a synthetic solution was investigated.

6.2 CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN A SYNTHETIC SOLUTION.

A synthetic solution was made up such that it contained iron and arsenic species only. Small quantities of sodium hydroxide (to dissolve As_2O_3), and sulphuric acid were added to the synthetic solution.

The synthetic solution was made up such that the molar ratio of Fe(III): As(III) was in excess of 2:1. The ratio used in all these experiments involving the synthetic solution was 5Fe(III): 1As(III), in keeping with the ratio used in experimental work done with the gold mine effluent. Fe(II) in the form of $FeSO_4.7H_2O$ was added such that the molar ratio of Fe(III): Fe(II) was 4:1. The solution was acidified to a pH of 1.3 using concentrated sulphuric acid. Refer to Appendix B-2 for the composition of the solution.

The results of the first chemical oxidation experiment using a synthetic solution (ChemSyn 1) are shown in Table 6.2-1. Detailed results are shown in Appendix C-2.

TIME (hr)	TEMP (°C)	pH	Red.Pot. (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	45.25	1.3	523.23	1153	4.71	275	0	498	1770
12	45.72	1.28	522.31	1193	14.14	255	7.26	518	1750
24	45.42	1.25	522.62	1273	4.71	215	21.79	535	1733
36	45.51	1.20	521.69	1312	1.18	196	28.75	546	1722
48	44.65	1.16	522.92	1333	0	185	32.68	530	1738
60	45.13	1.16	522.92	1340	2.36	182	33.89	551	1717
72	45.21	1.12	522.95	1352	1.18	176	36.01	563	1705

TABLE 6.2-1: Results - ChemSyn 1

Once again, the oxidation of arsenite was observed. A 36% conversion of arsenite was recorded. The decrease in the pH in the case of the synthetic solution was much more significant than in the case of the gold mine effluent. There was once again, no significant change in the redox potential of the reaction mixture. The standard deviation with respect to arsenate was within acceptable limits, except in the case of t = 12 hr. There was an increase in the ferrous ion concentration and a corresponding decrease in the ferric ion concentration, as would be expected if the ferric ion were oxidising arsenite to arsenate.

More experiments using synthetic solutions were conducted using different Fe(III)/Fe(II) ratios. The results of these experiments are shown in tables 6.2-2, 6.2-3 and 6.2-4. Detailed results are shown in Appendix C-2. Refer to Appendix B-2 for the composition of the solutions.

TIME (hr)	TEMP (°C)	pH	Red.Pot. (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	46.11	1.31	458.93	734	0	344	0	391	1659
12	45.63	1.26	480.16	762	3.54	330	4.11	426	1624
24	45.27	1.21	473.70	786	0	318	7.75	444	1606
36	44.80	1.15	480.77	788	1.18	317	7.99	370	1680
48	44.81	1.12	477.08	792	1.18	315	8.47	469	1581
60	45.05	1.10	494.0	828	1.18	297	13.80	455	1595
72	45.02	1.09	490.0	824	0	299	13.07	405	1645

TABLE 6.2-2: Results - ChemSyn 2

All the solutions were made up such that they initial concentrations of arsenite, arsenate and ferric ion were the same. However, analyses of the various mixtures show that there is variation amongst these concentrations. This may be due to incomplete dissolution of some of these species e.g. the arsenate concentration at t = 0 for ChemSyn 2 is 734 ppm whereas the solution was made up such that it should have a concentration of 1000 ppm arsenate. The concentration of the species could also be reduced if there was complex formation within the solution. If this was the case then, when the analysis was done, the ions that were still locked in the complex might not detected.

This is due to the fact that the molybdenum blue method relies on the formation of the molybdoarsenate complex which has the characteristic blue colouration, the intensity of which gives an indication of the concentration of arsenic in the solution. If the arsenate was instead locked in some other complex, then it might not be available to form this molybdoarsenate complex, hence affecting the concentration. Further, if the arsenic species were so strongly linked to a complex, then it is highly unlikely to be available for any chemical reaction.

The other factor that could result in a slight discrepancy in the arsenic concentration is that the reactor used to carry out this study was made of glass. Arsenic has a tendency to adsorb onto glass. This could have occurred to a small extent – this contribution was not deemed to be too significant due to the fact that the contents of the reactor were being mixed by the air that was being introduced at the bottom of the reactor. It is for this reason that samples removed from the reactor for chemical analysis were always stored in plastic bottles.

TIME (hr)	TEMP (^{0}C)	pH	Red.Pot. (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	46.10	1.27	491.54	993	7.07	617	0	369	1637
12	46.17	1.12	506.62	1030	4.71	580	5.94	397	1609
24	46.02	1.08	507.23	1048	5.89	563	8.78	324	1682
36	46.18	1.04	506.31	1123	4.71	487	21.07	467	1539
48	45.80	1.01	506.92	1118	3.54	493	20.13	385	1621
60	46.03	0.91	509.08	1176	3.54	434	29.58	417	1589
72	45.74	0.86	521.38	1213	4.71	397	35.66	361	1645

TABLE 6.2-3: Results - ChemSyn 3

A ratio of 5Fe(III): 1Fe(II) was used in ChemSyn 2 and ChemSyn 3. A chemical reaction was once again observed when the ratio of 5Fe(III): 1Fe(II) was used. Conversions of As(III) of 13% and 36% were observed in ChemSyn 2 and ChemSyn 3 respectively. The ferrous ion concentration was found to increase in the case of ChemSyn 2, whilst it fluctuated during ChemSyn 3.

A ratio of 3Fe(III): 1Fe(II) was used in ChemSyn 4. In the case of ChemSyn 4, no reaction was observed. This indicates that a molar ratio of 3Fe(III): 1Fe (II) does not favour the chemical oxidation of As(III). There was no significant change in the pH. The concentration of arsenite remained almost the same during the 72 hour period over which the experiment was conducted. There was a slight change in the redox potential of the reaction mixture. There was a slight fluctuation in the iron concentrations during this experiment.

TIME (hr)	TEMP (^{0}C)	pH	Red.Pot. (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	Fe(II) (ppm)	Fe(III) (ppm)
0	45.94	1.31	462.32	796	3.14	361	549	1573
12	45.74	1.26	463.85	782	3.14	368	523	1599
24	45.47	1.28	460.47	780	4.71	369	587	1535
36	45.46	1.28	459.85	784	4.71	367	558	1564
48	42.12	1.29	458.01	771	1.57	373	532	1590
60	45.23	1.28	473.08	769	3.14	374	507	1615
72	45.23	1.28	474.62	753	4.71	382	522	1600

TABLE 6.2-4: Results - ChemSyn 4

A drop in the pH of the reaction mixture was observed in all of the experiments in which the oxidation of arsenite was reported. When a ratio of 5Fe(III): 1Fe(II) was used, an increase in the redox potential as the reaction progressed was observed, whereas in the case of ChemSyn 1, when a ratio of 4Fe(III): 1Fe(II) was used, the redox potential remained almost the same throughout the experiment.

The standard deviation in most cases is well within acceptable limits, in fact in all but two cases, the standard deviation is below 5 %. This indicates very good precision.

All experiments involving the synthetic solution were carried out under conditions that were identical to those of the chemical oxidation in the gold mine effluent. Once again, the oxidation of arsenite was found to occur, at Fe(III): Fe(II) ratios of 4 and 5.

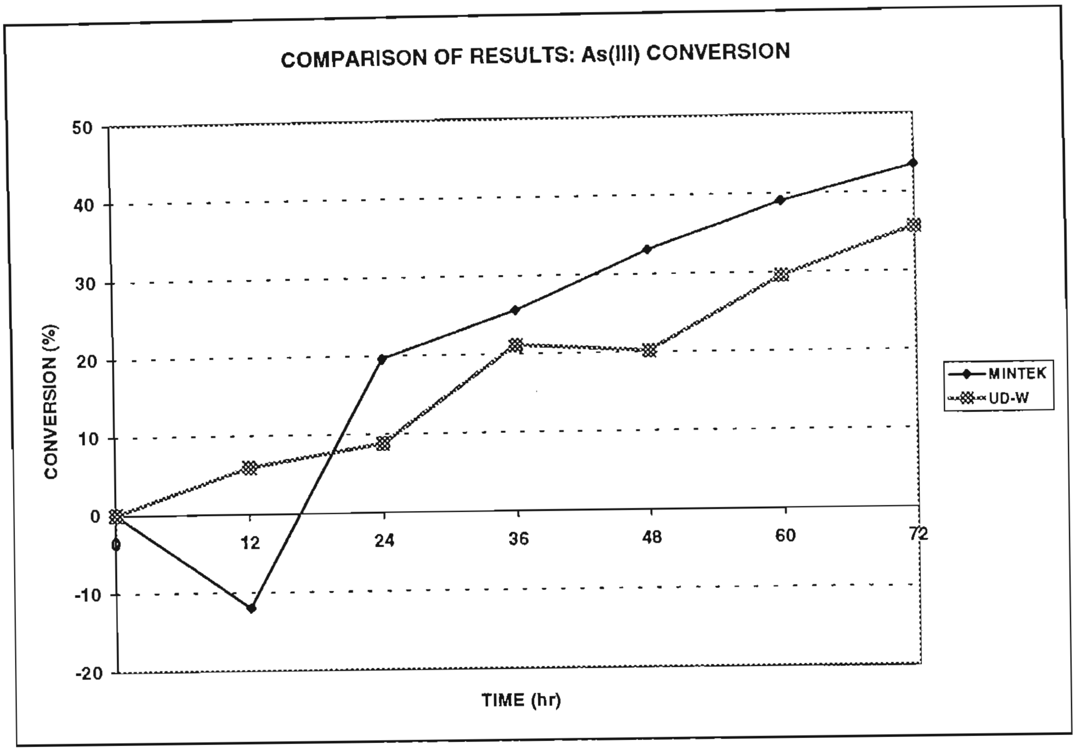
However, since the oxidation of arsenite was not supposed to occur, samples from the experiment ChemSyn 3 were sent to Mintek for analysis to make sure that the analytical methods being used were giving accurate results. The results of the Mintek analysis are shown in Table 6.2-5. The difference between the values obtained in the Mintek analysis and that obtained by the author is expressed as the percentage error and was calculated using the following formula:

$$Error = \frac{(MINTEK\ value) - (UDW\ value)}{(MINTEK\ value)} \times 100 \qquad \textbf{(6.2-1)}$$

The trend displayed for arsenite conversion for both the Mintek and UD-W results are shown in Graph 6.2-1.

TIME (hr)	As(V) (ppm) Mintek	As(V) %Error	As(III) (ppm) Mintek	As(III) %Error	%As(III) Conv. Mintek
0	1150	15	666	7	0
12	1070	4	746	22	-12.01
24	1280	17	536	5	19.52
36	1320	15	496	2	25.53
48	1370	19	446	11	33.03
60	1410	17	406	7	39.04
72	1440	15	376	6	43.54

TABLE 6.2-5: Comparison of analytical results for ChemSyn3



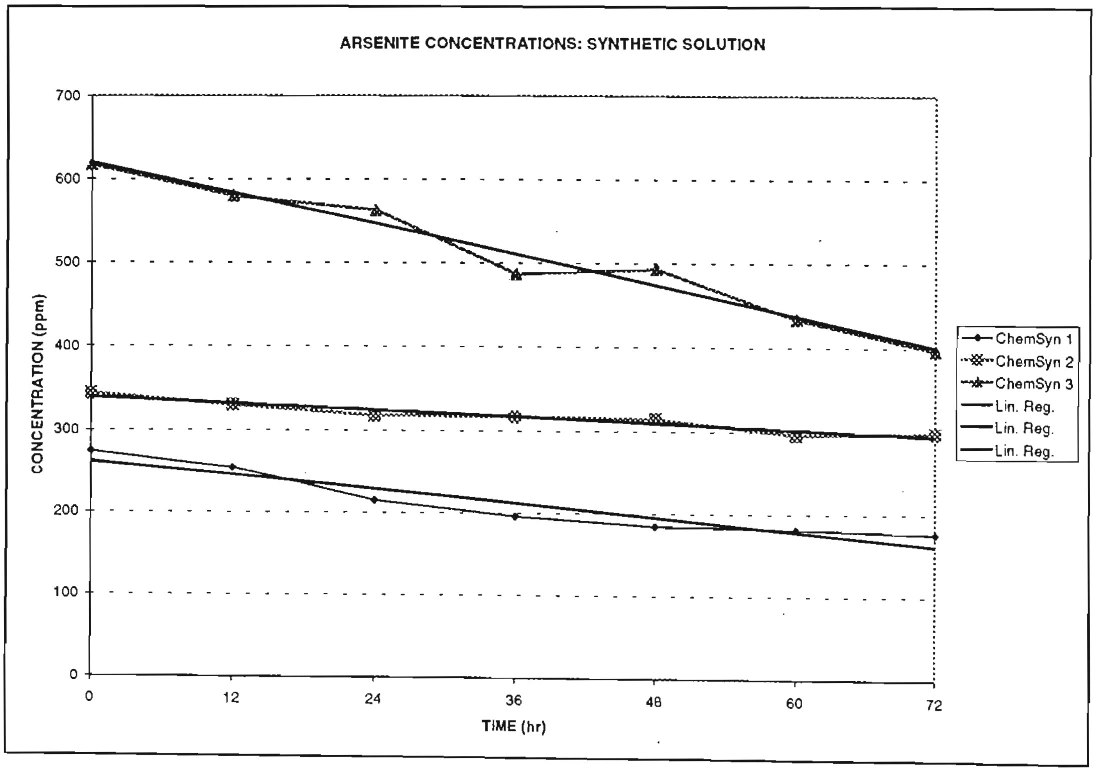
GRAPH 6.2-1: Comparison of arsenite conversion for ChemSyn3

Upon comparing the two sets of results, it is evident that they are not in complete agreement. However, the trends displayed in both sets of results are similar. There is one point only (at t=12 hr) that does not correspond with the trend obtained via the UD-W analysis. It is obvious that there is an error in the Mintek result for a time of 12 hours since that value gives a negative conversion which is not possible. In the case of analysis done at UD-W, an arsenite conversion of 36 % was recorded whilst the Mintek analysis showed a conversion of 43 %.

This may be attributed to the fact that the analytical methods used at Mintek were more sophisticated than those methods used by the student. Ion exclusion chromatography was used by Mintek to determine the arsenic concentration. This method is known to be one of the best for this application. It was therefore assumed that the Mintek values were more accurate than the UD-W values since a better method and more advanced equipment was used by their highly trained personnel to obtain these results. Thus although not in

complete agreement, the results show the same trend and lead to the same conclusion i.e. the oxidation of arsenite to arsenate is occurring.
It may therefore be concluded that there is no contribution by any of the chemical species present in the gold mine effluent to the arsenite oxidation since the oxidation was observed in the synthetic solution as well.

Graph 6.2-2 shows the variation of arsenite concentration with time for the chemical oxidation of arsenite in synthetic solutions for those experiments in which the oxidation was found to occur. Regression analyses on the data show once again that there is a linear relationship between the arsenite concentration and time, as was observed for ChemOx 1 (recall graph 6.1-1). This indicates once again that the rate of arsenite oxidation is zero order in As(III), in other words, the concentration of arsenite is not the rate limiting factor.



GRAPH 6.2-2: Regression analysis performed on arsenite concentration for chemical oxidation experiments on synthetic solutions

Results from ChemSyn 1 and ChemSyn 2 indicate that there is a drop in the pH of the reaction mixture (the oxidation of arsenite was found to occur in these experiments). If the equation for the oxidation of arsenite is examined:

$$HAsO_4 + 2H_2O + 2Fe^{3+} \Leftrightarrow H_3AsO_4 + 2H^+ + 2Fe^{2+} \qquad \textbf{(6.2-2),}$$

it is evident that acid is being generated. Since there is a nett production of acid (sulphuric acid), the pH of the solution should decrease, as was observed during the experiments. So the drop in pH also indicates that arsenite is being oxidised to arsenate.

The Nernst equation may be used to calculate electrode potentials under non-standard conditions. In the case of the reduction of Fe^{3+} to Fe^{2+}, the Nernst equation becomes:

$$2Fe^{3+} + 2e^- \Leftrightarrow 2Fe^{2+} \qquad \mathrm{E}^0 = 0.771\ \mathrm{V} \qquad \textbf{(6.2-3)}$$

$$E = E^0 - \frac{RT}{nF}\ln\left[\frac{\left(a_{Fe^{2+}}\right)^2}{\left(a_{Fe^{3+}}\right)^2}\right] \qquad \textbf{(6.2-4)}$$

$$E = 0.771 - \frac{RT}{nF}\ln\left[\frac{\left(a_{Fe^{2+}}\right)^2}{\left(a_{Fe^{3+}}\right)^2}\right] \qquad \textbf{(6.2-5)}$$

Recall, also that the activity is related to concentration by the relation:

$$a_i = \gamma_i c_i$$

From the above equations, it is evident that the ratio of the Fe^{2+}/Fe^{3+} concentrations will affect the redox potential of the solution. As the Fe^{3+} concentration increases, the redox potential of the solution will increase. This is the reason for investigating the effect of the Fe(III): Fe(II) ratio on the oxidation of arsenite.

Molar ratios of 3, 4 and 5 Fe(III): Fe(II) were investigated. In the case of ratios of 4 and 5, the oxidation of arsenite did occur, but when the ratio was decreased to 3, no reaction occurred. It may therefore be concluded that the minimum Fe(III): Fe(II) molar ratio, in order for the oxidation of arsenite to occur, lies somewhere between 3 and 4. C.Q.Zheng[37] reported that the rate of oxidation of pyrite increased with increasing Fe(III): Fe(II) ratio. This may also apply in the case of the oxidation of arsenite, with the threshold ratio lying somewhere between 3 and 4, below which the oxidation of arsenite does not occur.

An examination of the measured redox potentials at the beginning (t=0) of each of these experiments reveals that in the case of the ratio of 3:1, the redox potential is significantly lower than those recorded at higher iron ratios.

The values of the expected redox potentials of the synthetic reaction mixture were calculated using the concentrations of arsenic and iron species in the solution to obtain a theoretical redox potential. This value was then compared to the actual (measured) redox potential. The following half reactions were considered for the purpose of calculations:

$$HAsO_4 + 2H_2O \Leftrightarrow H_3AsO_4 + 2H^+ + 2e^- \qquad \textbf{(6.2-6)}$$

$$2Fe^{3+} + 2e^- \Leftrightarrow 2Fe^{2+} \qquad \textbf{(6.2-7)}$$

The overall reaction is:

$$HAsO_4 + 2H_2O + 2Fe^{3+} \Leftrightarrow H_3AsO_4 + 2H^+ + 2Fe^{2+} \qquad \textbf{(6.2-8)}$$

A comparison of the measured redox potentials and those calculated using the Nernst equation for reactions carried out in synthetic solution was done (A sample calculation is shown in Appendix D). The difference was calculated by subtracting the calculated value from the measured value. The values are shown in Table 6.2-6.

The general trend, as is evident from the table, is that except in the case of a few values for ChemSyn 1, the difference between the calculated and measured values of electrode potential are not large enough to be deemed significant. In most cases, the measured values are higher than the calculated values.

Experiment	Time (hr)	E (mV) Calculated	E (mV) Measured	Difference (mV)
ChemSyn1 Ratio = 4:1	0	481.41	523.23	41.82
	12	476.20	522.31	46.11
	24	467.75	522.62	54.87
	36	459.90	521.69	61.79
	48	455.58	522.92	67.34
	60	453.95	522.92	68.97
	72	448.78	522.95	74.17
ChemSyn 2 Ratio = 5:1	0	494.52	458.93	-35.59
	12	485.78	480.16	-5.62
	24	478.69	473.70	-4.99
	36	478.77	480.77	2.00
	48	468.80	477.08	8.28
	60	466.14	494.00	27.86
	72	469.07	490.00	20.93
ChemSyn 3 Ratio = 5:1	0	526.73	491.54	-35.19
	12	508.25	506.62	-1.63
	24	509.89	507.23	-2.66
	36	491.86	506.31	14.45
	48	495.36	506.92	11.56
	60	481.42	509.08	27.66
	72	479.69	521.38	41.69
ChemSyn 4 Ratio = 3:1	0	494.06	462.32	-31.74
	12	490.84	463.85	-26.99
	24	489.23	460.47	-28.76
	36	490.76	459.87	-30.89
	48	493.50	458.01	-35.49
	60	494.04	473.08	-20.96
	72	493.46	474.62	-18.84

TABLE 6.2-6: Comparison of electrode potentials

In the case of ChemSyn 1, the differences are generally higher than those for the other two experiments. The reason for this is not known since the precision for all three experiments was quite good – the standard deviation was less than 5 % in all but two instances as can be seen in from the results shown in section 6.2.

It is also evident that for ChemSyn 4, where no oxidation was recorded, the measured value of the redox potential is always lower than the calculated value i.e. for the case where no oxidation occurred, the calculated value is consistently higher than the measured one.

The difference between the calculated and measured values of redox potential may be attributed to several factors. The value of the standard redox potential at different pH values was obtained from the potential-pH diagrams which were constructed (Refer to Appendix E). It must be remembered that these diagrams were constructed using several approximations viz.

- In constructing the diagrams, it is assumed that the stoichiometric coefficients of the oxidised and reduced forms or the acid and base forms of the species under consideration are equal.
- The diagrams were constructed at a pressure of 1 atm
- It is assumed that the activities of the two forms (either oxidised and reduced forms or acid and base forms) are equal. This is true if both forms are either in the dissolved state or the gaseous state. In this case, it was assumed that they were both in the dissolved state.

Also, one should bear in mind that the potential-pH diagram is actually a 'predominance area' diagram. The outlined areas give an indication of those areas in which the designated species make up more than 50 % of the total concentration in solution.

Hence the values obtained from these diagrams will not be absolutely accurate and there will be a difference between the calculated and measured values. However; the difference between the calculated and measured values are not significant so it may be assumed that the reactions that were assumed to be taking place during the experiment are in fact occurring. It may therefore be safe to assume that there are no other side reactions affecting the oxidation of arsenite.

Furthermore, the synthetic solution also contained sodium hydroxide and concentrated sulphuric acid. Addition of sulphuric acid effected the pH and this was incorporated into the Nernst equation that was used in the calculation of the redox potential of the solution. In this way, the sulphuric acid was accounted for. However;. the sodium hydroxide was not incorporated into the Nernst equation because it was assumed that it did not effect the redox potential of the solution appreciably since such a small quantity (approximately 1 g) was added to the synthetic solution. If, however; this assumption is incorrect, then this would affect the calculated values of redox potential.

From the results of these experiments involving synthetic solutions of arsenic and iron, it was concluded that the oxidation of arsenite to arsenate by ferric cion did occur. The deduction that can be made from this is that there is no contribution by any other chemical species in the gold mine effluent that is effecting the oxidation of arsenite in the mine effluent.

6.3 CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION, IN THE PRESENCE OF A STAINLESS STEEL SURFACE, IN GOLD MINE EFFLUENT.

An investigation into the chemical oxidation of arsenite by ferric ion in the presence of a stainless steel surface was conducted in order to ascertain whether the stainless steel surface acted as an electron donor and thus made the oxidation of arsenite possible.

In a preliminary study conducted at the University of Durban-Westville in 1995, it was shown that the bacterial oxidation of arsenite in gold mine effluent in the presence of a stainless steel surface did occur. However, it was possible that the oxidation of arsenite occurred due to the stainless steel surface acting as an electron donor and not due to bacterial action. In order to ascertain if this was the case, the chemical oxidation in the presence of a stainless steel surface was investigated.

The reaction was carried out in gold mine effluent, to which ferric ion had been added such that the ratio of Fe(III) : As(III) was 5:1, as before. The reaction conditions were the same as those for the chemical oxidation without a surface, i.e. a temperature of 45 ^{0}C and pH of 1.3. The pH of the mixture was adjusted using concentrated sulphuric acid.

Results of this series of experiments are shown in Tables 6.3-1, 6.3-2 and 6.3-3. Detailed results are shown in Appendix C-3. The composition of the reaction mixture is given in Appendix B-3.

TIME (hr)	TEMP (^{0}C)	pH	Red.Pot(mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	Fe(II) (ppm)	Fe(III) (ppm)
0	46.50	1.38	570.20	1272	16.50	66	70	290
12	45.87	1.41	574.92	1162	2.36	176	73	287
24	45.73	1.38	569.38	1168	7.07	169	75	285
36	45.58	1.36	554.61	1213	0	124	74	286
48	45.36	1.35	554.61	1157	33.0	181	76	283
60	45.41	1.33	553.69	1185	2.36	153	75	285
72	45.39	1.32	557.69	1237	28.28	101	77	282

TABLE 6.3-1: Results - ChemSurf 1

TIME (hr)	TEMP (^{0}C)	pH	Red.Pot (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	Fe(II) (ppm)	Fe(III) (ppm)
0	46.97	1.33	585.99	997	0	14	69	448
12	45.66	1.34	577.07	970	4.71	41	77	440
24	45.52	1.33	568.76	982	2.36	29	77	440
36	44.84	1.33	570.0	908	7.07	102	75	442
48	45.64	1.30	572.15	935	2.36	76	68	449
60	45.43	1.29	570.30	907	9.43	104	67	450
72	45.51	1.31	570.92	852	2.36	159	68	449

TABLE 6.3-2: Results - ChemSurf 2

TIME (hr)	TEMP (^{0}C)	pH	Red.Pot (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	Fe(II) (ppm)	Fe(III) (ppm)
0	45.84	1.30	554.61	817	3.21	65	60	183
12	45.95	1.35	552.46	793	1.08	89	55	187
24	45.40	1.35	554.61	800	4.73	82	56	187
36	45.80	1.30	554.92	827	6.85	55	74	168
48	45.55	1.28	538.61	813	5.01	69	79	164
60	45.12	1.27	542.61	800	3.21	82	73	170
72	45.50	1.27	542.85	783	0	99	65	178

TABLE 6.3-3: Results - ChemSurf 3

Results of this investigation indicated that the oxidation of arsenite did not occur. In fact, in all the experiments conducted the concentration of arsenite increased!

The pH decreased slightly during all the experiments. Also, the redox potential decreased by about 12 to 15 mV in all the experiments. The standard deviation with respect to the arsenate concentration is within acceptable limits so the results of the analysis may be assumed to be fairly precise. The variation in the iron concentrations during all of these experiments was slight and therefore deemed insignificant.

The mass of the stainless steel was recorded before being inserted into the reactor and after it was removed from the reactor (Refer to Appendix B-3). In all of these cases, the mass of the stainless steel was found to increase slightly. The stainless steel surface was examined and no deposition of any material was visible to the naked eye, so no explanation for the slight increase in mass was found.

The results indicate an increase in the arsenite concentration and a corresponding decrease in the arsenate concentration. This is consistent with the reduction of arsenate to arsenite (the opposite of the aim of the exercise!).

McGeehan[36] studied the sorption of arsenite and arsenate in soils. Arsenate is strongly sorbed by soils under aerobic conditions. However, under anaerobic conditions, the arsenate is rapidly desorbed and is subsequently reduced to arsenite. The nature of the reduction is not clearly understood.

For his study, McGeehan[36] used soil which was immersed in water, to which he had added arsenate. In essence, he studied the effect of a surface (the soil) on the arsenic concentration. He found that the concentration of arsenate decreased and concurrently, arsenite appeared in the solution. This indicates that arsenite is being produced from the reduction of arsenate in the presence of a surface. He proposed two ways in which this could occur viz.:

- Arsenate, on the soil particle, is first reduced to arsenite and then desorption of arsenite into solution occurs
- Arsenate desorbs from the soil into solution and is subsequently reduced to arsenite

The first reaction sequence could explain the results obtained from experiments investigating the effect of a surface on the oxidation of arsenite. The concentration of arsenite increased, thus indicating that arsenate was being reduced. It is therefore possible that arsenate was sorbed onto the stainless steel surface, reduced to arsenite and then the arsenite desorbed into the solution.

The second reaction sequence could also be a possibility. However, if the arsenate is being reduced in solution then it must be assumed that this is happening due to the presence of the stainless steel in the reaction medium. This is because the chemical oxidation of arsenite by ferric ion in the absence of a surface did occur (as was discussed in the previous two sections). All these reactions were carried out under identical conditions, the only difference in this case being the presence of a surface in the reaction medium. If the second reaction sequence were true, then there must be some contribution from the stainless steel to this end. If not, then the reaction would not occur since the only difference between these reaction conditions and those of Sections 6.1 and 6.2 is the presence of the stainless steel mesh. It is possible that the stainless steel is acting as an electron donor, as would be required for the reduction of arsenate to arsenite according to the following equation:

$$H_3AsO_4 + 2H^+ + 2e^- \Leftrightarrow HAsO_4 + 2H_2O \qquad \textbf{(6.3-1)}$$

Since there appears to be no great variation in iron concentration - the oxidation of ferrous ion could provide the necessary electrons according to the equation:

$$2Fe^{2+} \Leftrightarrow 2Fe^{3+} + 2e^- \qquad \textbf{(6.3-2),}$$

there has to be an alternate electron donor and this could be the stainless steel. Thus it is possible that the second reaction mechanism could also explain the decrease in arsenate concentration.

It may therefore be concluded that the oxidation of arsenite, in the presence of a stainless steel surface, in gold mine effluent does not occur.

6.4 BACTERIAL OXIDATION OF ARSENITE IN A SYNTHETIC SOLUTION

An investigation into the bacterial oxidation of arsenite in a synthetic solution was undertaken. This signalled a change from the original plan i.e. the bacterial oxidation in the mine effluent and not a synthetic solution was supposed to have been studied.

This change was made due to the unexpected results of the chemical oxidation investigation. Now, the effect of one of the chemical species or any combination of the chemical species present in the mine effluent, had to be taken into account. Any one of these species could in some way affect the oxidation of arsenite (if it did occur). This contribution was even more crucial in the case of bacterial oxidation due to the bacteria being sensitive to the conditions in which they exist and grow.

It was therefore decided to investigate the bacterial oxidation in a synthetic solution, and depending on the outcome, the results of this investigation could then be applied to the mine effluent at a later stage.

The synthetic solution was made up in the same way as in the previous experiments, using a ratio of 5Fe(III): 1As(III). It was acidified to a pH of 1.8 using concentrated sulphuric acid. The synthetic solution in the reactor was inoculated with the bacterial culture which had been suspended in fresh medium. The bacteria was then given time to grow until the population had reached a sufficient size. This point was indicated by an increase in the cell number to approximately $1x10^8$ cells/ml and an increase in the redox potential.

High redox potentials are necessary for good oxidation rates and Dempsey et al reported that they aimed for a redox potential of between 550 and 600 mV.

An increase in redox potential indicates that the oxidation of ferrous to ferric ion is occurring and this is an indication that the bacteria are growing since they derive energy for growth and cell maintenance from the oxidation of ferrous to ferric ion.

Once the redox potential exceeded 600 mV and a cell count indicated that the culture was of a sufficient number, then the reaction mixture was monitored. Usually, it took the bacteria approximately four days to reach this point. Once this stage was reached, then samples were removed from the reactor every 24 hours and analysed for the various iron and arsenic species. Thus the time shown as zero in the table of results is actually the time at which the bacteria has reached a viable population size so that it was able to start affecting a change on the reaction mixture (i.e. this does not include the initial growth period of approximately 4 days).

The results of the first bacterial oxidation experiment are shown in Table 6.4-1. Detailed results are shown in Appendix C-4. The composition of the reaction mixture is given in Appendix B-4.

TIME (hr)	TEMP (^{0}C)	pH	Red.Pot. (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	37.68	1.90	512.46	468	0	408	0	633	1674
24	38.02	1.71	680.45	532	2.35	376	7.76	579	1728
48	38.03	1.77	677.99	550	1.18	367	10.01	562	1745
72	38.06	1.81	681.46	620	0.59	332	18.68	585	1722
96	38.04	1.79	664.14	644	1.18	321	21.44	542	1765
120	37.88	1.83	648.14	716	4.71	284	30.42	578	1729
144	37.93	1.75	647.53	710	1.77	286	29.71	601	1706
168	37.59	1.76	680.45	800	1.18	242	40.64	590	1717
192	35.45	1.76	676.75	832	1.18	226	44.52	553	1754

TABLE 6.4-1: Results - BacOx 1

The results indicate that a conversion of arsenite of almost 45 % was achieved over a period of eight days. There appears to be a slight discrepancy with respect to the conversion on day 5 (120 hr), when the conversion is 30.42 % and then decreased to 29.71 % on day 6 and then once again increased to 40.64 % on day 7. The value on day 5 appears to be incorrect. Since the standard deviation for this set of values is higher than those of days 4 and 6, it was assumed that there was an error with the measurement for day 5.

The standard deviation for all the measurements is well below 5 % indicating excellent precision. The pH of the solution decreased throughout the course of the experiment. The iron concentration fluctuated.

It is evident from the redox potential that the oxidation did not go to completion. If the redox potential had eventually levelled off and then started to drop then this would signal a decline in bacterial activity and hence the reaction would have to be stopped. This is because once the bacteria run out of nutrients, they will begin to die. Once they start dying, the redox potential will start decreasing. Since the experiment was carried out on a batch basis, the nutrients would eventually run out and this would happen. However, since the redox potential was still quite high on day 8, there was obviously still sufficient nutrients available.

The reaction was not allowed to go to completion because the experiment had to be stopped due to excessive loss of liquid from the reactor. This loss of liquid was not expected since the reaction was carried out at the relatively low temperature of 37 ^{0}C. One possible explanation for this loss of liquid was that droplets of liquid were being entrained within the gas leaving the reactor, thus resulting in excessive loss of liquid. In order to minimise this, a piece of glass wool was inserted on the exit line of the reactor so that any liquid leaving with the exhaust gases would hopefully be retained.

Results of the next bacterial oxidation experiment are shown in Table 6.4-2. Detailed results are shown in Appendix C-4. The composition of the reaction mixture is given in Appendix B-4.

A conversion of arsenite of almost 79 % was achieved over 10 days. There was a sharp increase in conversion from day 8 onwards. The conversion jumped from 38.76 % on day 7 to 54.87 on day 8. The conversion on days 9 and 10 also show large jumps in conversion. The iron concentrations fluctuated but no trend was evident. The pH decreased consistently during the experiment.

TIME (hr)	TEMP (^{0}C)	pH	Red.Pot. (mV)	As(V) (ppm)	Std. Deviation	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	37.80	1.69	630.60	412	1.18	734	0	701	1730
24	37.92	1.67	633.07	448	5.30	698	5.20	685	1746
48	37.68	1.64	628.76	456	5.30	689	6.47	652	1779
72	38.18	1.63	630.91	485	3.54	661	11.10	671	1760
96	38.16	1.62	633.07	515	4.12	631	16.31	643	1788
120	38.30	1.61	616.45	551	1.18	595	23.40	678	1753
144	38.41	1.60	613.07	562	0	584	25.69	712	1719
168	38.07	1.60	618.61	617	10.61	529	38.76	685	1746
192	37.92	1.58	599.22	672	2.36	474	54.87	658	1773
216	37.91	1.57	601.07	698	4.12	448	63.95	693	1738
240	38.06	1.56	600.15	735	2.94	411	78.58	659	1772

TABLE 6.4-2: Results - BacOx 2

The redox potential peaked at 633.07 mV on day 4 (96 hr) and remained around this value until day 7. From day 8 (192 hr), the redox potential appears to be dropping, thus indicating a decline in bacterial activity. This is probably due to the concentration of nutrients decreasing. The drop in the redox potential was not dramatic, thus indicating that there were still nutrients available. The experiment could therefore have probably gone on for a little longer, until the nutrients were totally depleted.

Here again, there was loss of liquid, but not as much as in the previous bacterial oxidation experiment. This indicates that the use of the glass wool did reduce the loss of liquid, but did not stop it altogether.

The decrease in the pH of the reaction mixture as the reaction progressed is consistent with the proposed mechanism of bacterial oxidation outlined in Section 3.5.2, during which sulphuric acid is generated.

Various researchers have reported on the effect of microbial interventions on the dissolution of minerals[32]. Ferrous ion can be rapidly oxidised by oxygen in the presence of bacteria, and the acceleration of this reaction can be of the order of 10^6 times that of the rate of reaction if the bacteria were not present. The bacteria derive the energy required for growth and cell maintenance from the oxidation of ferric to ferrous ion using oxygen as the oxidant.

$$Fe^{2+} + 0.25O_2 + H^+ \Leftrightarrow Fe^{3+} + 0.5H_2O \qquad \textbf{(6.4-1)}$$

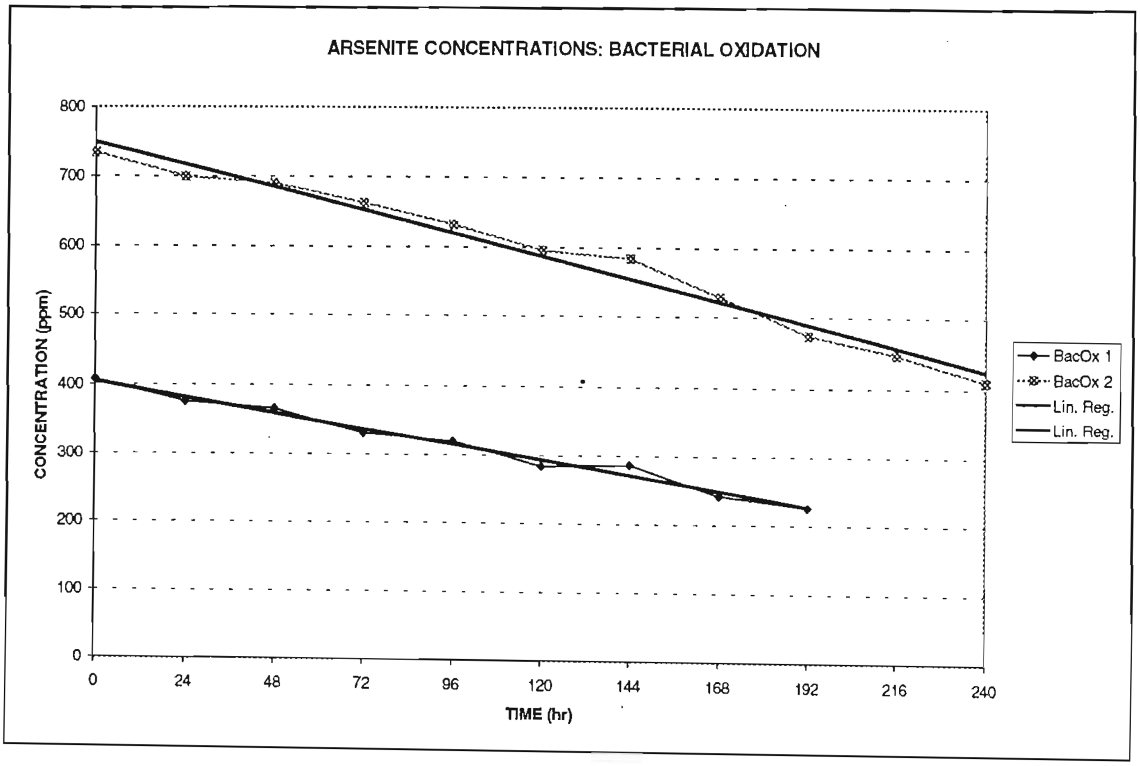
Ferric ion is known to be a good oxidising agent and it has been known to oxidise various sulphide minerals e.g. pyrite and arsenopyrite.

In order for the arsenite to be oxidised under these reaction conditions, the overall reaction that should be occurring is:

$$HAsO_4 + 2H_2O + 2Fe^{3+} \Leftrightarrow H_3AsO_4 + 2H^+ + 2Fe^{2+} \qquad \textbf{(6.4-2)}$$

The mechanism by which this reaction occurs could therefore involve two steps. In the first step, the bacterial culture oxidise ferrous to ferric ion, according to equation (6.4-1). Ferrous ion has been supplied to the reaction medium in two ways. Firstly, it is an ingredient of the medium in which the bacteria are suspended. The second way in which it has been supplies is, in making up the synthetic solution, ferrous ion was also added. Thus there should be an ample supply of ferrous ion available for the bacterial growth processes. Also, air is being supplied to the reactor, so sufficient oxygen will be available to the bacteria for this reaction to occur.

In the second step of this mechanism, the ferric ion oxidises the arsenite to arsenate and is itself reduced to ferrous ion. The bacteria may once again oxidise the ferrous ion to ferric ion and so the reaction will proceed in this manner. Since this is a cyclic process, whereby the bacteria oxidise the ferrous ion and the ferric ion then oxidises arsenite and is reduced to ferrous ion once again, fluctuations in the concentration of iron species (both ferric and ferrous ion) would be expected – as was observed.



GRAPH 6.4-1: Regression analysis performed on arsenite concentration for bacterial oxidation experiments on synthetic solutions

Graph 6.4-1 shows the variation of arsenite concentration with time for the bacterial oxidation of arsenite in synthetic solution. Regression analyses on the data show a linear relationship between the arsenite concentration with time. This indicates, yet again, that the oxidation of arsenite is zero order in As(III) and some other factor, other than the arsenite concentration is rate limiting.

Since both the chemical and bacterial processes were found to occur, it would be prudent to compare the two. The average conversion of arsenite achieved during the chemical oxidation in a synthetic solution was 28.25 % over 3 days, with the highest conversion of 36.01 % being achieved during ChemSyn 1. If the results of the bacterial oxidation were compared over the same time period i.e. over a period of 8 days, then the conversion achieved during BacOx 2 would be 54.87 % and the average conversion by bacterial oxidation would be 49.70 % over a period of 8 days (192 hr). The highest conversion of 78.58 % was achieved during BacOx 2, but this was over a period of 10 days.

If one compares the average conversion of 28.25 % for chemical oxidation (over 3 days) to the average conversion of 49.70 % for bacterial oxidation (over 8 days), an assessment as to whether the extra time required for the bacterial oxidation to occur is actually worthwhile, needs to be made. The chemical oxidation is known to be notoriously slow, so there is no guarantee that should the reaction be carried out over a longer period, the conversion will increase dramatically. Furthermore, the reaction needs to be carried out at a temperature of 45 ^{0}C as opposed to a temperature of 37 ^{0}C for bacterial oxidation. This means that there is a higher energy requirement for chemical oxidation.

The bacterial oxidation has shown that the initial change in conversion is a bit slow over the first few days, but accelerates considerably from around day 6. This indicates that the reaction could probably come a lot closer to achieving

100 % conversion if it is given a few more days. The energy requirement for the bacterial oxidation is obviously lower than that of the chemical oxidation. The only additional gas requirement is that the air supply be supplemented with carbon dioxide. This, however, need not be the case. Carbon dioxide is supplied to ensure that its concentration is not rate limiting. If the actual demand for carbon dioxide may be determined, then it may be found that additional carbon dioxide need not be supplied.

An important precaution that has to be borne in mind is that bacteria are sensitive, so potentially harmful substances should not be introduced into their environment. This means that air that is introduced into the reactor should be filtered. Also, high concentrations of certain chemicals are toxic to the bacteria e.g. this mixed culture cannot withstand concentrations of Zn of higher than 0.624 g/litre, so one has to take the necessary precautions when dealing with these chemicals.

It is important to note that these organisms will only be effective if they are in an environment that is conducive to their growth and survival. An advantage of using this mixed culture is that they thrive in a highly acidic environment so it is not necessary to sterilise the equipment since it is extremely unlikely that any other organisms will be able to survive in such an environment. If some other microorganisms were used, and they needed an environment that had a pH of say 5, then it would most probably have been necessary to sterilise all the equipment in order to ensure that there were no competitors present during the experiment.

It is obvious that one would want to achieve the highest possible conversion of arsenite in order to ensure complete removal of arsenic from solution. Therefore, although the bacterial oxidation process takes longer than the chemical oxidation, it may be well worth the effort if it gives a higher conversion of arsenite.

6.5 EXPERIMENTAL ERRORS

Errors may be classified as determinate or indeterminate. Determinate errors have a definite value and an assignable cause and it is possible to measure and account for these errors. Indeterminate errors cannot be positively identified nor can they be quantified. Indeterminate errors cause data from replicate measurements to fluctuate in a random manner whilst in the case of determinate errors, the error is mostly unidirectional.

Inherent in every physical measurement is some degree of uncertainty that can only be reduced to some acceptable level. Certain tools are used in the pursuit of this 'acceptable' level. The standard deviation is a measure of precision i.e. it is used to describe the reproducibility of results. The standard deviation describes the deviation of measurements from the mean. It must be noted that the application of classical statistics to a small number of replicate measurements (small being defined as 2 – 20) often leads to false conclusions with respect to indeterminate errors. Therefore, the usual standard deviation formula, $\sigma = \sqrt{\frac{\sum_1^N (x_i - \bar{x})^2}{N}}$; was not used to calculate standard deviation. Instead, the formula $s = \sqrt{\frac{\sum_1^N (x_i - \bar{x})^2}{N-1}}$ which applies to a small number of measurements; was used. A sample calculation is shown in Appendix F.

Errors in this study could only have arisen from physical measurements that were taken. This is because temperature, pH, redox potential and dissolved oxygen concentration were recorded automatically. Thus, it is indisputable that the only serious source of error in this study would have arisen from the chemical analyses that were performed.

Spectrochemical methods were used to determine the concentrations of arsenic and iron species. This involved the preparation of samples and the use of a spectrophotometer to read off values of absorbance. All analyses were done in triplicate and the mean of the closest two values were used in calculating the concentrations of the various species. The standard deviation with respect to these two values was calculated.

A blank determination was used in all the spectrochemical analyses. This is a correction factor which is used in order to offset any constant errors which affect physical measurements. In this case, all the analyses involved spectrochemical methods, hence there was room for error with regard to the measurements that were being taken. In all of the analyses, blanks were made up (i.e. the preparation of the blank was done in the same manner as for the samples being analysed, but there was no sample added) and all samples were measured against this blank. A standard deviation of between 5 and 10 % would have been considered as acceptable for this work.

Errors could have crept in in one of two ways: either during the preparation of samples or whilst taking an absorbance reading. The preparation of samples could have been affected if a slightly smaller or larger volume of sample was used. Recall that a 10 ml sample taken from the reactor was diluted to 100 ml. If either more or less than 10 ml was used then this would affect the concentrations of the various chemical species obtained after dilution and the effect would be magnified since a dilution factor of 10 was used.

The addition of incorrect amounts of reagents could affect the sample preparation and hence the absorbance. Since the absorbance is a direct indication of the concentration of the chemical species, this would affect results. An equipment malfunction would have resulted in incorrect absorbances and thus concentrations being recorded. However, this was not observed so this could not have been a factor that contributed to erroneous results.

It is therefore evident that errors could only have arisen as a result of human error. From the results, it is evident that better precision was obtained as the researcher gained more experience with the analytical methods that were used. The standard deviation in the first few experiments are at times quite high e.g. in ChemOx 1. However, the precision with respect to experiments performed later e.g. ChemSyn 2 was excellent.

CHAPTER 7

CONCLUSION AND RECOMMENDATIONS

The sulphide mineral arsenopyrite (FeAsS), is one of the most common host minerals in which gold is occluded. Ores of this nature are classified as refractory since they are not amenable to conventional gold extraction methods. During the processing of arsenical refractory ores, the arsenic is solubilised, thus resulting in high concentrations of arsenic in the gold mine effluent.

Arsenic is highly toxic, therefore it has to be removed from the mine effluent to prevent contamination of the environment. Many methods have been used for arsenic removal, but it has been found that most compounds of arsenic are unstable. They quickly decompose and go back into solution, thus re-creating the hazard situation. Arsenate compounds are more stable than arsenite compounds so it is therefore necessary to oxidise any arsenite in the mine effluent to arsenate prior to removal.

The chemical oxidation of arsenite by ferric ion should occur. Ferric ion is a strong oxidising agent and Barrett et al reported that the oxidation reaction should occur in an acidic medium. However, they found that although theoretically possible, the reaction did not occur. During this investigation, the chemical oxidation of arsenite in gold mine effluent was found to occur.

Since a chemical reaction was observed when none was expected, it was necessary to study this phenomenon more closely. It was possible that a contribution by one of the multitude of chemical species present in the effluent resulted in the oxidation of arsenite. In order to ascertain if this was the case, the chemical oxidation in a synthetic solution containing iron and arsenic species only was studied.

It was found that the chemical oxidation of arsenite in the synthetic solution did occur. Thus the conclusion that there is no outside contribution from one of the other chemical species in the mine effluent could be drawn. Furthermore, this confirms that the chemical oxidation of arsenite by ferric ion does occur.

The effect of the ferrric to ferrous ion ratio on the chemical oxidation of arsenite in the sythetic solution was also studied. It was found that the oxidation occurred at a ratio equal to or greater than 4. The threshold ratio, below which the oxidation does not occur lies somewhere between 3 and 4.

The Nernst equation was used to calculate the theoretical redox potential of the synthetic reaction solution. This value was then compared with the measured values and it was found in most cases that there was a small difference between the two values. This insignificant difference means that it is highly probable that the reaction that was proposed is actually taking place. Also, if any other interactions are occurring in the solution then these are not of any significance.

The effect of a stainless steel surface on the oxidation of arsenite in gold mine effluent was investigated. It was found that instead of the arsenite being oxidised, the arsenate was reduced to arsenite. McGeehan reported that the reduction of arsenate occurred in the presence of soil particles. He proposed two possible mechanisms by which this occurred. One of these mechanisms involved the sorption of arsenate onto the soil, where it was then reduced to arsenite and it then went back into solution. The other mechanism involved the reaction occurring in the solution itself.

It is the recommendation of the author that the same experiment be conducted using a non-conducting surface so it may be ascertained if the conducting (stainless steel) surface plays a role in the second mechanism. This is because if the second mechanism holds true, then there has to be a contribution by the stainless steel to the reaction, since this reaction was carried out under conditions which were identical to that of the chemical oxidation in the mine effluent.

The bacterial oxidation of arsenite in a synthetic solution was found to occur. Conversions of up to 79 % were achieved over a period of 10 days. Although this may be deemed a good outcome, the time taken to achieve this conversion may be a bit excessive. It is possible that the chemical oxidation could achieve the same results in much less time. It is therefore necessary to try to optimise the process and to try to prolong the lifespan of the bacterial culture. This could be difficult under batch conditions, since although there will (ideally) always be sufficient gas and ferrous ion present, the micro-nutrients will eventually run out, causing the bacteria to die.

Both the bacterial and chemical oxidation experiments showed that the oxidation of arsenite was zero order in arsenite and hence some other factor, other than arsenite concentration is rate limiting.

It took approximately five days from the time the bacterial culture was inoculated into the synthetic solution for the population to reach a population of 1×10^8 cells/ml. The total time it took to achieve the conversion of 79 % is therefore 15 days. This time is rather long and may pose problems in large scale operations. The conditions under which the bacterial oxidation was carried out should therefore be closely examined in order to ascertain what could be done in order to speed up the process so that the highest possible conversion may be achieved in the shortest possible time.

Conducting the bacterial oxidation on a continuous basis may be a viable alternative to the batch process and it is highly probable that better results may be achieved on a continuous basis. Since the bacterial process is an autocatalytic one i.e. one has to 'seed' the process with suitable bacteria initially, but the bacteria are thereafter produced by the process reactions; running this process on a continuous basis, need not be overly difficult.

The crucial factor in conducting this on a continuous basis is to not 'upset' the bacteria in any way. It is much easier to do this when running a continuous process since new medium is being supplied and some 'spent' and reacted fluid is being removed. Thus it is important to try to maintain optimum conditions for bacterial oxidation through all of this. It is therefore the recommendation of the author that this alternative to the batch process be investigated.

CHAPTER 8

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APPENDICES

APPENDIX A

CHEMICAL SPECIATION

APPENDIX A-1

METHOD FOR ARSENIC SPECIATION

Instrument: Spectrophotometer to read absorbance at 865 nm, providing a path length of 1 cm.

1. Reagents

All solutions were prepared from analytical grade reagents and distilled water was used throughout.

1.1 Ammonium molybdate 4,0%

Dissolve 4.0g of ammonium molybdate in 60ml of water and dilute to 100ml with water. Store the solution in a polyethylene bottle and reject if it becomes discoloured or if a precipitate forms.

1.2 Ascorbic acid 0.1M

Dissolve 1.32g of ascorbic acid in 75ml water.

1.3 Potassium antimonyl tartrate 0.274%

Dissolve 0.2743g of potassium antimonyl tartrate in distilled water and dilute to 100ml.

1.4 Sulphuric acid 2.5M

Dilute 70ml of concentrated sulphuric acid (relative density 1.84) to 500ml.

1.5 Mixed reagent

Mix the following reagents thoroughly:

- 125ml 2.5M sulphuric acid
- 37.5ml ammonium molybdate

Add the following:

- 75ml ascorbic acid
- 12.5ml potassium antimonyl tartrate

This reagent must be prepared fresh daily

1.6 Potassium iodate

Dissolve 0.8g of KI in 20ml water. Add 1 g of KIO_3 and dilute to 50 ml. Add 1ml conc. H_2SO_4. Store in a dark place.

2. Photometric determination of As(V) by the Molybdenum Blue method

Pipette 0.5 ml sample into a 50ml volumetric flask. Add 8ml of the mixed reagent and shake for 2 minutes. Add 2 drops of KIO_3 to the flask. Fill the flask to the mark with distilled water, leave for 4 hours for the colour to develop completely and measure photometrically at 865nm. Use a blank which has been prepared in an identical manner, except that no arsenic has been added. A series of standards for As(V) should be prepared and measured in the same way.

3. Photometric determination of total inorganic arsenic by the Molybdenum Blue method

Pipette 0.5 ml sample into a 50ml volumetric flask. Add 2 drops of KIO_3 and allow to stand for 15 minutes. Add 8ml of the mixed reagent to the flask and shake for 2 minutes. Allow to stand for 4 hours and measure photometrically at 865nm. Use a blank which has been prepared in an identical manner, except that no arsenic has been added. A series of standards for total As should be prepared and measured in the same way.

APPENDIX A-2

PREPARATION OF STANDARD SOLUTIONS OF ARSENIC

These standard solutions were used to obtain calibration curves (see Appendix A-5)

1. Preparation of As(III) standard solution (1000ppm)

1.1 Make up a 10% (mass/volume) sodium hydroxide (NaOH) solution by dissolving 1g NaOH in 10 cm^3 water.

1.2 Dissolve 0,1320g of arsenic(III) oxide (As_2O_3, molar mass 197.84 g/mol) in 10 cm^3 of 10% sodium hydroxide solution.

N.B. Arsenite is highly insoluble in water, so it has to dissolved in NaOH first.

1.3 Add 2 M H_2SO_4 dropwise until the solution is slightly acidic (pH = 6.8). Make up to 100 ml using distilled water.

1.4 Dilute as required.

VOL. STOCK SOLN. (ml)	DILUTE TO (ml)	ppm
5	100	50
5	50	100
7.5	50	150
10	50	200
12.5	50	250
15	50	300
17.5	50	350

Table A-2.1: Standard solutions of arsenite

2. Preparation of As(V) standard solution (1000ppm)

2.1 Dissolve 0.4160g of arsenic acid disodium salt heptahydrate ($Na_2HasO_4 \bullet 7H_2O$, molar mass 312.0 g/mol) in distilled water. Dilute to 100ml.

2.2 Dilute as required.

VOL. STOCK SOLN.(ml)	DILUTE TO(ml)	(ppm)
5	100	50
7	100	70
9	100	90
5	50	100
7.5	50	150
10	50	200
12.5	50	250
15	50	300
17.5	50	350

Table A-2.2: Standard solutions of arsenate

APPENDIX A-3

METHOD FOR IRON SPECIATION

All glassware must be washed with conc HCl and rinsed with distilled water prior to use.

Instrument: Spectrophotometer to read absorbance at 510 nm, providing a path length of 1 cm.

1. Reagents

Glass bottles are recommended for storage. The hydrochloric acid, ammonium acetate solution and stock iron solutions are stable indefinitely if tightly stoppered. The hydroxylamine and phenanthroline solutions are stable for several months. The working iron solutions are not stable and must be prepared freshly as needed by diluting the stock solution. Distilled water must be used throughout.

1.1 Hydrochloric acid, concentrated

1.2 Hydroxylamine reagent

Dissolve 10g $NH_2OH.HCl$ in 100ml distilled water

1.3 Ammonium acetate buffer solution

Dissolve 250g $NH_4C_2H_3O_2$ in 150 ml water. Add 700ml glacial acetic acid and dilute to 1 litre.

N.B. New reference standards should be prepared with each buffer preparation.

1.4 Phenanthroline solution (2.5%)

Dissolve 2.5g 1,10-phenanthroline monohydrate $C_{12}H_8N_2.H_2O$ in 100ml water by stirring and heating to 80°C; do not boil. Discard the solution if it darkens. Heating is not necessary if 2 drops conc HCl are added to the water.

N.B. 1ml of this reagent is sufficient for no more than 2mg Fe

1.5 0.1N Potassium permanganate solution

Weigh out 3.2-3.25g of A.R. potassium permanganate on a watch glass, transfer it to a 1500ml beaker, add 1 litre water, cover the beaker with a clock glass and boil gently for 15-30 mins. Allow the solution to cool to room temperature. Filter the solution through a sintered glass funnel and store the filtered solution in a clean glass-stoppered bottle kept in the dark or in a bottle of dark brown glass.

2. Determination of concentration of total iron

2.1 Transfer 0.5 ml of the sample to be analysed into a 50 ml volumetric flask.

2.2 Add 2 ml concentrated HCl and 2 ml hydroxylamine reagent. Allow to stand for 15 minutes.

2.3 Add 10 ml acetate buffer solution and 10 ml 2.5% phenanthroline solution and dilute to the mark with distilled water. Mix thoroughly.

2.4 Allow at least 10-15 min for maximum colour development.

2.5 Measure the absorbance of the solution at 510 nm

3. Determination of ferrous iron

3.1 Place 10 ml acetate buffer and 10 ml 2.5% phenanthroline solution in a 50 ml volumetric flask.

3.2 Add 0.5ml sample and dilute to the mark with distilled water.

3.3 Allow 10-15 min. for maximum colour development.

3.4 Measure the absorbance of the solution at 510 nm.

APPENDIX A-4

PREPARATION OF STANDARD SOLUTIONS OF IRON

These standard solutions were used to obtain calibration curves (see Appendix A-5)

1. Preparation of Fe(III) standard solution (1000ppm)

1.1 Slowly add 2ml conc H_2SO_4 to 10ml water and dissolve 0.7022g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in this solution.

1.2 Add 0.1N $KMnO_4$ dropwise until a faint pink colour persists (this indicates that all the Fe^{2+} has been oxidised to Fe^{3+}). Dilute with water to the 100ml mark and mix. This stock solution contains 1000ppm Fe^{3+} (1ml contains 1mg Fe^{3+}).

1.3 Dilute as required.

Volume stock solution (ml)	Dilute to (ml)	ppm Fe^{3+}
5	50	100
7.5	50	150
10	50	200
12.5	50	250
15	50	300
50	50	500
70	50	700

Table A-4.1: Standard solutions of Fe(III)

N.B. The standard solution should be slightly acidic, 6-6.8.

2. Preparation of Fe(II) standard solution (1000ppm)

2.1 Slowly add 2ml conc H_2SO_4 to 10ml water and dissolve 0.7022g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in this solution.

2.2 Dilute with water to the 100ml mark and mix. This stock solution contains 1000ppm Fe^{3+} (1ml contains 1mg Fe^{2+}).

2.3 Dilute as required.

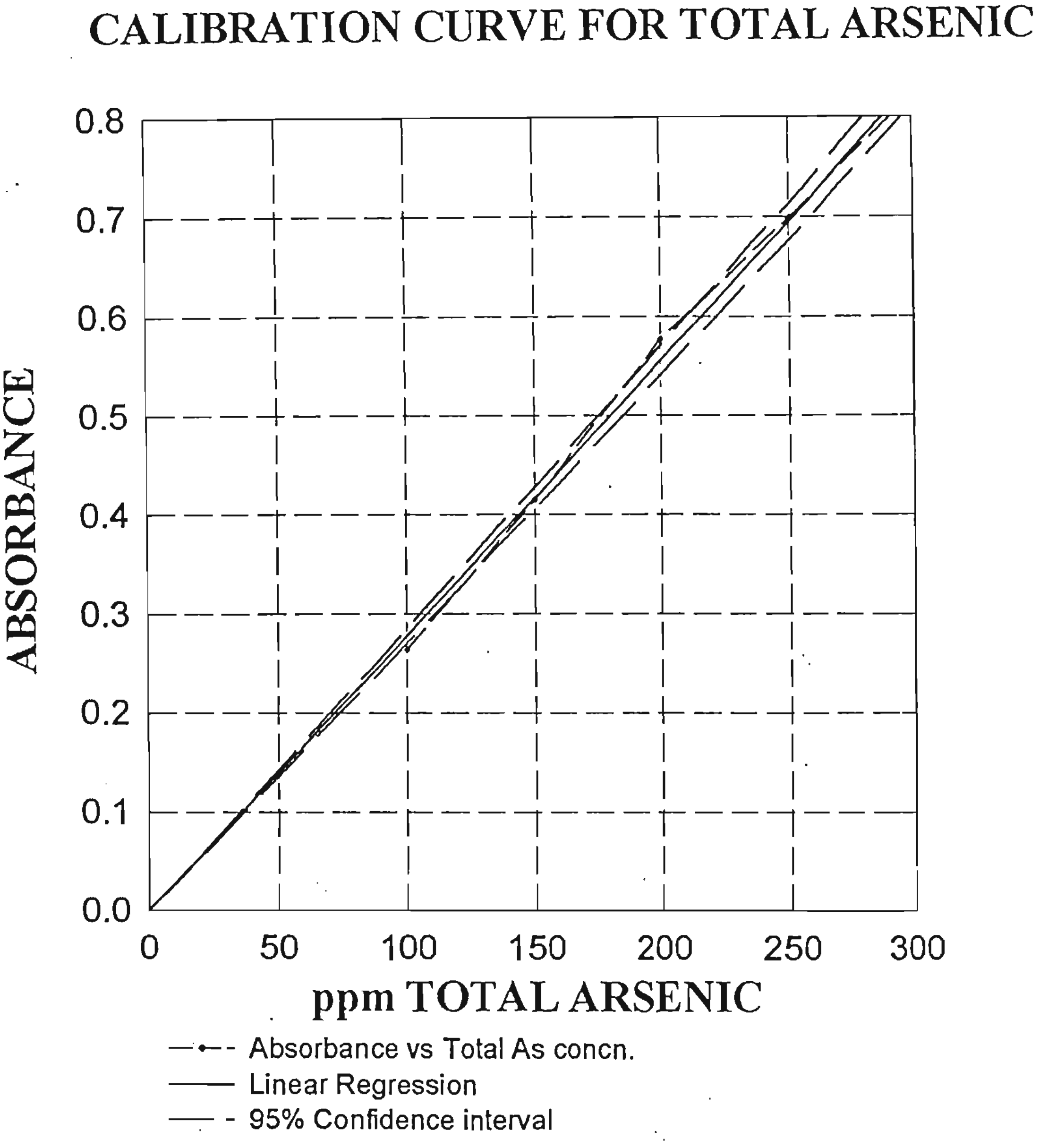
Volume stock solution (ml)	Dilute to (ml)	ppm Fe^{2+}
5	50	100
7.5	50	150
10	50	200
12.5	50	250
15	50	300
50	50	500
70	50	700

Table A-4.2: Standard solutions of Fe(II)

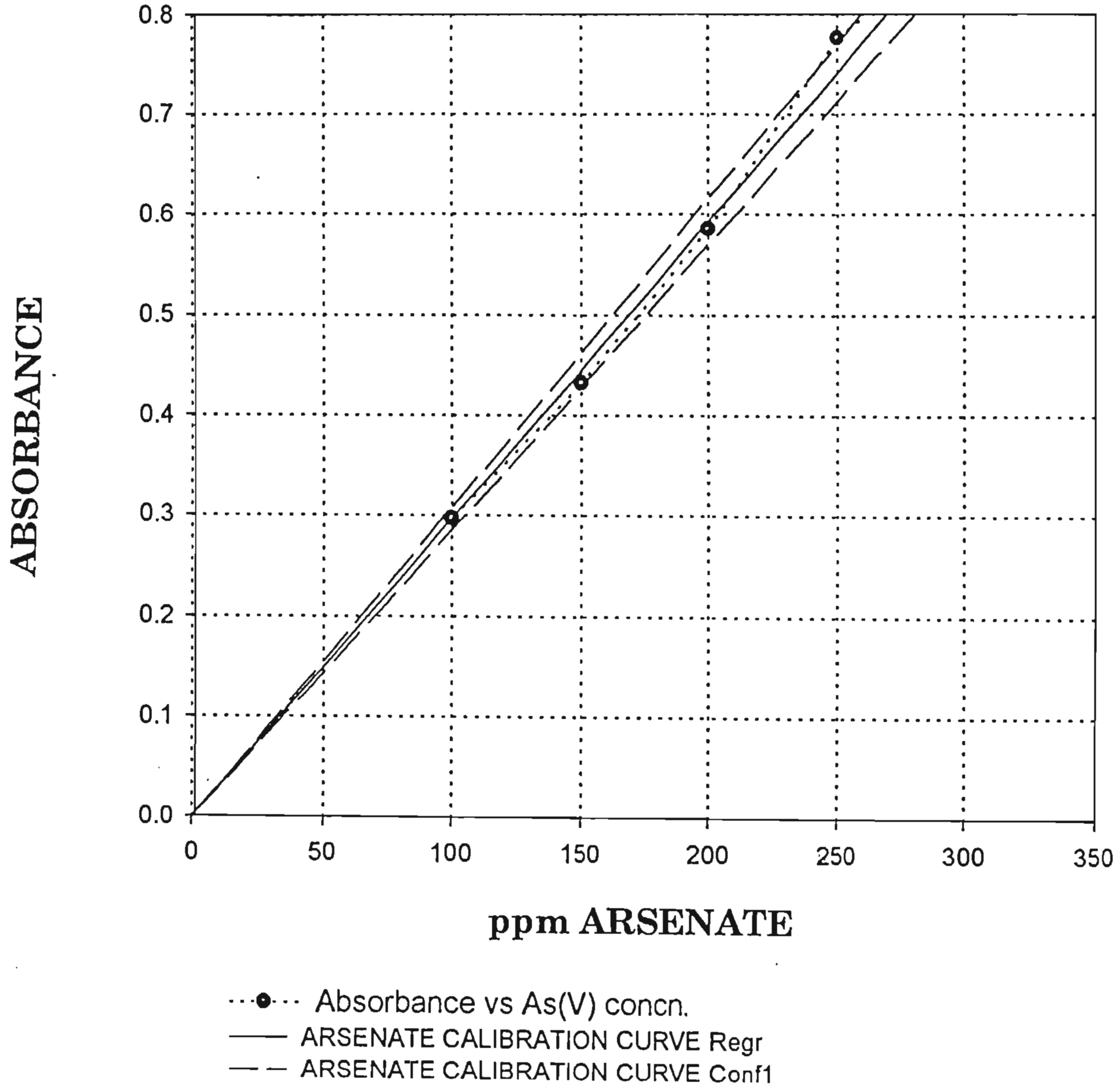
APPENDIX A-5

CALIBRATION CURVES

ARSENIC CALIBRATION CURVES

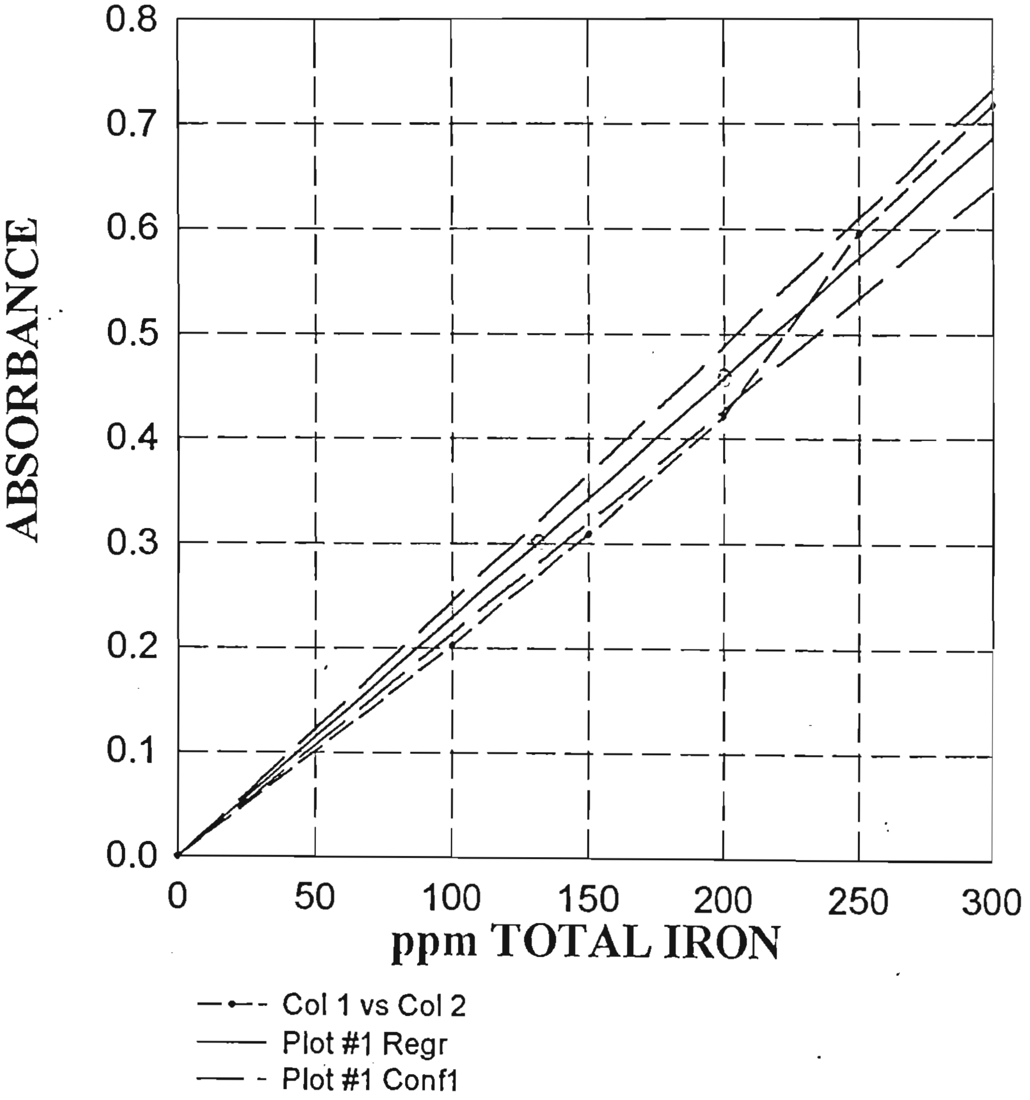


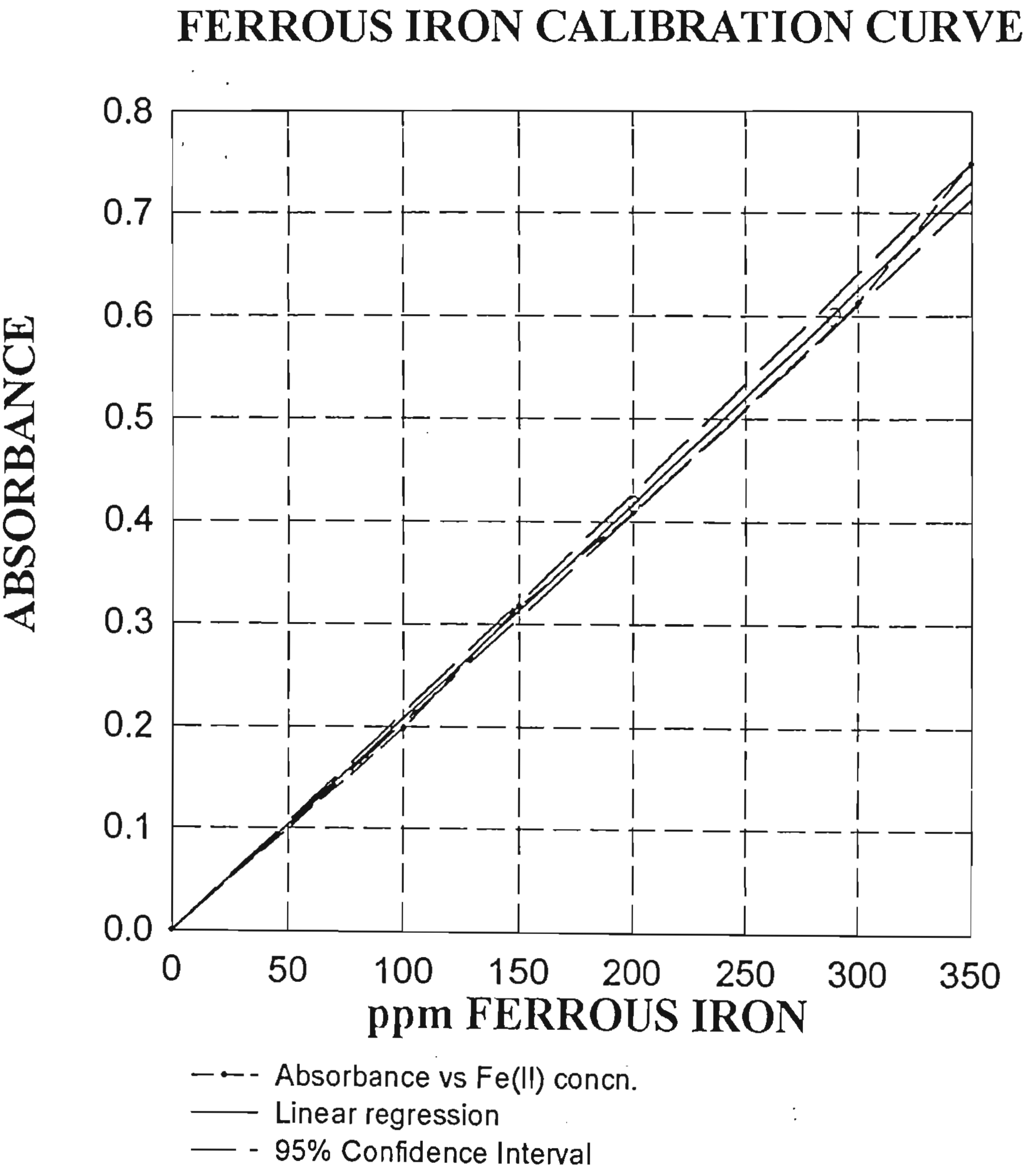
CALIBRATION CURVE FOR ARSENATE



IRON CALIBRATION CURVES

CALIBRATION CURVE FOR TOTAL IRON




FERROUS IRON CALIBRATION CURVE
ABSORBANCE
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
50
100
150
200
250
300
350
ppm FERROUS IRON
Absorbance vs Fe(II) concn.
Linear regression
95% Confidence Interval

APPENDIX B

COMPOSITION OF REACTION SOLUTIONS AND REACTION CONDITIONS

B-1 CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN GOLD MINE EFFLUENT

The composition of the mine effluent with respect to arsenic species and iron added are shown in the following table. The concentration of arsenite in the effluent was determined before experimentation and the amount of ferric ion that had to be added was then calculated using this.

	ChemOx1	ChemOx2	ChemOx3
Total As (ppm)	1476	1715	861
As(V) (ppm)	1107	1127	745
As(III) (ppm)	369	588	116
$FeCl_3.6H_2O$ added (g)	21.947	6.374	1.255
Fe(III):As(III) ratio	5:1	5:1	5:1
Liquid volume (ml)	600	600	600
Air flow rate (vvm)[1]	1	1	1
Setpoint: Temperature	45 °C	45 °C	45 °C
Setpoint: pH	1.3	1.3	1.3

TABLE B-1.1: Details for Chemical Oxidation experiments

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[1] vvm = (volume air)/(volume liquid).(minute)

B-2 CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN A SYNTHETIC SOLUTION

The solution used in this series of experiment was made up such that it consisted primarily of arsenic and iron species

The solution used in all of these experiments were made up using the following chemicals:

- Arsenite in the form of As_2O_3
- Arsenate in the form of $Na_2HAsO_4.7H_2O$
- Ferrous ion in the form of $FeSO_4.7H_2O$
- Ferric ion in the form of $Fe_2(SO_4)_3.6H_2O$

The ratio of ferric to ferrous ion in solution was varied. The compositions of these solutions are shown in the following table.

	ChemSyn1	ChemSyn2	ChemSyn3	ChemSyn4
As_2O_3	0.66	0.66	0.66	0.66
$Na_2HasO_4.7H_2O$	4.150	4.150	4.150	4.150
$FeSO_4.7H_2O$	2.321	1.857	1.857	3.095
$Fe_2(SO_4)_3.6H_2O$	8.483	8.483	8.483	8.483
Fe(III):As(III) ratio	5:1	5:1	5:1	5:1
Fe(III):Fe(II) ratio	4:1	5:1	5:1	3:1
Liquid volume (ml)	1000	1000	1000	1000
Air flow rate (vvm)	1	1	1	1
Setpoint: Temperature	45 °C	45 °C	45 °C	45 °C
Setpoint: pH	1.3	1.3	1.3	1.3

TABLE B-2.1: Details for synthetic Chemical Oxidation experiments

B-3 CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN THE PRESENCE OF A SURFACE IN GOLD MINE EFFLUENT

The composition of the mine effluent with respect to arsenic species and iron added are shown in the following table. The concentration of arsenite in the effluent was determined before experimentation and the amount of ferric ion that had to be added was then calculated using this.

	ChemSurf1	ChemSurf2	ChemSurf3
Total As (ppm)	1338	1011	882
As(V) (ppm)	1272	997	817
As(III) (ppm)	66	14	65
$FeCl_3.6H_2O$ added (g)	0.714	0.152	0.725
Fe(III):As(III) ratio	5:1	5:1	5:1
Liquid volume (ml)	1000	1000	1000
Air flow rate (vvm)	1	1	1
Setpoint: Temperature	45 ^{0}C	45 ^{0}C	45 ^{0}C
Setpoint: pH	1.3	1.3	1.3
Mass of stainless steel (before) (g)	9.9851	8.8138	8.8192
Mass of stainless steel (before) (g)	9.9852	8.8192	8.848
Difference (mg)	1.0 increase	5.4 increase	2.9 increase

TABLE B-3.1: Details for Chemical Oxidation experiments in the presence of a surface

B-4 BACTERIAL OXIDATION OF ARSENITE BY FERRIC ION IN A SYNTHETIC SOLUTION

The solution used in this series of experiment was made up such that it consisted primarily of arsenic and iron species

The solution used in all of these experiments were made up using the following chemicals:

- Arsenite in the form of As_2O_3
- Arsenate in the form of $Na_2HAsO_4.7H_2O$
- Ferrous ion in the form of $FeSO_4.7H_2O$
- Ferric ion in the form of $Fe_2(SO_4)_3.6H_2O$

The compositions of these solutions are shown in Table B-4.1. Air was supplied at a rate of 1 vvm and the carbon dioxide was supplemented by supplying pure CO_2 to the reaction mixture. The total volume of liquid in the reactor was made up such that it consisted of 80 % reaction mixture and 20 % inoculum (bacteria and fresh medium).

	BacOx1	**BacOx2**
As_2O_3 (g)	0.66	0.66
$Na_2HasO_4.7H_2O$ (g)	4.150	4.150
$FeSO_4.7H_2O$ (g)	3.095	3.095
$Fe(SO_4)_3.6H_2O$ (g)	8.483	8.483
Fe(III):As(III) ratio	5:1	5:1
Fe(III):Fe(II) ratio	3:1	3:1
Reaction mixture volume (ml)	1000	1000
Inoculum volume (ml)	250	250
Air flow rate	1vvm	1vvm
CO_2 flow rate		
Setpoint: Temperature	37 ^{0}C	37 ^{0}C
Setpoint: pH	1.8	1.8

TABLE B-4.1: Details for Bacterial Oxidation experiments

APPENDIX C

EXPERIMENTAL RESULTS

APPENDIX C-1

EXPERIMENTAL RESULTS

CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN GOLD MINE EFFLEUNT

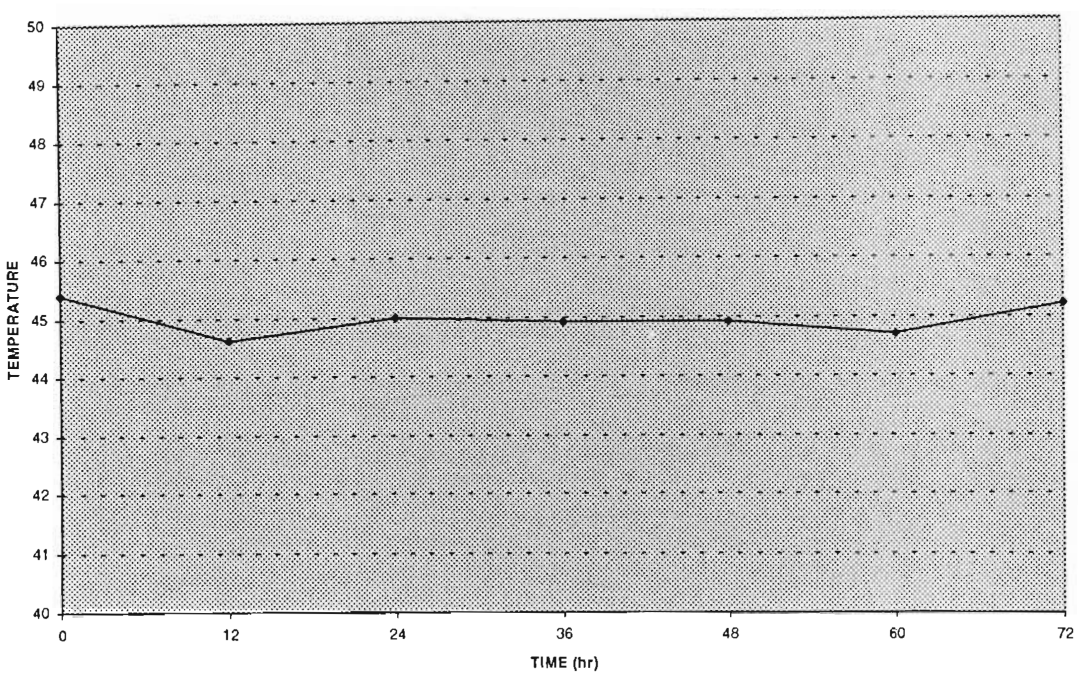
RESULTS: Chemox 1

TIME (hr)	TEMP (^0C)	pH	Redox Potential (mV)	As(V) (ppm)	As(III) (ppm)	% As(III) Conv.	Fe(II) (ppm)	Fe(III) (ppm)
0	45.40	1.29	358.40	1030	441	0	429	2242
12	44.60	1.26	359.10	1078	393	10.95	391	2280
24	45.0	1.27	359.30	1165	306	30.58	440	2232
36	44.90	1.27	358.80	1168	303	31.34	470	2202
48	44.90	1.27	359.40	1253	218	50.59	457	2215
60	44.70	1.24	360.60	1315	156	64.56	550	2122
72	45.20	1.23	362.10	1380	91	79.29	483	2189

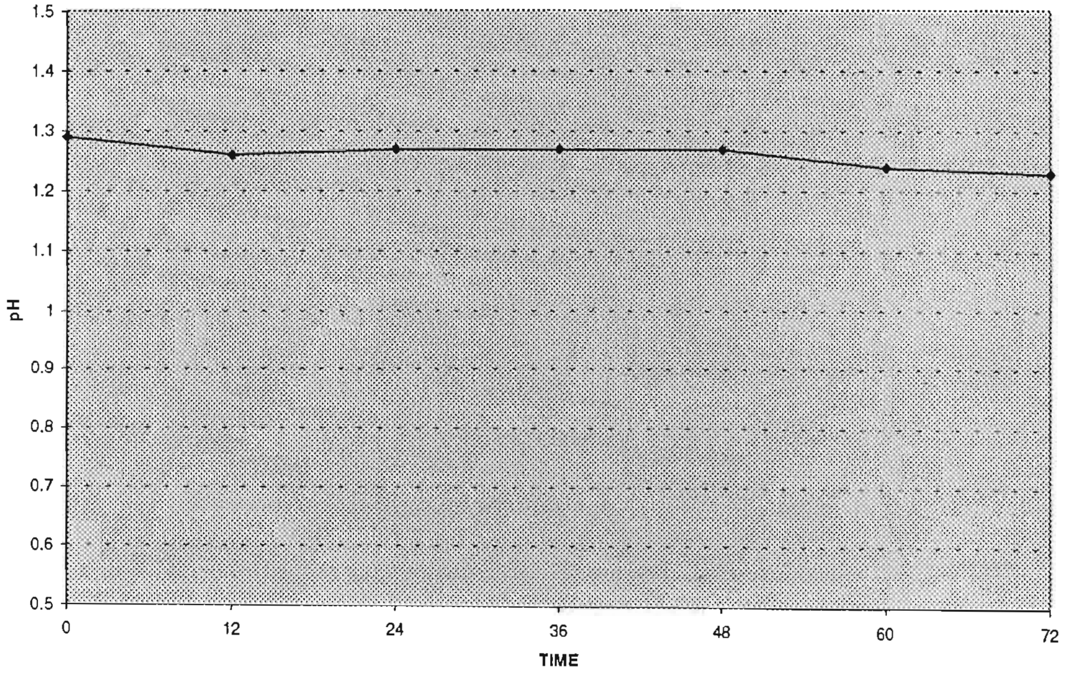
TABLE C–1.1: Results ChemOx 1

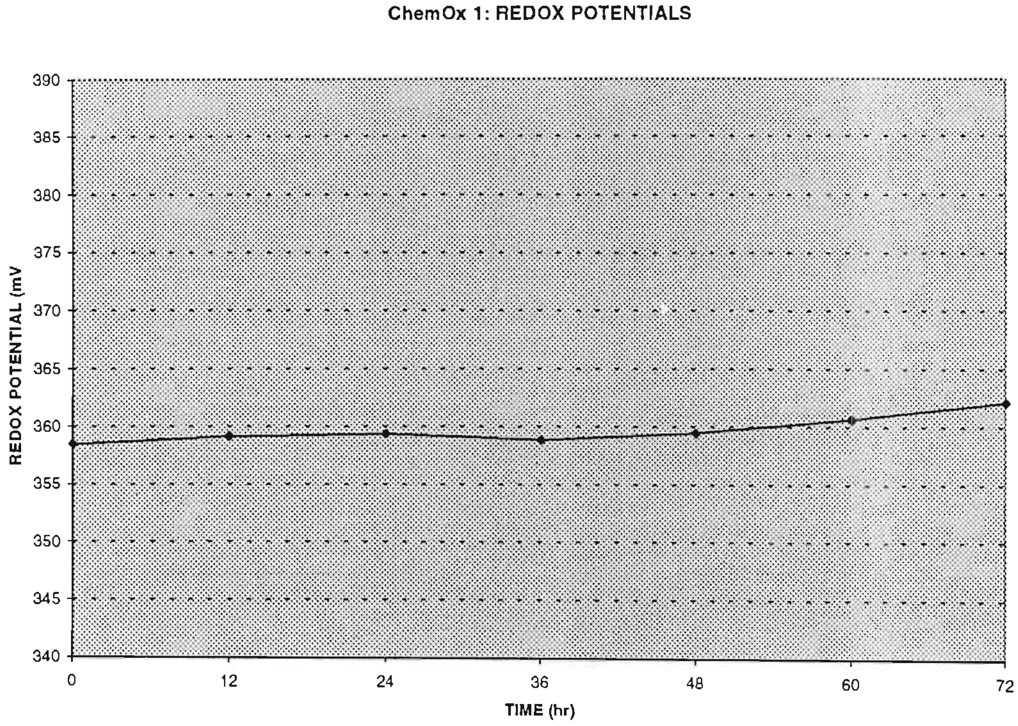
GRAPHS: ChemOx 1

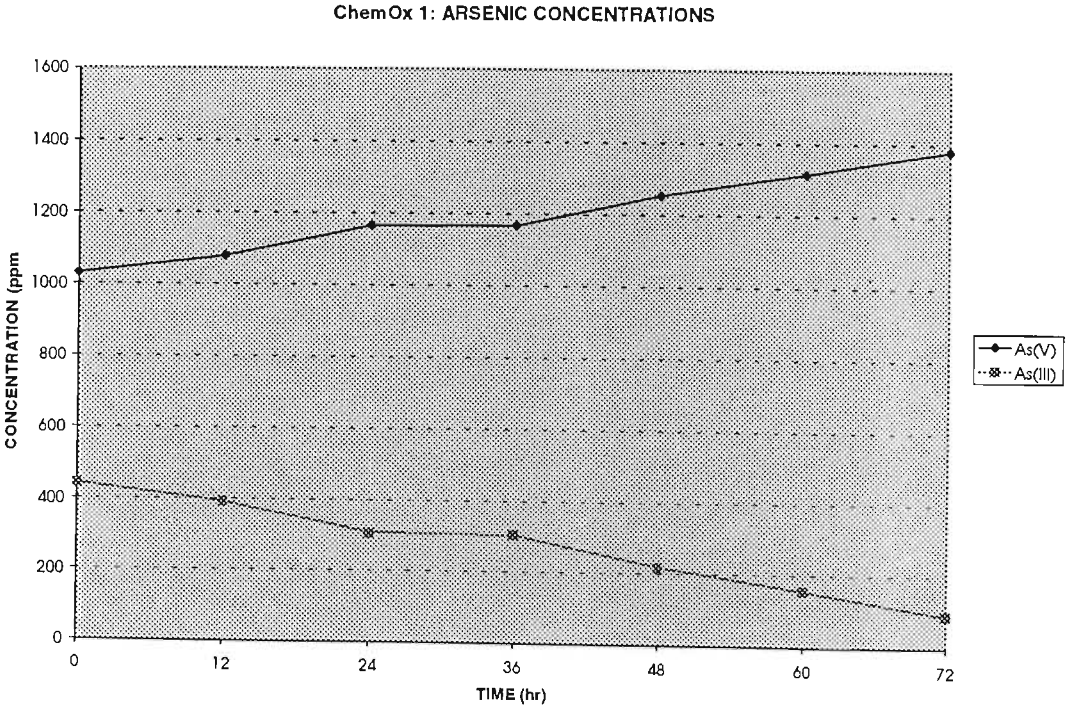
ChemOx 1: TEMPERATURE



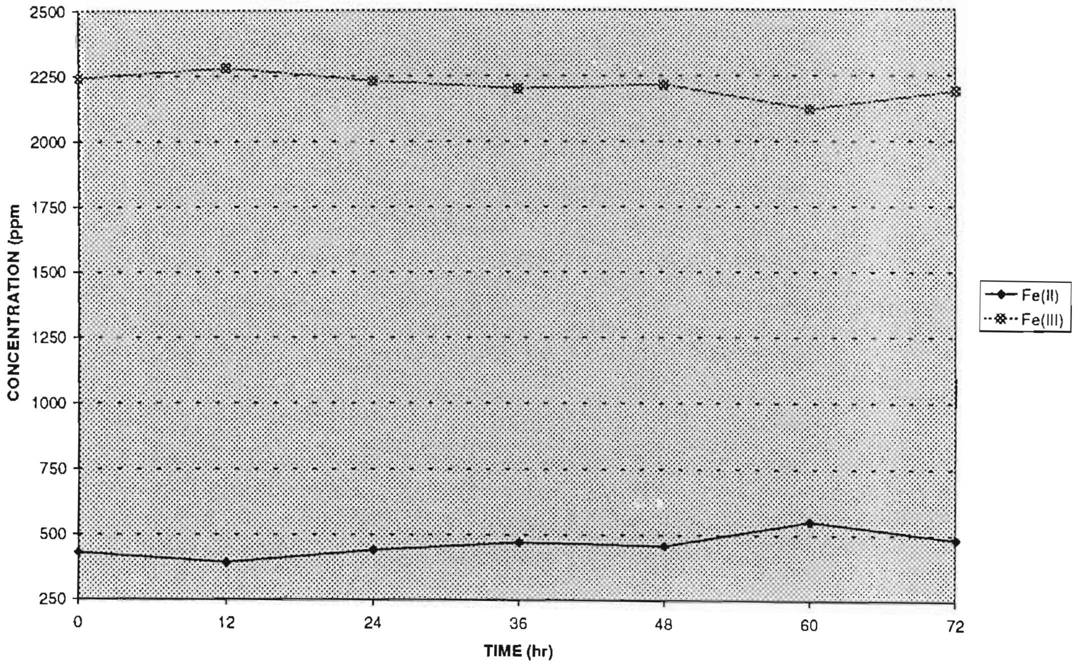
ChemOx 1: pH



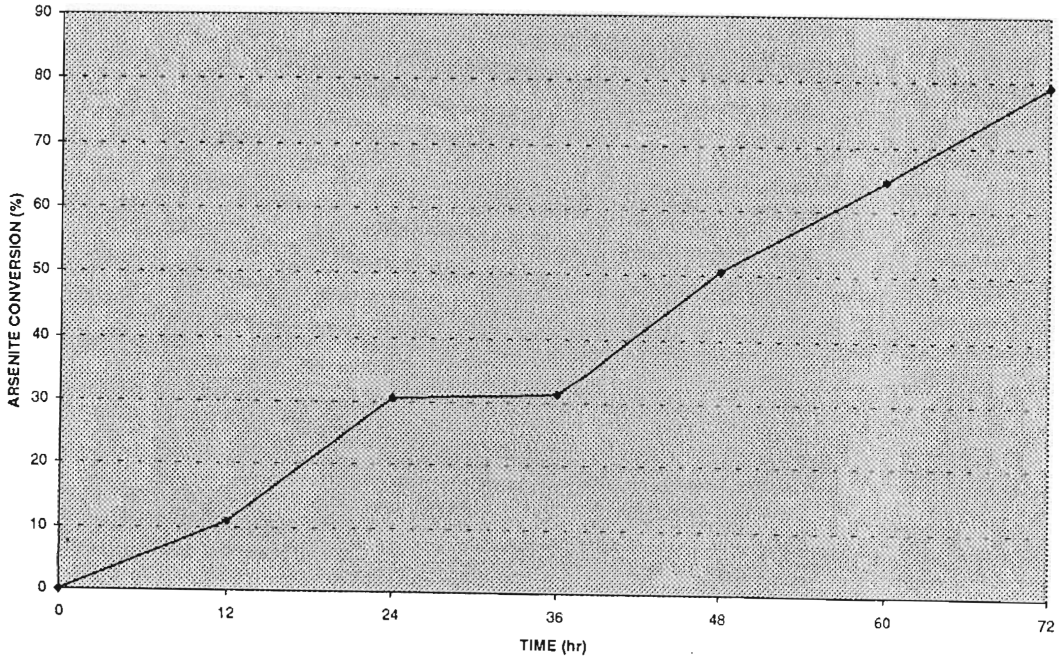

ChemOx 1: REDOX POTENTIALS
REDOX POTENTIAL (mV
390
385
380
375
370
365
360
355
350
345
340
0
12
24
36
48
60
72
TIME (hr)


ChemOx 1: ARSENIC CONCENTRATIONS
CONCENTRATION (ppm
1600
1400
1200
1000
800
600
400
200
0
0
12
24
36
48
60
72
TIME (hr)
As(V)
As(III)

ChemOx 1: IRON CONCENTRATIONS



ChemOx 1 : ARSENITE CONVERSION



RESULTS:ChemOx 2

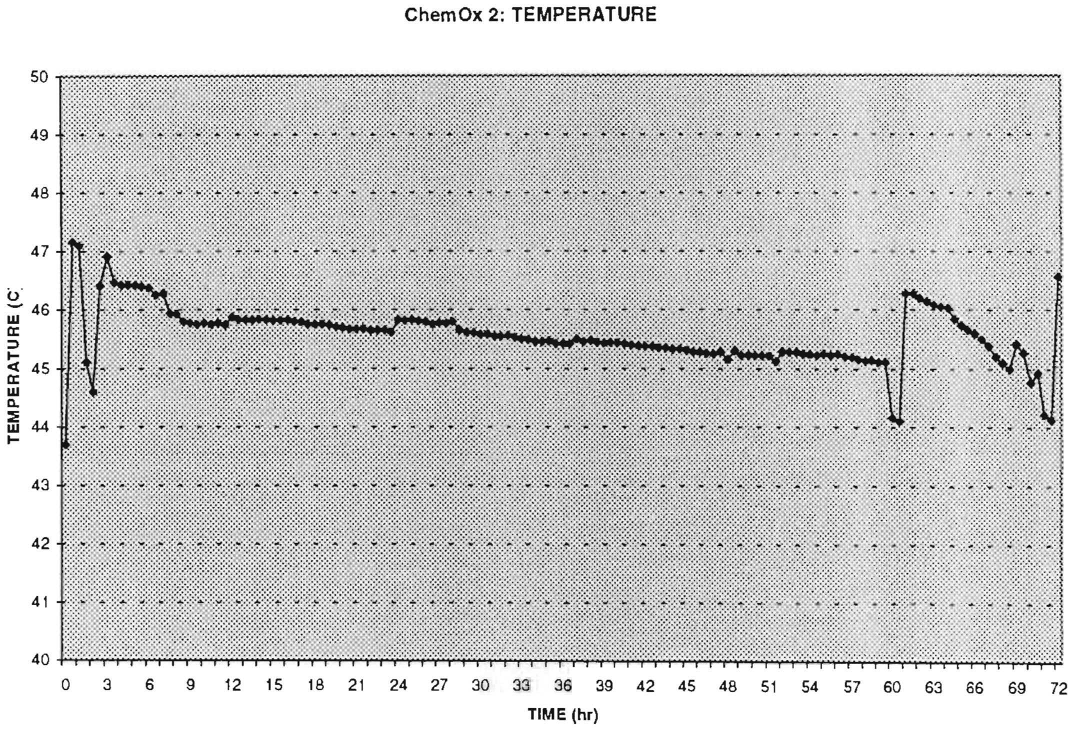
Time (hr)	Temperature (^{0} C)	pH	Redox Potential (mV)
0.0	43.68	1.27	572.76
0.5	47.15	1.21	591.22
1.0	47.09	1.22	585.07
1.5	45.11	1.29	571.53
2.0	44.6	1.3	575.84
2.5	46.41	1.23	572.15
3.0	46.91	1.23	568.15
3.5	46.47	1.25	570.3
4.0	46.42	1.25	574.3
4.5	46.42	1.25	570.3
5.0	46.42	1.25	568.46
5.5	46.39	1.26	569.69
6.0	46.38	1.26	572.46
6.5	46.25	1.26	569.69
7.0	46.28	1.25	569.38
7.5	45.94	1.26	571.23
8.0	45.92	1.26	570.3
8.5	45.79	1.28	569.07
9.0	45.77	1.27	568.76
9.5	45.74	1.26	569.69
10.0	45.77	1.26	575.84
10.5	45.74	1.25	569.69
11.0	45.76	1.26	571.84
11.5	45.73	1.25	569.38
12.0	45.87	1.23	569.07
12.5	45.82	1.24	572.46
13.0	45.82	1.24	576.15
13.5	45.82	1.24	569.07
14.0	45.83	1.24	577.69
14.5	45.82	1.25	567.23
15.0	45.81	1.25	568.15
15.5	45.81	1.24	576.76
16.0	45.82	1.24	570.61
16.5	45.79	1.24	576.76
17.0	45.79	1.24	570.92
17.5	45.74	1.24	570.3
18.0	45.74	1.24	571.23
18.5	45.74	1.24	573.07
19.0	45.73	1.24	570.3
19.5	45.7	1.24	570.61
20.0	45.69	1.24	569.07
20.5	45.67	1.24	567.23
21.0	45.66	1.24	572.76
21.5	45.66	1.23	572.15
22.0	45.64	1.24	570.61
22.5	45.64	1.23	569.69
23.0	45.64	1.23	570.61
23.5	45.61	1.23	568.76
24.0	45.82	1.19	569.38
24.5	45.81	1.19	571.84

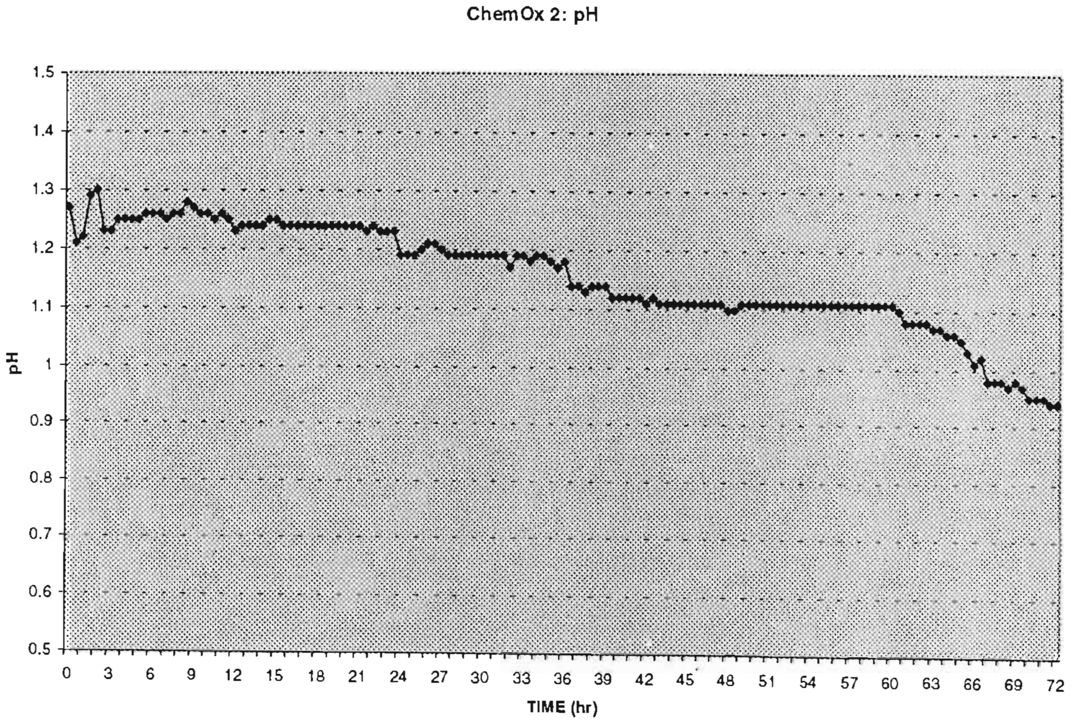
25.0	45.82	1.19	570.3
25.5	45.8	1.2	569.38
26.0	45.78	1.21	574.3
26.5	45.74	1.21	569.38
27.0	45.76	1.2	570.61
27.5	45.75	1.19	570
28.0	45.79	1.19	571
28.5	45.64	1.19	572.76
29.0	45.61	1.19	570.3
29.5	45.6	1.19	569.07
30.0	45.57	1.19	570
30.5	45.57	1.19	570.3
31.0	45.54	1.19	575.53
31.5	45.54	1.19	568.76
32.0	45.55	1.17	573.07
32.5	45.51	1.19	569.07
33.0	45.49	1.19	572.76
33.5	45.48	1.18	571.22
34.0	45.45	1.19	571.84
34.5	45.45	1.19	570
35.0	45.46	1.18	572.76
35.5	45.42	1.17	575.53
36.0	45.42	1.18	571.23
36.5	45.42	1.14	574.3
37.0	45.49	1.14	570.92
37.5	45.45	1.13	568.76
38.0	45.47	1.14	571.84
38.5	45.44	1.14	569.07
39.0	45.43	1.14	568.46
39.5	45.44	1.12	571.84
40.0	45.43	1.12	575.53
40.5	45.42	1.12	570
41.0	45.39	1.12	570.61
41.5	45.38	1.12	570.92
42.0	45.37	1.11	571.23
42.5	45.37	1.12	573.69
43.0	45.35	1.11	573.38
43.5	45.34	1.11	571.23
44.0	45.33	1.11	572.15
44.5	45.32	1.11	571.53
45.0	45.3	1.11	570.92
45.5	45.28	1.11	569.38
46.0	45.28	1.11	572.15
46.5	45.26	1.11	569.07
47.0	45.25	1.11	588.76
47.5	45.28	1.11	574.61
48.0	45.15	1.1	570.3
48.5	45.3	1.1	576.76
49.0	45.23	1.11	568.15
49.5	45.22	1.11	571.23
50.0	45.23	1.11	567.84
50.5	45.22	1.11	570.3
51.0	45.21	1.11	570
51.5	45.12	1.11	569.38

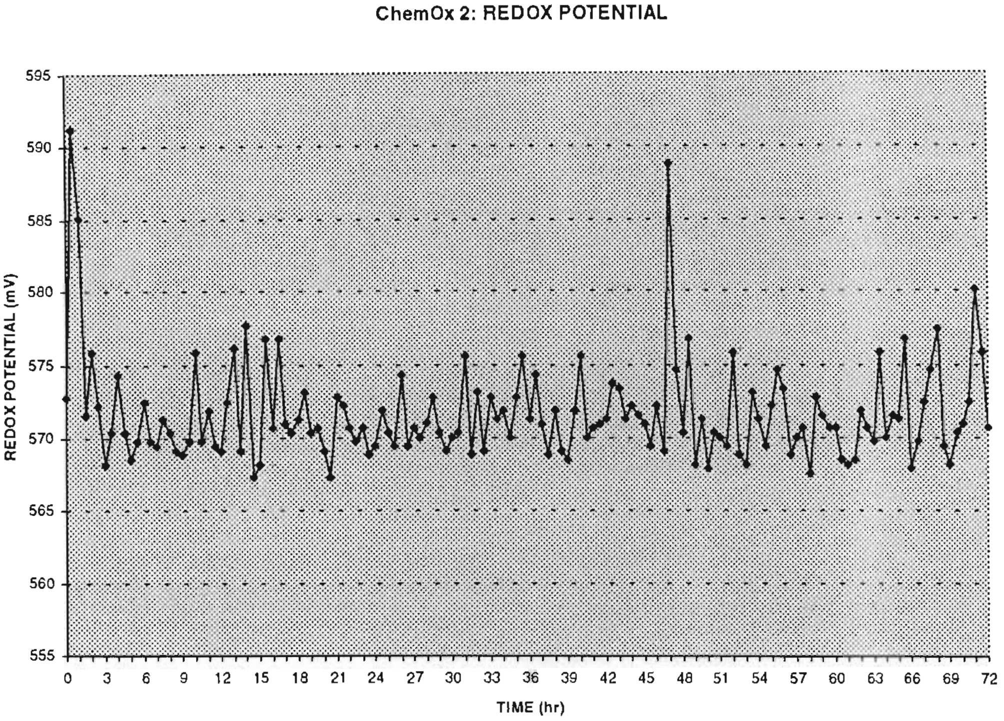
52.0	45.29	1.11	575.84
52.5	45.28	1.11	568.76
53.0	45.28	1.11	568.15
53.5	45.25	1.11	573.07
54.0	45.24	1.11	571.23
54.5	45.23	1.11	569.38
55.0	45.24	1.11	572.15
55.5	45.22	1.11	574.61
56.0	45.24	1.11	573.38
56.5	45.2	1.11	568.76
57.0	45.19	1.11	570
57.5	45.15	1.11	570.61
58.0	45.13	1.11	567.53
58.5	45.14	1.11	572.76
59.0	45.11	1.11	571.53
59.5	45.11	1.11	570.61
60.0	44.16	1.11	570.61
60.5	44.11	1.1	568.46
61.0	46.27	1.08	568.15
61.5	46.28	1.08	568.46
62.0	46.19	1.08	571.81
62.5	46.14	1.08	570.61
63.0	46.08	1.07	569.69
63.5	46.05	1.07	575.84
64.0	46.02	1.06	570
64.5	45.83	1.06	571.53
65.0	45.73	1.05	571.23
65.5	45.65	1.03	576.76
66.0	45.6	1.01	567.84
66.5	45.49	1.02	569.69
67.0	45.38	0.98	572.46
67.5	45.2	0.98	574.61
68.0	45.1	0.98	577.38
68.5	45	0.97	569.38
69.0	45.41	0.98	568.15
69.5	45.27	0.97	570.3
70.0	44.77	0.95	570.92
70.5	44.93	0.95	572.46
71.0	44.22	0.95	580.15
71.5	44.12	0.94	575.84
72.0	46.56	0.94	570.61

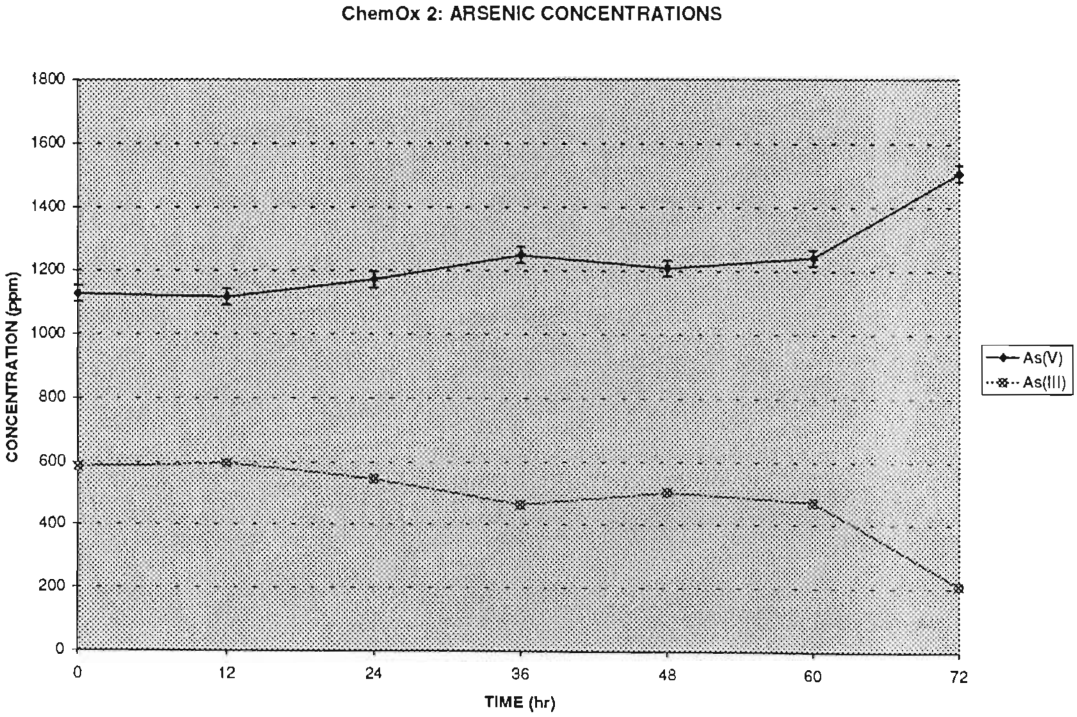
Table C-1.2: Results ChemOx2

GRAPHS: ChemOx2

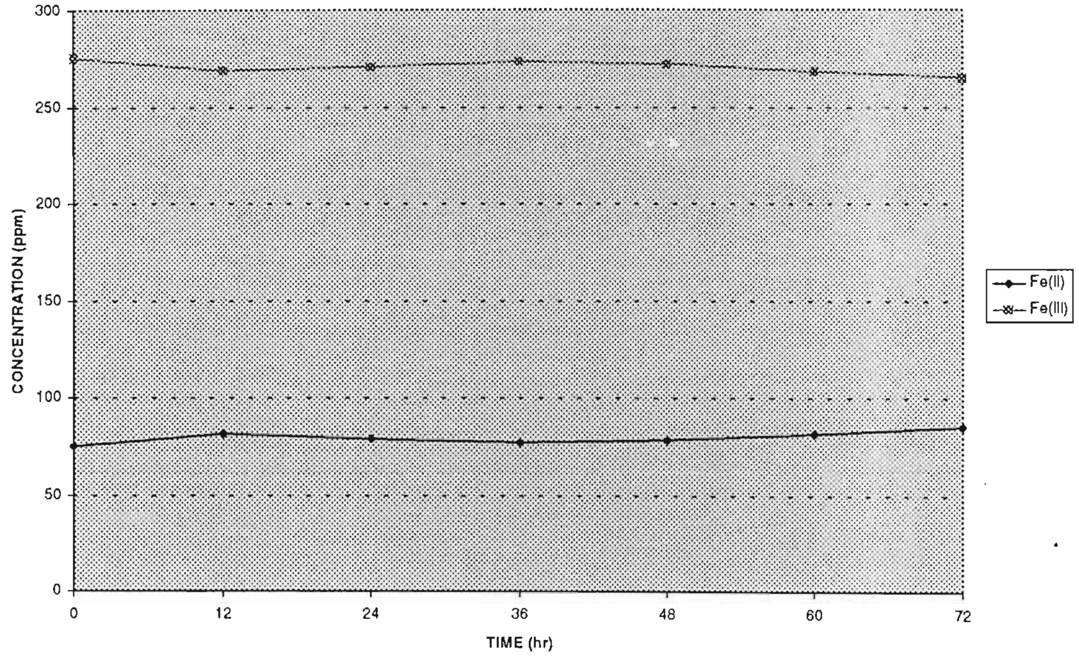




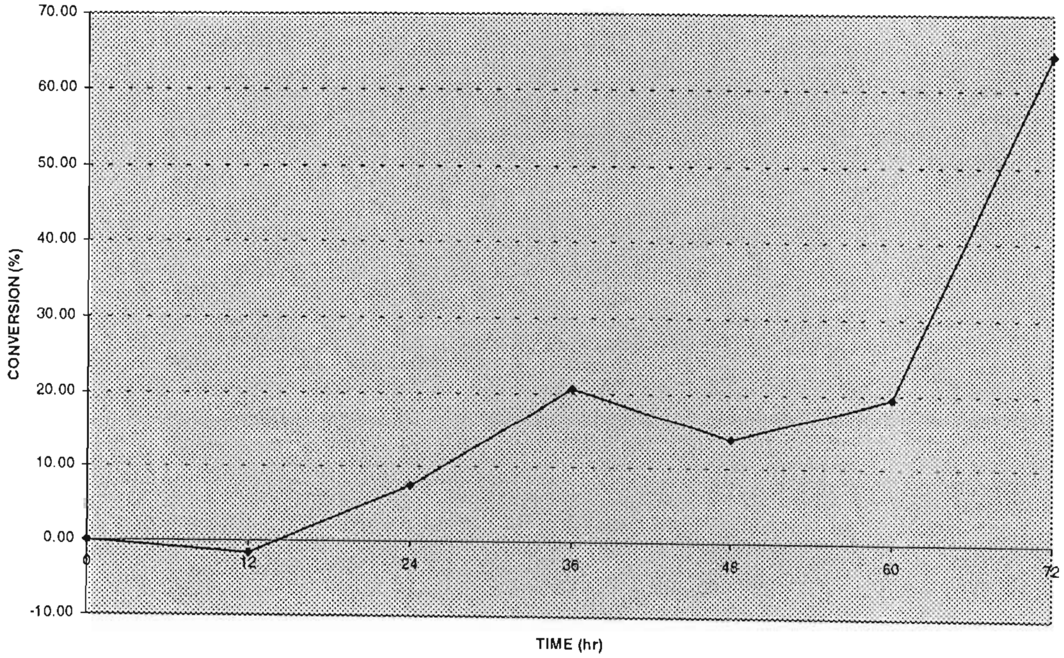

ChemOx 2: REDOX POTENTIAL
REDOX POTENTIAL (mV)
595
590
585
580
575
570
565
560
555
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
48
51
54
57
60
63
66
69
72
TIME (hr)


ChemOx 2: ARSENIC CONCENTRATIONS
CONCENTRATION (ppm)
1800
1600
1400
1200
1000
800
600
400
200
0
0
12
24
36
48
60
72
TIME (hr)
As(V)
As(III)

ChemOx 2 : IRON CONCENTRATIONS



ChemOx 2 : As(III) CONVERSION (%)



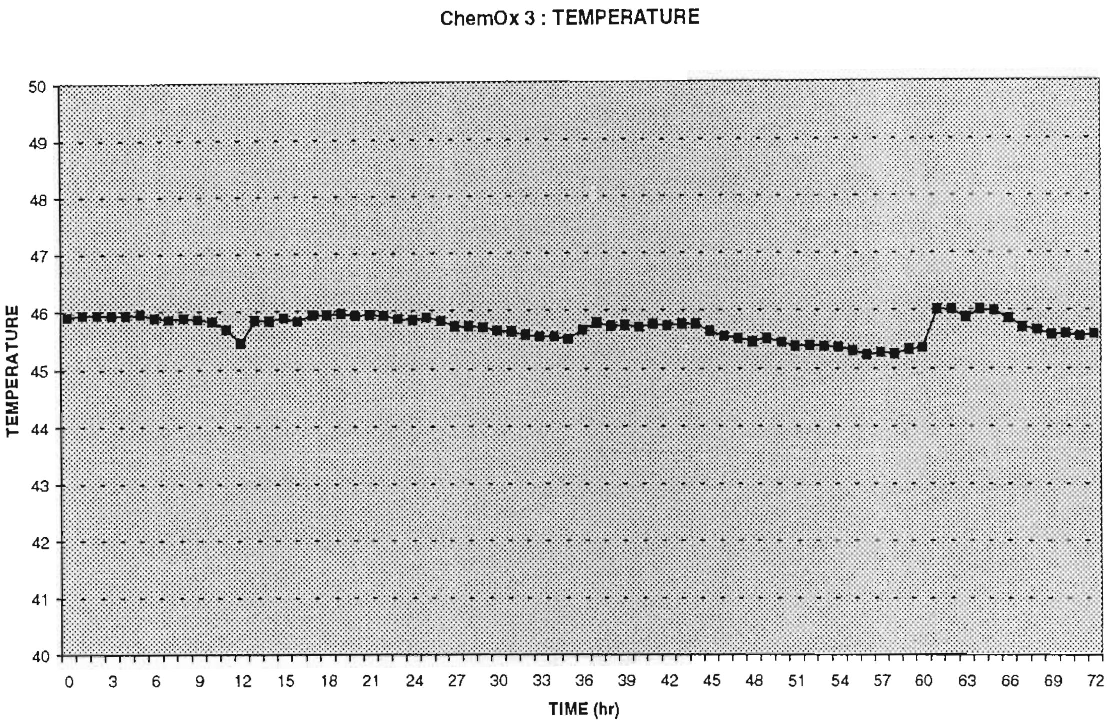
RESULTS: ChemOx 3

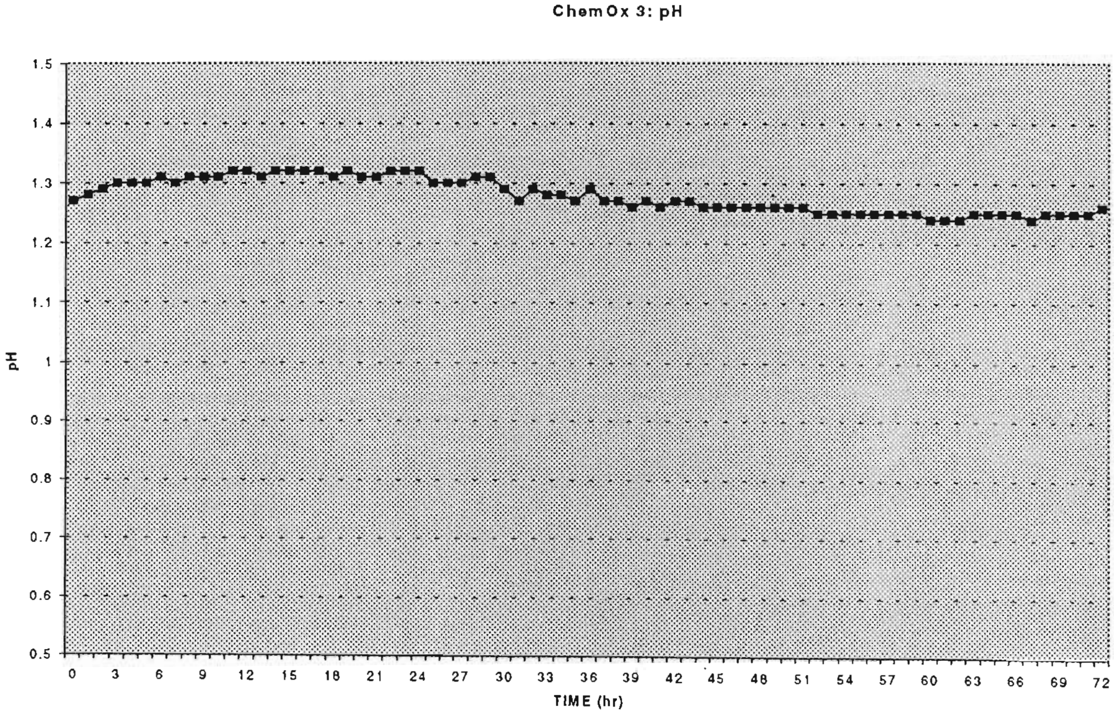
TIME (hr)	Temperature (^{0}C)	pH	Redox Potential (mV)
0	45.9	1.27	554.92
1	45.94	1.28	554.92
2	45.94	1.29	555.55
3	45.93	1.30	555.54
4	45.93	1.30	554.3
5	45.95	1.30	554.61
6	45.89	1.31	554.92
7	45.86	1.30	553.38
8	45.88	1.31	558.61
9	45.86	1.31	554.61
10	45.82	1.31	553.38
11	45.69	1.32	554.61
12	45.45	1.32	561.69
13	45.84	1.31	553.69
14	45.83	1.32	554.61
15	45.88	1.32	555.23
16	45.82	1.32	557.07
17	45.93	1.32	563.53
18	45.93	1.31	558.61
19	45.95	1.32	555.23
20	45.92	1.31	556.77
21	45.93	1.31	554.0
22	45.92	1.32	557.07
23	45.86	1.32	555.54
24	45.84	1.32	554.61
25	45.88	1.30	551.84
26	45.82	1.30	554.92
27	45.72	1.30	553.38
28	45.72	1.31	554.61
29	45.71	1.31	553.38
30	45.65	1.29	552.46
31	45.63	1.27	553.38
32	45.57	1.29	552.46
33	45.54	1.28	550.61
34	45.54	1.28	551.84
35	45.5	1.27	556.77
36	45.66	1.29	558.61
37	45.78	1.27	556.15
38	45.72	1.27	553.38
39	45.74	1.26	555.54
40	45.71	1.27	555.23
41	45.76	1.26	554.30
42	45.73	1.27	554.61
43	45.76	1.27	553.38
44	45.76	1.26	557.69
45	45.63	1.26	557.38
46	45.54	1.26	555.84
47	45.51	1.26	554.92

48	45.45	1.26	553.38
49	45.51	1.26	557.69
50	45.44	1.26	557.38
51	45.38	1.26	554.0
52	45.39	1.25	555.84
53	45.37	1.25	555.23
54	45.36	1.25	554.92
55	45.3	1.25	554.92
56	45.23	1.25	556.46
57	45.27	1.25	557.38
58	45.24	1.25	555.23
59	45.32	1.25	556.46
60	45.35	1.24	554.30
61	46.01	1.24	555.23
62	46.01	1.24	556.15
63	45.87	1.25	554.0
64	46.01	1.25	554.92
65	45.99	1.25	558.61
66	45.85	1.25	552.77
67	45.7	1.24	553.69
68	45.66	1.25	554.92
69	45.57	1.25	555.84
70	45.59	1.25	553.07
71	45.54	1.25	553.69
72	45.58	1.26	558.92

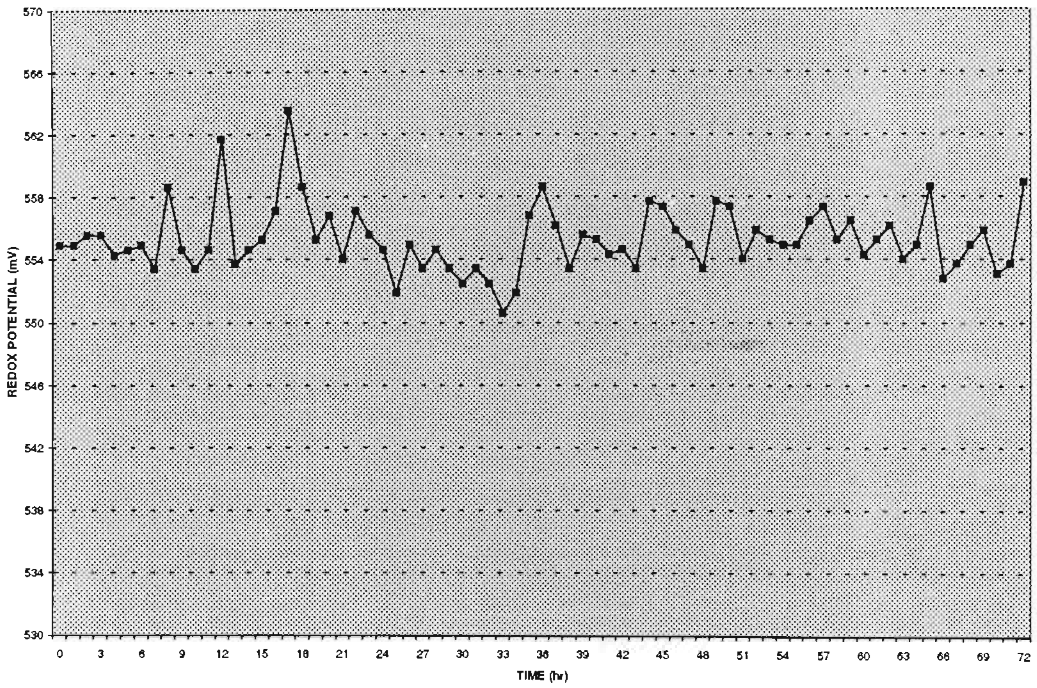
TABLE C–1.3: Results ChemOx 3

GRAPHS: ChemOx 3

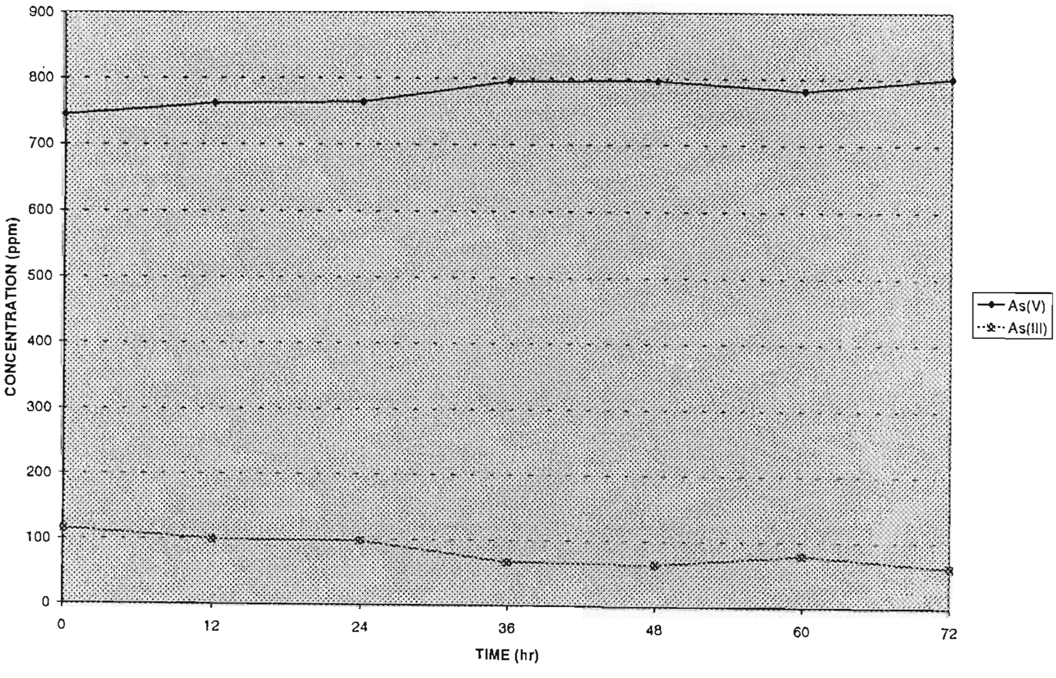


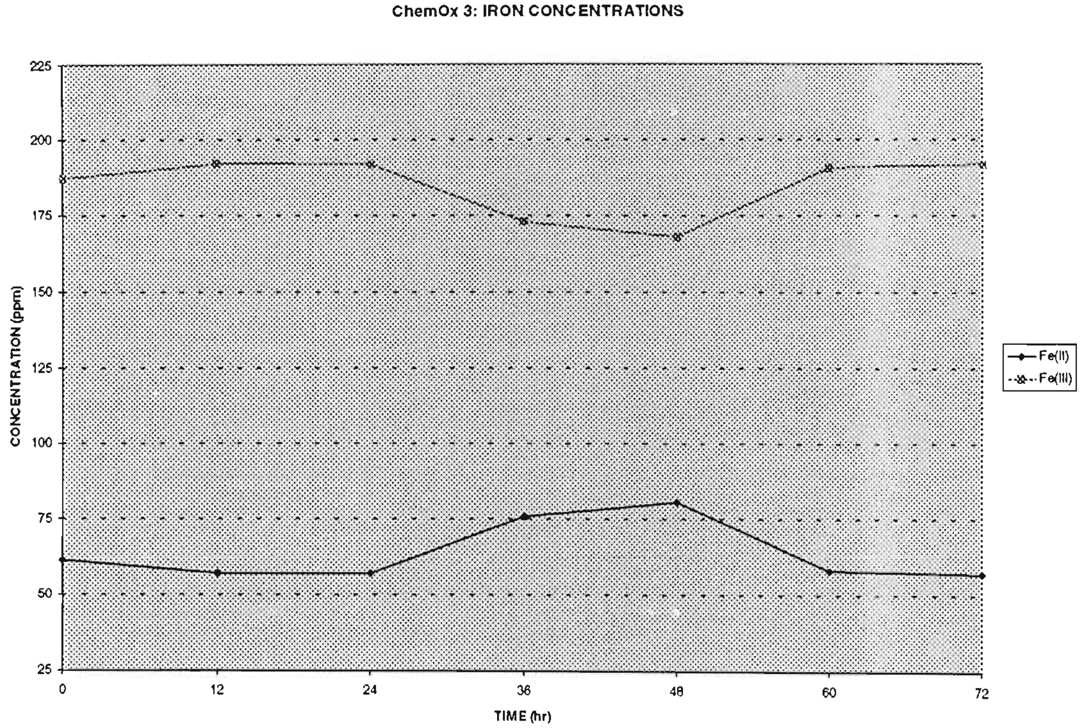


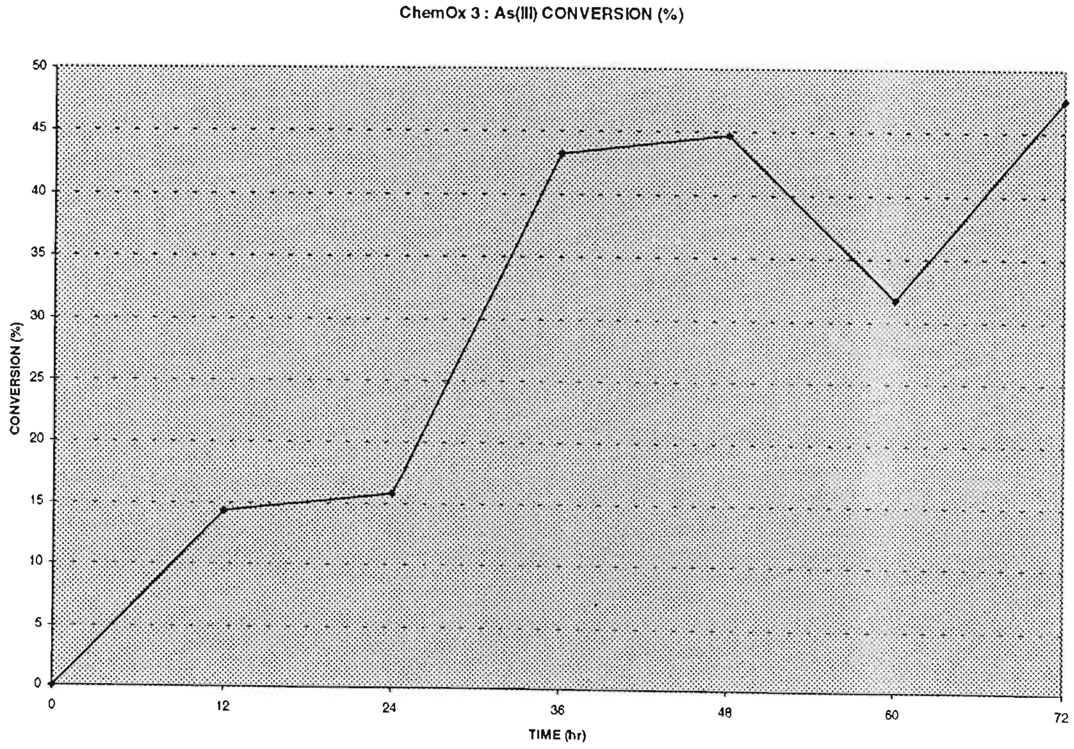
ChemOx 3: REDOX POTENTIAL



ChemOx 3 : ARSENIC CONCENTRATIONS




ChemOx 3: IRON CONCENTRATIONS
225
200
175
150
125
100
75
50
25
CONCENTRATION (ppm)
0
12
24
36
48
60
72
TIME (hr)
Fe(II)
Fe(III)


ChemOx 3 : As(III) CONVERSION (%)
50
45
40
35
30
25
20
15
10
5
0
CONVERSION (%)
0
12
24
36
48
60
72
TIME (hr)

APPENDIX C-2

EXPERIMENTAL RESULTS

CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN A SYNTHETIC SOLUTION

RESULTS: ChemSyn 1

Time (hr)	Temperature (^{0} C)	pH	Redox Potential (mV)
0.0	45.25	1.30	523.23
0.5	45.75	1.31	523.21
1.0	45.80	1.31	523.19
1.5	45.65	1.30	523.51
2.0	45.55	1.30	523.72
2.5	46.01	1.31	523.14
3.0	45.62	1.30	523.10
3.5	45.48	1.30	523.09
4.0	45.67	1.30	523.16
4.5	45.28	1.29	523.04
5.0	45.40	1.29	523.12
5.5	45.23	1.29	523.02
6.0	45.40	1.29	523.14
6.5	45.54	1.30	523.10
7.0	45.76	1.30	523.09
7.5	45.73	1.29	523.16
8.0	45.73	1.29	522.98
8.5	45.73	1.29	523.11
9.0	45.69	1.30	523.04
9.5	45.65	1.30	523.12
10.0	45.65	1.30	522.95
10.5	45.66	1.29	522.61
11.0	45.65	1.29	522.54
11.5	45.68	1.28	522.60
12.0	45.72	1.28	522.31
12.5	45.81	1.28	522.95
13.0	45.83	1.28	522.61
13.5	45.80	1.30	522.07
14.0	45.80	1.30	523.11
14.5	45.82	1.30	523.04
15.0	45.78	1.30	523.12
15.5	45.79	1.30	522.95
16.0	45.76	1.30	522.61
16.5	45.75	1.30	522.54
17.0	45.74	1.30	522.60
17.5	45.72	1.30	522.95
18.0	45.69	1.28	522.61
18.5	45.68	1.28	523.11
19.0	45.69	1.29	522.84
19.5	45.65	1.29	522.63
20.0	45.66	1.29	523.04
20.5	45.65	1.27	523.12
21.0	45.62	1.27	522.68
21.5	45.61	1.26	522.61
22.0	45.58	1.26	522.54
22.5	45.55	1.27	522.60
23.0	45.58	1.27	522.95

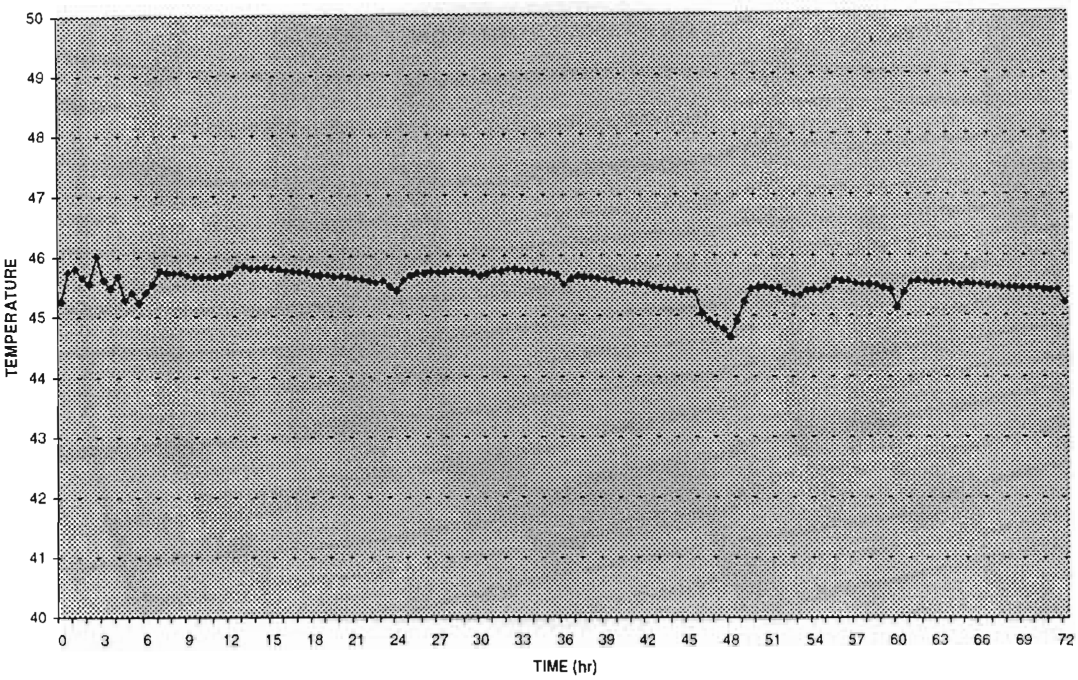
23.5	45.49	1.25	522.72
24.0	45.42	1.25	522.62
24.5	45.60	1.25	522.75
25.0	45.68	1.25	522.09
25.5	45.71	1.27	522.52
26.0	45.70	1.28	522.06
26.5	45.73	1.28	522.61
27.0	45.72	1.27	522.07
27.5	45.74	1.27	523.11
28.0	45.75	1.26	523.04
28.5	45.74	1.26	523.12
29.0	45.72	1.26	522.95
29.5	45.71	1.26	522.61
30.0	45.66	1.25	522.54
30.5	45.69	1.25	522.73
31.0	45.74	1.26	522.00
31.5	45.74	1.25	523.01
32.0	45.77	1.25	522.63
32.5	45.78	1.23	523.04
33.0	45.74	1.23	523.12
33.5	45.74	1.22	522.68
34.0	45.74	1.21	522.61
34.5	45.72	1.22	522.54
35.0	45.71	1.20	522.60
35.5	45.67	1.20	521.87
36.0	45.51	1.20	521.69
36.5	45.61	1.20	521.78
37.0	45.65	1.20	521.53
37.5	45.64	1.21	521.87
38.0	45.63	1.20	522.04
38.5	45.61	1.20	522.61
39.0	45.60	1.20	522.07
39.5	45.59	1.20	523.11
40.0	45.54	1.19	523.04
40.5	45.56	1.19	522.99
41.0	45.54	1.19	522.95
41.5	45.53	1.19	522.61
42.0	45.51	1.20	522.54
42.5	45.47	1.19	522.48
43.0	45.45	1.20	522.29
43.5	45.43	1.20	522.10
44.0	45.42	1.19	522.63
44.5	45.39	1.19	522.65
45.0	45.41	1.18	522.78
45.5	45.38	1.18	522.68
46.0	45.03	1.18	522.61
46.5	44.92	1.18	522.87
47.0	44.85	1.16	522.60
47.5	44.78	1.16	522.73
48.0	44.65	1.16	522.92
48.5	44.91	1.16	522.61
49.0	45.23	1.16	522.07
49.5	45.44	1.16	523.11

50.0	45.46	1.16	523.04
50.5	45.47	1.16	523.12
51.0	45.45	1.16	522.95
51.5	45.45	1.17	522.61
52.0	45.37	1.16	522.54
52.5	45.34	1.16	522.25
53.0	45.33	1.16	522.26
53.5	45.41	1.16	522.47
54.0	45.42	1.17	522.84
54.5	45.42	1.17	522.63
55.0	45.47	1.16	523.04
55.5	45.59	1.16	523.12
56.0	45.56	1.16	522.68
56.5	45.56	1.16	522.61
57.0	45.52	1.16	522.54
57.5	45.51	1.16	522.60
58.0	45.50	1.17	522.52
58.5	45.50	1.17	522.87
59.0	45.45	1.16	522.69
59.5	45.42	1.16	522.74
60.0	45.13	1.16	522.92
60.5	45.38	1.16	522.69
61.0	45.55	1.16	522.26
61.5	45.58	1.16	522.47
62.0	45.55	1.16	522.84
62.5	45.54	1.16	522.63
63.0	45.55	1.16	523.04
63.5	45.54	1.16	523.12
64.0	45.53	1.16	522.68
64.5	45.50	1.15	522.61
65.0	45.54	1.15	522.54
65.5	45.51	1.15	522.60
66.0	45.51	1.15	522.91
66.5	45.48	1.15	522.26
67.0	45.49	1.15	522.47
67.5	45.46	1.14	522.84
68.0	45.46	1.14	522.63
68.5	45.45	1.13	522.07
69.0	45.45	1.13	523.11
69.5	45.45	1.13	523.04
70.0	45.45	1.12	523.12
70.5	45.43	1.13	522.95
71.0	45.42	1.12	522.61
71.5	45.43	1.12	522.54
72.0	45.21	1.12	522.95

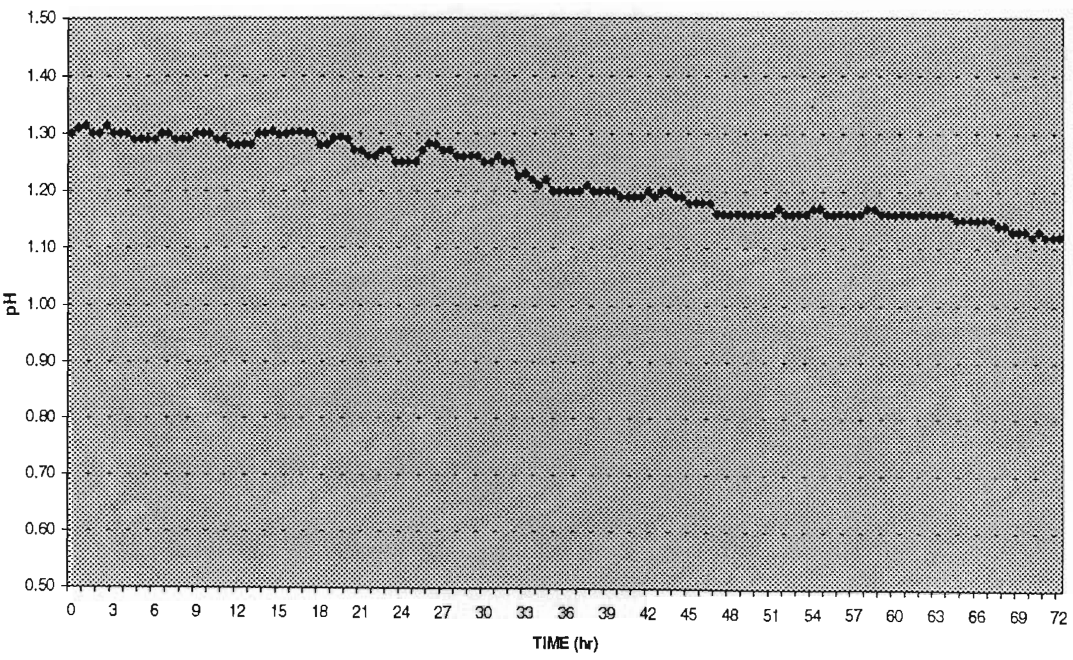
TABLE C-2.1: RESULTS ChemSyn 1

GRAPHS: ChemSyn 1

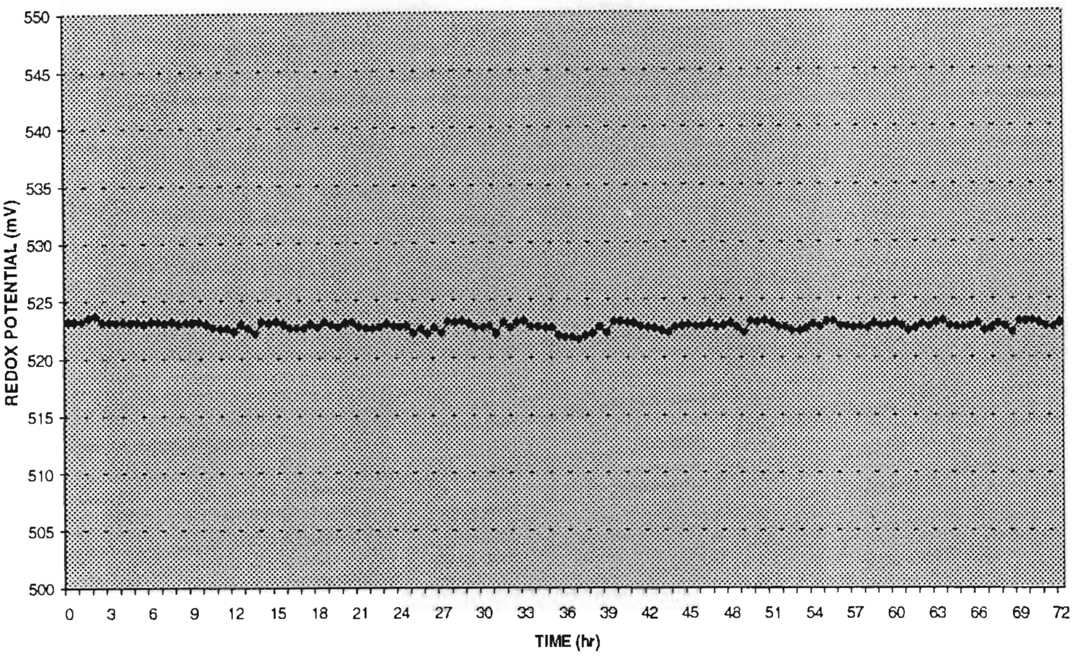
ChemSyn 1 : TEMPERATURE



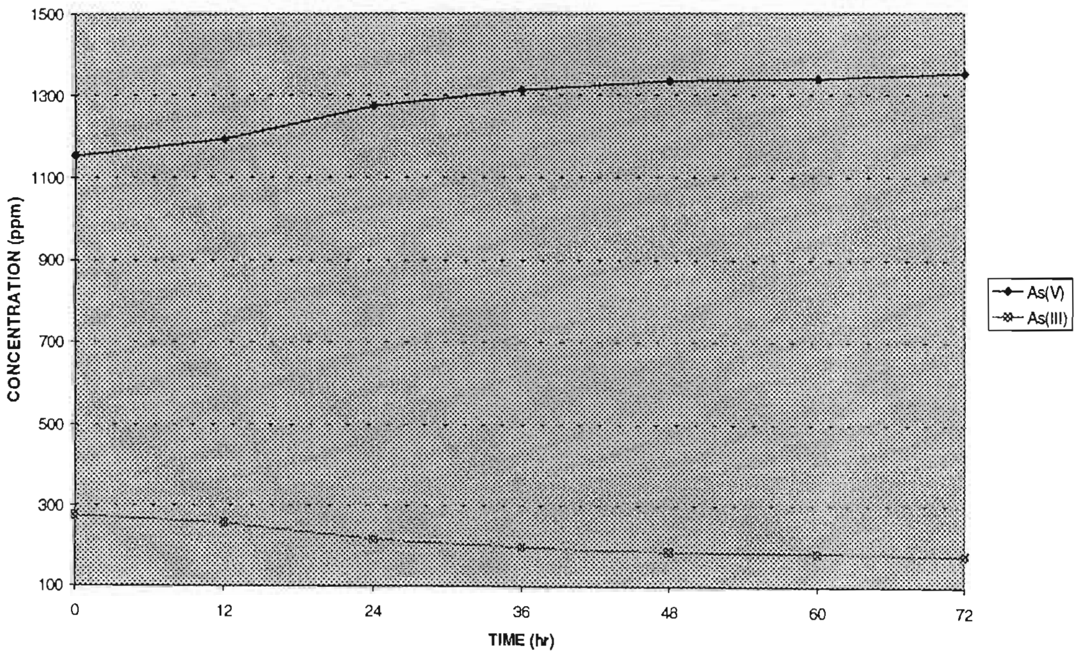
ChemSyn 1 : pH



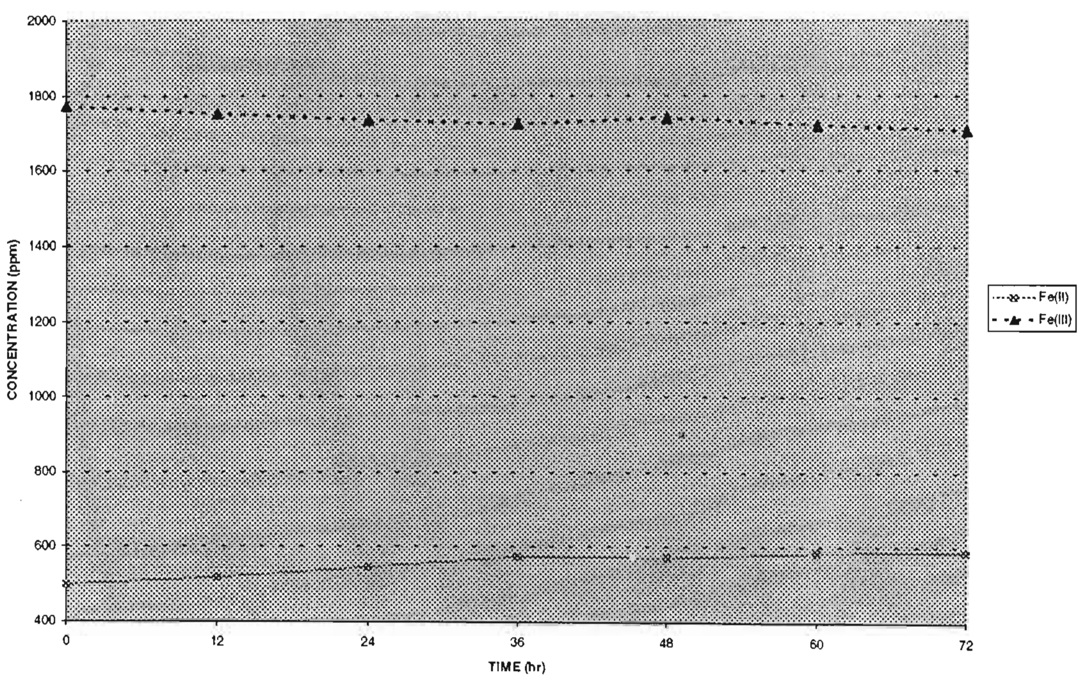
ChemSyn 1 : REDOX POTENTIAL



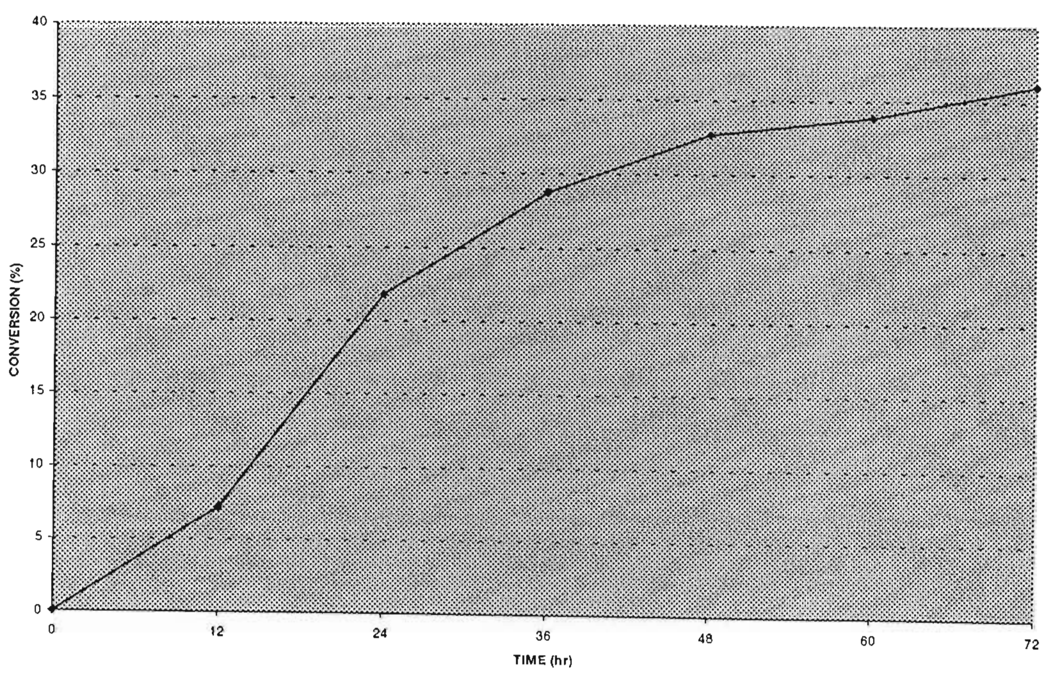
ChemSyn 1 : ARSENIC CONCENTRATIONS



ChemSyn 1: IRON CONCENTRATIONS



ChemSyn 1: As(III) CONVERSION



RESULTS: ChemSyn 2

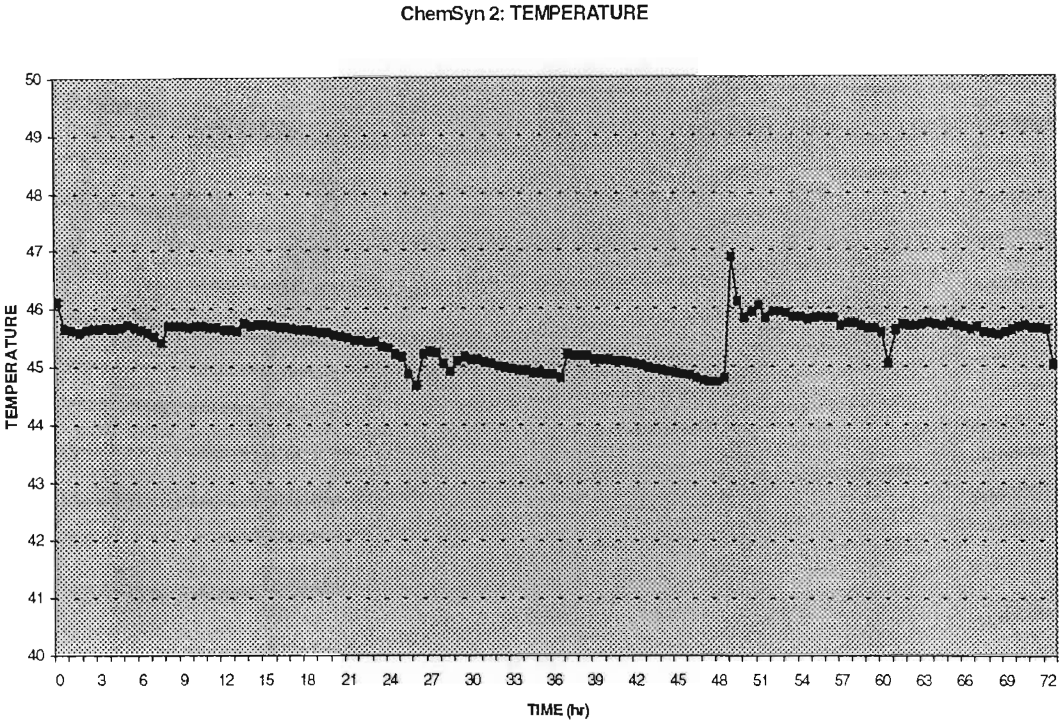
Time (hr)	Temperature (^{0} C)	pH	Redox Potential (mV)
0.0	46.11	1.31	458.93
0.5	45.64	1.38	462.62
1.0	45.63	1.36	459.85
1.5	45.59	1.35	466.62
2.0	45.62	1.33	462.01
2.5	45.65	1.33	457.70
3.0	45.64	1.32	482.93
3.5	45.68	1.31	473.70
4.0	45.65	1.31	475.24
4.5	45.68	1.30	476.77
5.0	45.71	1.29	472.77
5.5	45.67	1.29	476.16
6.0	45.62	1.29	482.00
6.5	45.58	1.28	475.24
7.0	45.51	1.28	473.70
7.5	45.40	1.28	472.47
8.0	45.68	1.27	478.62
8.5	45.69	1.27	479.85
9.0	45.69	1.27	476.47
9.5	45.66	1.27	474.31
10.0	45.68	1.27	476.16
10.5	45.69	1.26	473.70
11.0	45.67	1.26	478.62
11.5	45.68	1.26	477.39
12.0	45.63	1.26	480.16
12.0	45.63	1.26	480.16
12.5	45.60	1.25	479.85
13.0	45.73	1.24	474.00
13.5	45.70	1.25	478.93
14.0	45.71	1.24	475.85
14.5	45.72	1.24	475.54
15.0	45.68	1.24	478.62
15.5	45.67	1.24	474.00
16.0	45.67	1.24	474.62
16.5	45.65	1.24	482.00
17.0	45.63	1.23	474.93
17.5	45.63	1.23	475.24
18.0	45.59	1.23	475.85
18.5	45.57	1.23	476.16
19.0	45.58	1.23	477.70
19.5	45.54	1.22	475.85
20.0	45.51	1.22	471.24
20.5	45.49	1.22	478.62
21.0	45.45	1.22	475.54
21.5	45.45	1.22	475.54
22.0	45.39	1.21	474.93
22.5	45.41	1.21	474.62

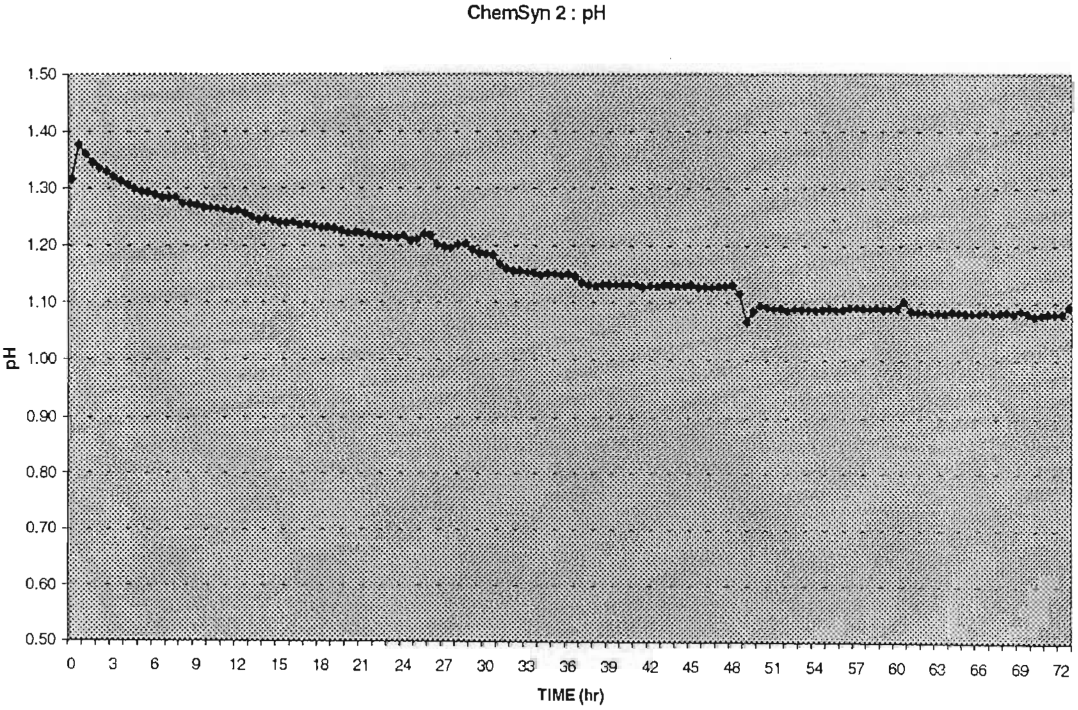
23.0	45.35	1.21	474.93
23.5	45.31	1.22	475.54
24.0	45.21	1.21	473.70
24.5	45.17	1.21	477.39
25.0	44.86	1.22	475.24
25.5	44.67	1.22	475.85
26.0	45.20	1.20	478.31
26.5	45.24	1.20	477.08
27.0	45.23	1.19	473.39
27.5	45.04	1.20	473.70
28.0	44.90	1.20	475.85
28.5	45.09	1.19	474.93
29.0	45.15	1.19	476.16
29.5	45.11	1.18	475.54
30.0	45.10	1.18	477.08
30.5	45.06	1.17	476.47
31.0	45.04	1.16	477.70
31.5	44.99	1.16	475.54
32.0	44.97	1.15	474.62
32.5	44.96	1.15	474.93
33.0	44.94	1.15	474.00
33.5	44.92	1.15	476.16
34.0	44.90	1.15	474.93
34.5	44.90	1.15	472.16
35.0	44.87	1.15	475.24
35.5	44.87	1.15	475.24
36.0	44.80	1.15	480.77
36.5	45.20	1.13	476.16
37.0	45.19	1.13	476.16
37.5	45.18	1.13	475.24
38.0	45.17	1.13	474.31
38.5	45.12	1.13	474.62
39.0	45.10	1.13	473.39
39.5	45.11	1.13	477.70
40.0	45.08	1.13	474.62
40.5	45.08	1.13	474.00
41.0	45.06	1.13	478.00
41.5	45.05	1.13	474.31
42.0	45.01	1.13	477.70
42.5	44.98	1.13	474.93
43.0	44.96	1.13	474.62
43.5	44.94	1.13	477.39
44.0	44.91	1.13	482.93
44.5	44.88	1.13	477.08
45.0	44.87	1.13	479.54
45.5	44.83	1.13	475.85
46.0	44.80	1.13	475.85
46.5	44.76	1.13	472.16
47.0	44.72	1.13	472.77
47.5	44.73	1.13	478.62
48.0	44.81	1.12	477.08
48.5	46.87	1.07	491.54

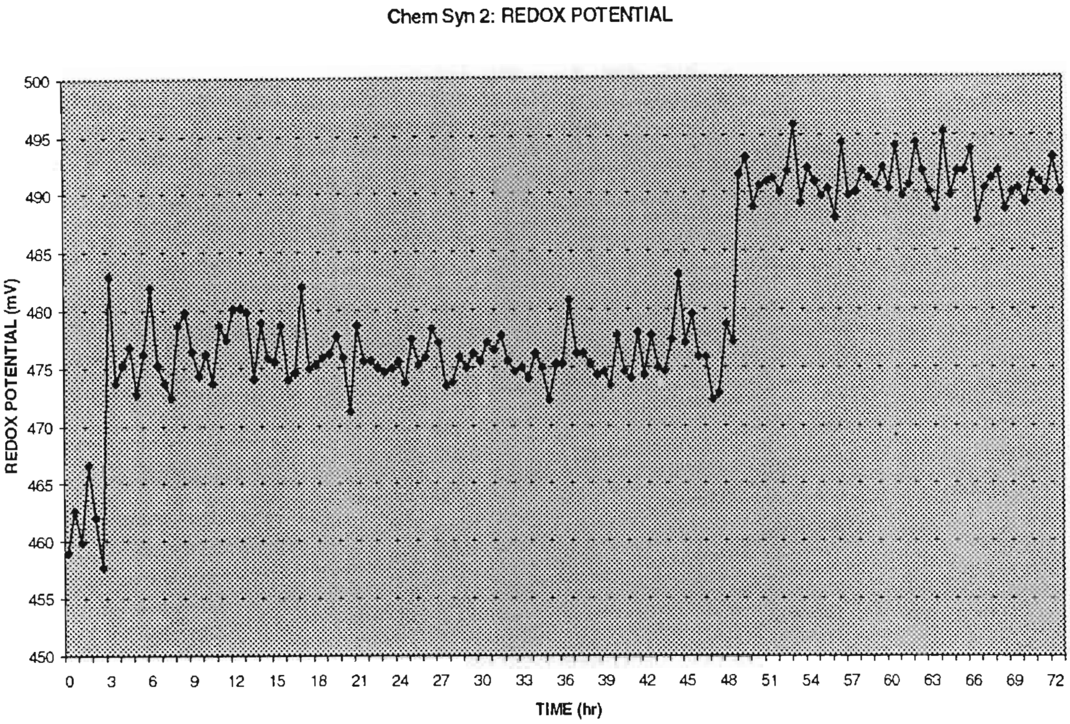
49.0	46.13	1.09	493.08
49.5	45.83	1.10	488.77
50.0	45.93	1.09	490.62
50.5	46.04	1.09	490.93
51.0	45.83	1.09	491.23
51.5	45.93	1.09	490.00
52.0	45.94	1.09	491.85
52.5	45.91	1.09	495.85
53.0	45.85	1.09	489.08
53.5	45.85	1.09	492.16
54.0	45.81	1.09	490.93
54.5	45.83	1.09	489.70
55.0	45.85	1.09	490.31
55.5	45.82	1.09	487.85
56.0	45.83	1.09	494.31
56.5	45.70	1.09	489.70
57.0	45.74	1.09	490.00
57.5	45.73	1.09	491.85
58.0	45.68	1.09	491.23
58.5	45.65	1.09	490.62
59.0	45.66	1.09	492.16
59.5	45.57	1.09	490.31
60.0	45.05	1.10	494.00
60.5	45.62	1.09	489.70
61.0	45.71	1.08	490.62
61.5	45.70	1.08	494.31
62.0	45.70	1.08	491.85
62.5	45.72	1.08	490.00
63.0	45.74	1.08	488.46
63.5	45.72	1.08	495.23
64.0	45.70	1.08	489.70
64.5	45.73	1.08	491.85
65.0	45.69	1.08	491.85
65.5	45.66	1.08	493.69
66.0	45.63	1.08	487.54
66.5	45.67	1.08	490.31
67.0	45.59	1.08	491.23
67.5	45.56	1.08	491.85
68.0	45.53	1.08	488.46
68.5	45.57	1.09	490.00
69.0	45.63	1.08	490.31
69.5	45.67	1.08	489.08
70.0	45.69	1.08	491.54
70.5	45.64	1.08	490.93
71.0	45.66	1.08	490.00
71.5	45.63	1.08	493.08
72.0	45.02	1.09	490.00

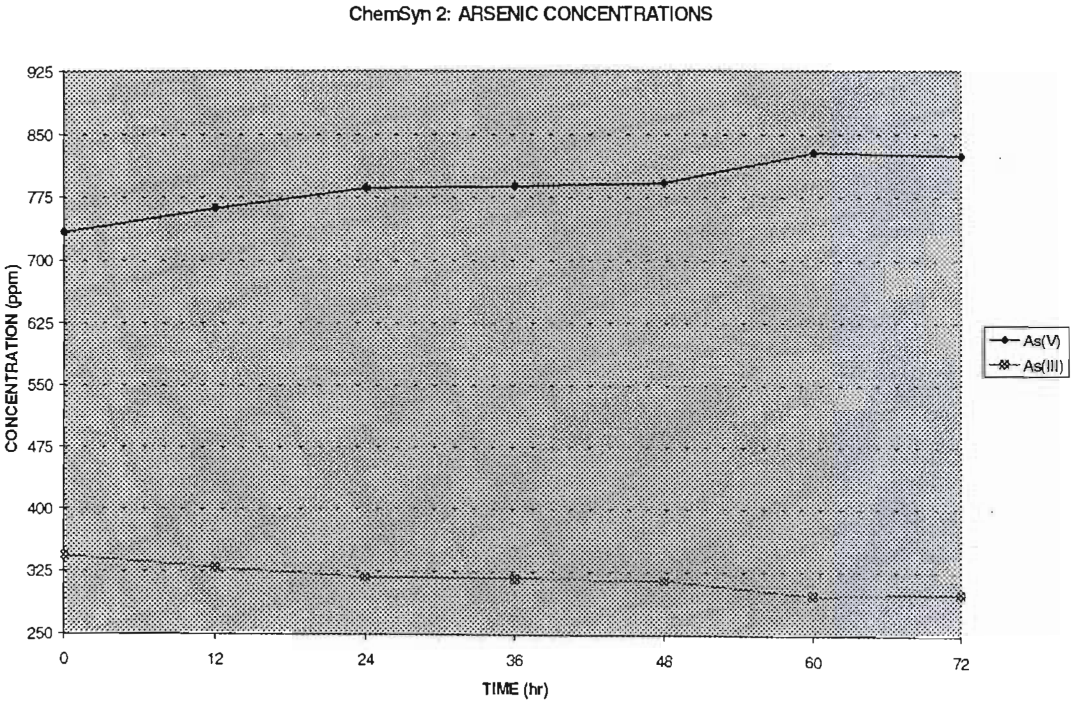
TABLE C-2.2: Results ChemSyn 2

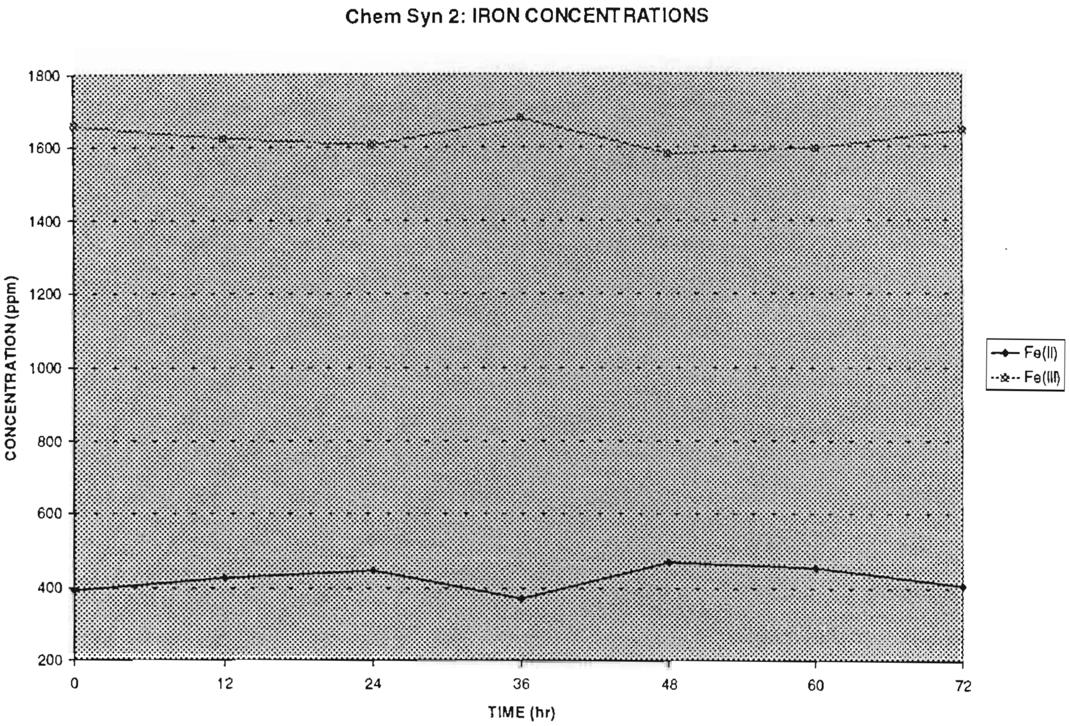
GRAPHS: ChemSyn 2

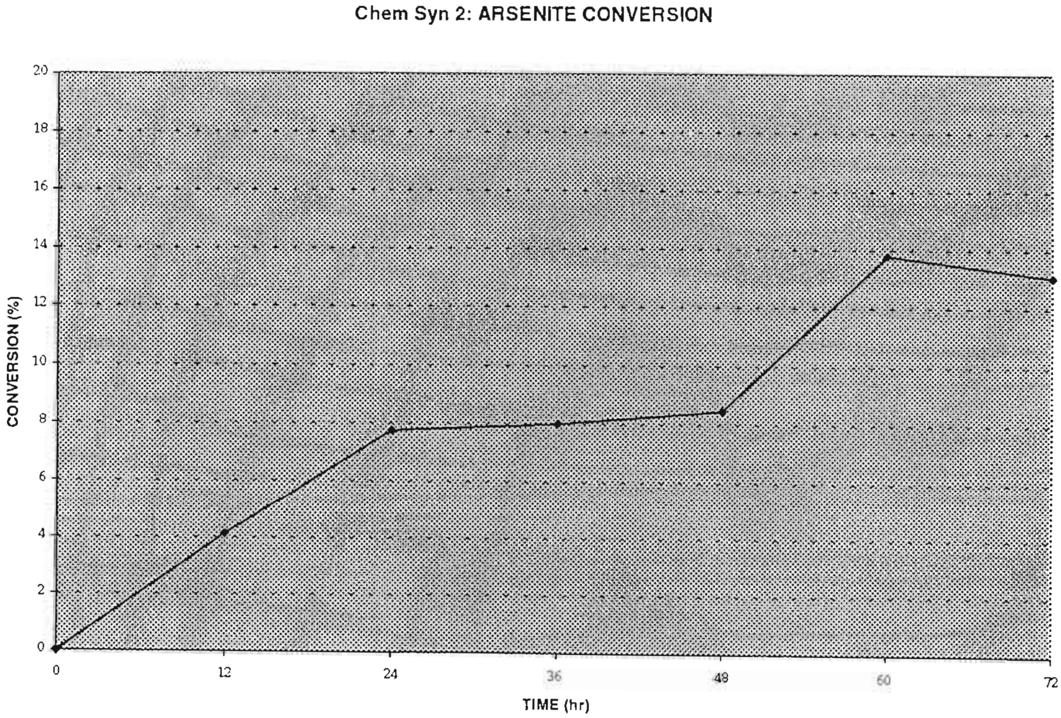





Chem Syn 2: REDOX POTENTIAL
REDOX POTENTIAL (mV)
500
495
490
485
480
475
470
465
460
455
450
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
48
51
54
57
60
63
66
69
72
TIME (hr)


ChemSyn 2: ARSENIC CONCENTRATIONS
CONCENTRATION (ppm)
925
850
775
700
625
550
475
400
325
250
0
12
24
36
48
60
72
TIME (hr)
As(V)
As(III)


Chem Syn 2: IRON CONCENTRATIONS
CONCENTRATION (ppm)
1800
1600
1400
1200
1000
800
600
400
200
0
12
24
36
48
60
72
TIME (hr)
Fe(II)
Fe(III)


Chem Syn 2: ARSENITE CONVERSION
CONVERSION (%)
20
18
16
14
12
10
8
6
4
2
0
0
12
24
36
48
60
72
TIME (hr)

RESULTS: ChemSyn 3

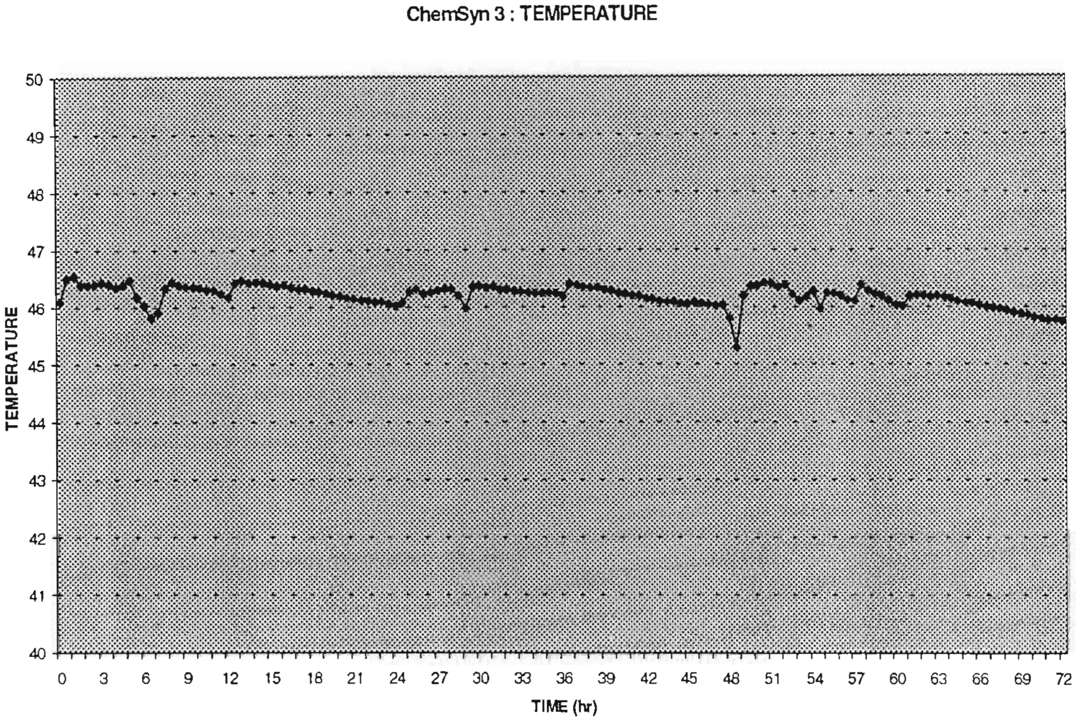
Time	Temperature (^{0} C)	pH	Redox Potential (mV)
0.0	46.10	1.27	491.54
0.5	46.51	1.22	505.69
1.0	46.55	1.20	510.31
1.5	46.39	1.19	507.23
2.0	46.38	1.19	509.69
2.5	46.39	1.19	507.23
3.0	46.43	1.19	508.46
3.5	46.40	1.17	506.92
4.0	46.34	1.17	507.23
4.5	46.39	1.16	506.00
5.0	46.48	1.15	516.15
5.5	46.18	1.16	510.92
6.0	46.02	1.16	508.77
6.5	45.81	1.16	506.31
7.0	45.91	1.15	506.92
7.5	46.34	1.14	508.46
8.0	46.44	1.13	507.23
8.5	46.39	1.13	505.69
9.0	46.36	1.13	508.46
9.5	46.35	1.13	510.00
10.0	46.33	1.13	506.92
10.5	46.30	1.13	506.31
11.0	46.30	1.13	506.85
11.5	46.23	1.13	506.72
12.0	46.17	1.12	506.62
12.5	46.42	1.11	506.62
13.0	46.46	1.11	506.00
13.5	46.42	1.10	506.31
14.0	46.42	1.10	508.16
14.5	46.43	1.10	508.77
15.0	46.39	1.11	507.54
15.5	46.37	1.10	505.08
16.0	46.38	1.10	509.08
16.5	46.33	1.09	504.77
17.0	46.31	1.10	510.00
17.5	46.32	1.09	508.46
18.0	46.28	1.09	507.23
18.5	46.26	1.09	506.92
19.0	46.25	1.09	509.08
19.5	46.20	1.09	509.08
20.0	46.19	1.09	508.77
20.5	46.16	1.09	505.08
21.0	46.14	1.09	509.08
21.5	46.11	1.09	512.46
22.0	46.10	1.09	506.92
22.5	46.09	1.09	505.69
23.0	46.09	1.08	506.32
23.5	46.05	1.08	505.82

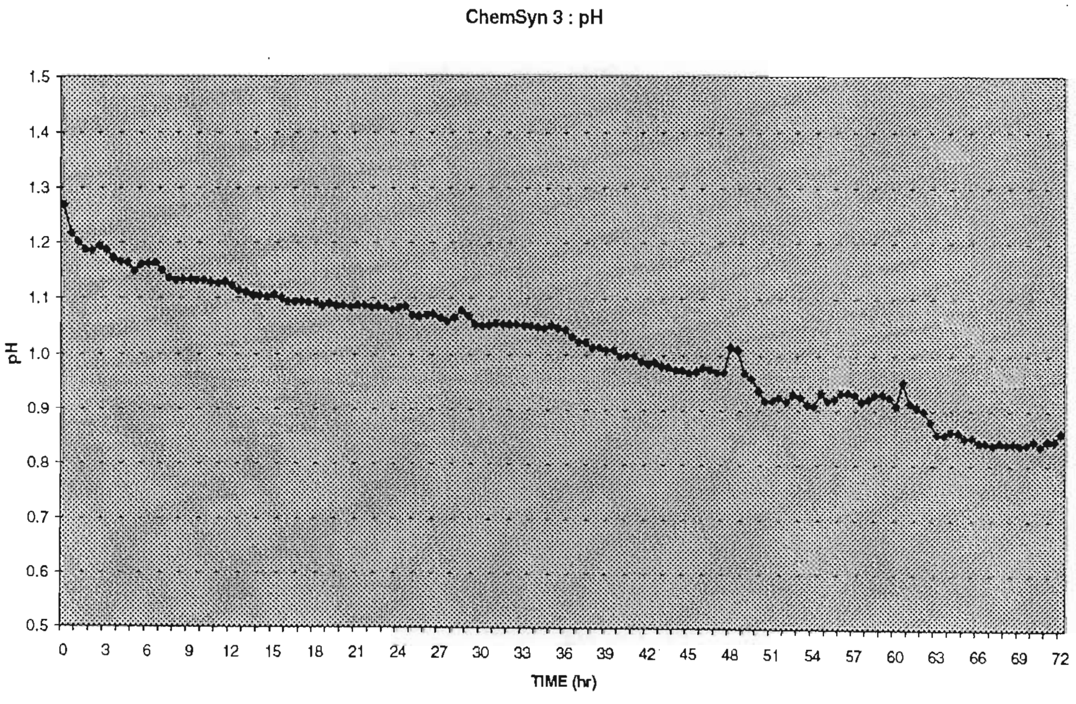
24.0	46.02	1.08	507.23
24.5	46.08	1.09	508.46
25.0	46.26	1.07	507.85
25.5	46.31	1.07	506.62
26.0	46.23	1.07	506.31
26.5	46.25	1.07	508.77
27.0	46.29	1.07	508.16
27.5	46.32	1.06	506.92
28.0	46.31	1.07	512.15
28.5	46.20	1.08	506.31
29.0	45.98	1.07	510.31
29.5	46.35	1.05	506.31
30.0	46.37	1.05	507.23
30.5	46.34	1.05	506.31
31.0	46.35	1.06	508.46
31.5	46.29	1.05	507.85
32.0	46.29	1.05	508.46
32.5	46.28	1.05	508.46
33.0	46.26	1.05	507.54
33.5	46.25	1.05	502.92
34.0	46.23	1.05	506.62
34.5	46.24	1.05	506.92
35.0	46.25	1.05	506.85
35.5	46.23	1.05	506.62
36.0	46.18	1.04	506.31
36.5	46.39	1.03	506.31
37.0	46.38	1.02	507.23
37.5	46.34	1.02	506.92
38.0	46.33	1.01	506.00
38.5	46.33	1.01	506.92
39.0	46.29	1.01	509.69
39.5	46.28	1.01	502.92
40.0	46.23	1.00	508.16
40.5	46.23	1.00	507.85
41.0	46.2	1	509.12
41.5	46.19	0.99	510.36
42.0	46.15	0.98	513.69
42.5	46.13	0.99	513.39
43.0	46.09	0.98	508.46
43.5	46.08	0.98	508.16
44.0	46.09	0.98	507.54
44.5	46.06	0.98	506.31
45.0	46.05	0.97	506.92
45.5	46.08	0.97	507.54
46.0	46.06	0.98	506.31
46.5	46.04	0.98	505.08
47.0	46.02	0.97	505.39
47.5	46.02	0.97	505.39
48.0	45.80	1.01	506.92
48.5	45.29	1.01	509.39
49.0	46.18	0.97	508.16
49.5	46.37	0.96	506.31
50.0	46.37	0.94	505.39

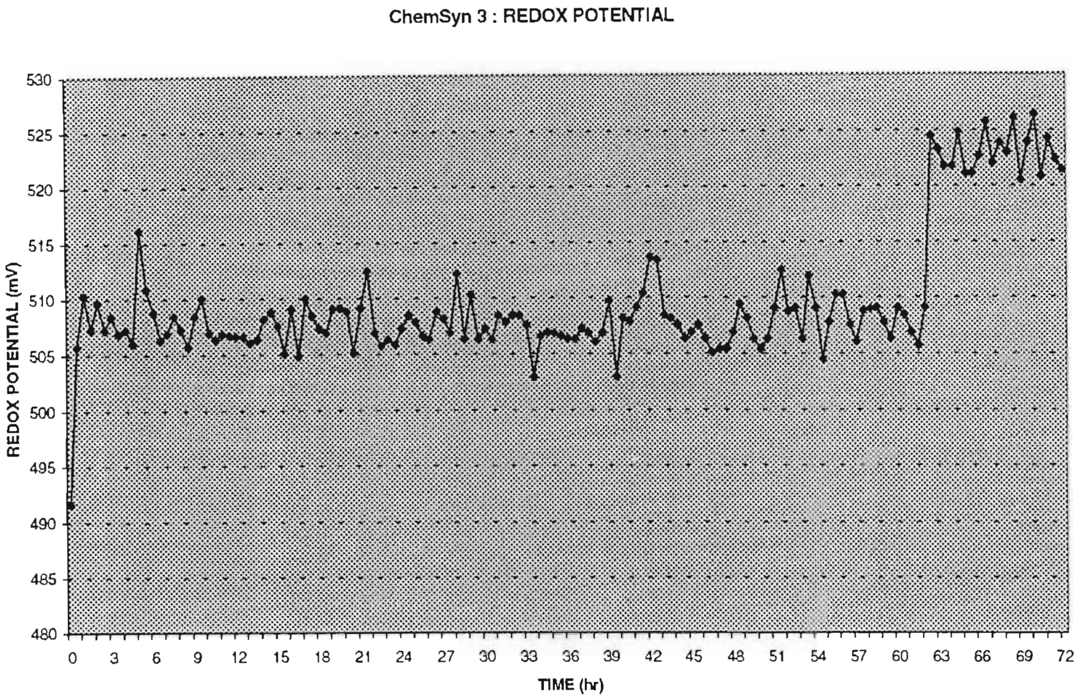
50.5	46.42	0.92	506.31
51.0	46.41	0.92	509.08
51.5	46.35	0.92	512.46
52.0	46.38	0.92	508.77
52.5	46.21	0.93	509.08
53.0	46.11	0.92	506.31
53.5	46.18	0.91	511.85
54.0	46.28	0.91	509.08
54.5	45.97	0.93	504.46
55.0	46.25	0.92	507.85
55.5	46.23	0.92	510.31
56.0	46.19	0.93	510.31
56.5	46.12	0.93	507.54
57.0	46.11	0.93	506.00
57.5	46.38	0.92	508.77
58.0	46.27	0.92	508.93
58.5	46.21	0.93	509.08
59.0	46.18	0.93	507.79
59.5	46.11	0.92	506.31
60.0	46.03	0.91	509.08
60.5	46.00	0.95	508.46
61.0	46.19	0.91	506.92
61.5	46.20	0.91	505.69
62.0	46.19	0.90	509.08
62.5	46.17	0.88	524.46
63.0	46.19	0.86	523.23
63.5	46.17	0.86	521.69
64.0	46.13	0.86	521.69
64.5	46.10	0.86	524.77
65.0	46.07	0.85	521.08
65.5	46.06	0.85	521.08
66.0	46.02	0.84	522.62
66.5	45.99	0.84	525.69
67.0	45.98	0.84	522.00
67.5	45.97	0.84	523.85
68.0	45.93	0.84	522.92
68.5	45.91	0.84	526.00
69.0	45.89	0.84	520.46
69.5	45.85	0.84	523.85
70.0	45.82	0.84	526.31
70.5	45.80	0.84	520.77
71.0	45.77	0.85	524.15
71.5	45.77	0.84	522.31
72.0	45.74	0.86	521.38

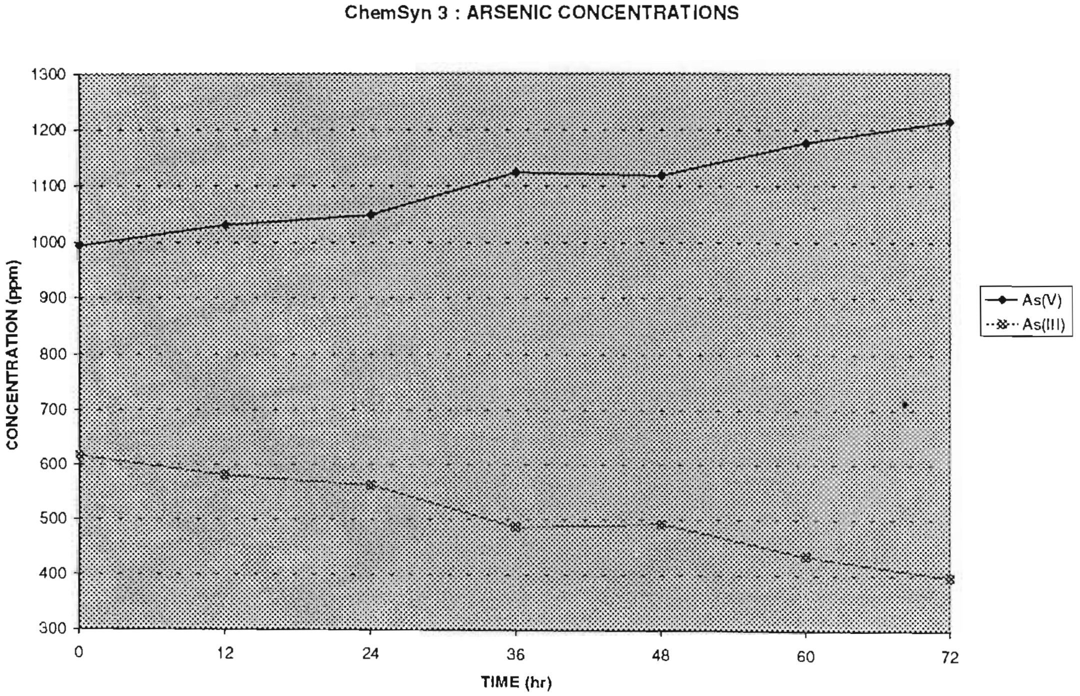
TABLE C-2.3: Results ChemSyn 3

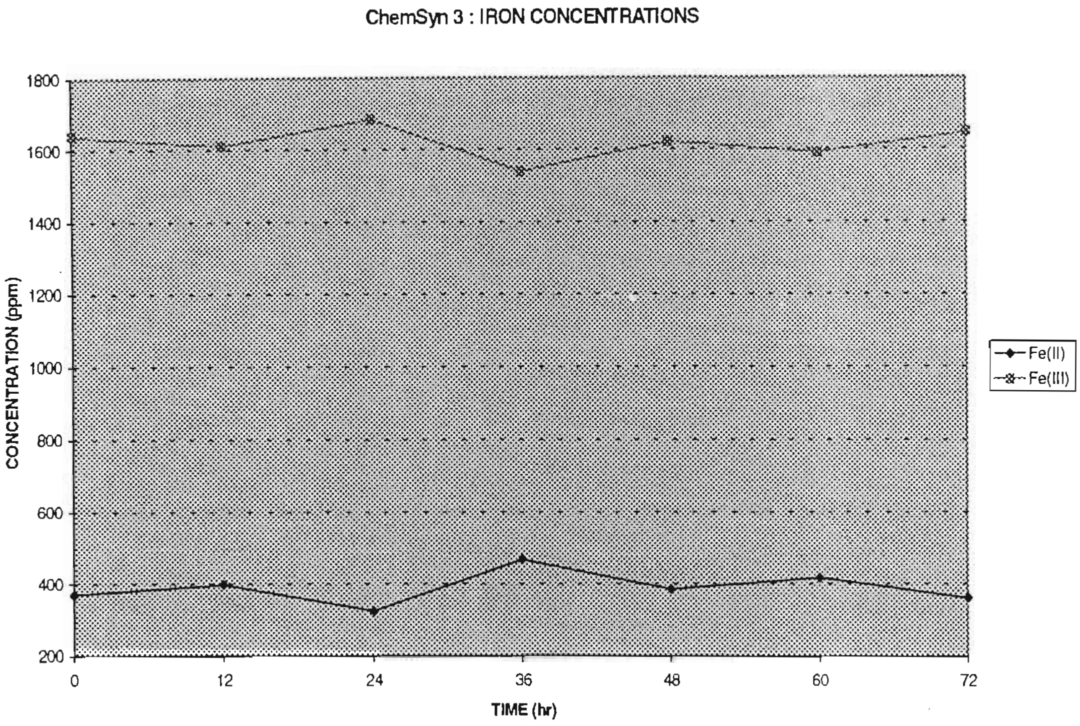
GRAPHS: ChemSyn 3

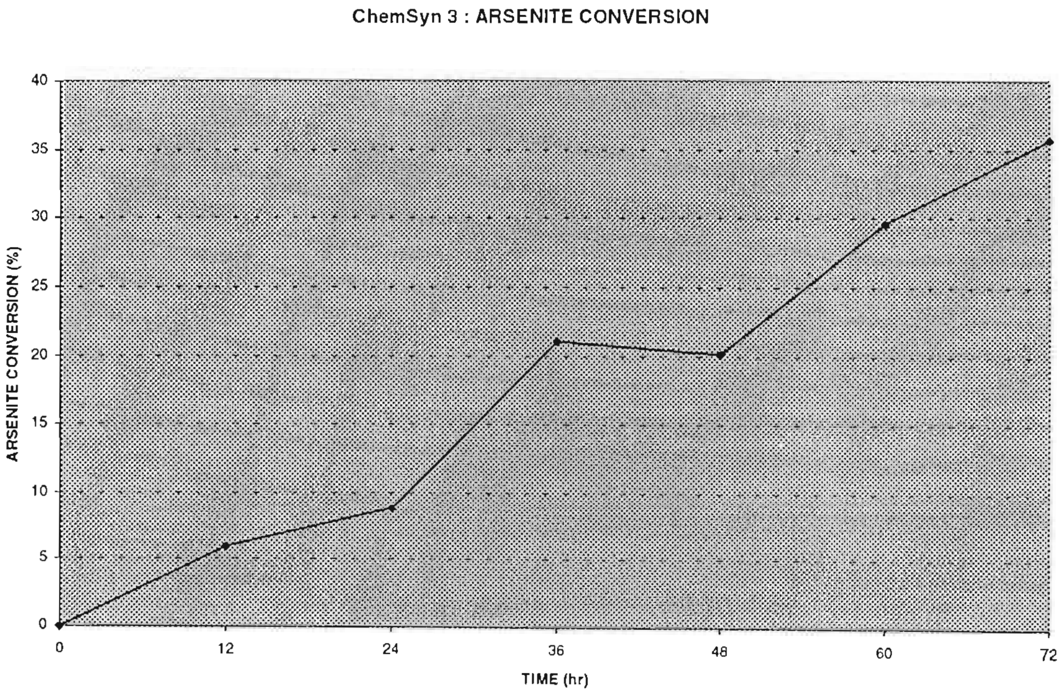





ChemSyn 3 : REDOX POTENTIAL
REDOX POTENTIAL (mV)
530
525
520
515
510
505
500
495
490
485
480
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
48
51
54
57
60
63
66
69
72
TIME (hr)


ChemSyn 3 : ARSENIC CONCENTRATIONS
CONCENTRATION (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
0
12
24
36
48
60
72
TIME (hr)
As(V)
As(III)


ChemSyn 3 : IRON CONCENTRATIONS
CONCENTRATION (ppm)
1800
1600
1400
1200
1000
800
600
400
200
0
12
24
36
48
60
72
TIME (hr)
Fe(II)
Fe(III)


ChemSyn 3 : ARSENITE CONVERSION
ARSENITE CONVERSION (%)
40
35
30
25
20
15
10
5
0
0
12
24
36
48
60
72
TIME (hr)

RESULTS: ChemSyn 4

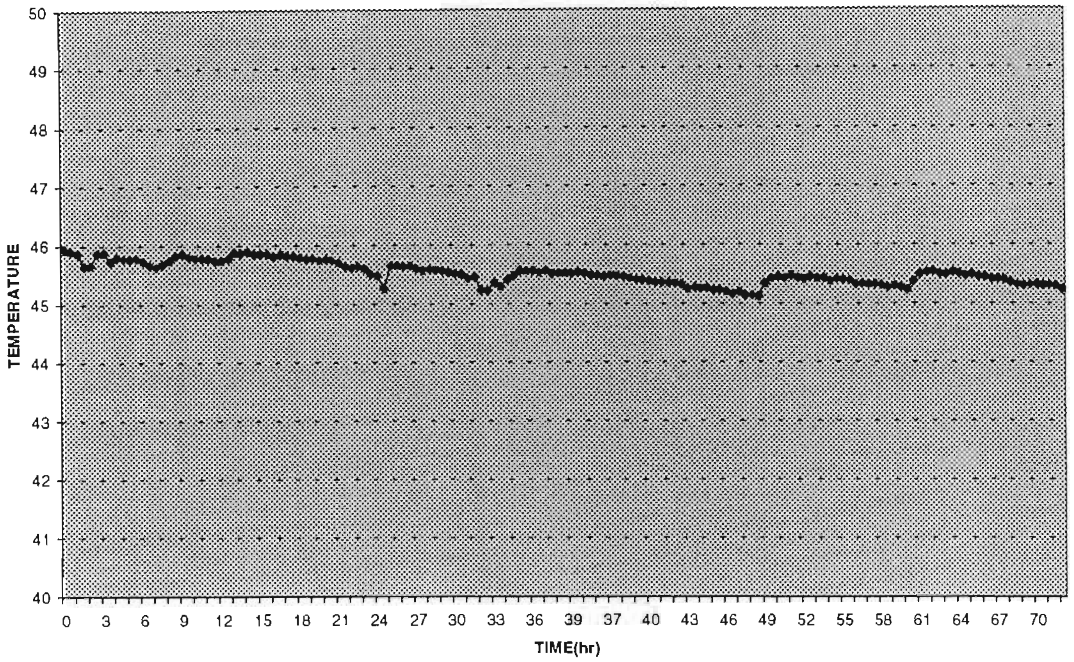
Time (hr)	Temperature (^{0} C)	pH	Redox Potential (mV)
0.0	45.94	1.28	426.32
0.5	45.90	1.24	442.32
1.0	45.86	1.23	445.39
1.5	45.64	1.23	442.93
2.0	45.66	1.24	443.55
2.5	45.86	1.22	443.24
3.0	45.88	1.24	458.01
3.5	45.72	1.24	456.47
4.0	45.79	1.24	458.31
4.5	45.77	1.24	462.01
5.0	45.77	1.24	460.16
5.5	45.78	1.24	459.24
6.0	45.73	1.24	456.16
6.5	45.66	1.24	461.08
7.0	45.62	1.24	458.01
7.5	45.68	1.25	458.01
8.0	45.75	1.25	458.01
8.5	45.82	1.24	459.54
9.0	45.85	1.25	459.54
9.5	45.79	1.25	460.77
10.0	45.77	1.25	457.08
10.5	45.78	1.25	458.62
11.0	45.77	1.26	462.31
11.5	45.73	1.26	460.16
12.0	45.74	1.26	463.85
12.5	45.77	1.26	459.85
13.0	45.88	1.25	458.01
13.5	45.86	1.26	459.85
14.0	45.88	1.26	460.47
14.5	45.84	1.26	457.70
15.0	45.84	1.26	456.78
15.5	45.85	1.26	461.39
16.0	45.80	1.26	457.39
16.5	45.83	1.26	459.85
17.0	45.81	1.26	459.24
17.5	45.81	1.26	456.78
18.0	45.78	1.27	462.93
18.5	45.75	1.27	461.08
19.0	45.77	1.27	459.54
19.5	45.74	1.27	462.62
20.0	45.75	1.27	458.01
20.5	45.73	1.27	459.85
21.0	45.70	1.27	459.24
21.5	45.62	1.27	462.93
22.0	45.60	1.27	459.54
22.5	45.63	1.28	457.70
23.0	45.59	1.28	458.69
23.5	45.50	1.28	459.03
24.0	45.47	1.28	460.47
24.5	45.26	1.29	462.93

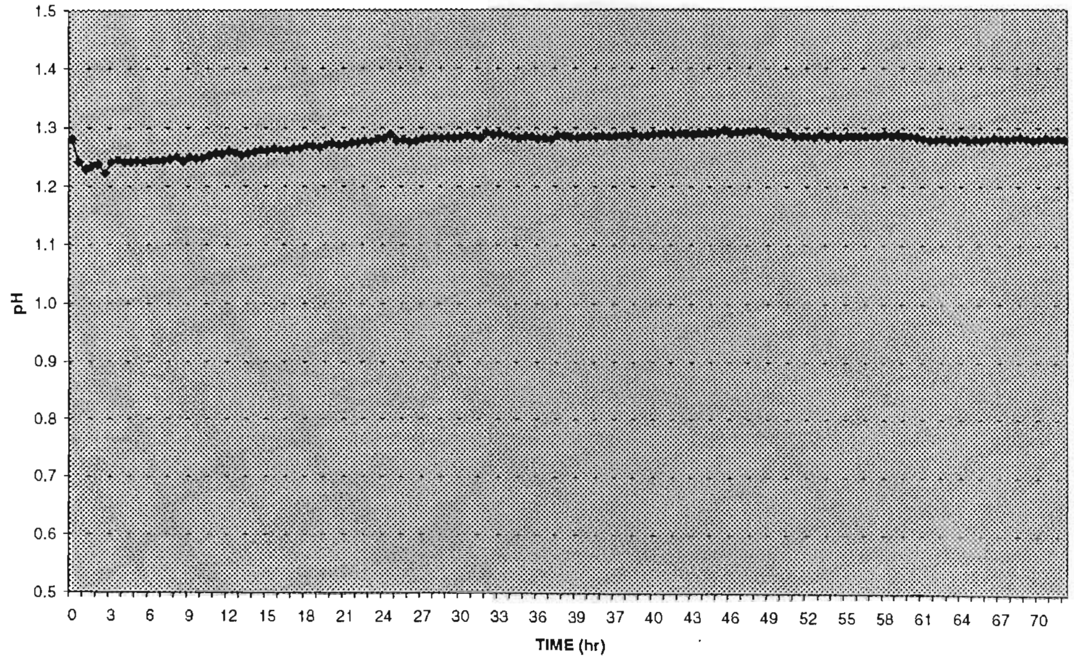
25.0	45.64	1.28	459.24
25.5	45.65	1.28	459.85
26.0	45.63	1.28	459.54
26.5	45.64	1.28	459.85
27.0	45.59	1.28	459.24
27.5	45.57	1.28	461.39
28.0	45.58	1.28	458.93
28.5	45.56	1.28	458.31
29.0	45.55	1.28	466.31
29.5	45.53	1.28	461.08
30.0	45.50	1.28	459.24
30.5	45.50	1.29	461.39
31.0	45.42	1.28	458.93
31.5	45.45	1.28	461.08
32.0	45.22	1.29	459.24
32.5	45.21	1.29	462.01
33.0	45.35	1.29	462.01
33.5	45.29	1.29	460.77
34.0	45.40	1.28	458.93
34.5	45.46	1.28	465.39
35.0	45.55	1.28	458.01
35.5	45.56	1.28	458.93
36.0	45.55	1.28	458.31
36.5	45.53	1.28	461.08
37.0	45.56	1.28	459.85
37.5	45.50	1.29	459.24
38.0	45.51	1.29	457.08
38.5	45.52	1.28	458.93
39.0	45.50	1.28	460.16
39.5	45.53	1.29	456.78
40.0	45.51	1.28	464.77
40.5	45.47	1.28	458.93
41.0	45.48	1.29	458.31
36.0	45.46	1.28	459.85
36.5	45.47	1.29	460.77
37.0	45.45	1.29	462.93
37.5	45.45	1.29	458.01
38.0	45.42	1.29	458.31
38.5	45.40	1.29	460.47
39.0	45.39	1.29	458.31
39.5	45.38	1.29	459.85
40.0	45.36	1.29	463.24
40.5	45.35	1.29	460.16
41.0	45.35	1.29	465.39
41.5	45.33	1.29	459.85
42.0	45.31	1.29	462.62
42.5	45.25	1.29	458.01
43.0	45.27	1.29	459.24
43.5	45.24	1.29	464.77
44.0	45.25	1.29	460.77
44.5	45.22	1.29	456.16
45.0	45.23	1.29	458.01
45.5	45.20	1.29	458.31
46.0	45.15	1.29	457.70

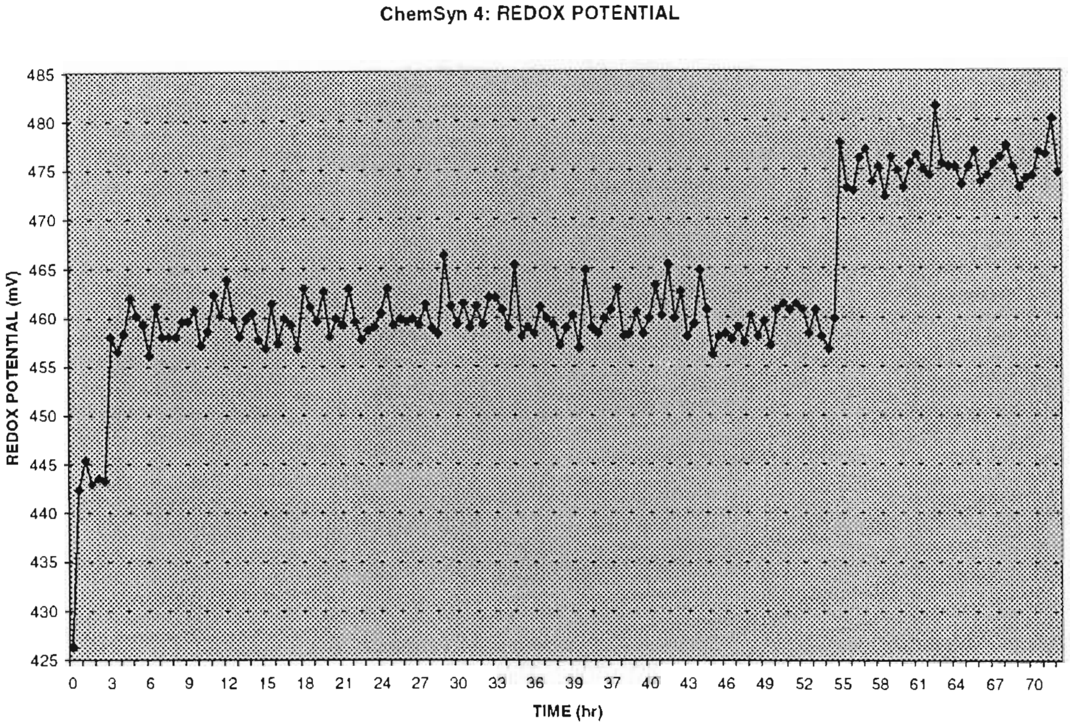
46.5	45.18	1.29	458.93
47.0	45.13	1.29	457.39
47.5	45.13	1.29	460.16
48.0	45.12	1.29	458.01
48.5	45.34	1.29	459.54
49.0	45.42	1.29	457.08
49.5	45.45	1.28	460.77
50.0	45.42	1.29	461.39
50.5	45.47	1.28	460.77
51.0	45.43	1.28	461.39
51.5	45.40	1.29	460.77
52.0	45.45	1.28	458.31
52.5	45.43	1.29	460.77
53.0	45.43	1.28	458.01
53.5	45.38	1.29	456.78
54.0	45.41	1.28	459.85
54.5	45.39	1.29	477.70
55.0	45.39	1.28	473.08
55.5	45.31	1.28	472.77
56.0	45.33	1.29	476.16
56.5	45.32	1.29	477.08
57.0	45.32	1.28	473.70
57.5	45.31	1.29	475.24
58.0	45.27	1.29	472.16
58.5	45.29	1.29	476.16
59.0	45.27	1.28	474.86
60.0	45.23	1.28	473.08
60.5	45.37	1.28	475.54
61.0	45.50	1.28	476.47
61.5	45.53	1.28	474.93
62.0	45.55	1.28	474.31
62.5	45.50	1.28	481.39
63.0	45.50	1.28	475.54
63.5	45.52	1.28	475.24
64.0	45.50	1.28	475.24
64.5	45.46	1.28	473.39
65.0	45.48	1.28	475.24
65.5	45.45	1.28	476.77
66.0	45.45	1.28	473.70
66.5	45.42	1.28	474.31
67.0	45.41	1.28	475.54
67.5	45.40	1.28	476.16
68.0	45.35	1.28	477.39
68.5	45.31	1.28	475.24
69.0	45.30	1.28	473.08
69.5	45.31	1.28	474.00
70.0	45.31	1.28	474.31
70.5	45.29	1.28	476.77
71.0	45.30	1.28	476.47
71.5	45.29	1.28	480.16
72.0	45.23	1.28	474.62

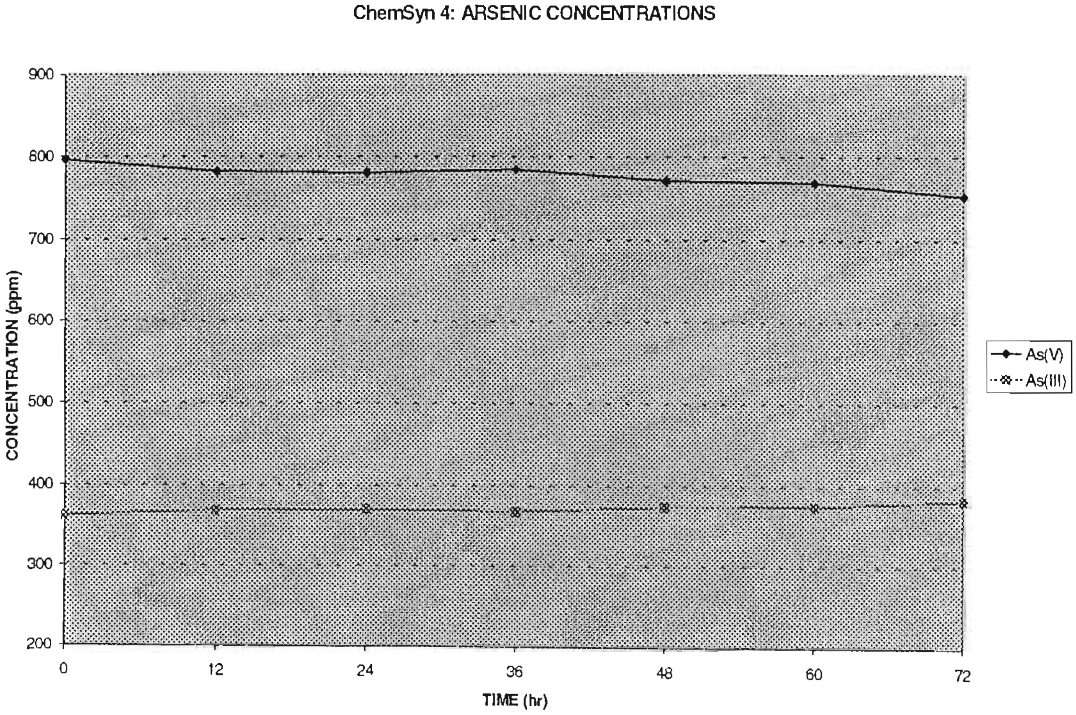
TABLE C-2.4: Results ChemSyn 4

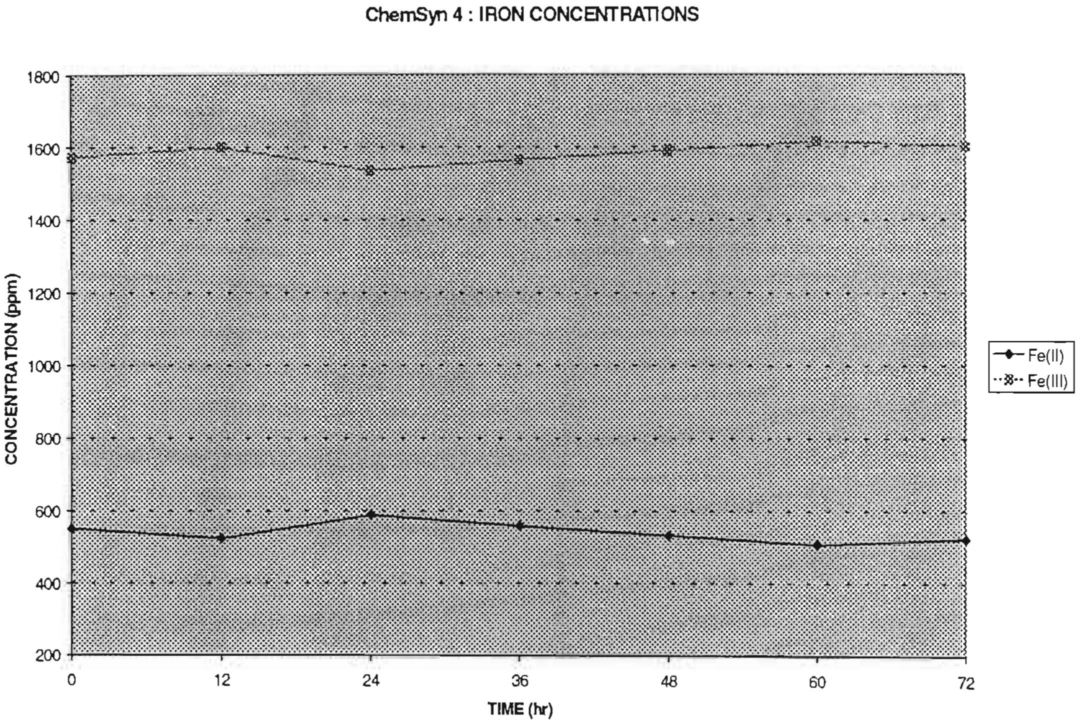
GRAPHS: ChemSyn 4


ChemSyn 4: TEMPERATURE


ChemSyn 4: pH


ChemSyn 4: REDOX POTENTIAL
REDOX POTENTIAL (mV)
485
480
475
470
465
460
455
450
445
440
435
430
425
0
3
6
9
12
15
18
21
24
27
30
33
36
39
37
40
43
46
49
52
55
58
61
64
67
70
TIME (hr)


ChemSyn 4: ARSENIC CONCENTRATIONS
CONCENTRATION (ppm)
900
800
700
600
500
400
300
200
0
12
24
36
48
60
72
TIME (hr)
As(V)
As(III)


ChemSyn 4 : IRON CONCENTRATIONS
CONCENTRATION (ppm)
1800
1600
1400
1200
1000
800
600
400
200
0
12
24
36
48
60
72
TIME (hr)
Fe(II)
Fe(III)

APPENDIX C-3

EXPERIMENTAL RESULTS

CHEMICAL OXIDATION OF ARSENITE BY FERRIC ION IN THE PRESENCE OF A SURFACE IN GOLD MINE EFFLUENT

RESULTS: ChemSurf 1

Time (hr)	Temperature (^{0} C)	pH	Redox Potential (mV)
0.0	46.5	1.38	570.20
0.5	46.0	1.38	570.41
1.0	46.0	1.38	570.62
1.5	45.5	1.38	570.52
2.0	45.6	1.39	570.10
2.5	45.6	1.39	571.25
3.0	45.8	1.39	571.62
3.5	45.6	1.39	571.35
4.0	45.7	1.39	570.81
4.5	45.6	1.39	570.77
5.0	45.7	1.39	570.70
5.5	45.7	1.39	571.35
6.0	45.7	1.39	571.26
6.5	45.6	1.39	571.24
7.0	45.6	1.39	570.91
7.5	45.7	1.39	570.75
8.0	45.7	1.39	570.81
8.5	45.6	1.39	571.85
9.0	45.7	1.39	572.15
9.5	45.7	1.39	572.52
10.0	45.8	1.39	572.35
10.5	45.8	1.39	572.81
11.0	45.7	1.40	572.91
11.5	45.8	1.40	573.29
12.0	45.9	1.41	574.92
12.5	45.8	1.40	574.81
13.0	45.8	1.39	574.45
13.5	45.6	1.39	573.91
14.0	45.7	1.39	573.65
14.5	45.7	1.39	573.83
15.0	45.7	1.39	573.26
15.5	45.7	1.39	573.91
16.0	45.7	1.39	573.56
16.5	45.7	1.39	573.14
17.0	45.7	1.39	573.81
17.5	45.7	1.39	573.62
18.0	45.6	1.39	573.20
18.5	45.7	1.39	572.91
19.0	45.6	1.39	572.81
19.5	45.7	1.39	572.72
20.0	45.7	1.39	572.81
20.5	45.6	1.39	572.63
21.0	45.7	1.39	572.81
21.5	45.7	1.39	572.61
22.0	45.7	1.39	572.30
22.5	45.7	1.38	572.61
23.0	45.7	1.38	572.55
23.5	45.7	1.39	572.46
24.0	45.7	1.38	569.38

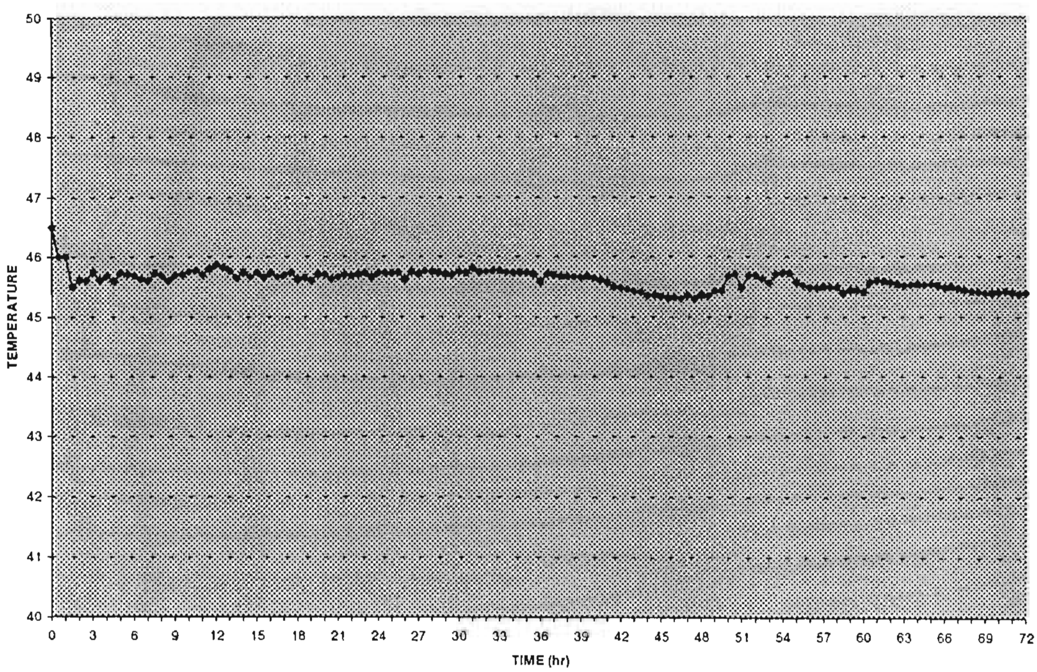
24.5	45.7	1.37	573.38
25.0	45.7	1.38	573.99
25.5	45.7	1.38	569.38
26.0	45.6	1.38	572.15
26.5	45.8	1.38	569.38
27.0	45.7	1.38	570.00
27.5	45.8	1.38	573.99
28.0	45.8	1.38	570.61
28.5	45.7	1.38	572.15
29.0	45.7	1.38	567.53
29.5	45.7	1.38	556.77
30.0	45.8	1.38	554.30
30.5	45.7	1.38	555.84
31.0	45.8	1.37	552.77
31.5	45.7	1.38	556.77
32.0	45.8	1.38	557.69
32.5	45.8	1.38	557.69
33.0	45.8	1.38	554.61
33.5	45.7	1.38	555.23
34.0	45.7	1.38	560.46
34.5	45.7	1.38	555.54
35.0	45.7	1.38	562.61
35.5	45.7	1.38	551.84
36.0	45.6	1.36	554.61
36.5	45.7	1.36	558.30
37.0	45.7	1.37	553.69
37.5	45.7	1.37	559.53
38.0	45.7	1.37	553.38
38.5	45.7	1.36	555.23
39.0	45.7	1.36	555.54
39.5	45.7	1.36	562.92
40.0	45.6	1.36	554.30
40.5	45.6	1.37	561.07
41.0	45.6	1.36	560.77
41.5	45.5	1.36	553.38
42.0	45.5	1.36	552.77
42.5	45.5	1.36	555.54
43.0	45.4	1.36	552.77
43.5	45.4	1.36	555.23
44.0	45.4	1.36	554.92
44.5	45.4	1.36	560.15
45.0	45.3	1.35	562.92
45.5	45.3	1.36	558.00
46.0	45.3	1.35	553.69
46.5	45.3	1.36	559.84
47.0	45.4	1.35	562.30
47.5	45.3	1.35	567.53
48.0	45.4	1.35	554.61
48.5	45.3	1.35	554.92
49.0	45.4	1.32	557.07
49.5	45.4	1.32	552.77
50.0	45.7	1.32	554.61
50.5	45.7	1.32	554.92
51.0	45.5	1.33	554.30

51.5	45.7	1.32	555.54
52.0	45.7	1.32	556.15
52.5	45.6	1.32	556.77
53.0	45.6	1.33	558.12
53.5	45.7	1.32	554.58
54.0	45.7	1.32	552.15
54.5	45.7	1.33	557.69
55.0	45.6	1.33	554.00
55.5	45.5	1.33	557.07
56.0	45.5	1.33	562.30
56.5	45.5	1.33	560.15
57.0	45.5	1.33	561.38
57.5	45.5	1.33	558.00
58.0	45.5	1.33	563.23
58.5	45.4	1.33	556.77
59.0	45.4	1.33	553.38
59.5	45.4	1.33	555.23
60.0	45.4	1.33	553.69
60.5	45.6	1.32	555.84
61.0	45.6	1.32	556.77
61.5	45.6	1.33	558.92
62.0	45.6	1.32	561.07
62.5	45.5	1.32	552.15
63.0	45.5	1.32	555.54
63.5	45.5	1.32	550.61
64.0	45.5	1.32	555.23
64.5	45.5	1.32	557.07
65.0	45.5	1.32	560.15
65.5	45.5	1.32	555.84
66.0	45.5	1.32	554.00
66.5	45.5	1.32	565.38
67.0	45.5	1.32	557.38
67.5	45.4	1.32	554.92
68.0	45.4	1.32	554.00
68.5	45.4	1.32	554.92
69.0	45.4	1.32	554.00
69.5	45.4	1.32	552.46
70.0	45.4	1.32	561.07
70.5	45.4	1.32	557.69
71.0	45.4	1.31	554.92
71.5	45.4	1.31	556.46
72.0	45.4	1.32	557.69

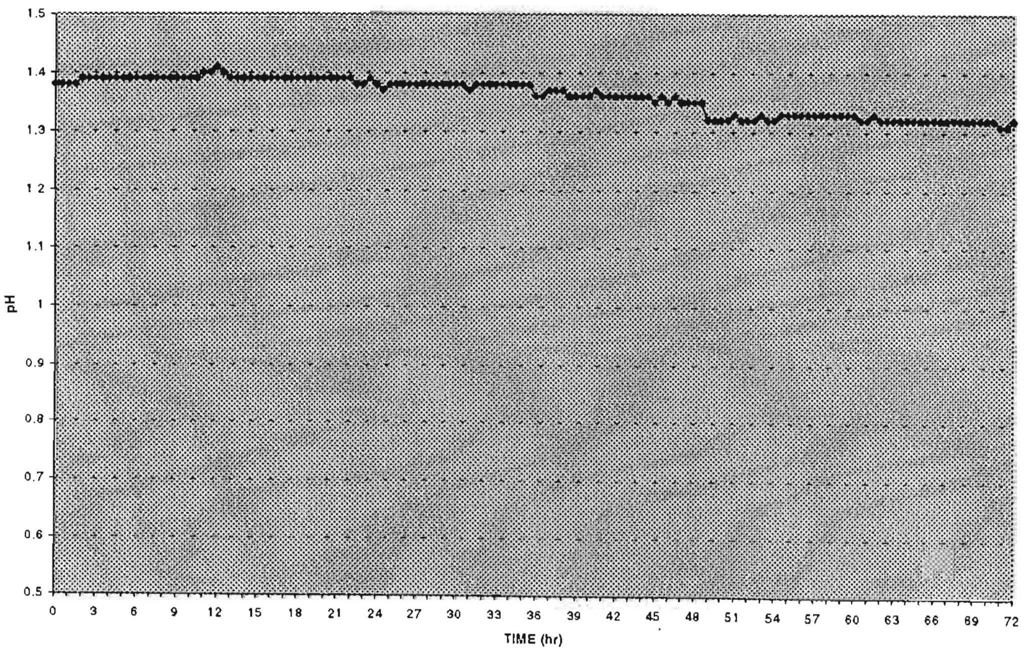
TABLE C-3.1: Results ChemSurf 1

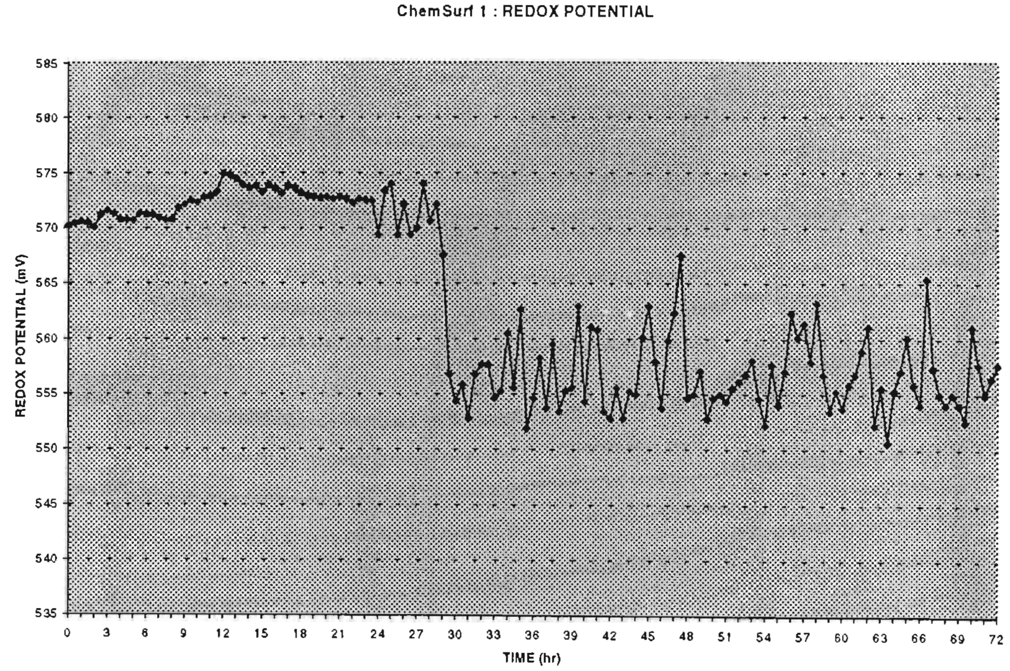
GRAPHS: ChemSurf 1

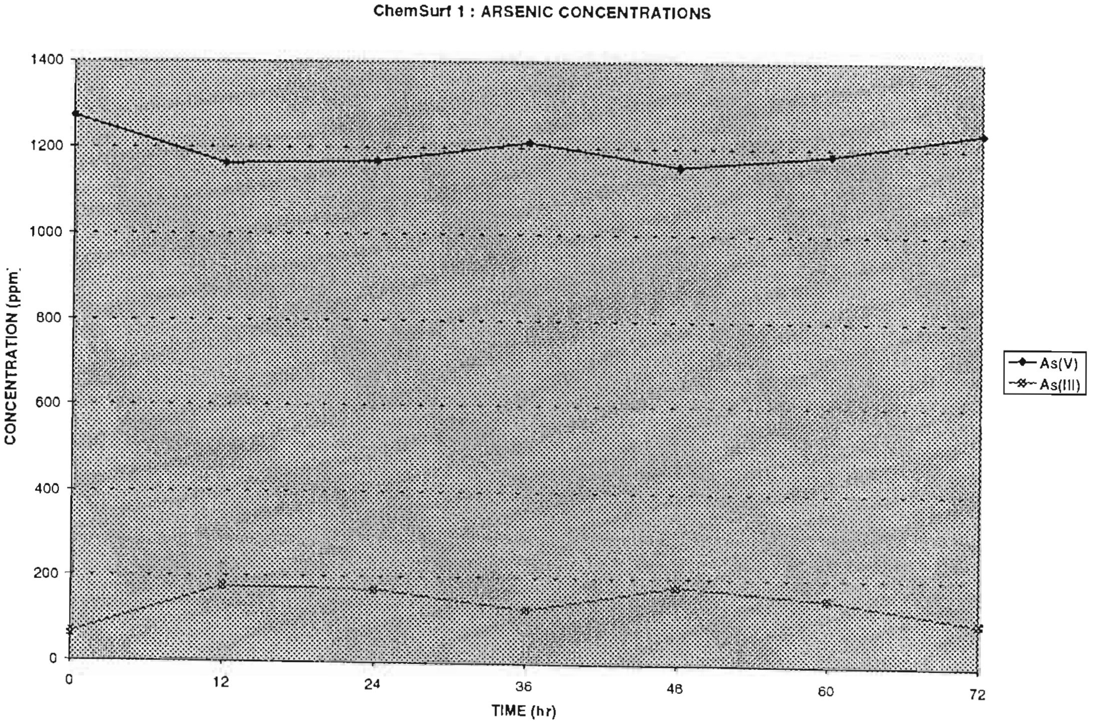
ChemSurf 1 : TEMPERATURE

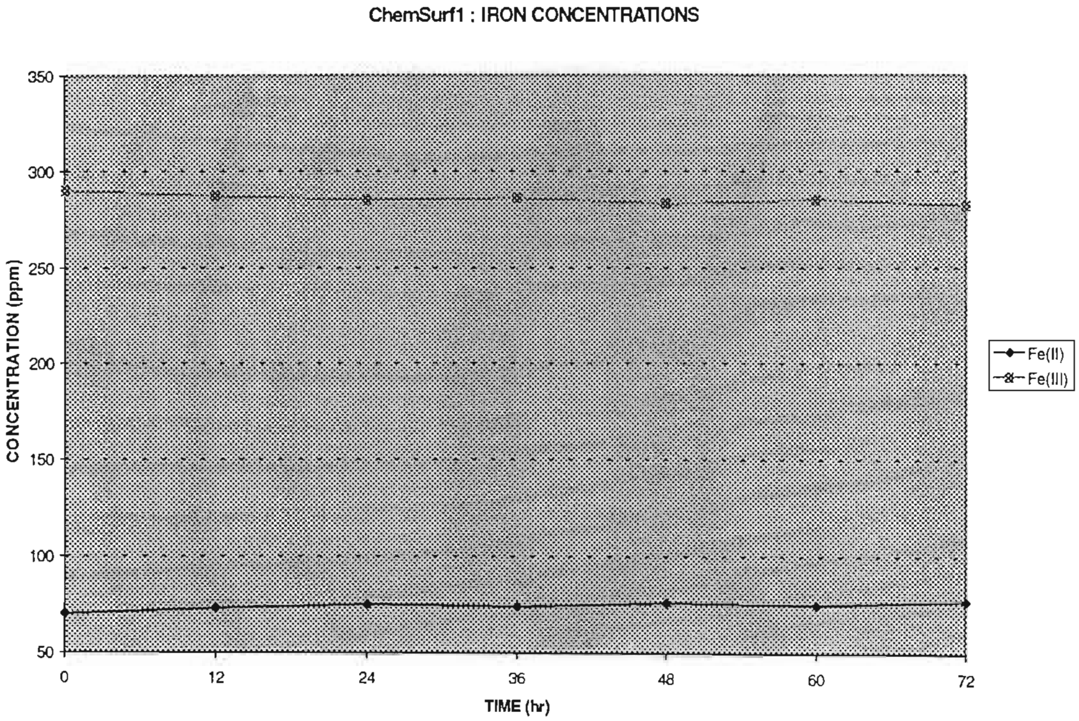


ChemSurf 1 : pH




ChemSurf 1 : REDOX POTENTIAL
REDOX POTENTIAL (mV)
585
580
575
570
565
560
555
550
545
540
535
TIME (hr)
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
48
51
54
57
60
63
66
69
72


ChemSurf 1 : ARSENIC CONCENTRATIONS
CONCENTRATION (ppm)
1400
1200
1000
800
600
400
200
0
TIME (hr)
0
12
24
36
48
60
72
As(V)
As(III)


ChemSurf1 : IRON CONCENTRATIONS
CONCENTRATION (ppm)
350
300
250
200
150
100
50
0
12
24
36
48
60
72
TIME (hr)
Fe(II)
Fe(III)

RESULTS: ChemSurf 2

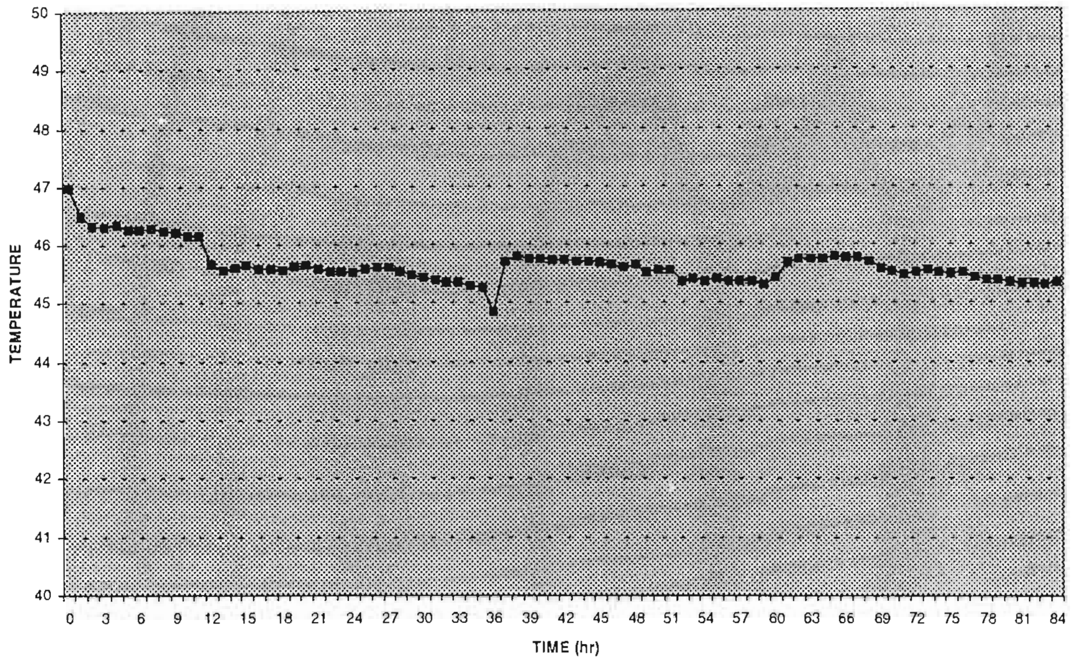
Time (hr)	Temperature (^{0} C)	pH	Redox Potential (mV)
0	46.97	1.33	585.99
1	46.48	1.34	576.76
2	46.32	1.34	570.3
3	46.29	1.34	567.72
4	46.34	1.34	570.61
5	46.25	1.35	568.15
6	46.25	1.35	570.61
7	46.27	1.35	571.53
8	46.23	1.34	568.76
9	46.21	1.34	572.76
10	46.16	1.35	571.53
11	46.16	1.34	571.84
12	45.66	1.34	577.07
13	45.56	1.34	568.76
14	45.61	1.34	575.53
15	45.64	1.34	573.38
16	45.58	1.33	572.15
17	45.58	1.34	571.53
18	45.55	1.34	573.69
19	45.62	1.34	571.84
20	45.64	1.33	569.38
21	45.58	1.34	570
22	45.54	1.34	571.53
23	45.54	1.34	570.61
24	45.52	1.33	568.76
25	45.59	1.34	569.37
26	45.61	1.34	570.92
27	45.6	1.34	570
28	45.53	1.34	572.15
29	45.47	1.34	571.84
30	45.43	1.34	575.53
31	45.4	1.34	570
32	45.35	1.34	570.92
33	45.34	1.33	569.69
34	45.29	1.34	570
35	45.27	1.33	570.3
36	44.84	1.33	570
37	45.7	1.3	569.38
38	45.8	1.31	566.92
39	45.76	1.31	570.61
40	45.76	1.31	570.3
41	45.73	1.32	570.61
42	45.73	1.31	575.53
43	45.71	1.31	571.84
44	45.71	1.32	572.76
45	45.68	1.32	569.38
46	45.65	1.32	571.53
47	45.61	1.32	567.53
48	45.64	1.3	572.15

49	45.51	1.3	572.76
50	45.57	1.31	569.07
51	45.56	1.31	569.38
52	45.37	1.31	570.3
53	45.42	1.31	573.38
54	45.38	1.3	570.92
55	45.42	1.31	569.69
56	45.37	1.31	569.69
57	45.36	1.3	569.38
58	45.37	1.3	570.92
59	45.31	1.31	572.46
60	45.43	1.29	570.3
61	45.69	1.31	569.69
62	45.74	1.31	570.3
63	45.74	1.31	567.84
64	45.76	1.31	571.84
65	45.8	1.31	570.61
66	45.78	1.31	569.38
67	45.77	1.31	570
68	45.7	1.31	575.84
69	45.59	1.31	569.38
70	45.53	1.31	570.3
71	45.48	1.31	574.61
72	45.51	1.31	570.92

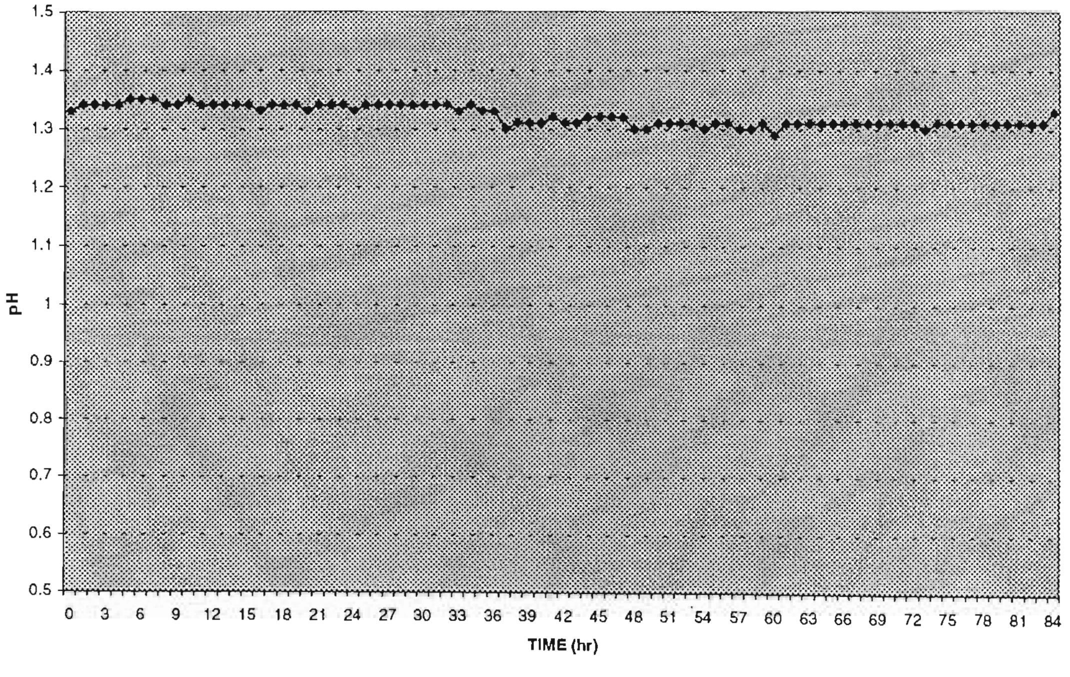
TABLE C-3.2 Results ChemSurf 2

GRAPHS: ChemSurf 2

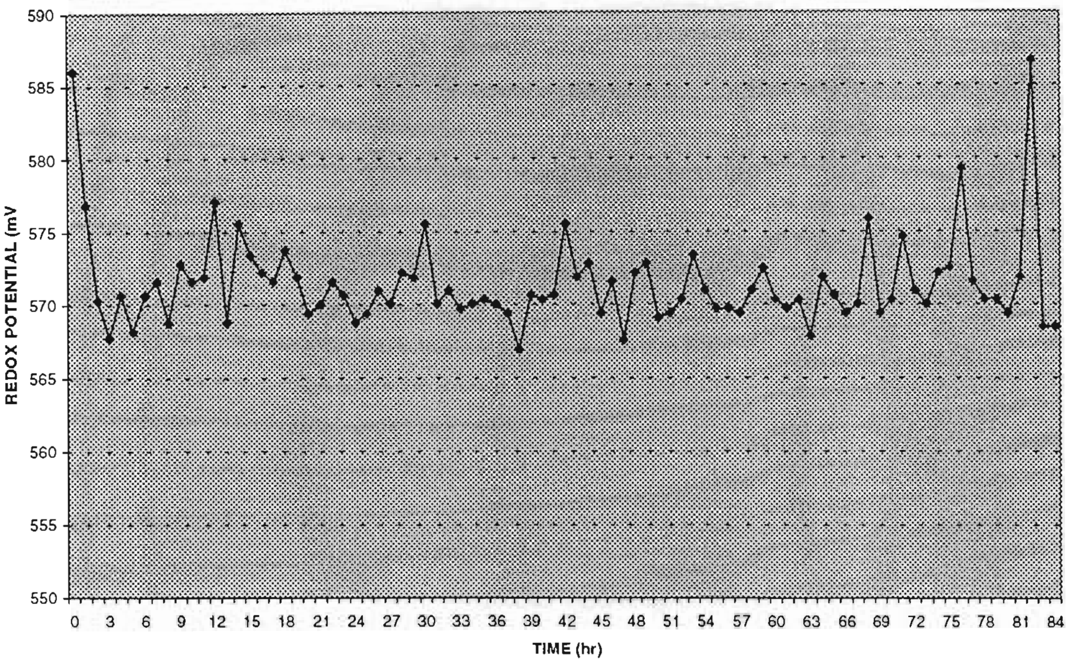
ChemSurf 2 : TEMPERATURE



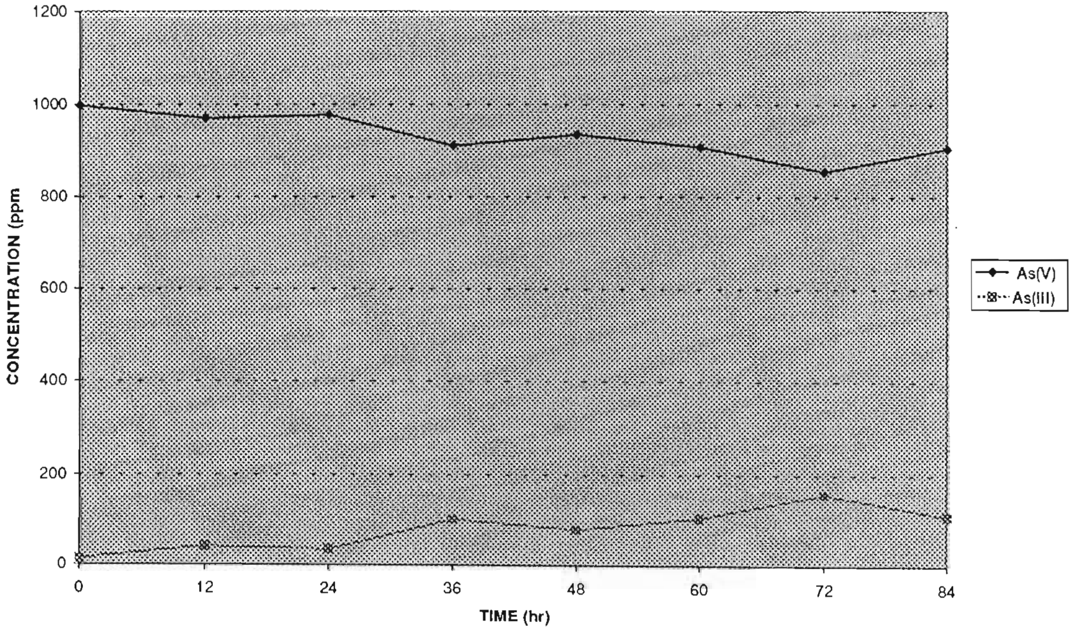
ChemSurf 2 : pH

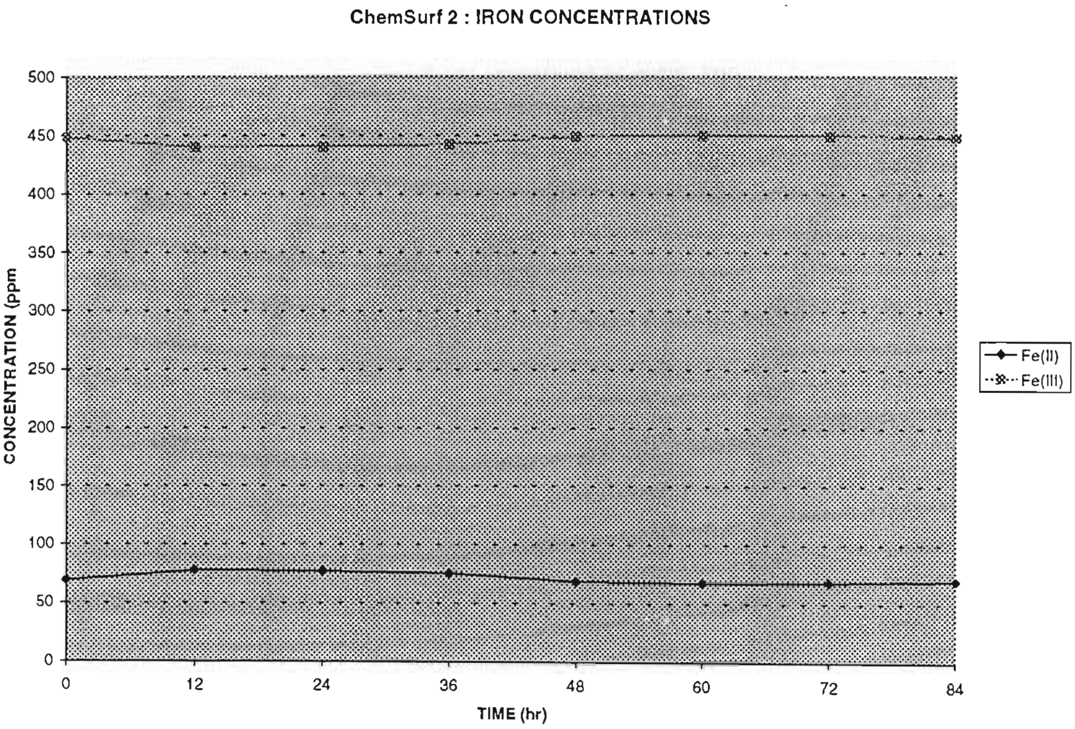


ChemSurf 2 : REDOX POTENTIAL



ChemSurf 2 : ARSENIC CONCENTRATIONS




ChemSurf 2 : IRON CONCENTRATIONS
CONCENTRATION (ppm
500
450
400
350
300
250
200
150
100
50
0
0
12
24
36
48
60
72
84
TIME (hr)
Fe(II)
Fe(III)

RESULTS: ChemSurf 3

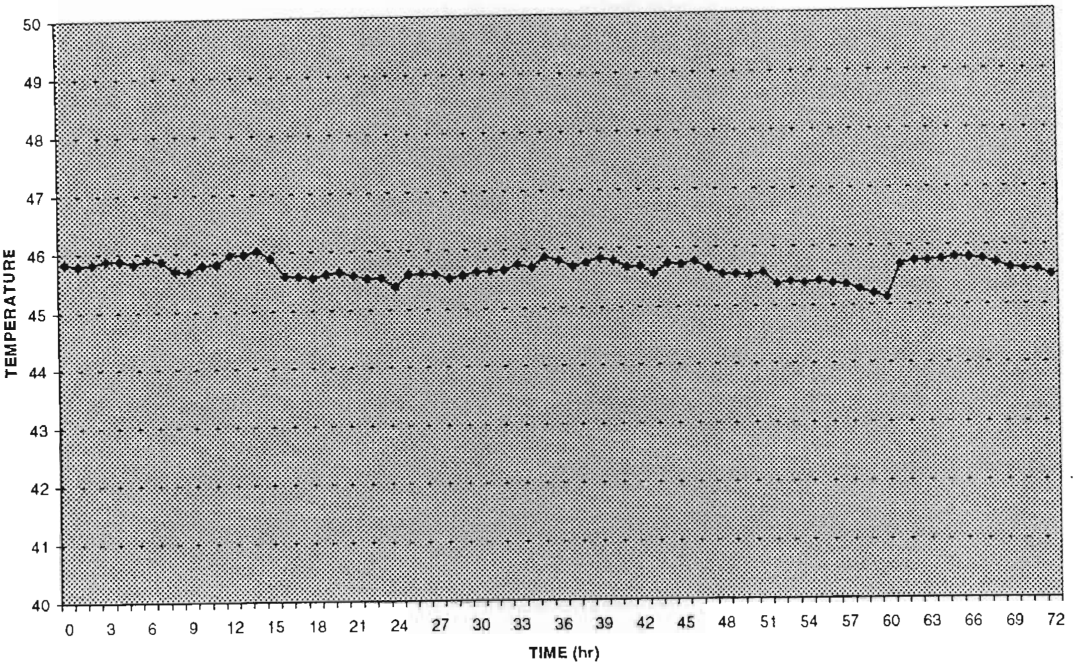
Time (hr)	Temperature (^{0}C)	pH	Redox Potential (mV)
0	45.84	1.30	554.61
1	45.80	1.34	554.69
2	45.82	1.34	553.85
3	45.88	1.34	554.60
4	45.88	1.34	553.67
5	45.82	1.35	553.19
6	45.89	1.35	552.89
7	45.85	1.35	553.17
8	45.70	1.34	552.56
9	45.69	1.34	552.89
10	45.79	1.35	553.79
11	45.80	1.34	553.98
12	45.95	1.35	552.46
13	45.96	1.35	555.23
14	46.02	1.35	558.92
15	45.89	1.34	558.19
16	45.58	1.34	557.14
17	45.58	1.34	556.28
18	45.55	1.34	558.52
19	45.62	1.34	556.47
20	45.64	1.34	554.98
21	45.58	1.34	557.25
22	45.54	1.34	554.89
23	45.54	1.34	554.23
24	45.40	1.35	554.61
25	45.59	1.34	554.87
26	45.61	1.34	554.97
27	45.60	1.34	554.25
28	45.53	1.33	554.65
29	45.57	1.33	556.32
30	45.63	1.33	555.89
31	45.64	1.31	554.92
32	45.65	1.31	556.78
33	45.74	1.32	557.02
34	45.68	1.32	555.78
35	45.87	1.3	555.14
36	45.80	1.30	554.92
37	45.70	1.30	553.87
38	45.76	1.31	553.38
39	45.83	1.31	551.36
40	45.78	1.31	549.67
41	45.69	1.29	547.00
42	45.68	1.30	543.38
43	45.56	1.29	548.69
44	45.73	1.29	543.07
45	45.72	1.28	539.53
46	45.77	1.28	541.23
47	45.64	1.28	539.84

48	45.55	1.28	538.61
49	45.54	1.29	541.08
50	45.52	1.29	540.15
51	45.56	1.29	540.85
52	45.37	1.29	542.02
53	45.42	1.29	541.08
54	45.38	1.28	542.74
55	45.42	1.28	540.41
56	45.37	1.28	542.08
57	45.36	1.28	543.87
58	45.27	1.29	542.59
59	45.19	1.27	542.42
60	45.12	1.27	542.61
61	45.69	1.27	543.69
62	45.74	1.28	542.41
63	45.74	1.28	541.08
64	45.76	1.28	540.78
65	45.80	1.28	543.09
66	45.78	1.28	542.86
67	45.77	1.28	542.74
68	45.70	1.28	543.07
69	45.62	1.27	541.95
70	45.6	1.27	542.45
71	45.58	1.27	543.98
72	45.50	1.27	542.85

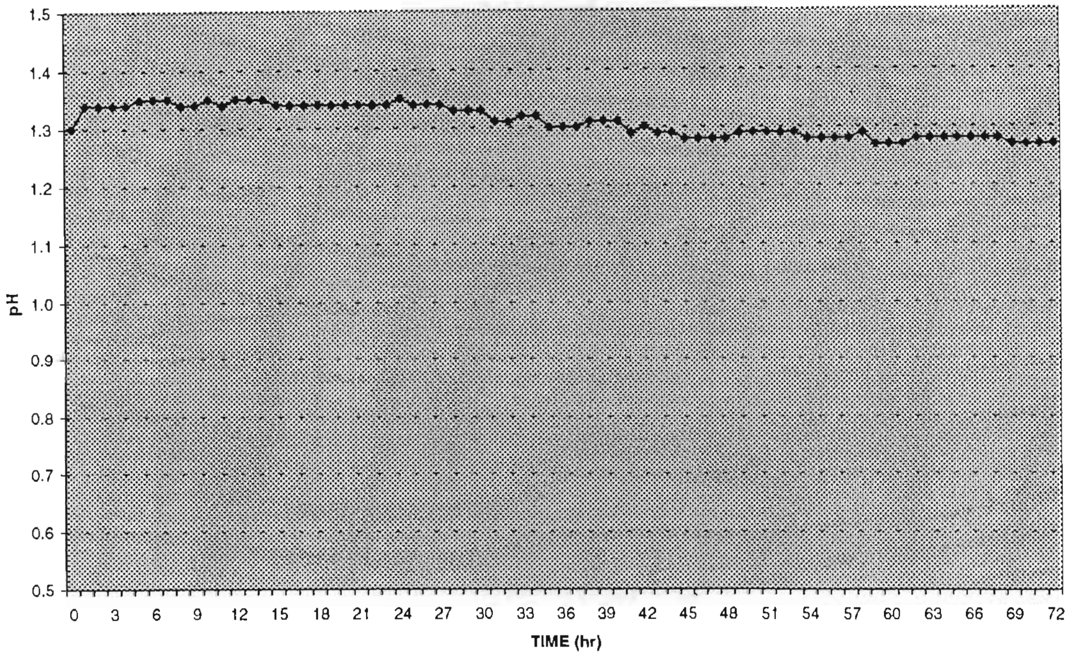
TABLE C-3.3: Results ChemSurf 3

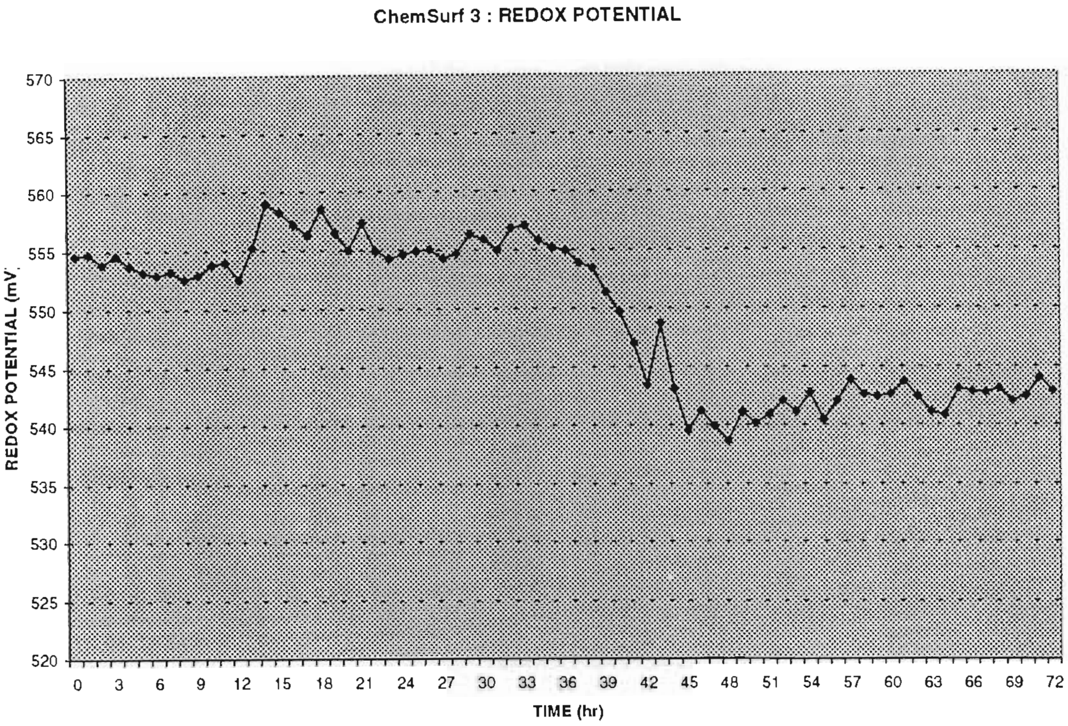
GRAPHS: ChemSurf 3

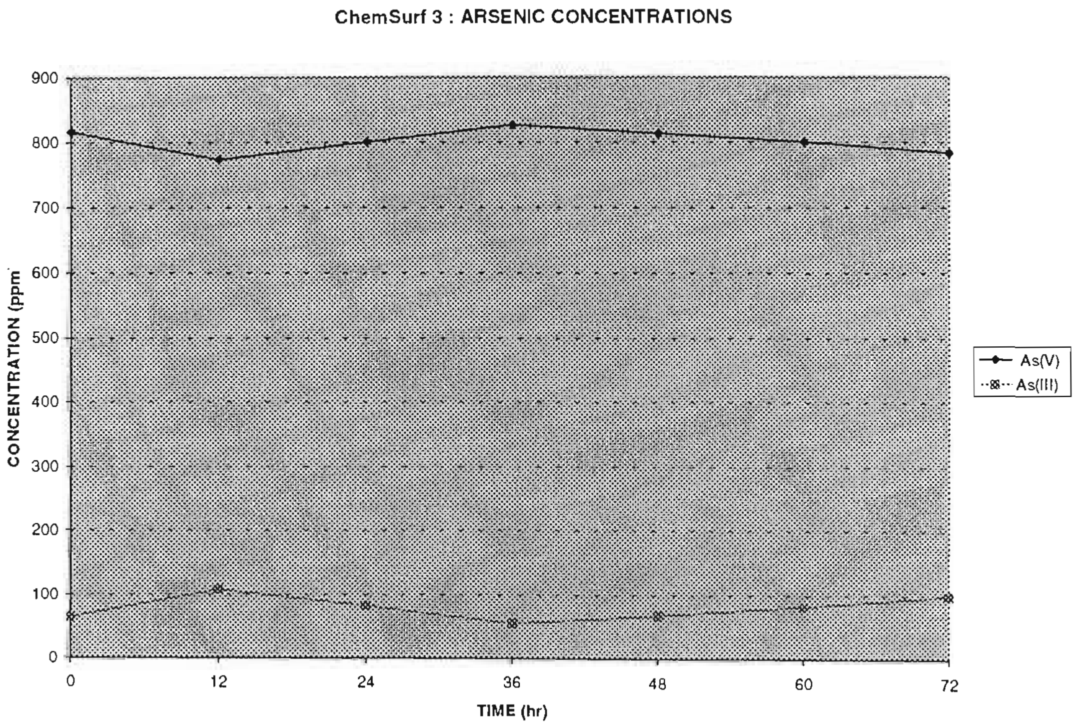
ChemSurf 3 : TEMPERATURE

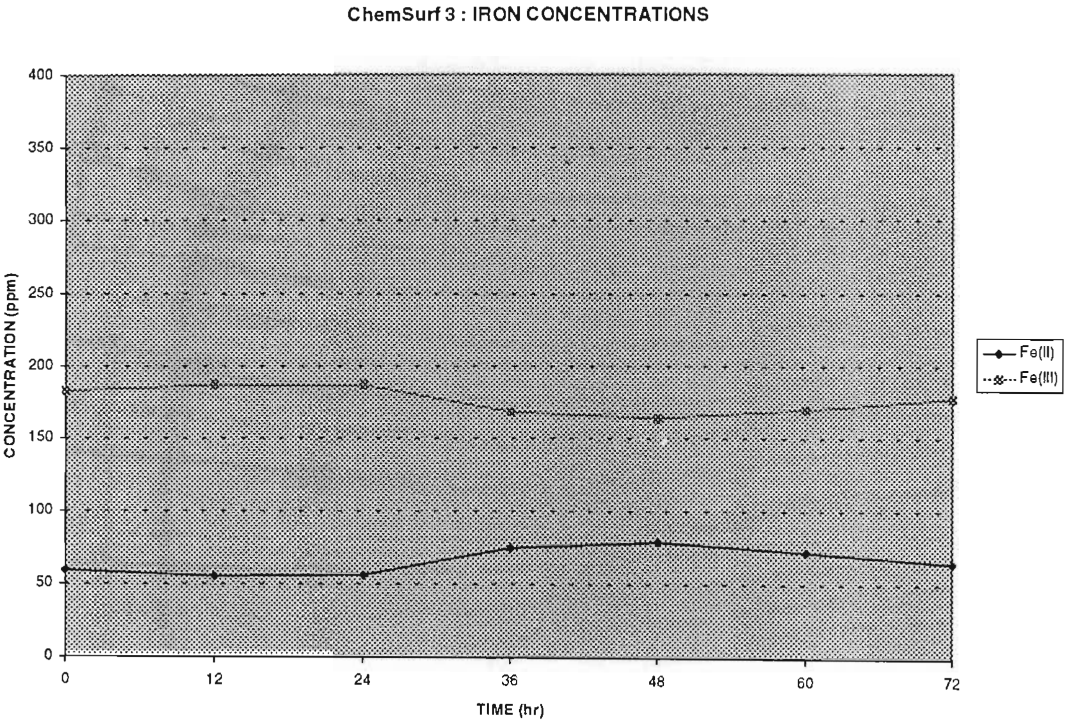


ChemSurf 3 : pH




ChemSurf 3 : REDOX POTENTIAL
REDOX POTENTIAL (mV)
570
565
560
555
550
545
540
535
530
525
520
0
3
6
9
12
15
18
21
24
27
30
33
36
39
42
45
48
51
54
57
60
63
66
69
72
TIME (hr)


ChemSurf 3 : ARSENIC CONCENTRATIONS
CONCENTRATION (ppm)
900
800
700
600
500
400
300
200
100
0
0
12
24
36
48
60
72
TIME (hr)
As(V)
As(III)


ChemSurf 3 : IRON CONCENTRATIONS
CONCENTRATION (ppm)
400
350
300
250
200
150
100
50
0
0
12
24
36
48
60
72
TIME (hr)
Fe(II)
Fe(III)

APPENDIX C-4

EXPERIMENTAL RESULTS

BACTERIAL OXIDATION OF ARSENITE IN A SYNTHETIC SOLUTION

RESULTS: BacOx1

Time (hr)	Temperature (^{0} C)	pH	Redox Potential (mV)	Dissolved Oxygen (mg/l)
0.0	37.68	1.90	512.46	7.58
0.5	38.03	1.93	522.92	7.47
1.0	38.07	1.90	519.23	7.53
1.5	38.11	1.93	540.77	7.60
2.0	38.09	1.95	587.22	7.54
2.5	38.11	1.94	664.45	7.53
3.0	38.07	1.93	665.06	7.00
3.5	38.04	1.87	676.45	7.58
4.0	38.07	1.83	676.75	7.44
4.5	38.01	1.81	677.68	7.24
5.0	38.04	1.80	675.52	6.88
5.5	38.12	1.79	676.14	6.83
6.0	38.12	1.79	676.14	7.49
6.5	38.09	1.79	675.22	7.55
7.0	38.08	1.78	676.45	7.36
7.5	38.04	1.78	677.99	6.94
8.0	38.07	1.78	676.75	7.13
8.5	38.07	1.78	677.37	7.47
9.0	38.05	1.78	677.37	7.52
9.5	38.07	1.78	677.68	6.65
10.0	38.03	1.79	677.68	7.33
10.5	38.03	1.78	676.75	7.13
11.0	38.02	1.78	683.83	7.54
11.5	37.99	1.78	678.29	7.15
12.0	38.03	1.78	679.52	7.31
12.5	38.05	1.74	676.75	7.49
13.0	38.08	1.78	676.75	6.69
13.5	38.07	1.78	677.68	7.28
14.0	38.09	1.77	677.06	7.54
14.5	38.09	1.78	681.06	7.15
15.0	38.04	1.77	679.52	6.91
15.5	38.02	1.78	680.45	7.40
16.0	38.06	1.78	676.45	7.22
16.5	38.06	1.77	676.45	7.27
17.0	38.01	1.78	677.99	7.40
17.5	37.99	1.78	679.52	7.03
18.0	38.03	1.78	680.75	7.55
18.5	38.06	1.78	675.52	7.03
19.0	38.06	1.77	677.99	6.82
19.5	38.05	1.78	677.99	6.94
20.0	38.06	1.76	677.68	7.06
20.5	38.05	1.78	677.06	7.52
21.0	38.07	1.78	678.29	8.19
21.5	38.05	1.78	677.99	7.38
22.0	38.08	1.78	685.06	7.37
22.5	38.05	1.78	678.29	6.62
23.0	38.06	1.77	678.60	8.02
23.5	38.04	1.69	691.21	7.25
24.0	38.02	1.71	680.45	7.57

24.5	38.02	1.74	681.68	7.67
25.0	38.13	1.78	681.98	7.70
25.5	38.18	1.77	677.68	7.70
26.0	38.23	1.78	677.06	7.63
26.5	38.26	1.67	686.29	7.59
27.0	38.22	1.76	684.14	7.65
27.5	38.19	1.78	675.52	7.65
28.0	38.20	1.79	677.68	7.69
28.5	38.21	1.77	684.75	7.65
29.0	38.25	1.75	683.83	7.61
29.5	38.27	1.73	678.91	7.65
30.0	38.26	1.73	677.37	7.65
30.5	38.26	1.72	676.14	7.61
31.0	38.23	1.75	676.45	7.64
31.5	38.18	1.76	676.45	7.69
32.0	38.18	1.70	679.22	7.69
32.5	38.18	1.76	675.22	7.72
33.0	38.16	1.78	681.06	7.71
33.5	38.03	1.78	674.91	7.77
34.0	38.00	1.78	677.37	7.83
34.5	38.07	1.75	684.14	7.73
35.0	38.06	1.78	683.83	7.75
35.5	38.02	1.78	677.68	7.79
36.0	38.01	1.75	684.45	7.76
36.5	38.03	1.76	677.06	7.76
37.0	37.99	1.77	678.29	7.79
37.5	37.99	1.74	679.22	7.77
38.0	37.97	1.69	681.98	7.78
38.5	37.92	1.78	678.29	7.83
39.0	37.92	1.78	679.22	7.82
39.5	37.92	1.78	678.29	7.83
40.0	37.92	1.78	679.22	7.82
40.5	37.92	1.78	678.29	7.83
41.0	37.92	1.78	679.22	7.82
41.5	37.95	1.76	681.68	7.87
42.0	37.90	1.80	677.68	7.85
42.5	37.96	1.77	681.68	7.76
43.0	37.92	1.78	678.29	7.83
43.5	37.92	1.78	679.22	7.82
44.0	37.95	1.76	681.68	7.87
44.5	37.99	1.74	679.83	7.80
45.0	38.06	1.78	674.91	7.73
45.5	38.03	1.72	677.68	7.76
46.0	38.03	1.74	678.29	7.83
46.5	38.06	1.78	679.22	7.82
47.0	38.03	1.76	681.68	7.87
47.5	38.03	1.76	679.83	7.80
48.0	38.03	1.77	677.99	7.71
48.5	38.03	1.78	677.06	7.77
49.0	38.05	1.73	677.68	7.76
49.5	38.08	1.71	678.60	7.78
50.0	38.09	1.77	673.99	7.77
50.5	38.12	1.78	675.52	7.67

51.0	38.18	1.78	679.83	7.66
51.5	38.17	1.78	682.29	7.66
52.0	38.22	1.75	676.45	7.66
52.5	38.17	1.78	680.75	7.69
53.0	38.15	1.81	677.37	7.63
53.5	38.15	1.77	675.83	7.74
54.0	38.15	1.77	677.68	7.72
54.5	38.16	1.76	677.06	7.69
55.0	38.14	1.78	676.75	7.68
55.5	38.16	1.77	676.75	7.69
56.0	38.16	1.76	681.98	7.65
56.5	38.14	1.78	677.37	7.70
57.0	38.16	1.72	679.52	7.69
57.5	38.16	1.78	678.29	7.69
58.0	38.13	1.78	682.60	7.67
58.5	38.14	1.78	676.75	7.68
59.0	38.12	1.77	677.06	7.72
59.5	38.14	1.77	679.22	7.70
60.0	38.13	1.78	678.29	7.69
60.5	38.12	1.77	680.14	7.71
61.0	38.09	1.78	678.91	7.72
61.5	38.12	1.75	677.99	7.71
62.0	38.11	1.79	680.75	7.71
62.5	38.10	1.78	676.14	7.71
63.0	38.10	1.77	679.83	7.74
63.5	38.10	1.75	678.91	7.73
64.0	38.06	1.78	681.06	7.74
64.5	38.02	1.80	683.22	7.76
65.0	38.02	1.76	667.83	7.78
65.5	38.01	1.79	674.60	7.75
66.0	38.01	1.79	675.22	7.74
66.5	37.99	1.79	680.14	7.77
67.0	38.05	1.78	680.75	7.76
67.5	37.98	1.79	680.14	7.76
68.0	37.96	1.79	676.45	7.78
68.5	37.93	1.79	677.06	7.79
69.0	37.92	1.81	675.83	7.76
69.5	37.95	1.80	681.68	7.78
70.0	37.92	1.81	677.68	7.80
70.5	37.96	1.79	682.60	7.77
71.0	37.92	1.80	677.68	7.78
71.5	38.01	1.80	676.14	7.72
72.0	38.06	1.81	681.06	7.70
72.5	37.96	1.77	662.91	7.69
73.0	38.18	1.81	661.06	7.70
73.5	38.16	1.78	668.45	7.65
74.0	38.18	1.81	669.37	7.65
74.5	38.19	1.81	661.06	7.65
75.0	38.19	1.75	662.60	7.64
75.5	38.17	1.81	662.91	7.67
76.0	38.17	1.79	662.60	7.65
76.5	38.13	1.79	659.83	7.64
77.0	38.13	1.83	664.45	7.63

77.5	38.11	1.81	662.91	7.65
78.0	38.11	1.80	661.99	7.68
78.5	38.08	1.74	673.68	7.72
79.0	38.07	1.82	661.99	7.66
79.5	38.10	1.79	664.14	7.69
80.0	38.03	1.81	665.68	7.71
80.5	38.06	1.81	660.14	7.67
81.0	38.06	1.74	664.14	7.66
81.5	38.03	1.81	661.99	7.67
82.0	38.00	1.82	663.22	7.69
82.5	38.02	1.82	663.22	7.71
83.0	37.97	1.83	661.68	7.72
83.5	38.00	1.81	665.37	7.73
84.0	37.97	1.81	662.60	7.76
84.5	37.98	1.82	667.83	7.72
85.0	37.99	1.81	661.37	7.70
85.5	37.98	1.79	660.14	7.73
86.0	37.96	1.84	665.37	7.74
86.5	37.96	1.80	664.45	7.71
87.0	37.93	1.81	662.29	7.75
87.5	37.90	1.76	663.52	7.76
88.0	37.88	1.82	660.45	7.76
88.5	37.91	1.83	662.29	7.77
89.0	37.88	1.82	664.14	7.81
89.5	37.87	1.80	663.83	7.78
90.0	37.85	1.82	660.14	7.78
90.5	37.85	1.81	660.76	7.82
91.0	37.95	1.83	661.68	7.67
91.5	37.95	1.80	663.52	7.76
92.0	37.92	1.82	666.29	7.74
92.5	37.96	1.76	665.68	7.71
93.0	37.96	1.82	660.76	7.72
93.5	37.92	1.88	660.45	7.70
94.0	37.89	1.75	666.91	7.71
94.5	37.89	1.83	665.99	7.72
95.0	37.93	1.84	662.91	7.70
95.5	38.03	1.81	661.06	7.63
96.0	38.04	1.79	664.14	7.63
96.5	38.09	1.82	665.68	7.68
97.0	38.09	1.84	663.83	7.63
97.5	38.08	1.83	661.37	7.61
98.0	38.07	1.80	661.68	7.58
98.5	38.09	1.85	663.52	7.59
99.0	38.06	1.79	664.76	7.60
99.5	38.03	1.83	662.60	7.63
100.0	38.02	1.80	663.83	7.64
100.5	37.94	1.64	661.99	7.64
101.0	38.00	1.85	649.06	7.68
101.5	37.97	1.84	657.99	7.65
102.0	37.98	1.85	660.76	7.67
102.5	37.97	1.67	661.99	7.66
103.0	37.96	1.83	653.06	7.66
103.5	37.97	1.85	645.07	7.65

104.0	37.98	1.83	650.60	7.66
104.5	37.95	1.76	662.60	7.65
105.0	37.93	1.64	661.37	7.70
105.5	37.93	1.81	666.29	7.67
106.0	37.92	1.82	653.06	7.68
106.5	37.93	1.81	645.07	7.67
107.0	37.91	1.82	646.91	7.67
107.5	37.89	1.78	650.91	7.67
108.0	37.89	1.82	649.68	7.70
108.5	37.86	1.82	648.45	7.66
109.0	37.85	1.83	646.91	7.68
109.5	37.85	1.80	645.68	7.67
110.0	37.85	1.79	644.76	7.65
110.5	37.82	1.83	648.45	7.68
111.0	37.82	1.65	649.68	7.67
111.5	37.81	1.83	650.60	7.69
112.0	37.81	1.78	646.91	7.67
112.5	37.78	1.83	647.22	7.67
113.0	37.78	1.74	649.68	7.68
113.5	37.78	1.81	657.37	7.62
114.0	37.79	1.77	649.06	7.66
114.5	37.82	1.84	649.37	7.65
115.0	37.80	1.82	652.45	7.64
115.5	37.84	1.81	649.68	7.66
116.0	37.81	1.85	650.30	7.65
116.5	37.85	1.82	649.06	7.62
117.0	37.85	1.85	645.68	7.64
117.5	37.88	1.88	649.06	7.62
118.0	37.80	1.82	652.45	7.64
118.5	37.84	1.81	649.68	7.66
119.0	37.85	1.85	645.68	7.64
119.5	37.88	1.88	649.06	7.62
120.0	37.88	1.83	648.14	7.62
120.5	37.93	1.85	646.60	7.60
121.0	37.98	1.81	645.07	7.57
121.5	38.05	1.80	648.45	7.53
122.0	38.07	1.77	649.06	7.46
122.5	38.10	1.74	662.60	7.44
123.0	38.10	1.75	655.83	7.45
123.5	38.08	1.67	660.14	7.45
124.0	38.07	1.71	672.75	7.44
124.5	38.05	1.73	662.29	7.42
125.0	38.03	1.74	650.60	7.45
125.5	38.03	1.69	663.83	7.44
126.0	38.00	1.75	647.22	7.45
126.5	37.99	1.71	649.37	7.43
127.0	37.95	1.74	651.83	7.44
127.5	37.96	1.71	645.37	7.45
128.0	37.92	1.65	647.22	7.44
128.5	37.93	1.75	647.53	7.42
129.0	37.94	1.72	646.60	7.37
129.5	37.94	1.66	659.22	7.33
130.0	37.95	1.75	661.37	7.24

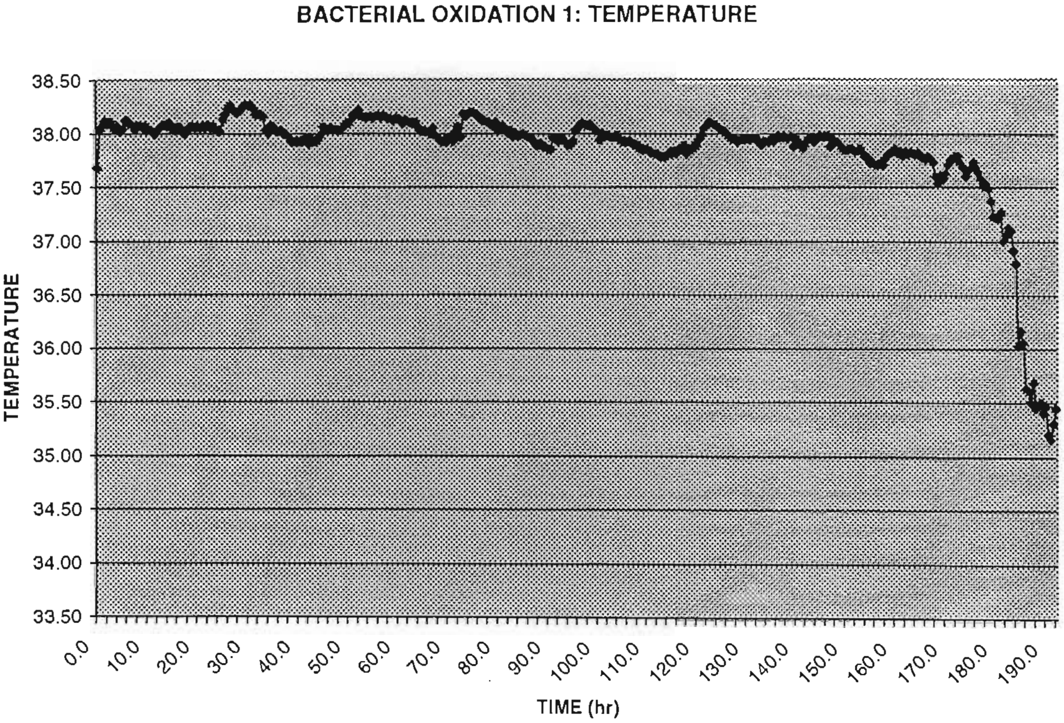
130.5	37.94	1.69	662.91	7.19
131.0	37.96	1.73	661.06	7.01
131.5	37.95	1.67	669.68	7.00
132.0	37.96	1.69	661.99	6.93
132.5	37.92	1.75	681.06	6.90
133.0	37.89	1.65	670.60	6.86
133.5	37.92	1.75	676.45	6.79
134.0	37.92	1.65	665.68	6.76
134.5	37.92	1.75	663.22	6.63
135.0	37.94	1.76	668.45	6.79
135.5	37.92	1.64	674.29	6.73
136.0	37.96	1.74	689.37	6.79
136.5	37.98	1.78	662.29	6.81
137.0	37.96	1.77	665.68	6.73
137.5	37.97	1.77	660.76	6.63
138.0	37.96	1.74	669.68	6.77
138.5	37.95	1.78	645.37	6.77
139.0	37.97	1.69	665.06	6.69
139.5	37.88	1.79	669.68	7.10
140.0	37.94	1.66	664.14	6.84
140.5	37.91	1.65	658.29	6.96
141.0	37.88	1.67	661.06	6.74
141.5	37.86	1.66	676.45	7.05
142.0	37.91	1.70	662.91	7.03
142.5	37.95	1.70	651.83	7.44
143.0	37.96	1.71	645.37	7.45
143.5	37.92	1.65	647.22	7.44
144.0	37.93	1.75	647.53	7.42
144.5	37.96	1.74	689.37	6.79
145.0	37.98	1.78	662.29	6.81
145.5	37.96	1.77	665.68	6.73
146.0	37.97	1.77	660.76	6.63
146.5	37.97	1.69	665.06	6.69
147.0	37.88	1.79	669.68	7.10
147.5	37.94	1.66	664.14	6.84
148.0	37.91	1.67	658.29	6.96
148.5	37.91	1.69	658.29	6.96
149.0	37.88	1.71	661.06	6.74
149.5	37.86	1.69	676.45	7.05
150.0	37.84	1.73	678.32	6.95
150.5	37.84	1.75	679.52	6.80
151.0	37.85	1.77	664.45	6.90
151.5	37.84	1.79	665.37	6.93
152.0	37.83	1.79	666.60	7.27
152.5	37.84	1.78	664.14	7.27
153.0	37.85	1.76	672.45	7.35
153.5	37.82	1.76	666.29	7.36
154.0	37.78	1.77	665.99	7.35
154.5	37.78	1.78	668.14	7.37
155.0	37.72	1.79	669.06	7.40
155.5	37.72	1.78	672.75	7.41
156.0	37.71	1.79	662.91	7.29
156.5	37.70	1.78	664.45	7.38

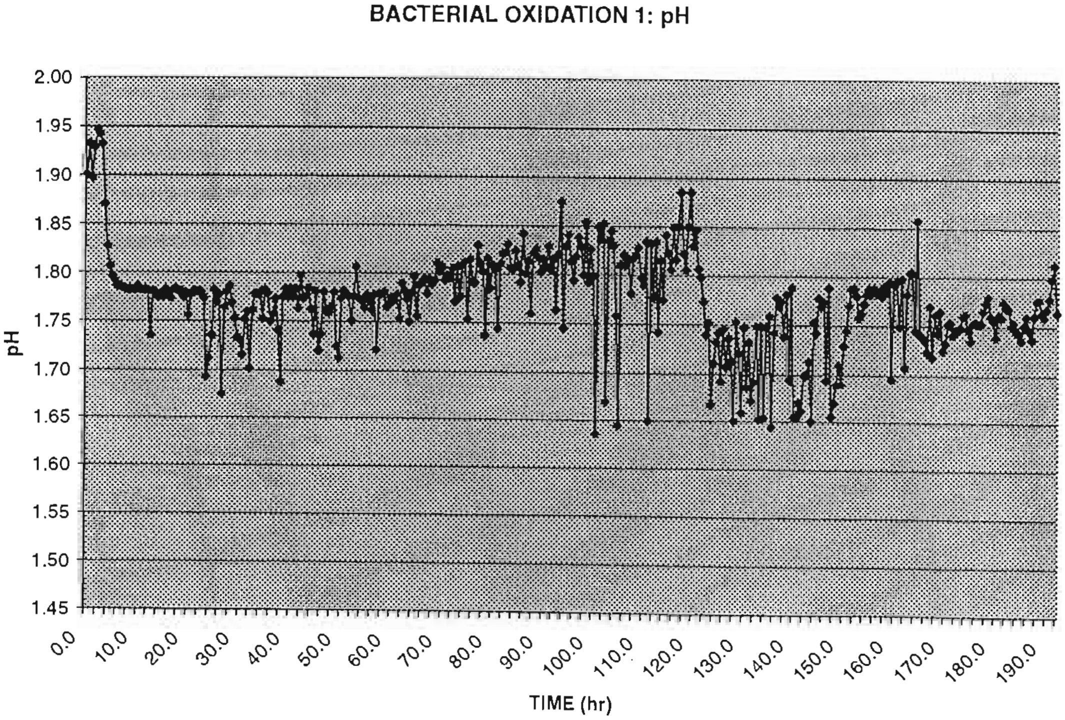
157.0	37.71	1.78	661.06	7.37
157.5	37.70	1.78	663.22	7.28
158.0	37.76	1.79	661.06	7.15
158.5	37.80	1.79	666.29	7.24
159.0	37.82	1.79	660.76	7.23
159.5	37.82	1.70	659.22	6.80
160.0	37.85	1.79	664.14	6.70
160.5	37.81	1.80	665.37	6.75
161.0	37.83	1.75	675.83	6.78
161.5	37.79	1.80	662.91	6.74
162.0	37.83	1.71	660.45	6.70
162.5	37.80	1.78	664.14	6.91
163.0	37.82	1.80	666.91	6.91
163.5	37.81	1.80	658.60	6.75
164.0	37.80	1.75	678.29	6.77
164.5	37.82	1.86	651.53	6.85
165.0	37.78	1.74	677.99	6.63
165.5	37.77	1.74	677.37	6.62
166.0	37.75	1.74	660.45	7.00
166.5	37.78	1.72	678.29	6.93
167.0	37.76	1.77	680.45	6.83
167.5	37.73	1.72	676.14	6.93
168.0	37.59	1.76	680.45	6.62
168.5	37.53	1.74	677.99	6.89
169.0	37.60	1.77	660.14	6.76
169.5	37.56	1.73	662.29	6.64
170.0	37.62	1.73	675.83	6.67
170.5	37.70	1.75	679.22	6.86
171.0	37.75	1.75	667.52	6.84
171.5	37.75	1.74	678.29	8.07
172.0	37.79	1.75	677.37	6.83
172.5	37.79	1.75	678.60	8.45
173.0	37.72	1.75	677.37	6.76
173.5	37.67	1.76	675.83	8.39
174.0	37.60	1.76	685.37	6.66
174.5	37.65	1.75	677.68	8.48
175.0	37.67	1.73	674.60	7.50
175.5	37.73	1.75	678.60	8.30
176.0	37.67	1.75	680.75	8.40
176.5	37.63	1.75	675.52	8.38
177.0	37.58	1.75	676.75	7.31
177.5	37.51	1.77	677.37	8.43
178.0	37.53	1.77	678.91	8.34
178.5	37.48	1.78	674.29	7.45
179.0	37.37	1.76	677.37	8.06
179.5	37.22	1.76	679.22	7.67
180.0	37.22	1.74	678.60	7.91
180.5	37.21	1.76	677.68	8.45
181.0	37.26	1.76	677.06	8.37
181.5	37.00	1.77	677.37	7.64
182.0	37.05	1.77	677.68	7.87
182.5	37.12	1.77	678.91	8.21
183.0	37.10	1.75	678.60	8.34

183.5	36.91	1.75	677.68	8.05
184.0	36.79	1.75	677.37	7.19
184.5	36.02	1.74	676.14	8.25
185.0	36.17	1.74	677.06	7.93
185.5	36.06	1.75	675.22	6.63
186.0	35.63	1.76	677.37	8.24
186.5	35.61	1.75	675.52	8.06
187.0	35.50	1.74	678.60	6.62
187.5	35.68	1.76	682.60	6.65
188.0	35.45	1.78	676.45	7.34
188.5	35.47	1.78	677.68	6.93
189.0	35.50	1.76	677.99	6.65
189.5	35.40	1.76	675.83	6.89
190.0	35.46	1.77	676.14	7.91
190.5	35.20	1.78	676.45	6.62
191.0	35.16	1.80	678.29	7.65
191.5	35.31	1.81	675.52	6.66
192.0	35.45	1.76	676.75	6.94

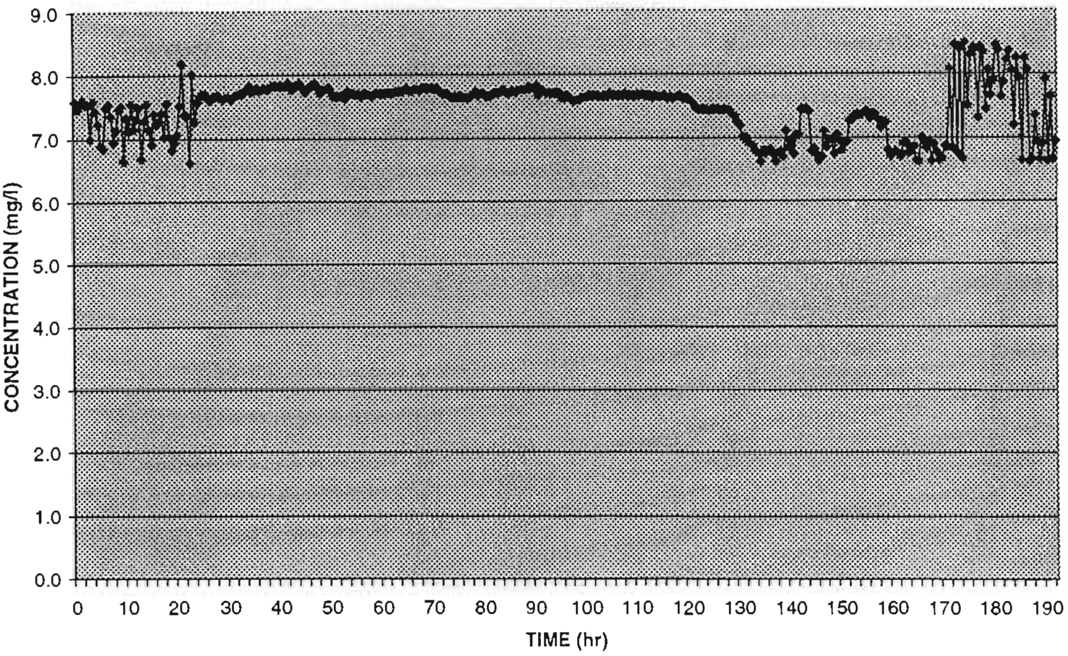
TABLE C-4.1: Results BacOx 1

GRAPHS: BacOx1

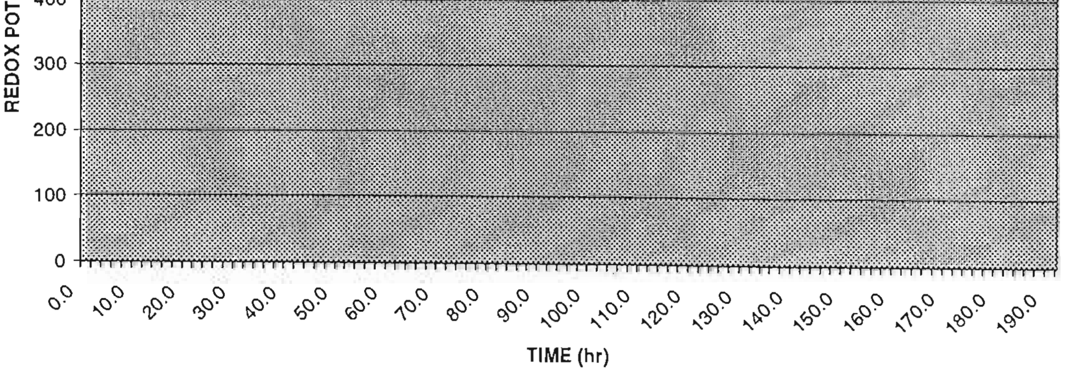




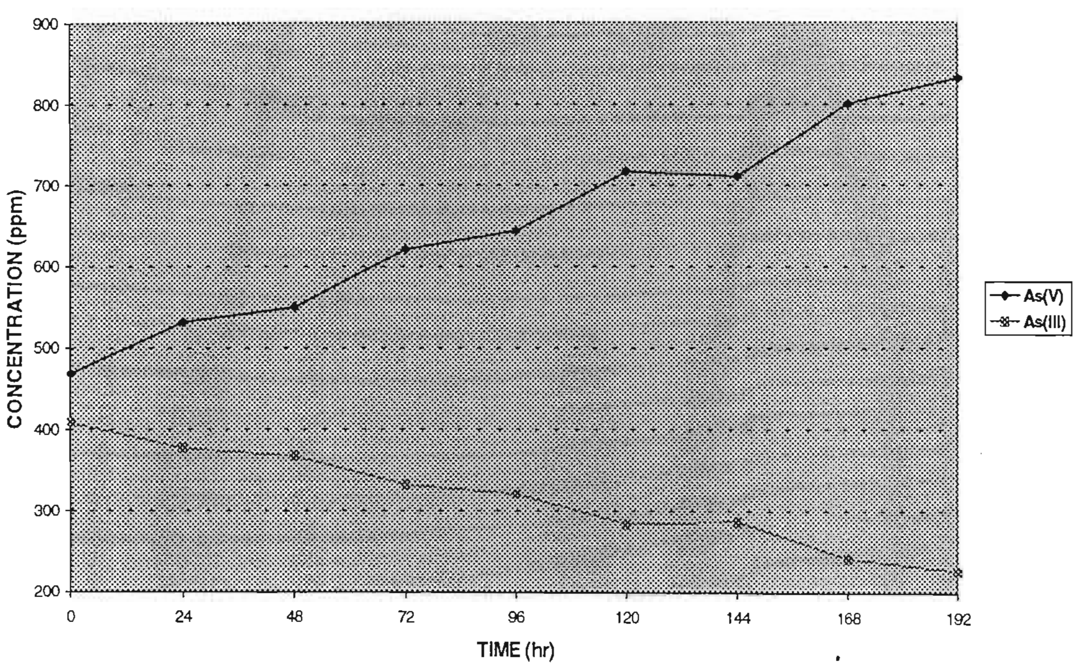
BACTERIAL OXIDATION 1: DISSOLVED OXYGEN CONCENTRATION



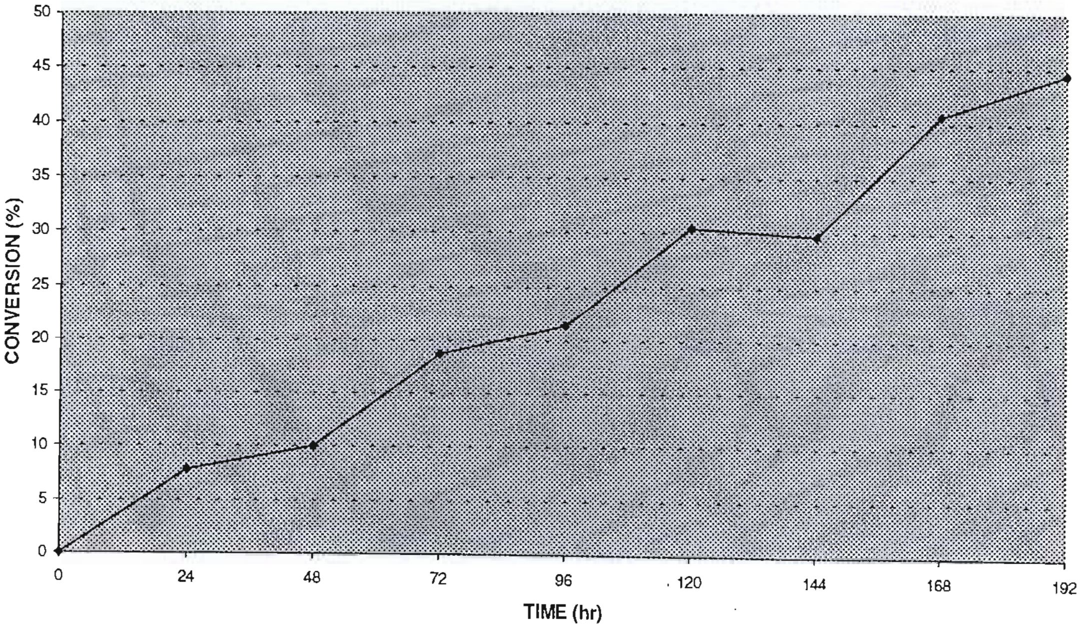
BACTERIAL OXIDATION 1 REDOX POTENTIAL

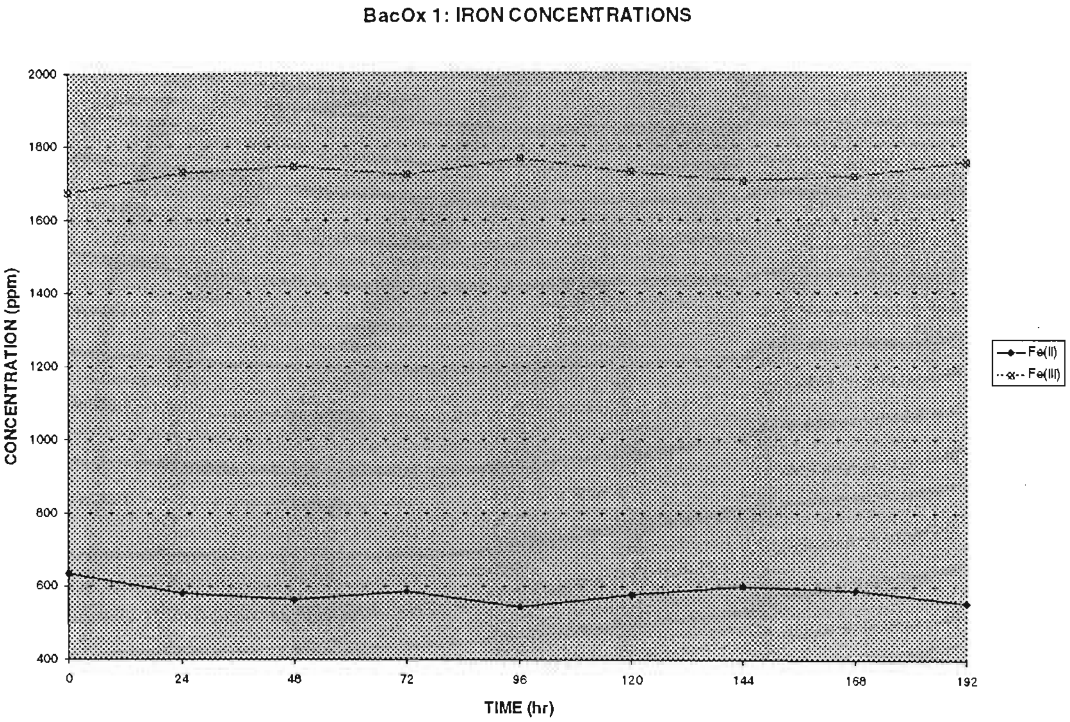


BacOx 1: ARSENIC CONCENTRATIONS



BacOx 1: ARSENITE CONVERSION




BacOx 1: IRON CONCENTRATIONS
CONCENTRATION (ppm)
2000
1800
1600
1400
1200
1000
800
600
400
0
24
48
72
96
120
144
168
192
TIME (hr)
Fe(II)
Fe(III)

RESULTS: BacOx2

Time (hr)	Temperature (^{0}C)	pH	Redox Pot.ential (mV)	Dissolved Oxygen (mg/l)
0.0	37.80	1.69	630.60	7.58
0.5	38.04	1.69	635.53	7.47
1.0	38.11	1.69	630.91	7.53
1.5	38.11	1.68	629.07	7.60
2.0	38.10	1.68	628.76	7.54
2.5	38.09	1.68	630.60	7.53
3.0	38.10	1.68	630.91	7.00
3.5	38.11	1.68	627.84	7.58
4.0	38.09	1.68	632.45	7.44
4.5	38.06	1.68	634.30	7.24
5.0	38.09	1.68	632.76	6.88
5.5	38.06	1.69	631.84	6.83
6.0	38.05	1.68	633.99	7.49
6.5	38.04	1.69	633.37	7.55
7.0	38.03	1.68	633.22	7.36
7.5	38.01	1.68	631.84	6.94
8.0	37.99	1.68	627.84	7.13
8.5	37.95	1.68	633.07	7.47
9.0	37.95	1.68	628.14	7.52
9.5	37.93	1.68	630.30	6.65
10.0	37.95	1.68	635.53	7.33
10.5	37.92	1.68	631.84	7.13
11.0	37.95	1.67	632.45	7.54
11.5	37.94	1.67	629.68	7.15
12.0	37.90	1.67	632.45	7.31
12.5	37.91	1.67	632.14	7.49
13.0	37.91	1.67	631.84	6.69
13.5	37.87	1.67	632.14	7.28
14.0	37.88	1.67	632.14	7.54
14.5	37.90	1.67	631.22	7.15
15.0	37.92	1.67	631.22	6.91
15.5	37.90	1.67	629.68	7.40
16.0	37.92	1.67	629.68	7.22
16.5	37.94	1.67	631.53	7.27
17.0	37.96	1.67	632.14	7.40
17.5	37.97	1.67	638.30	7.03
18.0	37.98	1.67	630.91	7.55
18.5	37.98	1.67	631.22	7.03
19.0	38.00	1.67	630.91	6.82
19.5	37.96	1.67	631.84	6.94
20.0	37.95	1.67	629.99	7.06
20.5	37.92	1.67	631.22	7.52
21.0	37.92	1.67	632.14	8.19
21.5	37.92	1.67	632.76	7.38
22.0	37.92	1.67	634.30	7.37
22.5	37.92	1.67	631.53	6.62
23.0	37.91	1.67	633.07	8.02
23.5	37.89	1.67	631.53	7.25
24.0	37.92	1.67	633.07	7.57

24.5	38.03	1.66	634.30	7.67
25.0	38.08	1.67	633.37	7.70
25.5	38.06	1.67	629.68	7.70
26.0	38.06	1.66	631.22	7.63
26.5	38.06	1.66	631.53	7.59
27.0	38.03	1.67	633.99	7.65
27.5	38.03	1.66	633.07	7.65
28.0	38.02	1.66	631.22	7.69
28.5	38.03	1.66	630.91	7.65
29.0	38.02	1.66	633.07	7.61
29.5	38.04	1.66	629.68	7.65
30.0	38.04	1.66	632.14	7.65
30.5	38.03	1.66	628.76	7.61
31.0	38.00	1.66	632.14	7.64
31.5	37.99	1.66	631.22	7.69
32.0	38.01	1.66	631.22	7.69
32.5	38.00	1.66	629.99	7.72
33.0	37.99	1.66	631.84	7.71
33.5	38.01	1.65	633.99	7.77
34.0	37.98	1.66	638.30	7.83
34.5	37.97	1.65	630.91	7.73
35.0	37.98	1.65	636.14	7.75
35.5	37.95	1.66	632.76	7.79
36.0	37.94	1.66	632.14	7.76
36.5	37.89	1.65	630.30	7.76
37.0	37.88	1.65	631.84	7.79
37.5	37.86	1.65	632.76	7.77
38.0	37.80	1.65	631.22	7.78
38.5	37.78	1.65	633.68	7.83
39.0	37.83	1.65	633.37	7.82
39.5	37.73	1.66	629.99	7.83
40.0	37.51	1.65	631.53	7.82
40.5	37.80	1.64	631.53	7.83
41.0	37.81	1.64	630.91	7.82
41.5	37.76	1.65	634.30	7.87
42.0	37.74	1.64	632.76	7.85
42.5	37.76	1.64	629.37	7.76
43.0	37.77	1.65	629.99	7.83
43.5	37.86	1.64	630.30	7.82
44.0	37.93	1.64	630.60	7.87
44.5	37.95	1.65	630.60	7.80
45.0	37.92	1.64	630.91	7.73
45.5	37.77	1.64	630.30	7.76
46.0	37.73	1.64	629.68	7.83
46.5	37.79	1.64	629.63	7.82
47.0	37.81	1.64	629.52	7.87
47.5	37.75	1.64	628.89	7.80
48.0	37.68	1.64	628.76	7.71
48.5	37.76	1.64	627.84	7.77
49.0	37.85	1.64	631.84	7.76
49.5	37.87	1.64	629.99	7.78
50.0	37.85	1.64	634.60	7.77
50.5	37.88	1.64	631.22	7.67

51.0	37.85	1.64	635.84	7.66
51.5	37.85	1.64	632.45	7.66
52.0	37.85	1.64	630.91	7.66
52.5	37.87	1.64	639.22	7.69
53.0	37.83	1.64	630.60	7.63
53.5	37.83	1.64	631.22	7.74
54.0	37.84	1.64	629.07	7.72
54.5	37.82	1.64	632.14	7.69
55.0	37.82	1.64	634.60	7.68
55.5	37.81	1.64	636.76	7.69
56.0	37.83	1.64	631.22	7.65
56.5	37.80	1.64	627.53	7.70
57.0	37.77	1.64	638.91	7.69
57.5	37.77	1.64	630.60	7.69
58.0	37.72	1.64	631.22	7.67
58.5	37.68	1.64	633.07	7.68
59.0	37.69	1.64	631.53	7.72
59.5	37.71	1.64	630.30	7.70
60.0	37.78	1.64	629.99	7.69
60.5	37.82	1.63	632.76	7.71
61.0	37.79	1.63	629.37	7.72
61.5	37.80	1.64	629.99	7.71
62.0	37.77	1.64	633.99	7.71
62.5	37.75	1.63	628.45	7.71
63.0	37.81	1.64	630.30	7.74
63.5	37.82	1.64	633.07	7.73
64.0	37.81	1.64	630.60	7.74
64.5	37.76	1.64	631.22	7.76
65.0	37.73	1.64	631.84	7.78
65.5	37.75	1.63	633.07	7.75
66.0	37.79	1.63	634.91	7.74
66.5	37.83	1.63	636.14	7.77
67.0	37.42	1.66	631.22	7.76
67.5	38.10	1.63	629.99	7.76
68.0	38.15	1.63	630.91	7.78
68.5	38.15	1.63	630.60	7.79
69.0	38.11	1.63	632.45	7.76
69.5	38.05	1.63	629.07	7.78
70.0	38.09	1.63	632.14	7.80
70.5	38.10	1.63	631.42	7.77
71.0	38.14	1.63	632.84	7.78
71.5	38.16	1.63	633.99	7.72
72.0	38.18	1.63	630.91	7.70
72.5	38.19	1.63	632.14	7.69
73.0	38.14	1.63	632.76	7.70
73.5	38.18	1.62	631.22	7.65
74.0	38.18	1.63	630.30	7.65
74.5	38.18	1.62	633.37	7.65
75.0	38.16	1.62	629.68	7.64
75.5	38.19	1.63	632.76	7.67
76.0	38.20	1.64	631.84	7.65
76.5	38.19	1.62	632.45	7.64
77.0	38.13	1.62	632.76	7.63

77.5	38.12	1.62	630.60	7.65
78.0	38.16	1.63	630.30	7.68
78.5	38.12	1.62	630.91	7.72
79.0	38.15	1.62	633.37	7.66
79.5	38.15	1.62	637.37	7.69
80.0	38.13	1.62	629.07	7.71
80.5	38.12	1.62	630.60	7.67
81.0	38.09	1.62	630.91	7.66
81.5	38.10	1.62	631.22	7.67
82.0	38.02	1.62	629.99	7.69
82.5	38.06	1.62	633.37	7.71
83.0	38.08	1.62	637.37	7.72
83.5	38.11	1.64	634.91	7.73
84.0	38.14	1.63	630.60	7.76
84.5	38.20	1.62	630.60	7.72
85.0	38.20	1.62	634.91	7.70
85.5	38.18	1.62	631.22	7.73
86.0	38.18	1.63	633.37	7.74
86.5	38.19	1.63	637.37	7.71
87.0	38.14	1.63	634.91	7.75
87.5	38.18	1.62	630.60	7.76
88.0	38.18	1.63	630.60	7.76
88.5	38.18	1.62	634.91	7.77
89.0	38.16	1.62	631.22	7.81
89.5	38.19	1.63	629.99	7.78
90.0	38.20	1.64	633.37	7.78
90.5	38.19	1.62	630.60	7.82
91.0	38.14	1.62	629.07	7.67
91.5	38.10	1.62	634.30	7.76
92.0	38.15	1.62	629.07	7.74
92.5	38.15	1.62	634.91	7.71
93.0	38.11	1.62	631.22	7.72
93.5	38.05	1.62	630.60	7.70
94.0	38.09	1.62	634.91	7.71
94.5	38.16	1.62	631.22	7.72
95.0	38.12	1.62	629.99	7.70
95.5	38.15	1.62	633.37	7.63
96.0	38.16	1.62	633.07	7.63
96.5	38.18	1.62	637.53	7.68
97.0	38.15	1.62	632.76	7.63
97.5	38.11	1.62	632.45	7.61
98.0	38.09	1.62	629.99	7.58
98.5	38.08	1.62	633.37	7.59
99.0	38.08	1.62	630.60	7.60
99.5	38.06	1.62	629.07	7.63
100.0	38.05	1.62	634.30	7.64
100.5	38.04	1.62	629.07	7.64
101.0	38.01	1.62	634.91	7.68
101.5	38.05	1.62	631.22	7.65
102.0	38.06	1.62	632.45	7.67
102.5	38.09	1.62	630.30	7.66
103.0	38.11	1.63	630.63	7.66
103.5	38.13	1.62	630.91	7.65

104.0	38.11	1.62	630.30	7.66
104.5	38.12	1.63	634.91	7.65
105.0	38.11	1.62	633.07	7.70
105.5	38.12	1.62	631.22	7.67
106.0	38.11	1.62	616.76	7.68
106.5	38.09	1.62	614.91	7.67
107.0	38.08	1.62	617.38	7.67
107.5	38.04	1.62	618.30	7.67
108.0	38.01	1.62	616.14	7.70
108.5	38.02	1.62	615.22	7.66
109.0	38.04	1.62	616.45	7.68
109.5	38.05	1.62	614.61	7.67
110.0	38.06	1.62	614.91	7.65
110.5	38.09	1.62	618.91	7.68
111.0	38.11	1.62	614.91	7.67
111.5	38.10	1.62	615.84	7.69
112.0	38.11	1.62	622.30	7.67
112.5	38.11	1.63	616.76	7.67
113.0	38.13	1.62	614.91	7.68
113.5	38.09	1.62	615.53	7.62
114.0	38.14	1.62	615.53	7.66
114.5	38.18	1.62	614.61	7.65
115.0	38.19	1.62	614.61	7.64
115.5	38.22	1.61	614.91	7.66
116.0	38.21	1.62	613.99	7.65
116.5	38.18	1.62	616.14	7.62
117.0	38.25	1.62	617.68	7.64
117.5	38.27	1.61	613.99	7.62
118.0	38.22	1.62	617.38	7.64
118.5	38.16	1.62	615.84	7.66
119.0	37.70	1.63	613.99	7.64
119.5	38.24	1.62	618.91	7.62
120.0	38.30	1.61	616.45	7.62
120.5	38.29	1.61	614.30	7.60
121.0	38.30	1.61	615.22	7.57
121.5	38.27	1.61	616.45	7.53
122.0	38.29	1.61	615.84	7.46
122.5	38.30	1.61	617.38	7.44
123.0	38.28	1.61	614.30	7.45
123.5	38.21	1.61	617.07	7.45
124.0	38.23	1.61	615.84	7.44
124.5	38.27	1.61	619.22	7.42
125.0	38.26	1.61	616.14	7.45
125.5	38.22	1.61	616.14	7.44
126.0	38.25	1.61	615.22	7.45
126.5	38.26	1.61	621.38	7.43
127.0	38.24	1.62	616.45	7.44
127.5	38.23	1.62	614.30	7.45
128.0	38.18	1.62	615.53	7.44
128.5	38.18	1.62	618.91	7.42
129.0	38.18	1.62	620.45	7.37
129.5	38.20	1.61	613.99	7.33
130.0	38.22	1.61	615.22	7.24

130.5	38.20	1.61	613.68	7.19
131.0	38.21	1.61	614.91	7.01
131.5	38.20	1.61	612.45	7.00
132.0	38.19	1.61	618.91	6.93
132.5	38.19	1.61	612.15	6.90
133.0	38.18	1.61	615.84	6.86
133.5	38.18	1.61	615.53	6.79
134.0	38.17	1.61	616.45	6.76
134.5	38.17	1.61	615.53	6.63
135.0	38.21	1.61	615.22	6.79
135.5	38.22	1.61	613.38	6.73
136.0	38.27	1.61	615.53	6.79
136.5	38.28	1.61	615.53	6.81
137.0	38.31	1.61	617.38	6.73
137.5	38.35	1.61	615.53	6.63
138.0	38.42	1.61	618.91	6.77
138.5	38.48	1.61	615.22	6.77
139.0	38.49	1.61	616.14	6.69
139.5	38.53	1.61	615.22	7.10
140.0	38.54	1.61	617.07	6.84
140.5	38.53	1.61	616.14	6.96
141.0	38.52	1.61	616.14	6.74
141.5	38.51	1.61	617.07	7.05
142.0	38.48	1.61	616.45	7.03
142.5	38.40	1.60	615.84	7.44
143.0	38.38	1.60	616.52	7.45
143.5	38.39	1.60	614.87	7.44
144.0	38.41	1.60	613.07	7.42
144.5	38.36	1.60	617.99	6.79
145.0	38.37	1.60	617.99	6.81
145.5	38.39	1.60	618.61	6.73
146.0	38.42	1.60	619.53	6.63
146.5	38.39	1.60	617.07	6.69
147.0	38.40	1.60	617.68	7.10
147.5	38.36	1.60	615.22	6.84
148.0	38.40	1.60	621.38	6.96
148.5	38.40	1.60	617.99	6.96
149.0	38.40	1.59	615.82	6.74
149.5	38.38	1.59	613.99	7.05
150.0	38.35	1.60	615.22	6.95
150.5	38.35	1.60	618.30	6.80
151.0	38.34	1.59	616.14	6.90
151.5	38.33	1.60	617.99	6.93
152.0	38.31	1.60	615.22	7.27
152.5	38.30	1.60	615.22	7.27
153.0	38.29	1.60	616.76	7.35
153.5	38.27	1.60	614.61	7.36
154.0	38.28	1.59	614.30	7.35
154.5	38.25	1.60	617.07	7.37
155.0	38.25	1.60	618.30	7.40
155.5	38.26	1.60	614.61	7.41
156.0	38.26	1.60	614.30	7.29
156.5	38.25	1.59	615.53	7.38

157.0	38.25	1.59	616.76	7.37
157.5	38.22	1.60	617.07	7.28
158.0	38.21	1.59	618.61	7.15
158.5	38.19	1.59	613.99	7.24
159.0	38.19	1.60	614.91	7.23
159.5	38.20	1.59	618.30	6.80
160.0	38.16	1.59	615.22	6.70
160.5	38.17	1.59	616.76	6.75
161.0	38.17	1.60	615.22	6.78
161.5	38.17	1.59	618.61	6.74
162.0	38.19	1.59	615.84	6.70
162.5	38.22	1.60	616.14	6.91
163.0	38.19	1.59	617.07	6.91
163.5	38.19	1.59	615.22	6.75
164.0	38.20	1.60	619.22	6.77
164.5	38.16	1.59	615.22	6.85
165.0	38.14	1.60	617.68	6.63
165.5	38.13	1.59	615.84	6.62
166.0	38.16	1.60	615.22	7.00
166.5	38.20	1.60	616.76	6.93
167.0	38.14	1.60	614.91	6.83
167.5	38.10	1.60	615.22	6.93
168.0	38.07	1.60	618.61	6.62
168.5	38.06	1.59	615.84	6.89
169.0	38.06	1.59	616.14	6.76
169.5	38.13	1.59	618.91	6.64
170.0	38.16	1.59	613.68	6.67
170.5	38.15	1.59	621.68	6.86
171.0	38.11	1.59	621.68	6.84
171.5	38.08	1.59	614.30	8.07
172.0	38.09	1.59	615.22	6.83
172.5	38.03	1.59	616.14	8.45
173.0	38.05	1.59	613.99	6.76
173.5	38.05	1.59	613.99	8.39
174.0	38.05	1.59	615.84	6.66
174.5	38.00	1.59	616.45	8.48
175.0	37.99	1.59	615.53	7.50
175.5	38.01	1.59	615.84	8.30
176.0	37.99	1.59	618.91	8.40
176.5	38.00	1.59	613.38	8.38
177.0	37.94	1.59	619.22	7.31
177.5	37.96	1.59	614.61	8.43
178.0	37.94	1.59	613.68	8.34
178.5	37.92	1.59	616.45	7.45
179.0	37.85	1.59	617.38	8.06
179.5	37.83	1.59	615.84	7.67
180.0	37.79	1.59	615.84	7.91
180.5	37.84	1.59	616.45	8.45
181.0	37.85	1.59	613.99	8.37
181.5	37.76	1.59	602.30	7.64
182.0	37.72	1.59	598.92	7.87
182.5	37.68	1.59	600.76	8.21
183.0	37.73	1.59	599.22	8.34

183.5	37.79	1.59	602.30	8.05
184.0	37.78	1.58	600.45	7.19
184.5	37.75	1.58	599.22	8.25
185.0	37.85	1.59	600.76	7.93
185.5	37.86	1.59	599.53	6.63
186.0	37.91	1.58	600.15	8.24
186.5	37.91	1.58	602.61	8.06
187.0	37.89	1.58	603.53	6.62
187.5	37.88	1.59	602.61	6.65
188.0	37.90	1.58	600.76	7.34
188.5	37.89	1.59	599.22	6.93
189.0	37.84	1.58	602.61	6.65
189.5	37.88	1.59	598.92	6.89
190.0	37.86	1.59	598.30	7.91
190.5	37.91	1.59	600.76	6.62
191.0	37.96	1.58	603.84	7.65
191.5	37.94	1.58	601.58	6.66
192.0	37.92	1.58	599.22	6.94
192.5	37.93	1.58	603.22	7.93
193.0	37.87	1.58	598.61	6.63
193.5	37.87	1.58	599.53	8.24
194.0	37.84	1.58	601.99	8.06
194.5	37.83	1.58	599.53	6.62
195.0	37.85	1.58	600.76	6.65
195.5	37.88	1.58	600.15	7.34
196.0	37.86	1.59	600.76	6.93
196.5	37.80	1.58	600.45	6.65
197.0	37.77	1.58	601.07	6.89
197.5	37.77	1.58	599.53	7.91
198.0	37.75	1.58	605.99	7.82
198.5	37.73	1.58	602.92	7.45
199.0	37.73	1.58	601.07	6.62
199.5	37.73	1.58	598.30	6.65
200.0	37.84	1.58	599.84	7.34
200.5	37.91	1.57	601.38	6.93
201.0	37.90	1.57	599.22	6.65
201.5	37.88	1.58	598.61	6.89
202.0	37.85	1.58	602.61	7.91
202.5	37.86	1.58	606.91	6.62
203.0	37.85	1.58	602.61	7.65
203.5	37.86	1.58	601.38	6.66
204.0	37.87	1.58	597.99	6.94
204.5	37.84	1.57	597.38	7.27
205.0	37.81	1.58	600.45	7.35
205.5	37.82	1.58	603.22	7.36
206.0	37.78	1.58	603.84	7.35
206.5	37.79	1.57	598.30	7.37
207.0	37.83	1.57	602.61	7.40
207.5	37.77	1.58	606.30	7.41
208.0	37.67	1.58	598.92	7.29
208.5	37.78	1.57	604.76	7.38
209.0	37.84	1.57	600.15	7.37
209.5	37.93	1.57	599.22	7.28

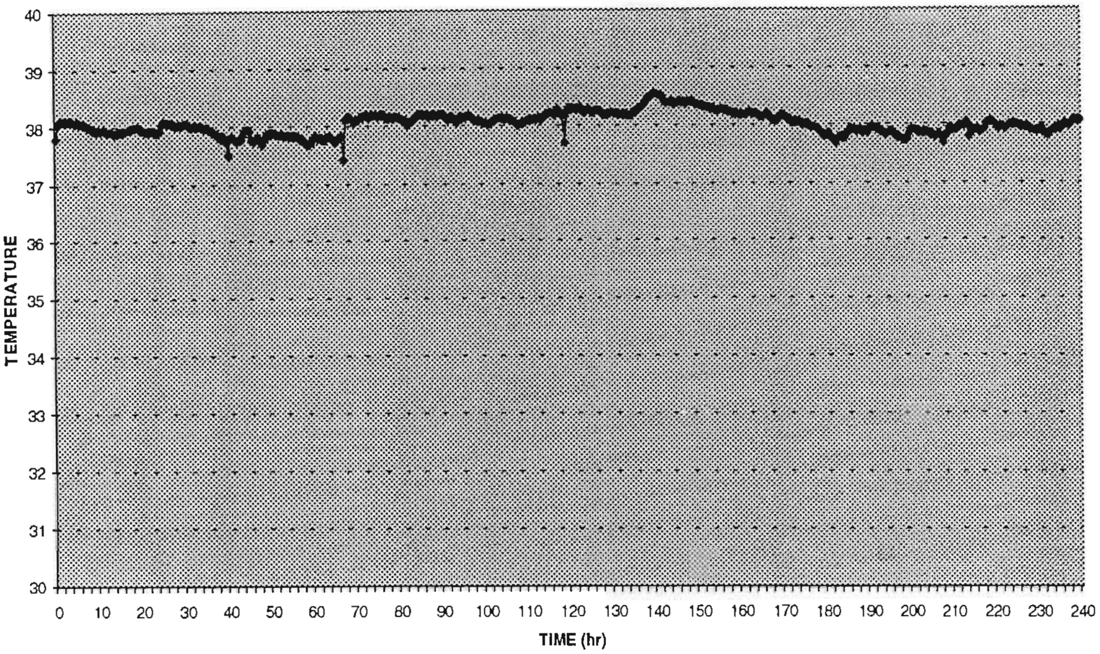
210.0	37.91	1.57	600.45	7.15
210.5	37.89	1.58	598.92	7.24
211.0	37.90	1.57	598.61	7.23
211.5	37.96	1.57	598.61	7.65
212.0	37.96	1.57	601.68	7.64
212.5	37.98	1.57	599.22	7.66
213.0	37.98	1.57	601.07	7.65
213.5	38.04	1.57	602.30	7.62
214.0	37.79	1.58	601.07	7.64
214.5	37.94	1.57	599.84	7.62
215.0	37.87	1.57	600.45	7.64
215.5	37.90	1.57	599.53	7.66
216.0	37.91	1.57	601.07	7.64
216.5	37.86	1.57	605.68	7.62
217.0	37.87	1.57	599.22	7.62
217.5	37.90	1.57	601.99	7.60
218.0	38.00	1.57	599.22	7.57
218.5	38.02	1.57	597.38	7.71
219.0	38.03	1.57	600.45	7.71
219.5	38.03	1.57	603.53	7.74
220.0	38.00	1.57	598.30	7.73
220.5	37.98	1.57	610.91	7.74
221.0	37.92	1.57	608.15	7.76
221.5	37.95	1.57	602.30	7.78
222.0	37.96	1.57	605.38	7.75
222.5	37.91	1.57	602.61	7.74
223.0	37.94	1.58	599.53	7.77
223.5	37.97	1.57	605.38	7.76
224.0	37.99	1.57	598.61	7.62
224.5	38.00	1.57	599.53	7.64
225.0	37.99	1.57	599.53	7.62
225.5	37.98	1.57	601.07	7.64
226.0	37.95	1.57	599.22	7.66
226.5	37.95	1.57	599.22	7.64
227.0	37.94	1.57	599.22	7.62
227.5	37.95	1.57	607.22	7.62
228.0	37.94	1.57	601.07	7.60
228.5	37.89	1.56	599.22	7.57
229.0	37.88	1.57	599.22	7.71
229.5	37.87	1.57	603.53	7.71
230.0	37.87	1.57	600.45	7.74
230.5	37.90	1.57	602.92	7.73
231.0	37.93	1.56	598.30	7.76
231.5	37.84	1.56	602.92	7.78
232.0	37.82	1.56	601.99	7.75
232.5	37.80	1.56	600.76	7.74
233.0	37.86	1.57	597.99	7.77
233.5	37.89	1.57	605.07	7.76
234.0	37.91	1.57	598.61	7.45
234.5	37.90	1.57	597.99	8.06
235.0	37.96	1.57	593.38	7.67
235.5	37.90	1.57	600.15	7.91
236.0	37.99	1.57	598.92	8.45

236.5	38.01	1.57	601.38	8.37
237.0	37.98	1.56	599.53	7.64
237.5	37.96	1.57	599.53	7.87
238.0	38.01	1.57	603.22	8.21
238.5	38.07	1.56	600.76	8.34
239.0	38.06	1.56	598.30	8.05
239.5	38.04	1.56	594.61	7.84
240.0	38.06	1.56	600.15	7.64

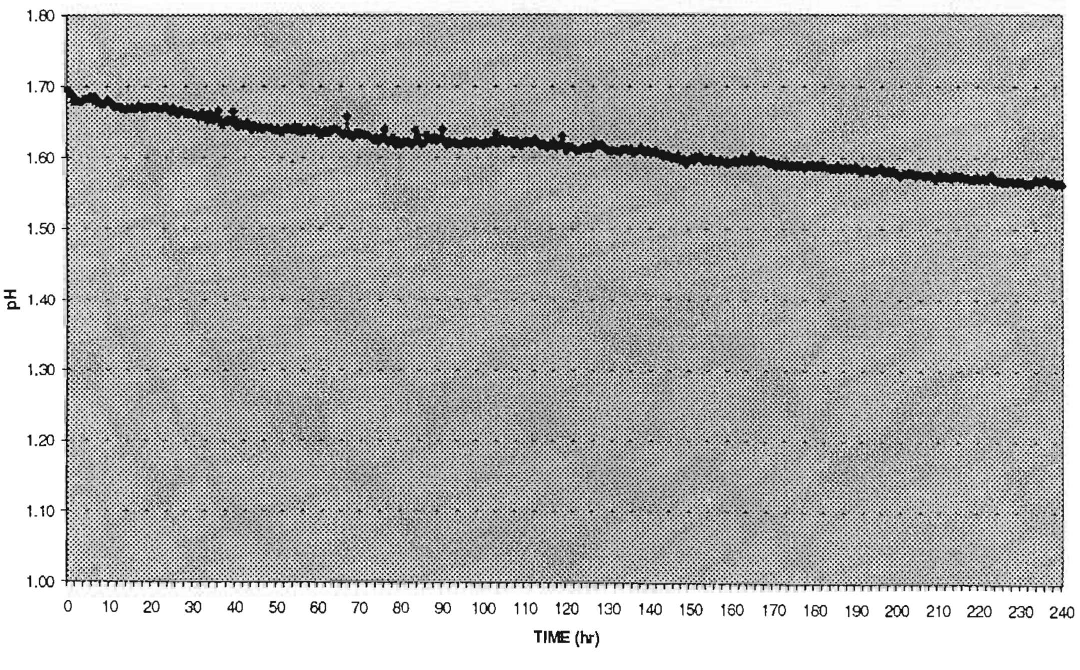
TABLE C-4.2: Results BacOx 2

GRAPHS : BacOx 2

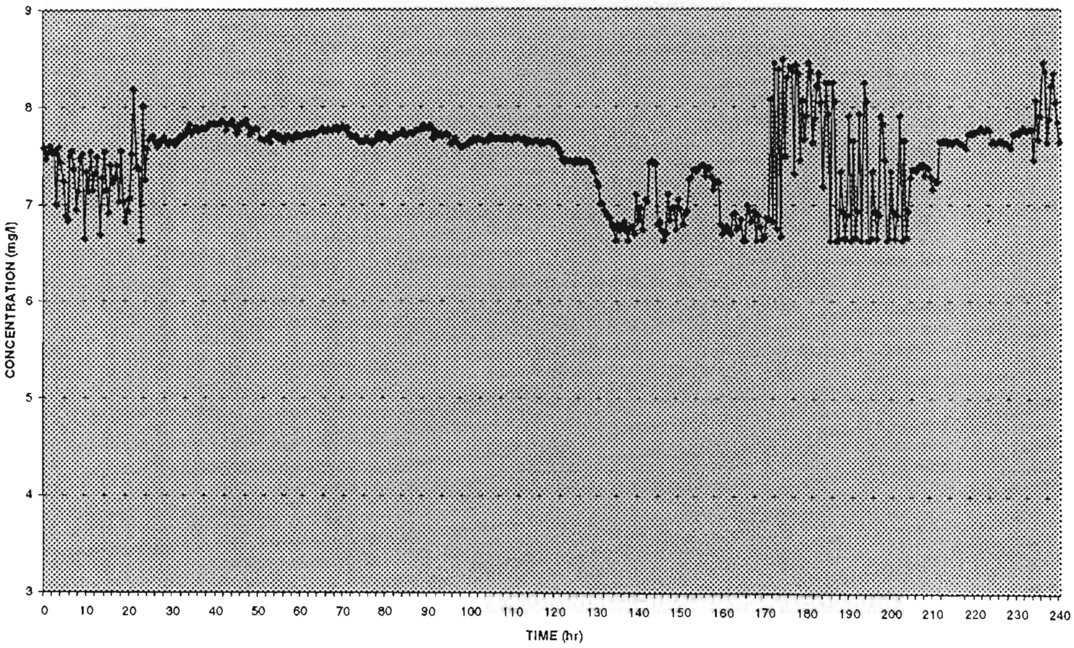
BacOx 2: TEMPERATURE



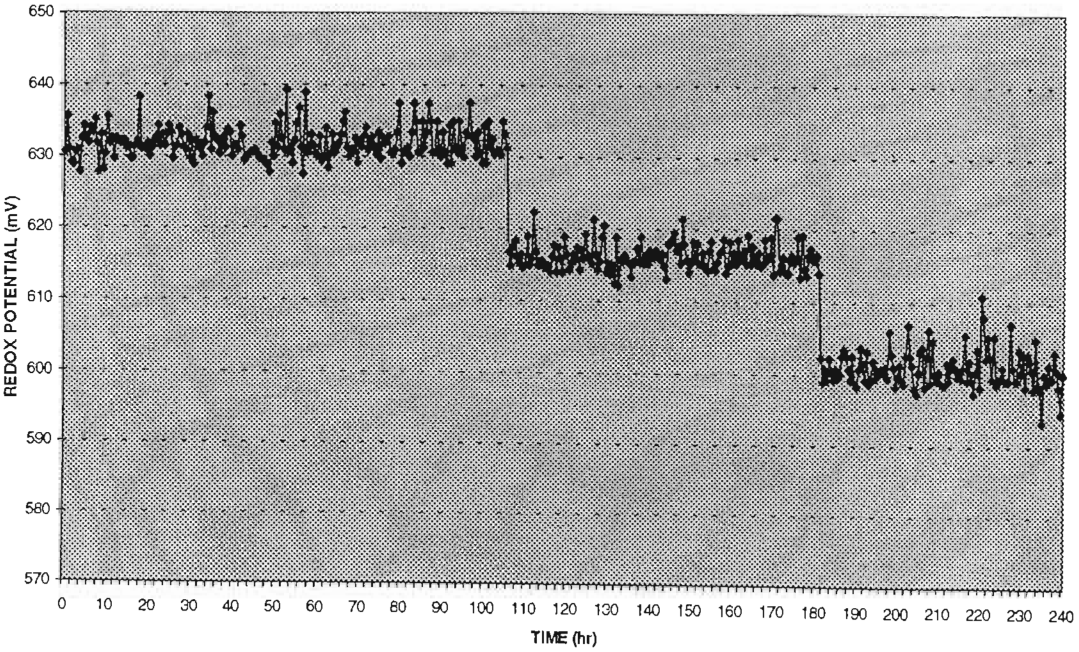
BacOx 2: pH

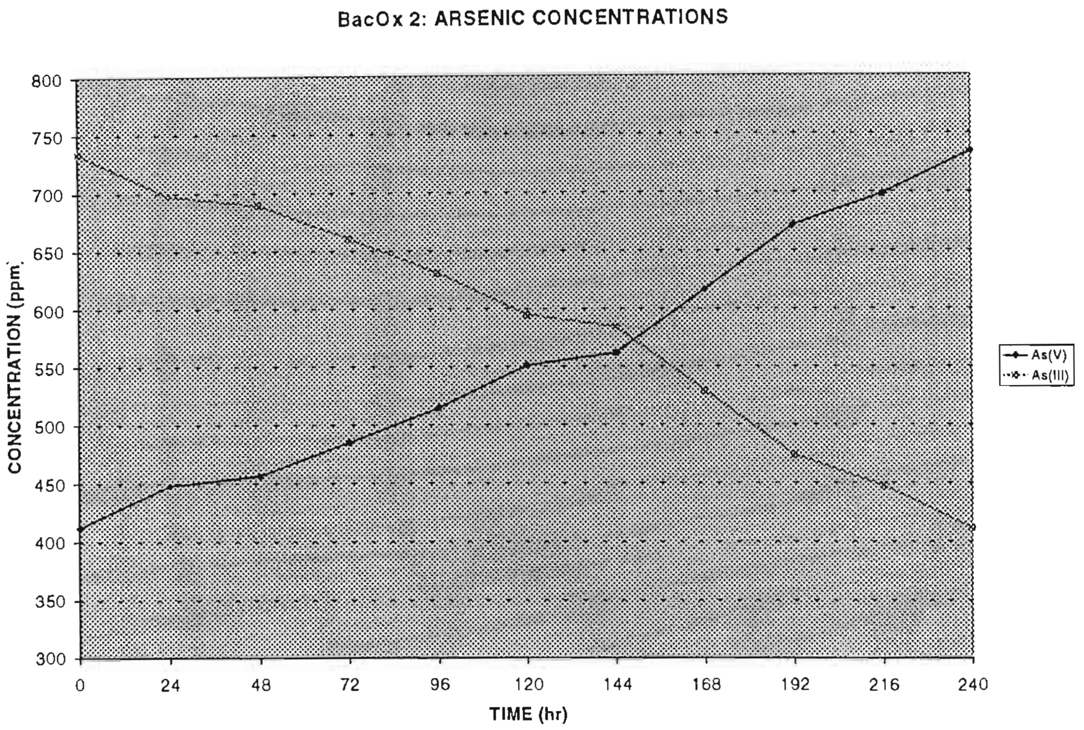


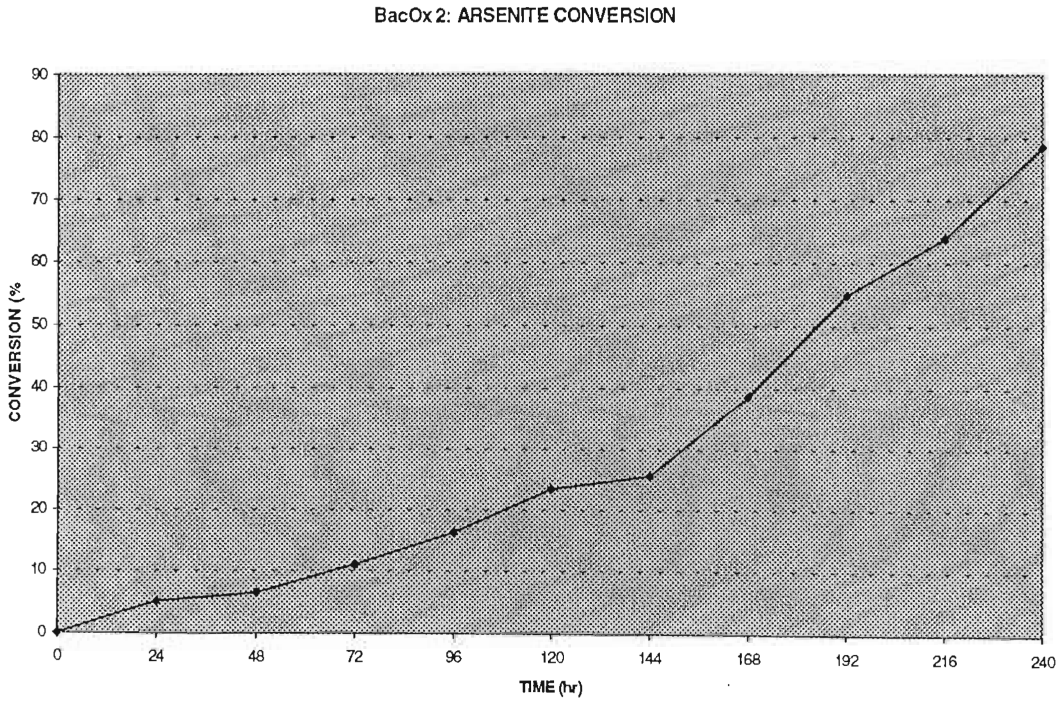
BacOx2: DISSOLVED OXYGEN CONCENTRATION

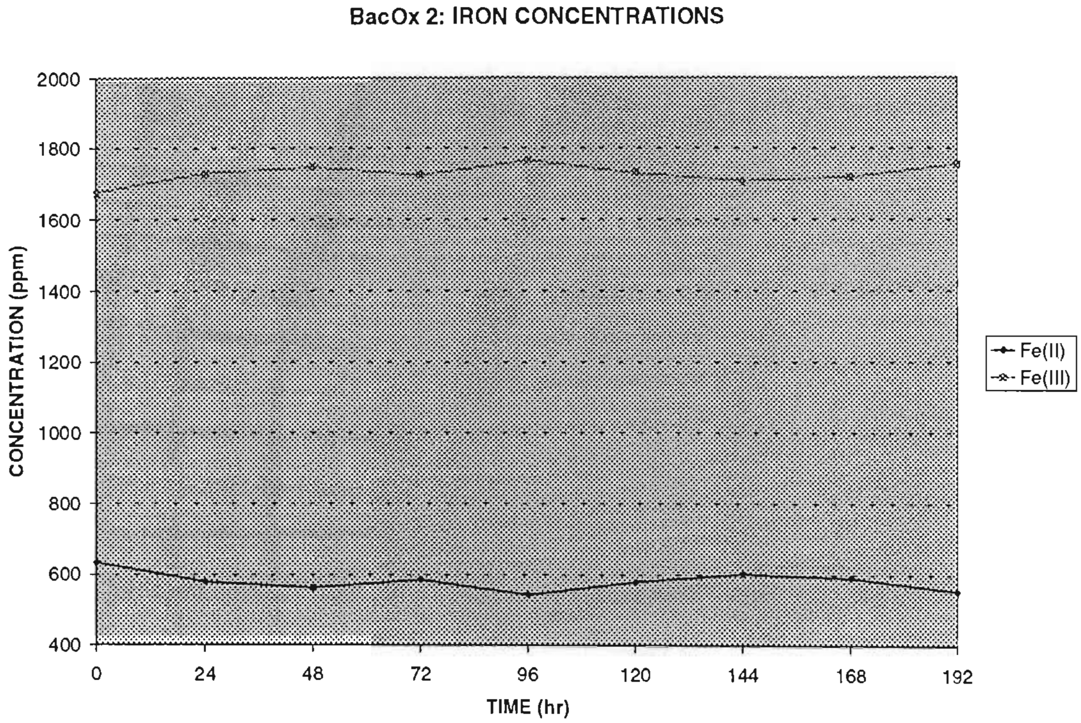


BacOx 2: REDOX POTENTIAL




BacOx 2: ARSENIC CONCENTRATIONS
800
750
700
650
600
550
500
450
400
350
300
CONCENTRATION (ppm)
0
24
48
72
96
120
144
168
192
216
240
TIME (hr)
As(V)
As(III)


BacOx 2: ARSENITE CONVERSION
90
80
70
60
50
40
30
20
10
0
CONVERSION (%
0
24
48
72
96
120
144
168
192
216
240
TIME (hr)


BacOx 2: IRON CONCENTRATIONS
CONCENTRATION (ppm)
2000
1800
1600
1400
1200
1000
800
600
400
TIME (hr)
0
24
48
72
96
120
144
168
192
Fe(II)
Fe(III)

APPENDIX D

NERNST EQUATION

APPENDIX D-1

SAMPLE CALCULATION USING NERNST EQUATION

Redox reaction:

$$HAsO_4 + 2H_2O \Leftrightarrow H_3AsO_4 + 2H^+ + 2e^- \quad E_0 = -0.559V \quad \text{(D-1.1)}$$

$$2Fe^{3+} + 2e^- \Leftrightarrow 2Fe^{2+} \; E_0 = 0.771V \quad \text{(D-1.2)}$$

Standard electrode potentials from Latimer[29]

Overall reaction:

$$HAsO_4 + 2H_2O + 2Fe^{3+} \Leftrightarrow H_3AsO_4 + 2H^+ + 2Fe^{2+} \qquad E_0 = 0.212V \qquad \text{(D-1.3)}$$

Sample calculation done for ChemSyn 1, at t=0

- Temperature = 45.25
- pH = 1.3
- Redox potential = 523 mV
- As(V) concentration = 577 ppm
- As(III) concentration = 275 ppm
- Fe(II) concentration = 498 ppm
- Fe(III) concentration = 1770 ppm

To calculate the theoretical redox potential, use the Nernst equation:

$$E = E^o - \frac{RT}{nF}\ln Q$$

Consider the As^{3+}/As^{5+} couple, equation (D-1.1):

$$Q = \frac{(a_{H_3AsO_4})(a_{H^+})^2}{(a_{HAsO_2})(a_{H_2O})^2}$$

For H_2O, $a = 1$ because pure liquid

At pH = 1.3, concentration of H^+ = 0.05 mol/dm^3

$I = 0.5\sum c_i z_i^2 = 0.138$

Debye and Huckel correlation:

$$-\log\gamma_i = \frac{A z_i^2\sqrt{I}}{1+\partial_i B\sqrt{I}}$$

At 45°C, A = 0.532

B = 0.333

For H^+

$\partial_i = 9\overset{0}{a}$

$\gamma_i = 0.762$

$a = 0.0381$

For As^{5+}

$\partial_i = 4\overset{0}{a}$

$\gamma_i = 2.01 \times 10^{-5}$

$a = 1.60 \times 10^{-7}$

For As^{3+}

$\partial_i = 4\overset{0}{a}$

$\gamma_i = 0.0204 \text{ x } 10^{-5}$

$a = 8.14 \text{ x } 10^{-5}$

$Q = 1.47 \text{ X } 10^{-6}$

From equation (E-2-7), Appendix E-2; $E_0 = 0.474$

Using the Nernst equation

$$E = 0.474 - \frac{(8.314 * 318)}{(2 * 96500)} \ln 1.47 * 10^{-6}$$

$$= 0.290 \text{ V}$$

So E for the As couple is −0.290V

Consider the Fe^{2+}/Fe^{3+} couple, equation (D-1.2):

$$Q = \frac{(a_{Fe^{2+}})^2}{(a_{Fe^{3+}})^2}$$

I = 0.160

For Fe^{2+}

$\partial_i = 6\overset{0}{a}$

$\gamma_i = 0.277$

$a = 2.49 \text{ x } 10^{-3}$

For Fe^{3+}

$\partial_i = 9\overset{0}{a}$

$\gamma_i = 0.101$

$a = 6.36 \times 10^{-3}$

$Q = 10.705$

From equation (E-1-4), Appendix E-1; $E_0 = 0.804$

Using the Nernst equation

$$E = 0.804 - -\frac{(8.314 * 318)}{(2 * 96500)} \ln 10.705$$

$$= 0.771 \text{ V}$$

So E for the Fe couple is 0.771 V

Adding the two to get the potential for the overall reaction gives:

E = 0.771-0.290

= 0.481 V

Difference = 523-481

= 42 mV

= difference between the measured value (from experiment) and calculated value (using Nernst equation)

APPENDIX E

CONSTRUCTION OF POTENTIAL – pH DIAGRAMS FOR IRON AND ARSENIC

These diagrams were constructed according to the method described in the literature survey (Refer to Section 3.10).

APPENDIX E-1

POTENTIAL-pH DIAGRAM FOR IRON

The following dissolved substances were considered:

Chemical Formula	Valence state	Standard chemical potential (cal)
Fe^{2+}	+2	-20 300
$HFeO_2^-$	+2	-90 627
Fe^{3+}	+3	-2 530
$FeOH^{2+}$	+3	-55 910
$Fe(OH)_2^+$	+3	-106 200

TABLE E-1.1 Chemical species used in the construction of potential-pH diagram

Source: Pourbaix[34]

Reactions and equilibrium formulae

z = +2

1.

$$Fe^{2+} + 2H_2O \Leftrightarrow HFeO_2^- + 3H^+$$

$$\log\frac{(HFeO_2^-)}{(Fe^{2+})} = -31.58 + 3pH \qquad \textbf{(E-1.1)}$$

z = +3

2.

$$Fe^{3+} + H_2O \Leftrightarrow FeOH^{2+} + H^+$$

$$\log\frac{(FeOH^{2+})}{(Fe^{3+})} = -2.43 + pH \qquad \textbf{(E-1.2)}$$

3.

$$FeOH^{2+} + H_2O \Leftrightarrow Fe(OH)_2^+ + H^+$$

$$\log\frac{(Fe(OH)_2^+)}{(FeOH^{2+})} = -4.69 + pH \qquad \textbf{(E-1.3)}$$

z = +2→+3

4.

$$Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$$

$$E_0 = 0.771 + 0.0591\log\frac{(Fe^{3+})}{(Fe^{2+})} \qquad \textbf{(E-1.4)}$$

5.

$$Fe^{2+} + H_2O \Leftrightarrow FeOH^{2+} + H^+ + e^-$$

$$E_0 = 0.914 + 0.0591pH + 0.0591\log\frac{(FeOH^{2+})}{(Fe^{2+})} \qquad \textbf{(E-1.5)}$$

6.

$$Fe^{2+} + 2H_2O \Leftrightarrow Fe(OH)_2^+ + 2H^+ + e^-$$

$$E_0 = 1.191 - 0.1182pH + 0.0591\log\frac{(Fe(OH)_2^+)}{(Fe^{2+})} \qquad \textbf{(E-1.6)}$$

7.

$$HFeO_2^- + H^+ \Leftrightarrow Fe(OH)_2^+ + e^-$$

$$E_0 = -0.675 + 0.0591pH + 0.0591\log\frac{(Fe(OH)_2^+)}{(HFeO_2^-)} \qquad \textbf{(E-1.7)}$$

8.

$$E_{0b} = 0 - 0.0591pH \qquad \textbf{(E-1.8)}$$

9. $$E_{0b} = 1.228 - 0.0591pH \qquad \textbf{(E-1.9)}$$

Limits of the domain of relative predominance of the dissolved substances.

1 $Fe^{2+}/HFeO_2^-$ pH = 10.33

2 $Fe^{3+}/FeOH^{2+}$ pH = 2.43

3 $FeOH^{2+}/Fe(OH)_2^+$ pH = 4.69

4 Fe^{2+}/Fe^{3+} $E_0 = 0.771$

5 $Fe^{2+}/FeOH^{2+}$ $E_0 = 0.914\text{-}0.0591pH$

6 $Fe^{2+}/Fe(OH)_2^+$ $E_0 = 1.191\text{-}0.1182pH$

7 $HFeO_2^-/Fe(OH)_2^+$ $E_0 = \text{-}0.675\text{+}0.0591pH$

Using these equations, the potential-pH diagram for iron was constructed (refer to fig. E-1.1).

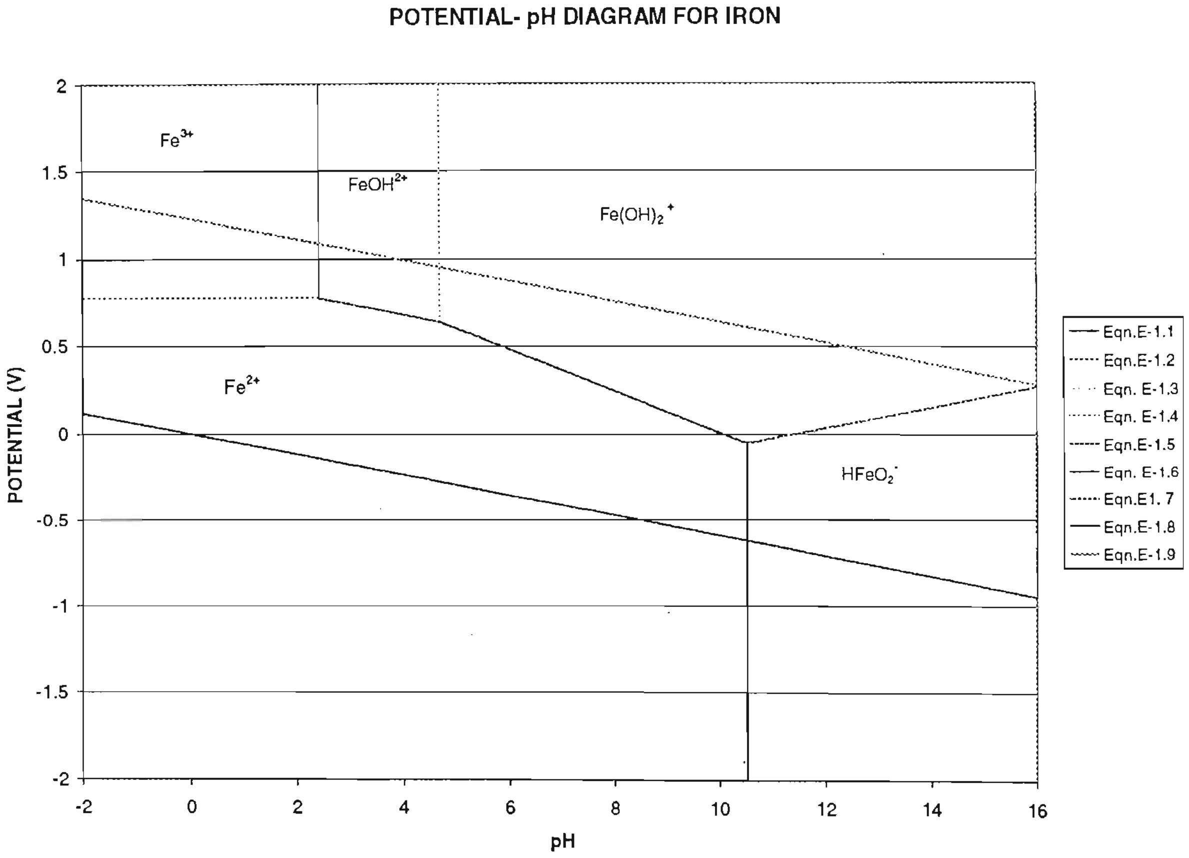


Figure E-1.1: Pourbaix diagram for Iron

APPENDIX E-2

POTENTIAL-pH DIAGRAM FOR ARSENIC

The following dissolved substances were considered:

Chemical Formula	Valence state	Standard chemical potential (cal)
AsO^+	+3	-39 100
$HasO_2$	+3	-96 250
AsO_2^-	+3	-83 700
H_3AsO_3	+3	-152 940
$H_2AsO_3^-$	+3	-140 400
H_3AsO_4	+5	-183 800
$H_2AsO_4^-$	+5	-178 900
$HAsO_4^{2-}$	+5	-169 000
AsO_4^{3-}	+5	-152 000

TABLE E-2.1 Chemical species used in the construction of potential-pH diagram

Source: Pourbaix[34]

Reactions and equilibrium formulae

$z = +3$

1.

$$AsO^{+} + H_2O \Leftrightarrow HAsO_2 + H^{+}$$

$$\log\frac{(HAsO_2)}{(AsO^{+})} = 0.34 + pH \qquad \textbf{(E-2.1)}$$

2.

$$HAsO_2 \Leftrightarrow AsO^{-} + H^{+}$$

$$\log\frac{(AsO_2^{-})}{(HAsO_2)} = -9.21 + pH \qquad \textbf{(E-2.2)}$$

$z = +5$

3.

$$H_3AsO_4 \Leftrightarrow H_2AsO_4^{-} + H^{+}$$

$$\log\frac{(H_2AsO_4^{-})}{(H_3AsO_4)} = -3.60 + pH \qquad \textbf{(E-2.3)}$$

4.

$$H_2AsO_4^{-} \Leftrightarrow HAsO_4^{2-} + H^{+}$$

$$\log\frac{(HAsO_4^{2-})}{(H_2AsO_4^{-})} = -7.26 + pH \qquad \textbf{(E-2.4)}$$

5.

$$HAsO_4^{2-} \Leftrightarrow AsO_4^{3-} + H^{+}$$

$$\log\frac{(AsO_4^{3-})}{(HAsO_4^{2-})} = -12.47 + pH \qquad \textbf{(E-2.5)}$$

$z = +3 \rightarrow +5$

6.

$$AsO^{+} + 3H_2O \Leftrightarrow H_3AsO_4 + 3H^{+} + 2e^{-}$$

$$E_0 = 0.550 - 0.0887pH + 0.0295\log\frac{(H_3AsO_4)}{(AsO^{+})} \qquad \textbf{(E-2.6)}$$

7.

$$HAsO_2 + 2H_2O \Leftrightarrow H_3AsO_4 + 2H^{+} + 2e^{-}$$

$$E_0 = 0.541 - 0.0591pH + 0.0295\log\frac{(H_3AsO_4)}{(HAsO_2)} \qquad \textbf{(E-2.7)}$$

8.

$$HAsO_2 + 2H_2O \Leftrightarrow H_2AsO_4^- + 3H^+ + 2e^-$$

$$E_0 = 0.666 - 0.0887pH + 0.0295\log\frac{(H_2AsO_4^-)}{(HAsO_2)} \qquad \textbf{(E-2.8)}$$

9.

$$HAsO_2 + 2H_2O \Leftrightarrow HAsO_4^{2-} + 4H^+ + 2e^-$$

$$E_0 = 0.881 - 0.1182pH + 0.0295\log\frac{(HAsO_4^{2-})}{(HAsO_2)} \qquad \textbf{(E-2.9)}$$

10.

$$AsO_2^- + 2H_2O \Leftrightarrow HAsO_4^{2-} + 3H^+ + 2e^-$$

$$E_0 = 0.609 - 0.0807pH + 0.0295\log\frac{(HAsO_4^{2-})}{(AsO_2^-)} \qquad \textbf{(E-2.10)}$$

11.

$$AsO_2^- + 2H_2O \Leftrightarrow AsO_4^{3-} + 4H^+ + 2e^-$$

$$E_0 = 0.977 - 0.1182pH + 0.0295\log\frac{(AsO_4^{3-})}{(AsO_2^-)} \qquad \textbf{(E-2.11)}$$

12.

$$E_{0b} = 0 - 0.0591pH \qquad \textbf{(E-2.12)}$$

13.

$$E_{0b} = 1.228 - 0.0591pH \qquad \textbf{(E-2.13)}$$

Limits of the domain of relative predominance of the dissolved substances

1. $AsO^+/HAsO_2$ pH = -0.34
2. $HAsO_2/AsO_2^-$ pH = 9.21
3. $H_3AsO_4/H_2AsO_4^-$ pH = 3.6
4. $H_2AsO_4^-/HAsO_4^{2-}$ pH = 7.26
5. $HAsO_4^{2-}/AsO_4^{3-}$ pH = 12.47
6. AsO^+/H_3AsO_4 $E_0 = 0.550-0.0887pH$
7. $HAsO_2/H_3AsO_4$ $E_0 = 0.541-0.0591pH$
8. $HAsO_2/H_2AsO_4^-$ $E_0 = 0.666-0.0887pH$
9. $HAsO_2/HAsO_4^{2-}$ $E_0 = 0.881-0.1182pH$
10. $AsO_2^-/HAsO_4^{2-}$ $E_0 = 0.609-0.0887pH$
11. AsO_2^-/AsO_4^{3-} $E_0 = 0.977-0.1182pH$

Using these equations, the potential-pH diagram for arsenic was constructed (refer to fig. E-2.1).

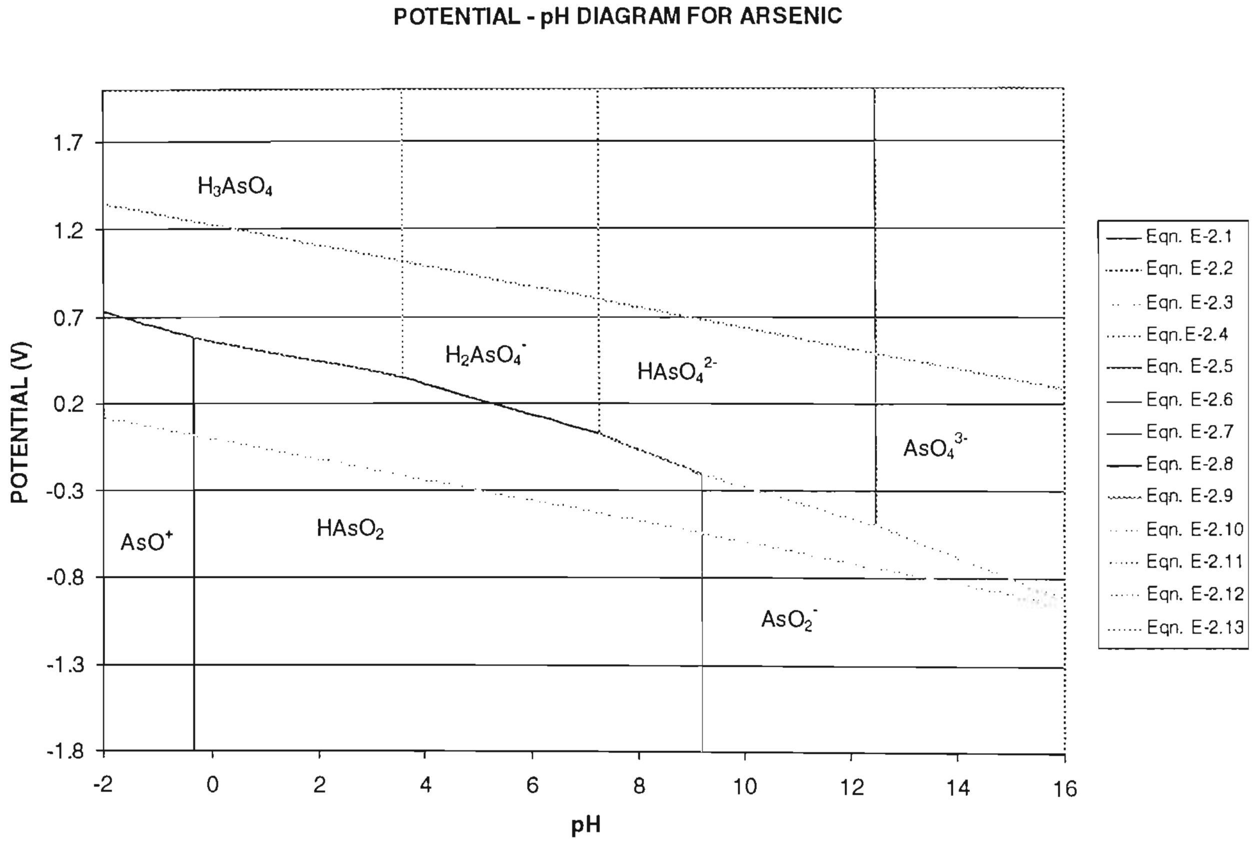


Figure E-2.1: Pourbaix diagram for Arsenic

APPENDIX F

STATISTICS

APPENDIX F-1

STATISTICS

The mean may be calculated from the formula:

$$Mean = \bar{x} = \left(\sum_{1}^{i} x\right)/i \qquad \text{(F-1.1)}$$

where *i* is the number of measurements taken.

The standard deviation for a small number of measurements (2 – 20) may be calculated from:

$$\text{Standard deviation} = s = \sqrt{\frac{\sum_{1}^{N}\left(x_i - \bar{x}\right)^2}{N-1}} \qquad \text{(F-1.1)}$$

Sample calculation for ChemOx 2 at time = 0

Concentrations: $C_1 = 1086.67$

$C_2 = 1116.67$

$C_3 = 1136.67$

Use A_2 and A_3 because these values are the closest to each other.

Mean (of A_2 and A_3) = (1116.67+1136.67)/2

= 1126.67

$$\text{Standard deviation} = \sqrt{\frac{(1116.67-1126.67)^2+(1136.67-1126.67)^2}{1}}$$

= 14.14