KINETICS OF NATURAL DEGRADATION OF CYANIDE FROM GOLD MILL EFFLUENTS

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by

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ABSTRACT

Most Canadian gold mining facilities utilize the cyanidation process in which cyanide is added to sequester gold from the ore. After zinc addition, gold is precipitated from a gold-cyanide complex. Waste streams from the process generally contain a sufficiently high concentration of cyanide and heavy metals that treatment is essential.

The oldest treatment method practiced by Canadian gold mines for cyanide destruction is "natural degradation".

Based on the literature review of the previous studies, the most important mechanism in the natural degradation of cyanide was recognized as being volatilization. Among the variables affecting the volatilization process the three most important were selected for this study, namely: temperature, UV light and aeration rate. The experimental pH chosen was 7.0. In order to evaluate the relative importance of these variables a full 2^3 factorial design was employed and appropriate experiments conducted over a period of one year.

The synthetic solutions examined were simple cyanide (NaCN), four single metallo-cyanide complexes (Cu, Zn, Ni and Fe) and two mixtures - a "low mix" containing a low concentration of metals relative to the total cyanide concentration and a "high mix", saturated with metals.

Analysis of the results of the experimental design led to the conclusion that temperature had the largest effect upon reaction kinetics. The rate of aeration together with temperature had a significant effect upon the volatilization rate within the first 48 to 72 hours. Ultraviolet irradiation only had a significant effect upon the decay rate of the iron cyanide complex and low mix.

A mathematical model for the degradation of a single metallo-cyanide complex solution was postulated for a batch reactor taking into consideration the law of conservation of mass, and assuming that chemical equilibrium existed between hydrocyanic acid (HCN) and cyanide ion (CN^-). The rate of volatilization of HCN and metal decay rate were the mechanisms assumed to be controlling the cyanide degradation process.

The best estimates of the metal decay coefficients from single metallo-cyanide solutions used to simulate the experimental data of the mixed metallo-cyanide solutions are as follows:

	k_1 at 4°C (h^{-1})	k_1 at 20°C (h^{-1})
$Na_2Cu(CN)_3$	0.00295	0.00753
$Na_2Zn(CN)_4$	0.01783	0.04496
$Na_2Ni(CN)_4$	0.00044	0.00095
$K_3Fe(CN)_6$	0.00143	0.00473

The model fits the data at the 95% confidence level for five of the eight test conditions; however, for the other three it is poorer.

The model, calibrated using coefficients from the synthetic solutions, has been applied to actual gold mill effluents. Results show that the model can be used for the basic estimate of the cyanide degradation rate. For a more precise result, a recalibration of the model is necessary as a function of the particular gold mill effluent's metal content.

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1 INTRODUCTION

Cyanide and cyanide compounds are found throughout the environment. The natural origins of cyanide and its derivatives are many plants containing cyanogenic glycosides, which when hydrolyzed release hydrogen cyanide (Ecological Analysts Inc., 1979). Historically, however, cyanide in the environment has been associated with industrial point sources. Cyanides are extensively employed in industry and occur in effluents from many different industrial processes such as the case hardening of steel, electroplating and metal-finishing, the scrubbing of coke-oven or blast furnace gases, photography and the extraction of precious metals such as silver and gold.

A reasonable amount of information on the treatment of cyanide-bearing wastes from plating industry and iron and steel subprocesses is available. But little information is available on the treatment of gold milling effluents.

Most of the gold mined in Canada is extracted from the ore by the process of cyanidation. The cyanide-bearing waste streams from the process are the barren bleed and the washed tailings containing the waste rock. Typically, these wastes contain simple cyanides of sodium or calcium, the cyanide complexes of copper, iron (less frequently), nickel, and zinc, thiocyanates and at some mines, arsenic. In addition to the toxic effects of cyanide these heavy metals can pose toxic problems. Their discharge may exceed the water quality criteria.

The methods considered to offer the greatest possibility for cyanide removal from gold mill effluents are: natural degradation, oxidation processes (using chlorine gas, hypochlorite, ozone or hydrogen peroxide), acidification/volatilization/reneutralization, electrolytic processes, ion exchange and conversion to less toxic forms (such as ferrocyanide, thiocyanate, etc).

For a long time, natural degradation in tailings ponds has been the only method practiced by Canadian gold mines for cyanide destruction. When this method is applied, usually all cyanide-bearing waste streams are pumped to a common tailings pond. In this pond the solids settle and a clear solution, the tailings pond overflow, is discharged to the environment. The liquid residence time in the tailings pond may be of the order of several days or months during which time the process of natural degradation of cyanide occurs.

For a long time an engineering goal has been to evaluate the efficiency of tailings ponds in cyanide removal from a mechanistic point of view, in order to develop criteria for pond design. In this study, it was decided, that one way to accomplish this would be to substitute synthetic mixtures for actual gold mill effluents and examine the phenomenon of natural degradation of cyanide in more detail. For this purpose, the study uses a laboratory and modelling approach. The objectives of this research are as follows:

(1) to examine the natural degradation of cyanide in synthetic solutions;

(2) to delineate major factors affecting cyanide removal, and mechanisms involved; and

(3) to model the kinetics of cyanide removal and compare the results with observations on actual systems.

2 LITERATURE REVIEW

2.1 Cyanidation

Over 90% of the gold mined in Canada is extracted from the ore by the process of cyanidation. This process consists of addition of sodium or calcium cyanide solution to the crushed and slurried ore in agitated and aerated tanks for up to 50 hours under alkali conditions (Figure 2.1). Elsner's equation has been suggested as being representative of the reaction that takes place during the dissolution of gold in dilute cyanide solutions (Hedley and Tabachnick, 1958):

$$4\ Au + 8\ NaCN + O_2 + 2\ H_2O = 4\ NaAu\ (CN)_2 + 4\ NaOH$$

The solution pH is controlled at a high level (pH=11) using lime additions to prevent the volatilization of hydrogen cyanide gas.

After clarification and filtration the pregnant solution containing gold is separated from the solids, and gold is precipitated from it by the addition of zinc dust. Zinc precipitation of gold is represented by the following equation:

$$2\ NaAu(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2\ Au$$

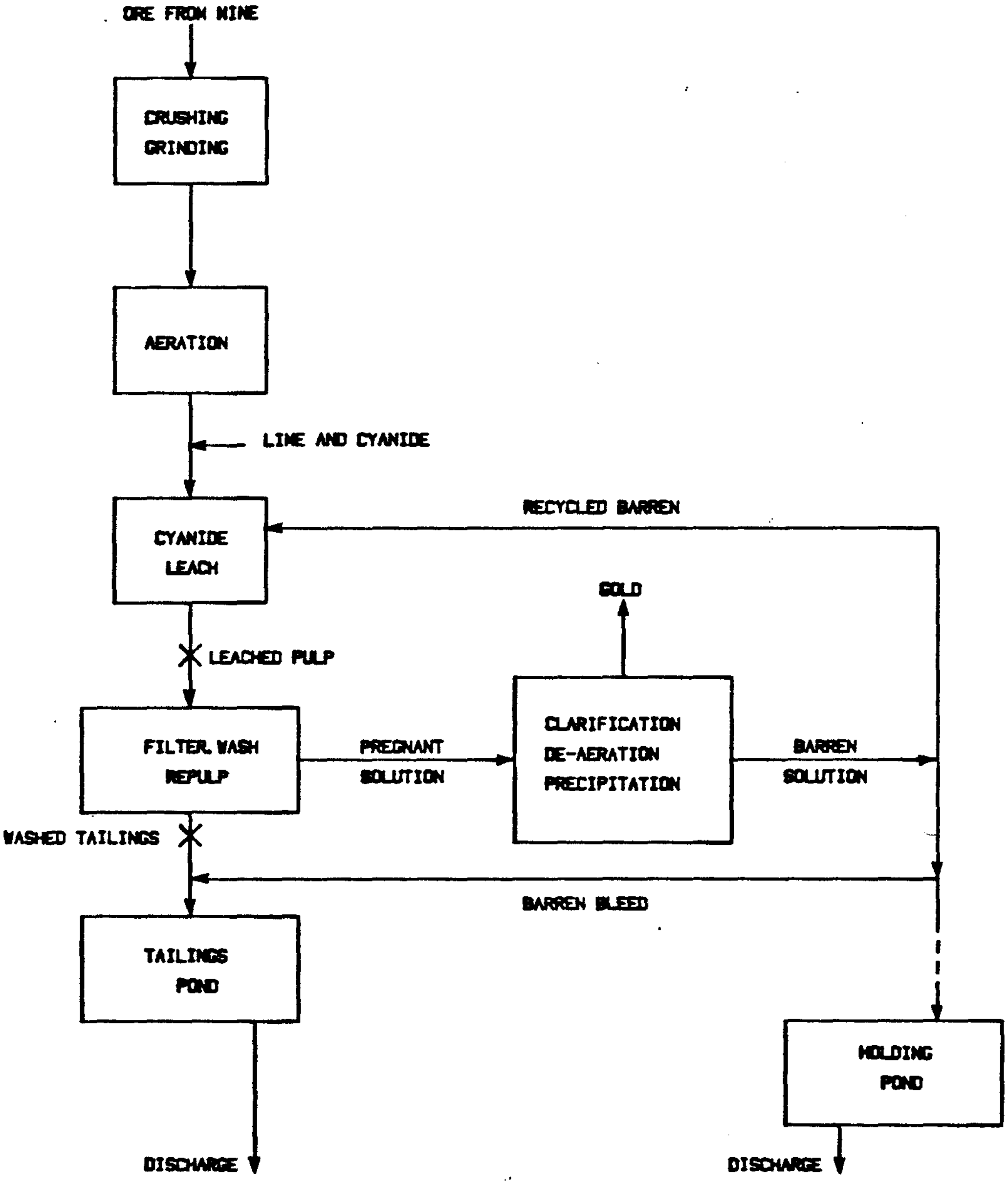

Figure 2.1 Simplified Gold Mill Flowsheet

A gold free solution, called "the barren solution" is produced following precipitation. The barren solution contains cyanide, heavy metals (Cu, Zn, Ni and Fe), thiocyanates, cyanates and sometimes arsenic.

Part of the barren solution is returned to the crushing and grinding circuit to aid in the cyanidation process. The remainder, called "the barren bleed" is discharged in order to avoid excessive accumulation of heavy metals in process waters.

As shown in Figure 2.1, the barren bleed constitutes only a portion of the total cyanide-bearing effluent to be disposed of - the other main effluent source is the washed filter residue containing the leached solids (tailings) plus repulping water and other miscellaneous streams (see Table 2.1). The barren bleed and washed tailings are usually combined and discharged to the tailings pond. After settling of solids, the tailings pond supernatant is left in the pond for a prolonged period of time to enhance natural degradation of cyanide. At some mines (e.g., Dome Mines Ltd. and Pamour-Schumacher Mines), waste barren solution (the effluent with the highest cyanide content) is segregated from the other cyanide-bearing solutions and retained in a separate pond for the purpose of natural degradation of cyanide.

TABLE 2.1. SUMMARY OF COMPOSITION OF PROCESS STREAMS AND MILL EFFLUENTS FOR SELECTED CANADIAN GOLD MILLING OPERATIONS

	Flow x 10^{-3} L/d	pH	Total CN (mg/L)	Cu (mg/L)	Zn (mg/L)	Ni (mg/L)	Fe (mg/L)	CNS^- (mg/L)
Barren Solution	150 to 560	11.3 to 12.2	86 to 650	6 to 275	10.2 to 237	0.28 to 10.0	0.1 to 35.7	42 to 510
Filtered* Tailings	191 to 2,300	10.2 to 11.7	27 to 150	3.0 15.0	1.02 to 22.9	0.1 to 2.36	0.1 to 7.14	16 to 120
Tailings Pond Effluents	0 to 13,600	7.2 to 8.3	0.2 to 48	0.02 to 37.3	0.04 to 0.82	0.07 to 0.7	0.4 to 5.2	2 to 72

Source: IEC, 1979.

* Samples filtered; results indicate soluble components.

2.2 Forms of Cyanides and Metals in Mining Wastes

2.2.1 Cyanide

The forms of cyanide in process waters are a result of reactions during gold cyanidation process. These forms are not well known. The cyanide may be chemically or physically adsorbed on tailings mineral surfaces and/or it may have reacted with metallic and nonmetallic constituents in tailings to produce cyano complexes, thiocyanates and cyanates at the mineral surfaces or in the interstitial solutions (Huiatt et al., 1983).

Metal-cyanide complexes are produced by the reaction of cyanide with a variety of mineral types: oxides, carbonates, silicates and sulphides of copper, zinc, nickel and iron. In Canadian ores it is the sulphide minerals that usually predominate in the feed to the cyanidation process (Scott and Ingles, 1981).

It is usually thought that most of cyanide is in solution rather than adsorbed on suspended particles. The fact that cyanide is used to leach gold from the ore supports that theory. The large fraction of metal sulphides in solution oxidize to polysulphides and thiosulphates. Some cyanide reacting with them becomes converted to thiocyanate and as insoluble precipitates but much of it remains in metallo-cyanide complexes and free cyanide forms (Schmidt et al., 1981; Conn, 1984). Even if adsorbed on suspended particles, some of the cyanide ion can be slowly re-released into the water assuming that such adsorption phenomena are reversible (Caruso, 1975).

2.2.2 Copper

Many precious metal ores contain copper minerals such as: azurite, $2CuCO \cdot Cu(OH)_2$; malachite, $CuCO_3 \cdot Cu(OH)_2$; chalcocite, Cu_2S; chalcopyrite, $CuFeS_2$; cuprite, Cu_2O, etc. In these minerals copper may have an oxidation state ranging from +1 to +2. Under the conditions normally used in cyanidation these minerals are readily and completely solubilized in weak cyanide solutions (Table 2.2). Copper combined with cyanide forms a variety of complexes. The complexation is particularly rapid at high pH values (Caruso, 1975). The complexes include simple complexes such as cupric and cuprous forms of cyanide and thiocyanate $\left(Cu(CN)_2, CuCN, Cu(CNS)_2 \text{ and } CuCNS\right)$ and double copper cyanides with complex ions such as $Cu(CN)_2^{1-}$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$. Of the complex ions $Cu(CN)_3^{2-}$ is considered the most probable to occur (Hedley and Tabachnick, 1958). Copper sulphides are readily oxidized to sulphates, and copper then released as Cu^{2+}. If Cu^{2+} is present in the ore, some of the cyanide may be oxidized to cyanate (CNO^-) in reducing combined Cu^{2+} to Cu^{1+}. For each two cupric ions reduced, one cyanide ion is converted to cyanate. Cyanide consumed in this way is not recoverable (Fairbridge, 1972).

Cuprous ion has a complete outer shell of 18 electrons and as such does not absorb radiation in solution. Cupric ion, however, has 17 electrons in its M-shell and can absorb radiation of suitable wavelength (3630, 7580 and 11900Å), (Noblitt, 1973).

TABLE 2.2. SOLUBILITY OF MINERALS IN CYANIDE SOLUTION

Main Element		Mineral	% Dissolved in 24 hours
Gold	Calaverite	$AuTe_2$	Readily soluble
Silver	Argentite	Ag_2S	Readily soluble
	Cerargyrite	$AgCl$	Readily soluble
	Proustite	Ag_3AsS_3)Ruby	Sparingly soluble
	Pyrargyrite	Ag_3SbS_3)silver	Sparingly soluble
Copper	Azurite	$2CuCO\cdot Cu(OH)_2$	94.5
	Malachite	$CuCO_3\cdot Cu(OH)_2$	90.2
	Chalcocite	Cu_2S	90.2
	Cuprite	Cu_2O	85.5
	Bornite	$FeS\cdot 2Cu_2S\cdot CuS$	70.0
	Enargite	$3CuS\cdot As_2S_5$	65.8
	Tetrahedrite	$4Cu_2S\cdot Sb_2S_3$	21.9
	Chrysocolla	$CuSiO_3$	11.8
	Chalcopyrite	$CuFeS_2$	5.6
Zinc	Smithsonite	$ZnCO_3$	40.2
	Zincite	ZnO	35.2
	Hydrozincite	$3ZnCO_3\cdot 2H_2O$	35.1
	Franklinite	$(Fe, Mn, Zn)O\cdot(Fe, Mn)_2O_3$	29.2
	Sphalerite	ZnS	18.4
	Gelamine	$H_2Zn_2SiO_4$	13.4
	Willemite	Zn_2SiO_4	13.1
Iron	Pyrrhotite	FeS or Fe_5S_6	Readily soluble
	Pyrite	FeS_2 (isometric)	Sparingly soluble
	Hematite	Fe_2O_3	Sparingly soluble
	Magnetite	Fe_3O_4	Practically insoluble
	Siderite	$FeCO_3$	Readily soluble
	Marcasite	FeS_2 (orthorhombic)	Readily soluble

Source: R. Tremblay, 1983.

2.2.3 Zinc

Zinc occurs in a precious metal ore in a number of minerals - smithsonite, $ZnCO_3$; sphalerite, ZnS; willemite, Zn_2SiO_4; zincite, ZnO and several others. These zinc minerals are sufficiently soluble under normal cyanidation conditions. The reaction of cyanide with sphalerite for example (Ingles, 1981a), proceeds according to the equation:

$$ZnS + 4\ CN^- + H_2O \rightarrow Zn(CN)_4 + HS^- + OH^-$$

In the presence of oxygen, sulphites and other intermediate products such as thiosulphate and thionates may be formed (Hedley and Tabachnick, 1958). Zinc forms complexes in aqueous solution but these are not particularly stable or inert (Fairbridge, 1972).

Sodium zinc cyanide is soluble in water (Hedley and Tabachnick, 1958) dissociating at any pH to some extent as follows:

$$Na_2Zn(CN)_4 \rightleftarrows 2Na^+ + Zn(CN)_4^{2-} \rightleftarrows Zn(CN)_2 \downarrow + 2CN^-$$

Another source of Zn in mill effluent is from the gold precipitation process. The amount of Zn dust used for the precipitation of precious metals depends to a large extent on the amount of precious metal in solution although other factors such as oxygen content, cyanide strength and alkalinity play an important part. During the reactions involved in precipitation, the greater part of the zinc dissolves in the cyanide solution and forms various complexes such as sodium or calcium zinc cyanide, zinc cyanide, zinc thiocyanate and zinc ferrocyanide (Hedley and Tabachnick, 1958).

Zinc's chemical behaviour is dictated by the existence of a single oxidation state, i.e., Zn^{2+}. In a crystal zinc has the tendency to form covalent bonds which show a distinct preference for tetrahedral coordination. The octahedral coordination does not commonly occur. The Zn^{2+} ion is normally found with ferrous ion and apparently competes with it during fractionation for vacant octahedral lattice sites (Fairbridge, 1972).

2.2.4 Nickel

Nickel is most frequently found in certain varieties of the iron mineral pyrrhotite (3 to 5% Ni) or in combination with sulphur as millerite NiS. Although nickel can achieve oxidation states of -1, 0, +1, +3 and +4, the majority of the nickel compounds are of the Ni(II) oxidation state.

The kinetics of formation and decomposition of the tetracyanonickelate (II) complex ion have been studied in some detail (Kolski and Margerum, 1968). The rate of formation is a fifth-order reaction, first-order in nickel and fourth-order in total cyanide; HCN is a reactant as well as CN^-. In the pH range 5.5 to 7.5 the rate is proportional to $[Ni^{2+}][CN^-]^2[HCN]^2$. By the use of iodine as a CN^- ion scavenger, the first-order rate constant for dissociation of the $Ni(CN)_4^{2-}$ ion at pH 3 to 8 in $\mu = 0.1$ $NaClO_4$ is estimated as $4.8 \times 10^{-4}(s^{-1})$. The yellow $Ni(CN)_4^{2-}$ ion (a square-planar complex) is both thermodynamically very stable and kinetically slow to release CN^- ion (Crouse and Margerum, 1974). Nickel is able to displace Zn and Cd from their cyanide complexes, forming the more stable tetracyanonickelate (II) complex (Broderius, 1973).

Nickel thiocyanate is also know to form. It is a yellow-brown hydrated solid that reacts with an excess of SCN^- to form complex ions $Ni(SCN)_4^{2-}$ and $Ni(SCN)_6^{4-}$ (Cotton and Wilkinson, 1962). A mixed cyano thiocyanato complex $K_2[Ni(CN)_2(SCN)_2]$ is obtained from nickel thiocyanate and potassium cyanide (nitrogen atom of the thiocyanate ion acts as ligand) (Sharpe, 1976).

The chemistry of nickel is not simple because of the existence of complex interconversions of various structures, i.e., octahedral, tetrahedral and square (Cotton and Wilkinson, 1962).

2.2.5 Iron

The principle sources of iron are the iron sulphide minerals: pyrite FeS_2 (isometric), marcasite FeS_2 (orthorhombic) and pyrrhotite Fe_5S_6. Their reactivities increase in that order (Ingles, 1981b). Cyanide reacts with iron (II) and iron (III) to form extremely stable octahedral complexes: ferrocyanide $Fe(CN)_6^{4-}$ and ferricyanide $Fe(CN)_6^{3-}$, respectively. These reactions are slow and incomplete at high pH values (Caruso, 1975). Together these two complexes form an oxidation-reduction couple; ferrocyanide, which is the usual form in solution at normal environmental oxidation potential levels, being fairly easily oxidized to ferricyanide (Ingles, 1981b). In addition to the difference in their stability constants (see Table 2.3), ferrocyanide forms an insoluble zinc salt while ferricyanide does not.

Perhaps the best-known reaction of aqueous Fe^{3+} is with thiocyanate ion to form one or more intensely red coloured thiocyanate complexes.

The principal iron mineral of concern, pyrrhotite, is reported to react first via its labile sulphur atom to yield thiocyanate and ferrous sulphide:

$$Fe_5S_6 + CN^- \rightarrow CNS^- + 5\ FeS$$

The ferrous sulphide formed oxidizes rapidly to ferrous sulphate and the ferrous iron then combines with cyanide

$$FeS + 2O_2 \rightarrow Fe^{2+} + SO_4^{2-}$$
$$Fe^{2+} + 6\ CN^- \rightarrow Fe(CN)_6^{4-}$$

These reactions will be competing, of course, with the hydrolysis-oxidation reactions leading to the precipitation of ferrous and ferric hydroxides (Ingles, 1981b).

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2(s)$$
$$4\ Fe(OH)_2(s) + O_2 + 2H_2O \rightarrow 4\ Fe(OH)_3(s)$$

TABLE 2.3. SOLUBILITY PRODUCTS AND FORMATION CONSTANTS OF CYANIDE COMPOUNDS (Ingles, 1981a)

Metal	Compound	Solubility Product log Ksp	Cumulative Formation Constants				
			log K_1	log K_2	log K_3	log K_4	log K_6
Cadmium II	$Cd(CN)_2$	8.0	5.48	10.60	15.23	18.78	-
Cobalt II	-	-	-	-	-	-	very large
Copper I	Cu,CN	19.49	-	24.0	28.59	30.30	-
Gold I	-	-	-	38.3	-	-	-
Iron II	-	-	-	-	-	-	35 (47)**
Iron III	-	-	-	-	-	-	42 (52)
Mercury I	$Hg_2(CN)_2$*	39.3	-	-	-	-	-
Mercury II	-	-	-	-	-	41.4	-
Nickel II	$Ni_2(CN)_4$+ $Ni^+ + Ni(CN)_4^{2-}$	8.77				22.0	-
Silver I	Ag, CN	15.92	-	21.1	21.7	20.6	-
Zinc II	-	-	-	-	-	16.7	-

* Excess cyanide gives metallic mercury and the Hg^{2+} complex, Hg $(CN)_4^{2-}$.

** Values in parentheses from Broderius, 1973.

Chemically, there is no evidence that any definite hydroxide, $Fe(OH)_3$ exists, and the red-brown precipitate commonly called ferric hydroxide is best described as hydrous ferric oxide, $Fe_2O_3 \cdot n\ H_2O$ (Cotton and Wilkinson, 1962).

2.3 Cyanide Chemistry

2.3.1 Free cyanide

Cyanide exists in water in several forms. The term "free cyanide" refers to a summation of the ionic form CN^- and the molecular form, hydrocyanic acid, HCN. The equilibrium between HCN and CN^- is pH dependent.

$$[HCN] \rightleftarrows [H^+] + [CN^-] \qquad K_a = \frac{[H^+]\ [CN^-]}{[HCN]} = \begin{array}{l} 4.36 \times 10^{-10} \\ \text{(at } 20°\text{C)} \end{array} \qquad (2.1)$$

At the pH value of 9.36 (equal to the pKa) the concentration of HCN and CN^- ion are equal (Broderius, 1973). With an increase in pH of one pH unit there is a tenfold decrease in the $[HCN]/[CN^-]$ ratio. At lower pH values (pH 7.0) most cyanide exists as molecular HCN (99.5%) (see Figure 2.2) which is the major toxic form of cyanide. Molecular HCN has a relatively high vapour pressure (53.1 kPa at 10.2°C), and therefore can readily be volatilized to the atmosphere, even from stagnant solutions.

The equilibrium constant K_a varies slightly with temperature. Extrapolating to a temperature more characteristic of northern

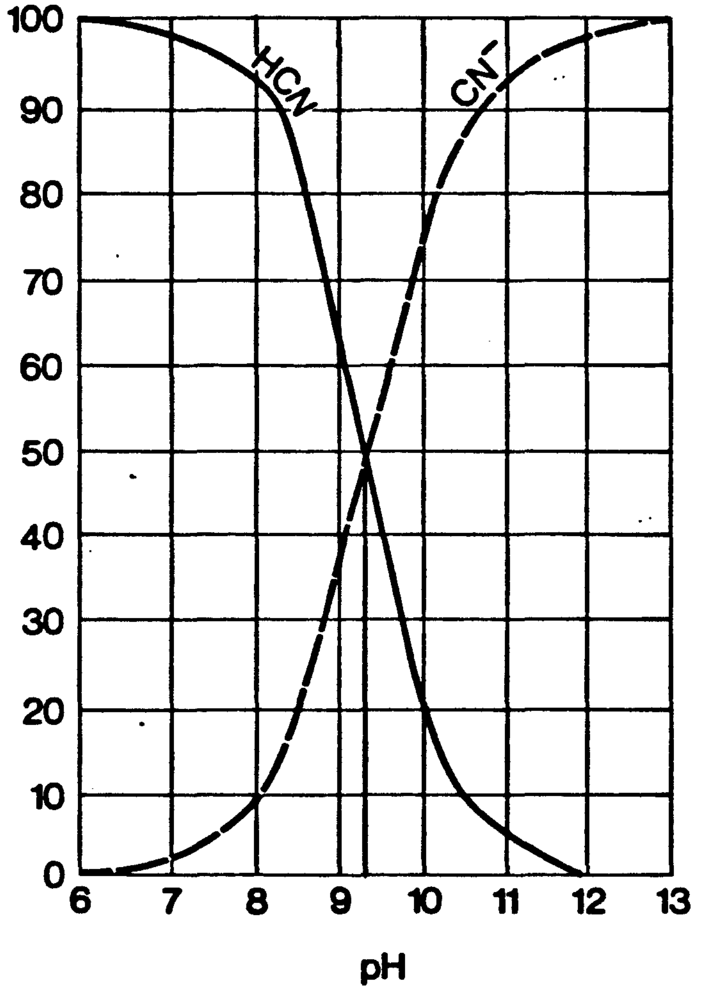

Figure 2.2 **Relative Percentage of Hydrocyanic Acid and Cyanide Ion in Solution as a Function of pH**

Canada or winter conditions in southern Canada, approximately 94% of free cyanide would be in the form of HCN at 4°C and pH 8.5 (Leduc et al., 1982).

Free cyanide in milling solutions may react with various forms of sulphur (polysulphide or thiosulphate) from pyrites and other mineral constituents to form thiocyanate (Luthy and Bruce, 1979).

$$CN^- + S_X^{2-} \rightleftarrows [S_{(X-1)}]^{2-} + SCN^-$$

$$CN^- + S_2O_3^{2-} \rightleftarrows SO_3^{2-} + SCN^-$$

In lower concentrations in the environment free cyanide will oxidize to cyanate, and this will degrade chemically to carbon dioxide and ammonia (Hendrickson and Diagnault, 1973).

$$HCNO + H_2O \rightarrow NH_3 + CO_2$$

This reaction can occur at pH's up to 8.5 but is greatly accelerated at lower pH's (Hendrickson and Daignault, 1973).

2.3.2 Simple cyanides

Most of the cyanide used in gold milling is in the form of alkaline metal salts. They are <u>simple cyanide</u> compounds represented by the formula $A(CN)_x$ where A can be alkali (sodium, potassium or ammonium) or metal, and x, the valence of A, represents the number of cyano groups present in the molecule.

The aqueous hydrolysis of simple cyanides has been examined by several investigators, e.g., Milne (1950a), Hyatt (1976) etc. Being the salts of a strong base (NaOH or KOH) and a weak acid (HCN) their dissolution in water results in the dissociation of the ionic lattice followed by the hydrolysis of the cyanide ion to form HCN:

$$NaCN \rightarrow Na^+ + CN^- \quad (2.2)$$

$$Na^+ + CN^- + H_2O \rightleftarrows Na^+ + OH^- + HCN \quad (2.3)$$

As the very weakly dissociated hydrocyanic acid permits little free hydrogen ions in solution, hydroxyl ion will predominate to produce an alkaline solution. The reduction of pH of these cyanide solutions will always lead to the preferential formation of undissociated HCN (Ecological Analysts Inc., 1979). Subsequent behaviour would then be the same as for HCN explained in Section 2.3.1 for free cyanide.

2.3.3 Complex cyanides

There are 28 elements found (Table 2.4) and more than 64 oxidation states of these elements which may form complex cyanides (Ford-Smith, 1964). The stability of the complex cyanides varies greatly from one element to another and from one oxidation state to another (see Table 2.4). The complexes form in stepwise fashion, with

TABLE 2.4. OXIDATION STATES OF METALS FORMING CYANIDE COMPLEXES

M	M(0)	M(I)	M(II)	M(III)	M(IV)	M(V)	M(VI)	M(VII)
Ti(22)				Ti(III)				
V (23)			V(II)	V(III)	V(IV)			
Cr(24)	Cr(I)	Cr(II)	Cr(III)	Cr(IV)				
Mn(25	Mn(0)	Mn(I)	Mn(II)	Mn(III)	Mn(IV)			
Fe(26)	Fe(I)?	Fe(II)	Fe(III)					
Co(27)	Co(0)	Co(I)	Co(II)	Co(III)	Co(IV)			
Ni(28)	Ni(0)	Ni(I)	Ni(II)					
Cu(29)		Cu(I)	Cu(II)					
Zn			Zn(II)					
Ge(32)					Ge(IV)			
Mo(42)			Mo(II)	Mo(III)	Mo(IV)	Mo(V)		
Tc(43)		Tc(I)			Tc(IV)			
Ru(44)			Ru(II)	Ru(III)				
Rh	Rh(0)	Rh(I)		Rh(III)				
Pd(46)	Pd(0)	Pd(I)	Pd(II)					
Ag(47)		Ag(I)						
Cd(48)			Cd(II)					
W (74)					W(IV)	W(V)		
Re(75)	Re(0)	Re(I)	Re(II)	Re(III)	Re(IV)	Re(V)	Re(VI)	Re(VII)
Os(76)			Os(II)	Os(III)?			Os(VI)	
Ir(77)			Ir(II)	Ir(III)				
Pt(78)	Pt(0)?	Pt(I)?	Pt(II)	Pt(III)	Pt(IV)			
Au(79)		Au(I)		Au(III)				
Hg(80)			Hg(II)					
Tl(81)		Tl(I)		Tl(III)				
Pb(82)		Pb(II)						
Po(84)					Po(IV)?			
U(92)							U(VI)	

Source: Ford-Smith, 1964.

successively higher cyanide contents, as the cyanide ion concentration of the solution is increased.

Under certain conditions which are a function of such factors as pH, temperature, and total cyanide concentration, complex metallo-cyanides will dissociate in water. This dissociation generates a complex cyanide ion which may further dissociate to release cyanide ions. But many complex ions are, in general, more stable than their original compounds and hence the extent of their subsequent dissociations may be relatively small (Caruso, 1975). Although a simple equation may be written to describe the overall dissociation of a complex cyanide ion, such one-step reactions are rare.

The actual process usually involves a number of intermediate steps. To appreciate the quantitative effect of altering conditions on an equilibrium, all intermediate species need be considered from a kinetic point of view. Although one species could predominate at any given time, other species could also be present. Unfortunately, very little work has been done on the elucidation of all intermediate reactions of the metallo-cyanide species thus far and, hence, one must rely upon overall or cumulative dissociation or equilibrium constants for many complex ions (Leduc et al., 1982).

According to Broderius (1973) the extent to which a complex cyanide dissociates is of little importance in environmental systems; the important factor is the rate at which cyanide bound in the complex exchanges with free cyanide in solution as illustrated in Eq. 2.4:

$$[M(CN)_X]^{-a} + H_2O \rightleftarrows [M(CN)_{X-1} \cdot H_2O]^{-a+1} + CN^- \qquad (2.4)$$

The rate of exchange is independent of total cyanide concentration and is governed by the pH of the medium and perhaps light intensity. A decrease in pH increases the rate of exchange. Complex ions such as $Fe(CN)_6^{4-}$, and $Fe(CN)_6^{3-}$ exhibit slow exchange with cyanide, while complex ions such as $Ni(CN)_4^{2-}$, $Cu(CN)_3^{2-}$ and $Ag(CN)_2$ exhibit immeasurably rapid exchange with cyanide (MacDiarmid and Hall, 1953). The thermodynamic stability of a complex should not necessarily be expected to show a relationship with its rate of exchange (Adamson et al., 1950).

Most of the tests carried out on metallo-cyanide complexes (Asperger, 1952; Doudoroff, 1956, etc.) revealed that irregardless of how stable the complexes are (e.g., iron or nickel cyanide complex), they must be regarded as delayed sources of free cyanide which will be released under specific conditions (UV irradiation or decreased pH). This free cyanide is then subject to various natural removal mechanisms.

Since the most common heavy metals present in mill tailing solutions are copper, zinc, nickel and iron, their chemistry will be discussed in detail in the following paragraphs.

a) Copper-Cyanide Complexes (Cu-CN)

High levels of copper are often found in cyanide-containing effluents. Common aqueous species include $Cu(CN)_2^{1-}$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. Copper-cyanide complexes in solution undergo a moderate degree of dissociation depending upon numerous factors such as: pH, temperature, dissolved oxygen concentration, initial cyanide concentration, etc. (Broderius, 1973; Caruso, 1975; Amax of Canada Ltd., 1980).

When a copper cyanide solution was prepared having the mole ratio CN:Cu = 2.0, equilibrium was established within two to three days. However, equilibrium was not attained at CN:Cu mole ratios of 2.5 and 3.0 after an extended period (110 days). This finding was interpreted as a sign of the slow formation and dissociation of the $Cu(CN)_3^{2-}$ complex in comparison with $Cu(CN)_2^{1-}$ (Broderius, 1973).

b) Zinc-Cyanide Complexes (Zn-CN)

Zinc-cyanide is a complex that readily dissociates in an aqueous solution. In very dilute solutions, virtually complete dissociation of these complex ions is to be expected at any pH value (Broderius, 1973). The tetracyano-complex of zinc (II) may exist in highly concentrated process waters but is expected to dissociate readily during in-plant effluent treatment. The equilibrium constant ($K_a = 1.3 \times 10^{-17}$) indicates that the complex will almost totally dissociate upon effluent dilution (total cyanide concentration less than 0.3 mg/L as CN^-) and, therefore, will be a significant source of free cyanide and metals (Doudoroff, 1976).

c) Nickel-Cyanide Complexes (Ni-CN)

For all practical purposes, the $Ni(CN)_5^{3-}$ and $Ni(CN)_6^{4-}$ species are only present at very high CN^- concentrations. In dilute nickelo-cyanide solutions in which the cyanide to nickel molar ratio is 4 to 1, the $Ni(CN)_4^{2-}$ ion is the only significant stable complex species (Penneman et al., 1962). The dissociation of nickel-cyanide complexes is very pH dependent. As the pH decreases, the dissociation of the $Ni(CN)_4^{2-}$ complex ion increases (Doudoroff, 1976). Broderius (1973) examined in detail the rates of dissociation and formation of the tetracyanonickelate (II) complex ion in solutions of varying total cyanide concentration and pH. He assumed that cyanonickelate (II) exists in equilibrium with cyanide and nickel ions:

$$Ni(CN)_4^{2-} \rightleftarrows Ni^{2+} + 4\ CN^- \qquad (2.5)$$

$$4\ CN^- + 4\ H^+ \rightleftarrows 4\ HCN$$

and calculated the dissociation constant as $K_D = 1.004 \pm 0.375 \times 10^{-31}$. He found that formation and dissociation of the complex are very slow; as much as ten days may be required to achieve dissociation equilibrium. Hence, Eq. (2.5) is actually the summation of several reactions, each with its own dissociation constant. He observed that the exposure of a dilute nickel-cyanide complex solution to bright sunlight does not result in any photodecomposition of the complex.

Long (1951) studied the exchange of nickel between tetracyanonickelate (II) ion and hydrated nickel ion. He noticed that at pH values ranging from 4 to 8, the exchange is slow compared to the rate of precipitation of nickel cyanide. However, the exchange of labelled cyanide between $Ni(CN)_4^{2-}$ and aqueous cyanide is fast, being completed in 30 s at pH 6.5 to 10.5.

d) Iron-Cyanide Complexes (Fe-CN)

Iron forms two complexes with cyanide, hexacyanoferrate (II) ion, $Fe(CN)_6^{4-}$, usually referred to as ferrocyanide, and hexacyanoferrate (III) ion, $Fe(CN)_6^{3-}$, commonly known as ferricyanide.

Potassium ferrocyanide and ferricyanide, the otherwise highly stable complexes, photodecompose when exposed to bright sunlight particularly in the presence of oxygen (Broderius, 1973). The actual decrease in the concentration of hexacyanoferrates in effluents due to photolysis will depend on the clarity of the effluent, the extent of contact between the effluent and the air, as well as the rate of air movement (rate of HCN removal) over the surface of the tailings pond (Ingles, 1981b).

Specific reports of studies on the natural degradation of pure hexacyanoferrates solutions, or of effluents containing high concentration levels of these compounds, are relatively rare. The works of Broderius (1973), Broderius and Smith (1980) and others, focussing on their photolytic decomposition, provide valuable and relevant background information. In their detailed and extensive studies on the rate and extent of photolysis of hexacyanoferrates (II) and (III) Broderius and Smith (1980) concluded that the maximum amounts of total cyanide that can be photochemically released as HCN from these complexes (each containing 6 mol CN^-) are 85 and 49%, respectively, corresponding to 5 moles of CN^- for hexacyanoferrate (II), and 3 moles of CN^- for hexacyanoferrate (III). They quote Balzani and Carassiti (1970) in stating that under prolonged irradiation of aerated and relatively concentrated hexacyanoferrate (II) and (III) solutions, $Fe(OH)_3$ (in alkaline solutions) and Prussian Blue (in acid solutions) are formed. At the same time they support these authors' contention that the overall chemical changes and the reaction mechanisms for the photolysis of hexacyanoferrate complexes are not well defined.

The removal methods of iron-cyanide complex other than photolysis do not appear to have received much attention. One would anticipate, for example, that in an effluent containing a relatively high proportion of labile metal cyanide complexes (such as those of zinc or copper), the release of the metal ions resulting from a drop in pH would be accompanied by precipitation of the corresponding metal ferrocyanide (Ingles, 1981b).

Although apparently never investigated, it is possible that ferrocyanide could be adsorbed on constituents of the tailings solids. For example, Gaudin (1932) and Taggart (1945) have both indicated that soluble prussiates (hexacyanoferrates) tend to form relatively stable, insoluble, polar films of copper ferrocyanide or ferricyanide on copper sulphide particles.

Hendrickson and Daignault (1973) studied the use of heavy metal ions to precipitate hexacyanoferrates for removal by precipitation or centrifugation. The metal ions tested were Fe^{2+}, Mn^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}. Copper and zinc were the most effective for precipitating hexacyanoferrate (II). Hexacyanoferrate (III) did not precipitate well by itself. Ferrous iron gave 90% removal but the other metals only removed about 60%. However, with both hexacyanoferrates present, precipitation of 99.5% or better in both forms was obtained with Fe^{2+}, Cd^{2+} and Cu^{2+}.

2.4 Removal of Cyanide by Natural Degradation

For the removal of cyanide from gold mill effluents, the oldest treatment practiced to date has been natural degradation.

The natural degradation process consists of impounding cyanide-bearing waste solutions in large shallow ponds, thus allowing the hydrogen cyanide to escape. Depending upon present cyanide species and physicochemical conditions, such interactions as hydrolysis, dissociation, volatilization, photodegradation, chemical and bacteriological oxidation, and precipitation-dissolution may be important. They are discussed in the following sections.

2.4.1 Volatilization

The rate of volatilization of HCN from a pond is dependent on the pH value of the waste and on prevailing atmospheric conditions. In general, decreased pH, increased temperature, reduced liquid-depth to surface-area ratios and increased turbulence will accelerate volatilization.

Taking into consideration the fact that atmospheric conditions vary widely, and that the cyanide-containing gold mill wastewater is strongly alkaline, it would be difficult, but not impossible, to predict the time necessary for complete removal of cyanide (Dodge and Reams, 1949).

Since the equilibrium reaction between HCN and CN^- is so pH dependent (Eq. 2.1) the presence of air and CO_2 (air normally contains 300 g/m^3 of CO_2) will have an effect on the formation of HCN (Clevenger and Morgan, 1916). The pH will decrease as the absorption of carbon dioxide from the air occurs and carbonic acid is produced by hydrolysis:

$$CO_2 + H_2O \rightarrow H_2CO_3^*$$

Carbon dioxide will convert the hydroxide alkalinity as rapidly as it is formed to bicarbonate alkalinity. The reactions are:

$$Ca(OH)_2 + H_2CO_3^* \rightarrow CaCO_3 \downarrow + 2\ H_2O$$

$$2\ NaOH + H_2CO_3^* \rightarrow Na_2CO_3 + 2\ H_2O$$

$$Na_2CO_3 + H_2CO_3^* \rightarrow 2\ NaHCO_3 \qquad pH = 8.3$$

Due to the formation of the bicarbonate-carbonic acid buffer system, further decreases in pH below 8.3 will be relatively slow. However, at equi-molar concentrations of H_2CO_3 and HCO_3^- the pH would be 6.5, and small changes in pH in this range (8.3 to 6.5) result in large changes in the HCN/CN^- ratio (Milne, 1950a) (see Figure 2.2).

The carbonic acid produced by dissolving CO_2 from the air in the water will also furnish hydrogen ions necessary to the formation of hydrogen cyanide.

The pH value can be used as an indicator of the percentage of total cyanide which has been converted into hydrogen cyanide. The concentration of cyanide in solution determines the amount of volatile HCN produced and consequently the partial pressure of HCN at the interface between the liquid and the surrounding gas. The partial pressure is related to the concentration of HCN in the liquid by an equilibrium constant (H) called the Henry's Law constant (Dodge and Zabban, 1952). H may be independent of concentration in a very dilute solution and of total pressure, provided the latter is nearly atmospheric; however, it is affected by the temperature of the solution.

Hydrogen cyanide in solution will maintain an equilibrium with atmospheric HCN. In general the amount of contact required to bring two phases into equilibrium is dependent on the rate of mass transfer. The rate at which mass is transferred between phases (in this case gas and liquid) is controlled by the driving force for mass transfer, the resistance to mass transfer and the interfacial area between phases (Perry, 1976) according to:

$$N_A = K_L (X - X_i) = K_G (Y_i - Y)$$

where N_A = mass transfer rate;

K_L, K_G = liquid and gas phase mass transfer coefficients;

X, Y = bulk liquid and gas mole fractions;

X_i, Y_i = liquid and gas mole fractions at the interface.

Looking at the problem from the viewpoint of chemical-engineering unit operations, the objective to be achieved in the cyanide removal process, based upon release of cyanide as hydrogen cyanide would be to bring about intimate contact first between cyanide in the pond and atmospheric pollutants (such as CO_2) to decrease the pH and promote the formation of HCN in solution and then between the solution and air to volatilize HCN.

In batch operations, volatilization of cyanide may occur in two ways:

i) By keeping the solution stagnant, in which case the solution is exposed to the surrounding air and the volatile solute is allowed to escape into the atmosphere. As soon as the surface of the solution becomes depleted of HCN the rate of removal of cyanide from the solution by volatilization becomes entirely dependent on the rate of the molecular diffusion of HCN (Palaty and Horokova-Jakubu, 1959; Lur'e and Panova, 1962).

When working with stagnant solutions wind effects and stratification have to be taken into consideration.

ii) By aerating the solution with a gas (usually air) which is introduced into the solution in fine bubbles. Even gentle aeration of alkaline cyanide wastes will increase the mass transfer rate and cause a decrease of the pH of the solution by natural recarbonation with a concomitant shift of the HCN/CN^- equilibrium to favour the formation and volatilization of HCN (Doudoroff et al, 1966). The difference between the partial pressure of hydrogen cyanide (which is in equilibrium with the concentration of HCN in the solution) and that in the gas used for stripping is one of the factors determining the rate at which the hydrogen cyanide is stripped from the solution. Stripping can only occur if the former partial pressure is higher than the latter, and the rate increases as this difference increases (Dodge and Zabban, 1952).

In all the experiments to date carried out on aerated solutions, air was used as a stripping agent. This improved the contact between atmospheric CO_2, the alkaline compounds in solution and HCN, decreased the pH, enhanced hydrolysis and brought about loss of HCN (Lur'e and Panova, 1962).

2.4.2 Photodegradation

Photodegradation occurs naturally in any shallow pond or lagoon where light can penetrate. Factors such as light penetration, affected by turbidity, colour, depth and many other parameters, will determine the impact of photodegradation in a specific body of water. Factors which enhance photolysis also enhance HCN removal. For example, water turbulence will enhance mixing and expose more metallo-cyanide complexes to sunlight. This will enhance volatilization of HCN by increasing the exposed surface area and the rate of mass transfer

(Ecological Analysts Inc. 1979). Numerous metallo-cyanide complex ions are relatively stable in aqueous solution in the absence of ultraviolet and visible light. However, under certain conditions, photodecomposition, with subsequent release of cyanide ions, will occur.

Ultraviolet (UV) and visible radiation cause the decomposition of complex iron cyanides, especially in the presence of dissolved oxygen (Burdick and Lipschuetz, 1950). After prolonged irradiation, HCN is released from its iron-cyanide complex. Iron may precipitate in basic solution as ferrous hydroxide (a white precipitate), or as ferric ferro-cyanide (Prussian Blue) in acidic solutions (Broderius, 1973). The pH, temperature and cyanide concentration all have a varying affect on the photolysis reaction of both iron-cyanide complexes (ferro- and ferri-). The lower the concentration of the iron complex ion, the faster the rate of photodegradation (Broderius and Smith, 1980).

The rate of volatilization of HCN from the surface of waters containing iron-cyanide complexes subjected to photolysis was found to be approximately first order. Half-lives for hexacyanoferrate (II) solutions containing 100 µg/L CN of 50 and 18 min were observed for fall and summer mid-day conditions, respectively, for a lake surface in Minnesota. In comparable hexacyanoferrate (III) solutions, the mid-day half-life ranged from 160 min in late fall to a minimum of about 64 min in mid-summer (Broderius and Smith, 1980).

2.4.3 Chemical oxidation

Chemical oxidation of cyanide using different oxidizing agents is a commonly employed treatment method for cyanide-bearing wastewaters but little data are available on the chemical oxidation of free cyanide under natural conditions.

Cyanide can be oxidized to cyanate by ozone, which is produced in water from ultraviolet irradiation by sunlight. Once cyanate is formed it will not revert to free cyanide, but because of its extreme instability it will decompose to ammonium ion and carbon dioxide (Amex of Canada Ltd., 1980; Resnick et al., 1958; Hendrickson and Daignault, 1973).

It is thermodynamically possible to oxidize free cyanide with molecular oxygen to yield cyanate, but unless catalyzed the reaction is impracticably slow. For example, Cu, activated carbon, enzymes, photo-redox reaction or microorganisms can be used as catalysts. (Pol'kin and Krylova, 1979; Weber and Corapcioglu, 1981; Schmidt et al., 1981).

2.4.4 Microbial oxidation

Many microorganisms are resistant, or can induce resistance, to cyanide by degrading it to nontoxic products (Knowles, 1976). It has been shown, primarily through studies of biological wastewater treatment systems, that bacterial, fungal and algal species can convert cyanide under either aerobic or anaerobic conditions to carbon dioxide and ammonia, nitrite or nitrate (Towill et al., 1978; Brunker, 1980; Ludzack and Schaffer, 1960).

The need for gradual acclimation of the system is usually stressed as well as an additional source of metabolic energy such as dextrose, glucose, etc. (Howe, 1965; Raef et al., 1977).

The fact that cyanide can be removed from various effluents by biological treatment has been confirmed on many occasions. Murphy and Nesbitt (1964) found that 2/3 of the cyanide carbon used was incorporated into bacterial cellular material and 1/3 was used for cell respiration.Kunz et al., (1978) still had doubts whether the removal is caused by bio-adsorption or by bio-oxidation.

Cyanate and thiocyanate can be broken down by bacteriological treatment. The products of decomposition are incoorporated into cellular constituents within the organism as either a nitrogen or carbon source or both. It has been proven that CNO^- was more difficult to treat biologically than CN^- and CNS^- and that the process is very sensitive to changes in pH and temperature (Ludzack and Schaffer, 1960).

The extent of microbial degradation of cyanide in mine tailings ponds is not well documented. Gold mill effluents are not only dominated by high concentrations of cyanide but they usually contain cyanate, ammonia, thiosalts, thiocyanate, and high concentrations of metallo-cyanide complexes which may not be amenable to bacterial attack as well as toxic chemicals such as heavy metals (Cu, Zn, Ni, Fe). In addition, they are typically initially characterized by a high pH

(>10), low nutrient levels, low number of microorganisms and high concentration of suspended solids.

The initial loss of cyanide from the cyanide-containing wastes in these ponds has been attributed to volatilization because it was found to be too rapid for strictly biological activity (Ludzack et al., 1951; Tarzwell, 1955).

After a prolonged period of time (some ponds have retention times of one to two years) the degradation of free cyanide could be enhanced by some biodegradation because the stagnant solution in the pond is bound to accumulate some microorganisms from the air, soil or plants. In order to enhance the process, some researchers have suggested the enrichment of the effluent organic substances by growing water plants (e.g., bulrushes) and the introduction of organic carbon material (such as molasses), and the maximization of oxygen availability by aerating the pond (Ilyalemdinov et al., 1977).

2.4.5 Thiocyanate formation

Cyanide can react with polysulphides or thiosulphate to form thiocyanate. Both polysulphide and thiosulphate are oxidation products of sulphides which are abundant in minerals (Amax of Canada Ltd, 1980; Luthy and Bruce, 1979).

If both CN^- and CNS^- are present in solution, the metallocyanide complexes will exist in solution preferentially to the respective thiocyanate complexes because the formation constants for metal-thiocyanide complexes tend to be much lower than the corresponding metal-cyanate complexes (Dean, 1973).

Many of the metal-thiocyanate complexes are insoluble, therefore, they will precipiate. This mechanism might play a role in the removal of Zn, Ni and Cu in effluent holding ponds (Schmidt et al., 1981).

2.4.6 Cyanide in soil

Some metal cyanides in gold mill effluents remain in solution, while others adsorb onto solids and settle from solution (IEC, 1979; Ingles, 1981a). Little information is available on the movement of either free or complex cyanides at low concentrations through soils or tailings (Renn, 1955).

An EPA laboratory study of cyanide movement in different soils (Alesii and Fuller, 1976) showed that some cyanides are quite immobile while others may be more mobile. Ferric ammonium hexacyanoferrate was apparently very immobile. Cyanide as $Fe(CN)_6^{3-}$ and CN^- in water were found to be very mobile in soils. Cyanide as KCN in a natural landfill leachate was found to be less mobile. Soil properties such as low pH and percent free-iron oxide, and kaolin, chlorite, and gibbsite type clays, tend to increase the attenuation of cyanide in the three forms tested. High pH, presence of free $CaCO_3$, low clay content and the presence of montmorillonite clay tend to increase the mobility of the cyanide forms (Alesii and Fuller, 1976).

The movement of cyanide in soil is usually quite limited because it is either complexed by trace metals or metabolized by various microorganisms (Towill et al., 1978).

2.4.7 Conclusion

A review of the literature shows that cyanide in an aquatic environment is not persistent. Very little information is available in the literature on the fate of cyanide in gold mill tailings ponds.

In general, the oxidation of cyanide with atmospheric oxygen is possible but, unless catalyzed, the reaction is impracticably slow. If it comes in contact with some oxidizing agents (e.g., chlorine, ozone), cyanide may be oxidized to a harmless level, but these oxidizing agents are not at hand in any of the mine tailings ponds.

Microbial degradation of cyanide in mine tailings ponds is not well documented in the literature. Microorganisms can convert cyanide (up to 200 mg/L) to CO_2, ammonia, nitrite and nitrate, in biological wastewater treatment systems, particularly if they are acclimatized to cyanide and there is an additional source of metabolic energy present. The possibility of microbial degradation in normally operated tailings ponds upon release of the mill effluent is remote because of the high levels of cyanide, heavy metals, pH and suspended solids, and the low number of microorganisms and low nutrient levels, found in the effluent. Therefore, microbial degradation cannot be considered as a removal mechanism during the initial period when natural degradation of cyanide seems to be most rapid. After a prolonged period of time the number of microorganisms may increase, but their effect on cyanide will depend upon their ability to oxidize it and break down metal cyanide complexes.

The only information that is well documented is the ability of free cyanide to volatilize in an aquatic environment. Basically, most of the potential cyanide degradation or removal mechanisms apply to free cyanide. Thus, it is necessary that the metallo-cyanide complexes dissociate or break down to the metal and free cyanide components before cyanide removal from an aquatic system can occur. Regardless of its form, simple or complexed, cyanide has to be treated as a potential source of HCN. After the initial quantity of free cyanide is released from a solution, the remaining cyanide forms will be converted into HCN, the volatile form of cyanide, as a function of the specific conditions occurring, e.g., sunlight, increased temperature, decrease in pH, presence of air.

Based on the above considerations, the major focus of this research was concentrated on volatilization and the metallo-cyanide complex dissociation (metal cyanide decay) as most important mechanisms for the removal of cyanide from the gold mill tailings ponds, keeping in mind all the other possible mechanisms.

3 ANALYTICAL METHODOLOGY

Cyanide terminology is defined in Appendix A and used consistently throughout this thesis. All chemical analyses for this project were carried out by the staff of the Laboratory Services Section at the Wastewater Technology Centre (WTC).

3.1 Cyanide Determinations

Samples taken during each experimental run were collected in polyethylene bottles, preserved with NaOH to a pH of 12, stored at 4°C and analyzed at the earliest possible time. The samples from all the solutions, except the iron cyanide complex solutions, were analyzed for total cyanide by the picric acid method (Appendix B.1). The picric acid method recovers all cyanides in the solution except iron cyanides (Conn, 1981). In this method, reagents are added to the sample directly and a colour develops which is directly related to cyanide concentration. Although with standard solutions the method was found to be both accurate and precise to levels of approximately 0.2 mg/L CN^- a concentration of 1 mg/L was adopted as a lower limit in this research for application of this method.

Below the 1 mg/L level the distillation method was applied (Appendix B.2). Iron-cyanide complex solutions were also analyzed by the distillation method.

A modified version of the conventional acid distillation technique, using hydrochloric acid and hydroxylamine hydrochloride as reagents at pH 2.0 is the more accurate analytical procedure for total cyanide than the picric acid method used at WTC (Conn, 1981). The cyanide measurements after distillation are either colorimetric or titrimetric, depending on the concentration of cyanide. The interlaboratory standard deviation was determined to be 0.01 mg/L at the 0.1 mg/L level for synthetic samples and 0.1 mg/L at the 2.6 mg/L level and 0.003 mg/L at the 0.030 mg/L level for four real samples.

The same distillation procedure is used for the determination of weak acid dissociable cyanides (all but iron-cyanides) except the reagents used in this case are an acetic acid - sodium acetate solution buffered at pH 4.5 and zinc acetate. The purpose of the zinc acetate is to prevent decomposition of any ferrocyanide present. Cyanide has been reported to be totally recovered from zinc and nickel complexes but only about 70% recoverable from copper complexes and 30% recoverable from cadmium complexes. No recovery is reported from ferro, ferri and cobalt complexes and thiocyanate is not an interference. The interlaboratory relative standard deviation on an actual effluent sample was determined to be 5.5% at a cyanide concentration of 2.5 mg/L CN^-.

3.2 Cyanate and Thiocyanate Determination

Cyanate hydrolyses to ammonia when heated at a low pH. This phenomenon is used in the cyanate determinations. The ammonia content is measured before and after hydrolysis of cyanate using ammonia-selective electrodes. The cyanate results have, for a 10 mL aliquot, a detection limit of 0.3 mg/L with a ±3% precision at 100 mg/L.

Thiocyanate forms an intense red color with ferric ion at an acidic pH, which is suitable for colorimetric determination. The thiocyanate results have, for a 10 mL aliquot, a detection limit of 1 mg/L. The precision, depending on the sample concentration, is as follows: ±3.7% at 7 mg/L ; ±0.6% at 35 mg/L and ±0.8% at 70 mg/L . More detailed descriptions of the methods are available in "Standard Methods" (APHA-AWWA-WPCF, 1980).

3.3 Metals Determination

Samples for the determination of metals were collected in acid washed polyethylene bottles preserved with nitric acid (pH ~2) and stored at 4°C. All metal analyses were performed by atomic absorption (AA) flame analysis (APHA-AWWA-WPCF, 1980). The detection limits, working range and precision for the results obtained by AA are as follows:

	Detection Limits (mg/L)	Linear Working Range (mg/L)
Cu	0.01 ± 0.005	0.01 - 10.0
Zn	0.01 ± 0.005	0.01 - 3.0
Ni	0.10 ± 0.02	0.10 - 10.0
Fe	0.10 ± 0.02	0.10 - 7.0

The precision varies with the sample concentration and its matrix. Precisions at the top end of the linear working ranges for Cu, Zn, Ni and Fe are: ±1%, ±1%, ±3% and ±3%, respectively.

4 SCREENING EXPERIMENTS

The review of the literature revealed that the processes of volatilization of HCN from cyanide solution and the dissociation of metallo-cyanide complexes were dependent upon many factors, such as pH, temperature, ultraviolet irradiation, contact with air (aeration), initial cyanide concentration, metal content, depth of the solution, etc. In this research, the three factors that were considered to be the most important were selected: temperature, UV light and aeration. The effect of depth upon irradiation was taken into consideration later when UV irradiation rate constant was calculated, and upon other factors was eliminated by having the solutions well mixed. The assumption was made that the pH effect on metallo-cyanide complexes was insignificant and only its effect on HCN/CN^- ratio was considered later in the modelling process.

The following sections explain how the temperature, UV light and concentration ranges used in this research were selected and present the results of the preliminary tests that were carried out in order to determine suitable pH and air flow levels for the experimental design.

4.1 The Effect of Temperature, UV Light and Concentration

In order to examine the effect of <u>temperature</u>, all bench scale experiments were carried out at 4°C and 20°C. The 20°C temperature was selected to be representative of warmer conditions and was easily obtained as a set room temperature. The 4°C temperature was chosen to be representative of cold weather conditions at many Canadian gold mines and was also the lowest temperature that the equipment available in the laboratory (cold water bath) could handle.

Considering that iron commonly occurs in the mill effluents and that an iron-cyanide complex solution is photodegradable (see Section 2.4.2), the effect of UV irradiation had to be examined to reproduce the sunlight effect. Samples tested under UV light were exposed to an intensity of 2 mW/cm^2; this intensity of sunlight is typical of southern Ontario in summer for the 300 to 400 nm range (Shaw, 1983). Since the experiments were carried out in graduated cylinders made of 2 mm thick Pyrex glass, it filtered out all radiation below 300 nm (Table 4.1). The range of UV irradiation from sunlight was reproduced with B-100A Black Ray Ultraviolet lamp (wavelength 366 nm) mounted 18 cm above the cylinder (Figure 4.1). The intensity was measured with a "Black Ray" Ultraviolet Meter, Model J-221, with absolute accuracy of ±15% and a precision of ±5%.

In order to examine the effect of concentration, the fact that the quality of the actual mill effluent would depend on the type of ore available, the treatment used on that ore, and chemicals applied in the process has to be taken into consideration. It would be difficult to carry out laboratory experiments on one specific mill effluent and apply the findings to others. Therefore, it was decided to produce a

TABLE 4.1. APPROXIMATE WAVELENGTH LIMITS FOR TRANSMISSION OF VARIOUS OPTICAL MATERIALS NEAR ROOM TEMPERATURE

Material	Thickness, mm	Approx. λ for cutoff, Å
Window glass (standard)	1	3070
	3	3140
	10	3300
Optical (white crown) glass	1.8	3090
Pyrex (Corning 774)	1	2800
	2	2970

Source: Shaw, 1983.

"synthetic effluent", i.e., to emulate the general characteristics of an actual gold mill effluent and use this solution in the experiments performed under controlled laboratory conditions.

The important metals found in the mill effluent at the selected gold mine complexed about 17% of the cyanide present. Based on the large amount of data available on this effluent, the individual metals most often found in the mill effluent typically tied up: Cu about 4%, Zn 8%, Ni 2% and Fe 3% of the available total cyanide.

Therefore, the level of 17% was chosen (i.e., metal cyanide to total cyanide ratio of 0.17) for sodium cyanide and the selected single metallo-cyanide solutions, which were:

i)	Sodium Tricyanocuprate	$Na_2Cu(CN)_3$
ii)	Sodium Tetracyanozincate	$Na_2Zn(CN)_4$
iii)	Sodium Tetracyanonickelate	$Na_2Ni(CN)_4$
iv)	Potassium Hexacyanoferrate	$K_3Fe(CN)_6$

The four particular metallo-cyanide complexes were selected for the following reasons:

i) Upon addition of cyanide in the cyanidation process, copper sulphides are readily oxidized to sulphates and Cu^{2+} is released. When cyanide is oxidized to cyanate, Cu^{2+} is reduced to Cu^{1+} (Fairbridge, 1972). Therefore, of all the complex ions formed, $Cu(CN)_3^{2-}$ is considered the most probable to occur in the mill effluents (Hedley and Tobachnick, 1958).

ii) Zinc's chemical behaviour is dictated by the existence of a single oxidation state, i.e., Zn^{2+}. Zinc minerals are sufficiently soluble under normal cyanidation conditions. Zinc forms complexes in aqueous solution but these are never particularly stable or inert (Fairbridge, 1972). During the reactions involved in gold precipitation, the greater part of the zinc dissolves in the cyanide solution and forms various complexes, the most common being $Na_2Zn(CN)_4$ (Hedley and Tobachnick, 1958).

iii) The chemistry of nickel is not simple because of the existence of the variety of its structures (octahedral, tetrahedral and square) (Cotton and Wilkinson, 1962). Although nickel can achieve various oxidation states (see Section 2.2.4) the majority of its compounds are of the Ni(II) oxidation state (Nriagu, 1980). Since the formation of tetracyanonickelate (II) complex is a very fast reaction (a fifth-order reaction) and this complex is considered to be thermodynamically very stable, this is the nickel-cyanide complex most likely to occur in the mill effluents (Kolski and Margerum, 1968).

iv) Cyanide reacts with iron (II) and iron (III) to form extremely stable ferro- and ferricyanide complexes, respectively (Broderius, 1973). The common form in the cyanidation process would be ferrocyanide but in an aquatic environment ferrocyanate would fairly easily oxidize to ferricyanide (Ingles, 1981b).

The simple sodium cyanide solution and these metallo-cyanide solutions were tested in anticipation that the results would assist in the interpretation of the data from more complex solutions.

For more complex solutions low and high mixes were tested. The "low mix" contained 200 mg/L of TCN, of which 17% was in a complex with the four metals mentioned above according to their exact stoichiometric proportions. The "high mix" was oversaturated with the same number of metals, hence, it did not contain any free cyanide (calculations were performed assuming that 117% of available cyanide was complexed with these four metals).

In order to determine suitable conditions for the experimental design, several preliminary tests were carried out. The results were used to delineate the choice of buffer and pH level, and to examine the effects of aeration and CO_2 on cyanide removal.

4.2 Selection of Buffer and pH Level

Objective - Molecular HCN and the cyanide ion CN^- (the free cyanide), exist in water in a definite relationship dependent upon the pH of the system (Eq. 2.1). Since the pH of cyanide solution changes when open to the atmosphere, a buffer has to be used in order to maintain the pH at the certain level. The objective of this experiment was to determine the type of buffer which could be used for the experiments with simple and metallo-cyanide complex solutions. The pH's that were considered were 7.0, 9.0 and 11.0. From Figure 2.2 it can be seen that at pH 7.0 approximately 99.5% of the free cyanide in solution is present as HCN, about 64% at pH 9.0 and about 5% at pH of 11.

Conditions - For safety reasons all the experiments were performed in a fume hood. All the preliminary tests were carried out at room temperature (20°C) and under fluorescent light. The conditions of the test are presented in Table 4.2, and the setup used is illustrated in Figure 4.1. All cyanide solutions were made on the day of the experiment. The air flow rate used in this test was 1000 cm^3/min (arbitrarily chosen).

Discussion - The results of the experiments are presented in Table 4.3. These show that at pH 7.0 the rate of reaction is the fastest and as the pH increases the reaction rate slows down substantially. There were some difficulties encountered in maintaining the pH at 11.0. During the latter part of the tests (after about 17 h) NaOH had to be added intermittently to maintain the pH constant. Because of these difficulties the results of the second set of tests are not available.

The equation used to calculate buffering capacity for the phosphate buffer (pKa = 7.2) was

$$pH = pKa + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} \quad \text{(Freiser and Fernando, 1963)}$$

The calculated concentration of the phosphate buffer (see Table 4.2) had a sufficient buffering capacity to maintain the pH at the desired level of 7.0.

TABLE 4.2. THE TEST CONDITIONS FOR BENCH SCALE EXPERIMENTS

Apparatus (Fig. 4.1)	Graduate cylinder (2000 mL) (As* = 47.78 cm^2)	
	pH meter	
	Fritted glass diffuser	
	Air flow meter	for aerated samples
	Glass impinger (water)	
	Glass impinger (1N KOH) - used for CO_2 trap	
	UV lamp - used for conditions with UV light	
Sample Source	2000 mL NaCN (100 mg/L TCN**)	
	2000 mL $Na_2Cu(CN)_3$ (100 mg/L TCN)	
Buffers	For pH 7.0 : 0.25M KH_2PO_4 and 0.16M Na_2HPO_4	
	For pH 9.0 : 0.1M H_3BO_3 and 0.1M NaOH	
	For pH 11.0 : 0.05M $Na_2HPO_4 \cdot 7H_2O$ and 0.1M NaOH	

* Surface area.
** Total cyanide.

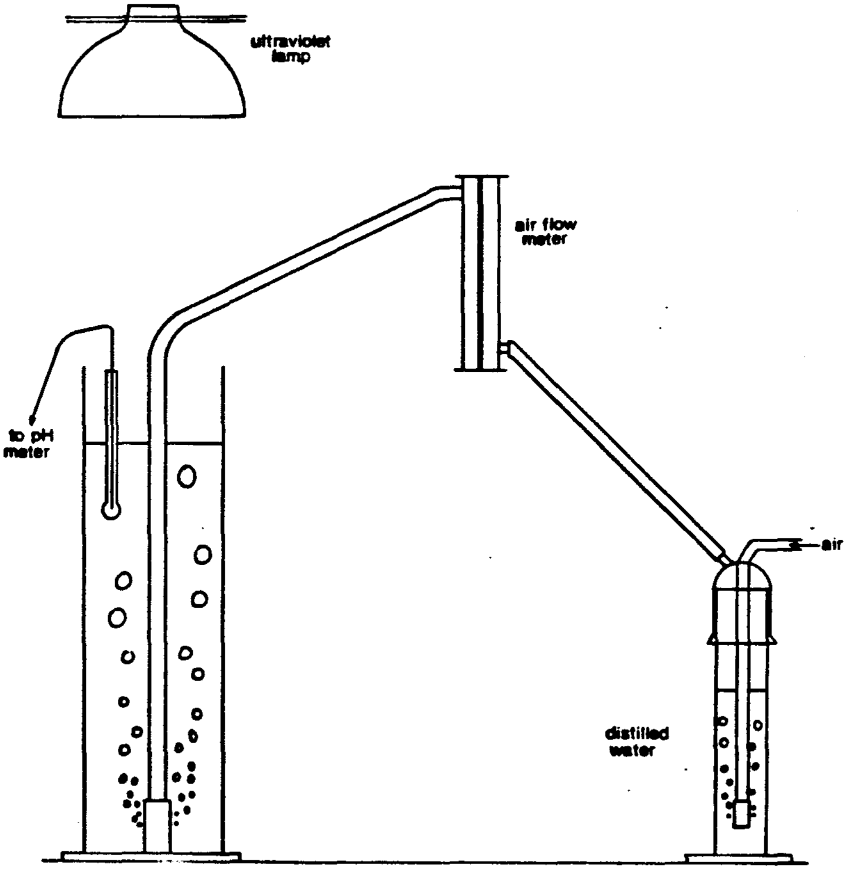

Figure 4.1 The Setup for Bench Scale Experiments

TABLE 4.3. THE EFFECT OF pH ON THE RATE OF CYANIDE REMOVAL (CHOICE OF BUFFER)

Cyanide Solutions	pH 7.0 0.25M K H_2PO_4 0.16M Na_2 HPO_4		pH 9.0 0.1M H_3BO_3 0.1M NaOH		pH 11.0 0.05M Na_2 HPO_4 0.1M NaOH	
	$k_v(h^{-1})$	$t_{1/2}(h)$	$k_v(h^{-1})$	$t_{1/2}(h)$	$k_v(h^{-1})$	$t_{1/2}(h)$
NaCN	0.2493	2.8	0.0776	8.9	0.0155	48.8
	0.2512	2.8	0.0858	8.1	NA	NA
Cu-CN	0.0356	19.5	0.0035	197.8	0.0014	498.1
	0.0328	21.1	0.0020	340.7	NA	NA

NA - not available.
k_v - volatilization rate constant calculated assuming first order reaction.
$t_{1/2}$ - half life.

In order to check if the PO_4^{3-} ligand had any effect on the removal reaction of cyanide (i.e., if PO_4^{3-} was competing with CN^- for metals) parallel experiments were carried out using either phosphate buffer or 1.2M HCl for pH control. The results are presented in Table 4.4 and they show the same rate of cyanide removal in both experiments.

Conclusion - Taking into consideration the ease of running the test at pH 7.0 and the fact that the rate of reaction was the fastest at that pH (Table 4.3), it was decided to run future tests at pH 7.0. From the results presented in Table 4.4 the conclusion is that phosphate buffer had no effect on cyanide removal - same rates of reaction involving Cl^- and PO_4^{3-}.

4.3 The Effect of Aeration

Objective - To determine if the presence of air had any effect on cyanide removal rate and, if so, to decide on the air flow rate to be used in subsequent experiments.

Conditions - For consistency the same setup was used for the experiments with and without air addition (Table 4.2). In the experiments with air addition, two air flow rates were used: 100 cm^3/min and 1000 cm^3/min.

Observations - Since the non-aerated samples were stagnant for the duration of the test, it was necessary to stir the solution before every sample was taken to avoid stratification effects. Cyanide concentrations in the layer closest to the surface always were lower

TABLE 4.4. EFFECTS OF Cl^- And PO_4^{3-} ON CYANIDE REMOVAL RATE

Cyanide Solutions		k_v (h^{-1})	$t_{1/2}$ (h)
NaCN	1.2M HCl	0.2638	2.6
	$H_2PO_4^-$ and HPO_4^{2-}	0.2512	2.8
$Na_2Cu(CN)_3$	1.2M HCl	0.0101	68.6
	$H_2PO_4^-$ and HPO_4^{2-}	0.0112	62.0

than the average cyanide concentration. Hence, there was some inconsistency in the results obtained on non-aerated samples.

There was a disadvantage in using an air flow rate of 1000 cm^3/min under laboratory conditions. The sample splashed around and the evaporation was 5% over 24 h. Compared to this, the evaporation of 2% per 24 h in case of 100 cm^3/min air flow was considerably lower, and in addition there were no problems with splashing during these tests.

Discussion

i) Air versus no air - From the results shown in Table 4.5 it is apparent that the presence of air had a definite effect on cyanide removal. Much longer times were required for cyanide removal from stagnant solutions.

ii) 1000 cm^3/min versus 100 cm^3/min - Cyanide from the solutions receiving the higher air flow rate was removed faster (about four times faster from NaCN and two times faster from Cu-CN solution) than from the solution with 100 cm^3/min of air.

Conclusions - The tests show that the presence and rate of availability of air have significant effects on the removal of cyanide. The only dilemma was whether air contributed only to stripping off cyanide from the solution, whether there was oxidation of cyanide going on, or a possible reaction with CO_2 from the air. To determine if cyanide oxidation to cyanate (CNO^-) was occurring, chemical analyses were performed and in all the cases CNO^- concentrations were <0.1 mg/L. Therefore, it is assumed that at the applied air

TABLE 4.5. THE EFFECT OF AERATION

Cyanide Solutions	AIR				NO AIR	
	1000 (cm^3/min)		100 (cm^3/min)			
	k_v (h^{-1})	$t_{1/2}$ (h)	k_v (h^{-1})	$t_{1/2}$ (h)	k_v (h^{-1})	$t_{1/2}$ (h)
NaCN	0.2493	2.8	0.0686	10.1	0.0228	30.4
	0.2512	2.8	0.0597	11.6	0.0269	25.8
Cu-CN	0.0356	19.5	0.0211	32.8*	0.0033	210.0*
	0.0328	21.1	0.0402	17.2	0.0086	80.6

* Inconsistent result.
Experiments were carried out at the pH of 7.0.

flows and for the duration of these experiments (4 to 30 h) there was no CNO^- produced.

4.4 The CO_2 Effect

Objective - To see if there was any effect from CO_2 in the air, causing a decrease in pH in spite of the phosphate buffer present in the solution.

Conditions - The conditions of the test are described in Table 4.2. One solution was examined having a CO_2 trap (1N KOH) on the air line, and the other solution was without CO_2 trap. The length of test runs was 103.6 h.

Observations - The results from this test are presented in Table 4.6. After four days the pH in both solutions went through essentially the same change (i.e., decreased from 6.94 (6.92) to 6.86) indicating that there was a reduction of 1% in the pH under the applied conditions. Because the permitted change in the experiments was decided to be ±0.5 at pH of 7.0 (±7%), this reduction was negligible.

Conclusion - Since the oxidation of cyanide to cyanate was not detected and there was a negligible effect of CO_2 on the cyanide solution pH level for the duration of these experiments, the positive effect of aeration was attributed to agitation of the cyanide solution and the stripping off of free cyanide.

TABLE 4.6. THE EFFECT OF CO_2 ON THE pH READINGS

	Experiment #1 (without CO_2 trap)	Experiment #2 (with CO_2 trap)
Time (h)	pH	pH
0.0	6.94	6.92
3.7	6.94	6.92
7.1	6.95	6.91
25.7	6.94	6.88
30.9	6.93	6.91
50.7	6.91	6.86
55.2	6.86	6.86
95.9	6.84	6.85
103.6	6.86	6.86

5 EXPERIMENTAL PROCEDURES AND ANALYSES OF EXPERIMENTAL RESULTS

5.1 Introduction

From the seven variables found in the literature to be affecting the process of natural degradation of cyanide (pH, temperature, UV light, contact with air, surface area versus depth of pond, initial cyanide concentration and metal content) only three, considered to be the most important factors, were selected to be examined under previously determined pH of 7.0. These are: UV light, aeration and temperature.

5.2 Full 2^3 Factorial Design

A full 2^3 factorial design was used for the three chosen variables to determine which variable had the highest effect on the rate of cyanide degradation. This design required 8 experimental runs to evaluate all combinations of two levels of each of the three variables (Box et al., 1978).

Table 5.1 shows the factorial design matrix ($k = 3$ columns and $N = 2^k$ rows) used for these experiments (a minus sign represents the low level and a plus sign the high level of each variable). The criteria used to determine the range for low and high levels was explained in Section 4.1.

TABLE 5.1. FACTORIAL DESIGN MATRIX

	Variables		
Run No.	UV Light (mW/cm^2) A	Air (cm^3/min) B	Temp. (°C) C
8	−	−	−
6	+	−	−
7	−	+	−
5	+	+	−
4	−	−	+
2	+	−	+
3	−	+	+
1	+	+	+

Experimental	UV light		Air		Temperature	
Settings	−	+	−	+	−	+
	0	2	0	100	4	20

5.3 Inspection of the Data

Upon completion of the experiments, plots of temporal changes in total cyanide concentrations in the single cyanide solutions were produced and visually examined. Two examples of these plots are given in Figures 5.1 and 5.2.

The resulting graphs show that the total cyanide concentration drastically decreased after 48 to 72 hours under all conditions. The decrease varied between 20 to 90% for the seven cyanide solutions examined (see Appendix C, Tables C.1 to C.14).

Sodium cyanide is a typical representative of water soluble simple cyanides. It will ionize rapidly and completely when dissolved in water to release CN^- and form HCN and, is therefore, considered as free cyanide. Consequently, if volatile HCN was to be released from any of the solutions examined, it would be derived initially from NaCN, then from the metallo-cyanide complex solutions. Therefore, it was concluded that the initial decrease in cyanide concentration in metallo-cyanide solutions should be compared to the rate of decrease of cyanide in NaCN solution since it occurred relatively quickly as the free cyanide was volatilizing from the solutions.

After the common initial decrease of the first part of the curve, the slopes of the second part of the curves varied among different metals, as well as within individual metallo-cyanides under different experimental conditions. This was attributed to the different length of time necessary for the dissociation of these

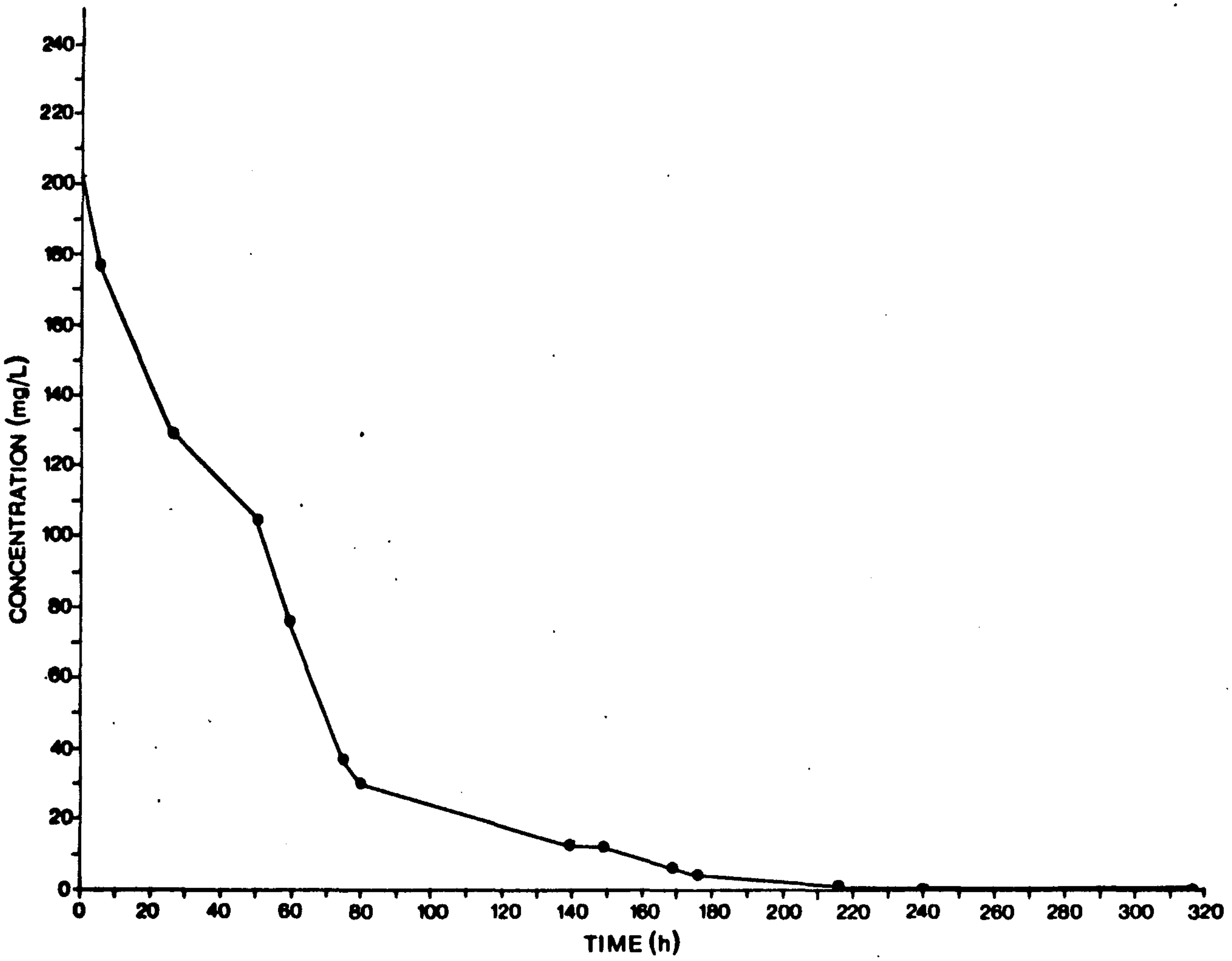

Figure 5.1 Total Cyanide Degradation in Sodium Cyanide Solution

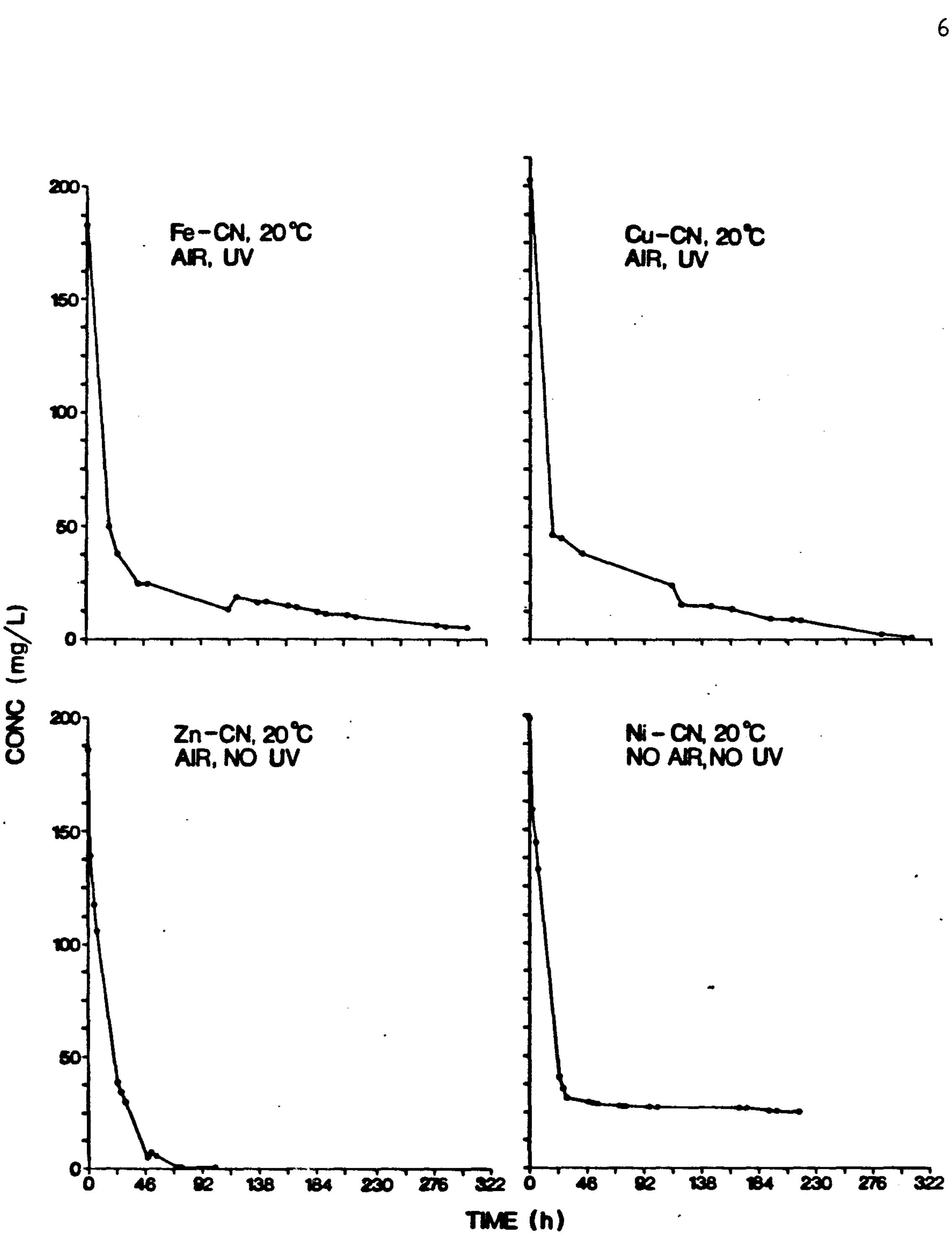

Figure 5.2 Typical Results of Total Cyanide Degradation in Fe, Cu, Zn and Ni Cyanide Complex Solutions

metallo-cyanide complexes (Table 2.2), the release of CN^- ion and formation of the volatile HCN.

5.4 Rates of Reaction

5.4.1 General

The objective of every study of chemical reaction kinetics is the determination of the order of a reaction and the provision of one or more rate equations to adequately describe the reaction at hand. The rate of reaction and the algebra for describing it is obtained by observing the change of concentration of reactant as a function of time.

If the mechanism of a reaction is known it is usually possible to postulate a rate equation and, hence, the order of reaction. The mechanism is the sequence of elementary steps that describes how the final products are formed from the original reactants. The rates of the individual steps will normally differ from each other, and the rate of the overall reaction will be determined primarily by the slowest of the steps.

It has been found experimentally that reaction rates are proportional to the concentrations of the reactants raised to an appropriate power. Expressing this mathematically for the irreversible reaction $aA + bB \rightarrow cC + dD$ the rate is (Smith, 1981):

$$r_A = - \frac{dc_A}{dt} = k\ C_A^{\alpha}\ C_B^{\beta} \tag{5.1}$$

α is the order of the reaction with respect to A and β is the order with respect to B. The proportionality constant k, called the reaction rate constant, is dependent on temperature and independent of concentration.

5.4.2 Rate calculations

The following first-order rate reaction was applied to both parts of the curve - the initial part caused by rapid volatilization of free cyanide (see Figures 5.1 and 5.2), and the second part representing the slow decrease of total cyanide concentration due to metal cyanide decay rate:

$$\frac{dC_A}{dt} = - k_1\ C_A \tag{5.2}$$

If the initial concentration is C_{Ao}, integration yields

$$\ln \frac{C_A}{C_{Ao}} = -k_1 t \qquad (5.3)$$

This implies a linear relationship between ln C_A/C_{Ao} and t.

In order to select the cut-off point between volatilization and metal cyanide decay, the break point on the curve, and determine the k value for both parts of the curve the computer program BACKRAT (Appendix D) was applied. In this program linear regression was carried out on every set of data from Time 0 to the end of the experiment and backwards from the last data point to Time 0. The residual sum of squares (RSS) was calculated and its average value monitored. When the change in cyanide removal mechanisms occurs RSS value suddenly changes, and this point is considered to be the cut-off point. The same check was made on the results of the average residual sum of squares obtained using backwards regression.

When the cut-off point was determined, the k_v value (rate constant from 0 time to the cut-off point) was available from the same forward regression analysis. In order to determine the k_1 value (the rate of reaction constant for the second part of the curve) the data set was analyzed by the RATE program (Appendix E). This program performs linear regression from the cut-off point to the end of the data set. The values of k's (the rate constants) determined this way had the units of $[h^{-1}]$.

5.5 Examination of the Factors Affecting Volatilization of Free Cyanide

The values of the volatilization mass transfer coefficients k_v (determined for all 7 solutions examined under 8 different conditions) tabulated in Appendix C (Tables C.1 to C.14), were used to construct the dot diagrams given in Figures 5.3a,b,c. The diagrams show the general location of the volatilization mass transfer coefficient with respect to temperature (Figure 5.3a), UV light (Figure 5.3b) and air (Figure 5.3c).

The effect of temperature on the rate of volatilization of cyanide from all examined solutions was very pronounced (higher rates at 20°C), particularly in the reactions with aeration present (Figure 5.3a). At 4°C the reaction was generally slow.

The energy of activation E, the minimum energy the reacting substances must have for the reaction to occur, was calculated for the NaCN solution using the semitheoretical relationship of Arrhenius for the specific rate constant (Perry, 1976):

$$k = A\,e^{-E/RT} \qquad (5.4)$$

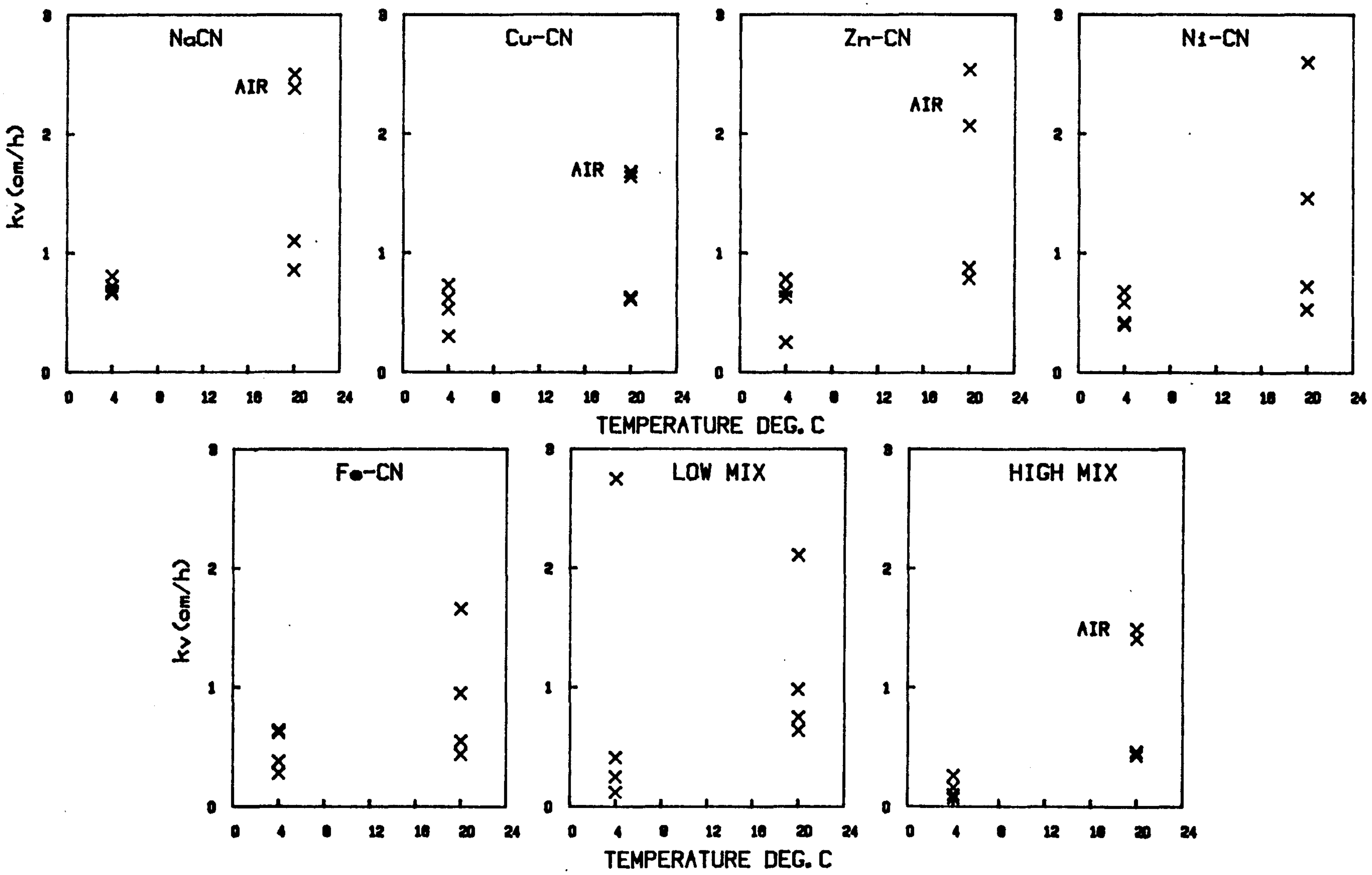

Figure 5.3a Volatilization Mass Transfer Coefficient k_v versus Temperature

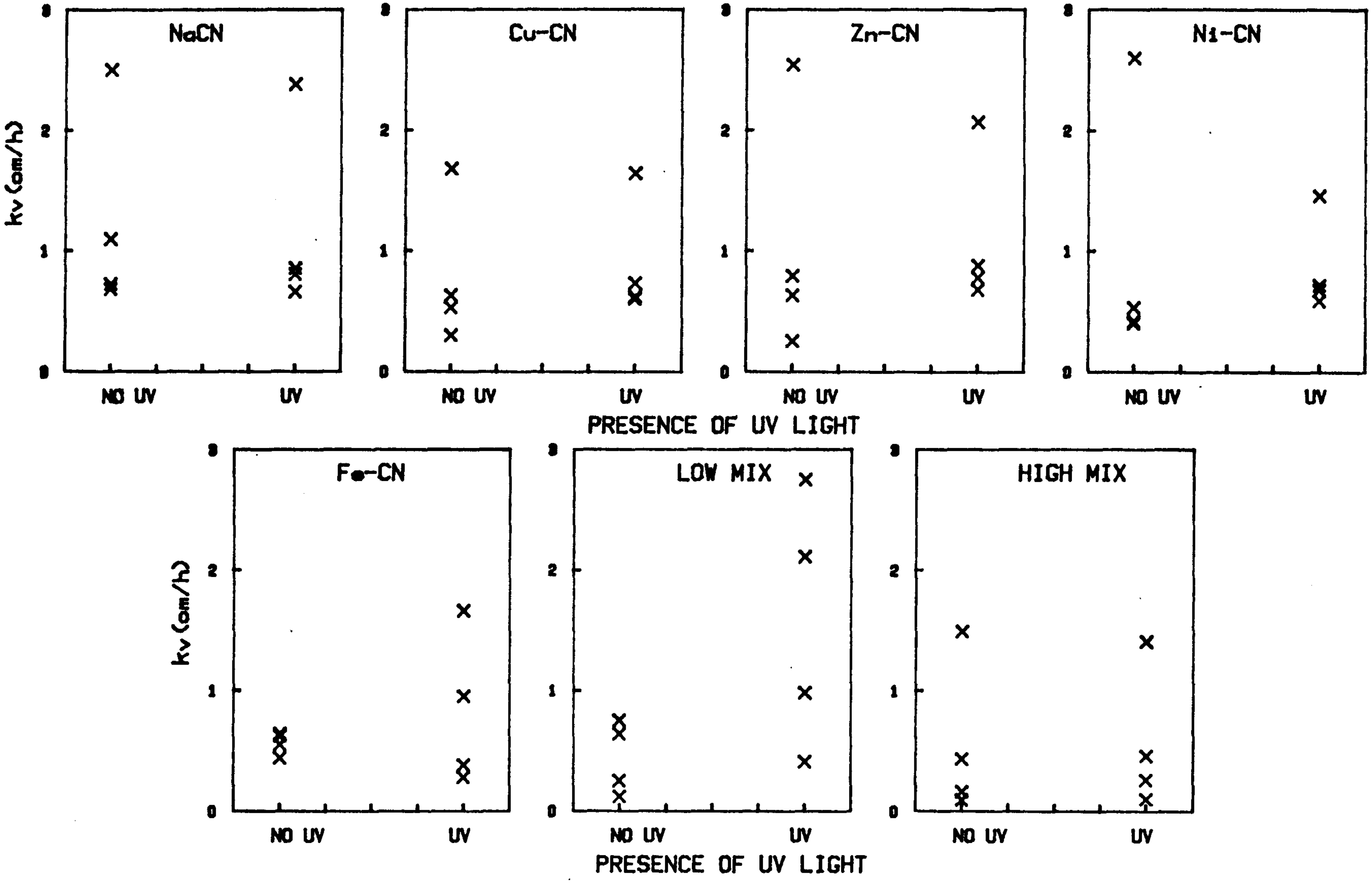

Figure 5.3b Volatilization Mass Transfer Coefficient k_v versus UV Light

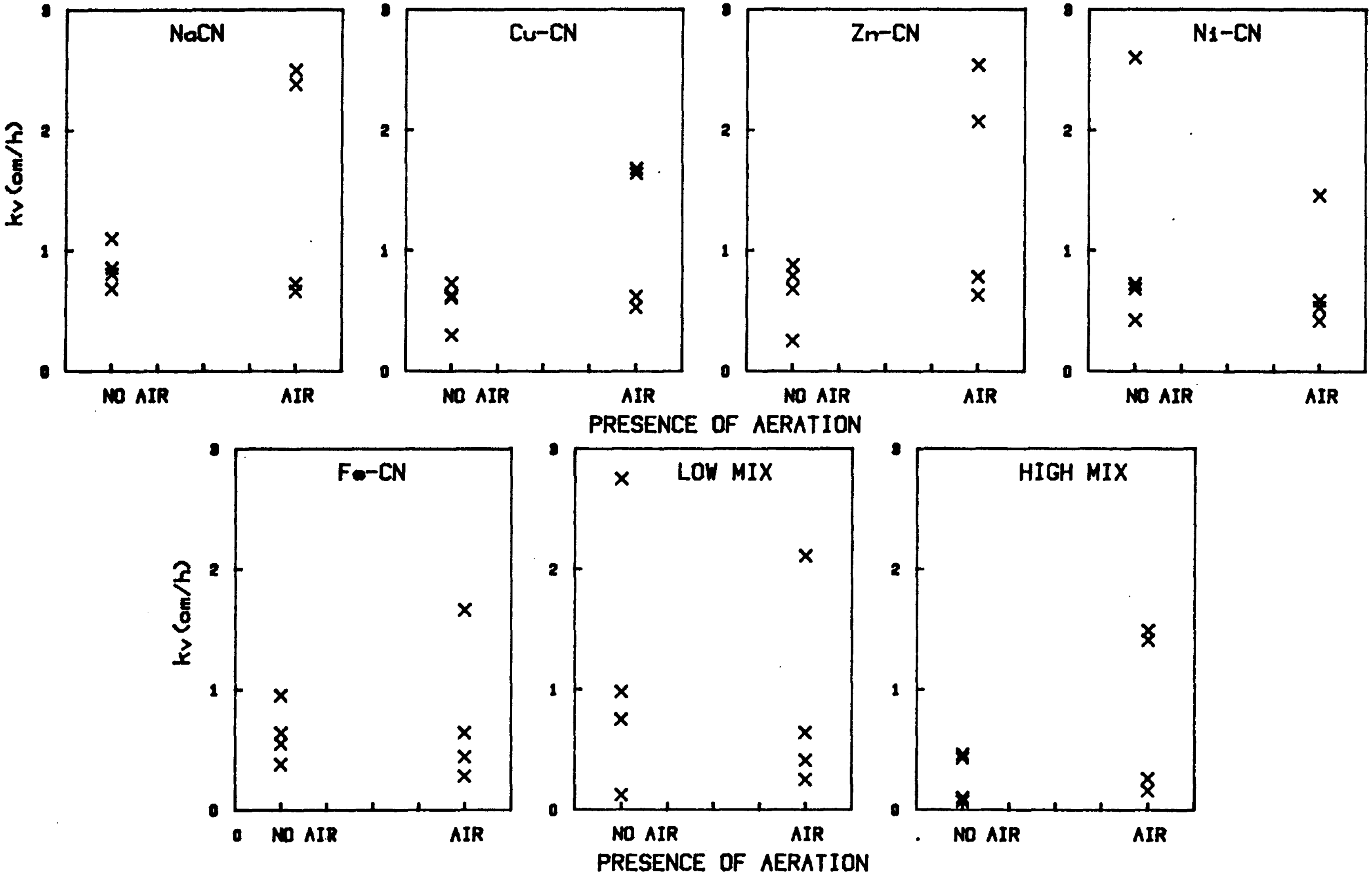

Figure 5.3c Volatilization Mass Transfer Coefficient k_v versus Aeration

where A is the frequency factor, R is the gas constant (R = 8.314 J/°K mol), T is the absolute temperature (°K) and E is the energy of activation of the reaction (kJ/mol). Taking the logarithms of Eq. 5.4, gives

$$\log k = \log A - \frac{E}{2.303RT} \qquad (5.5)$$

Thus a plot of log k against 1/T yields a slope that represents -E/2.303R. If the rate constants are available for only two temperatures, Eq. 5.5 is applied and when the two resulting expressions are subtracted from one another, the equation becomes (Perry, 1976):

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \frac{T_2 - T_1}{T_1 T_2} \qquad (5.6)$$

In this research, the activation energy for NaCN was calculated by applying Eq. 5.6, and using the rate constant values determined at 4°C (T_1 = 277°K) and 20°C (T_2 = 293°K), and solved for E the results were:

Conditions	E (kJ/mol)
AIR - UV	21.4
NO AIR - UV	25.3
AIR - NO UV	70.5
NO AIR - NO UV	65.9

The E value is always positive, therefore, the rate constant always increases with temperature. A rough working guide that the rate constant is doubled for every increase of 10°C has often been applied. In practice E may range from 4.2 to 418.4 kJ/mol or even wider and a 10°C change in temperature may lead to a smaller or greater factor than two in the rate constant (Perry, 1976). In the above case, for the temperature increase of 16°C (E = 21 to 25 kJ/mol) the factor was about 2 with UV light present, and a factor of about 5 was calculated with no UV applied (E = 66 to 70 kJ/mol).

The effect of UV irradiation was evident on the k_v of iron cyanide and low mix (Figure 5.3b).

Considering the effect of aeration (Figure 5.3c) the reaction rate was increased in most cases with the air being present, including NaCN.

The summarized results of the dot diagram analyses of factors affecting the volatilization rate of free cyanide from all cyanide solutions are presented in Table 5.2. The + and - signs in the table mean that the rate of volatilization was higher or lower, respectively, when the particular factor was present in the experiment.

5.6 Comparison of Volatilization Rates

When the values for the volatilization rate constant k_v were determined for NaCN and for metallo-cyanide solutions (see Appendix C, Tables C.1 to C.14) it was possible to compare them and at the same time check if the rate of volatilization of HCN from single

TABLE 5.2. FACTORS AFFECTING THE RATE OF VOLATILIZATION OF FREE CYANIDE (RESULTS OF THE DOT DIAGRAM ANALYSES)

	Temp.	Air	UV
NaCN	+	+	-
Cu-CN	+	+	-
Zn - CN	+	+	-
Ni - CN	+	+	-
Fe - CN	+	+	+
Low Mix	+	+	+
High Mix	+	+	-

metallo-cyanide solutions was within the 95% confidence limit of the volatilization rate of HCN from a solution of NaCN. The computer program VOLCONF (Appendix F) was used to do linear regression analyses and calculate the 95% confidence interval on the first part of the curve of all the data sets under the same condition, e.g., sodium cyanide is compared to Cu, Zn, Ni and Fe cyanide complex solutions under 20°C, NO AIR, UV (example, Figure 5.4). The general observation was that the values were within the 95% confidence level. Therefore, the statement made previously (Section 5.3) that the first part of the curve was attributed to the volatilization of free cyanide from NaCN as well as from metallo-cyanide complex solutions is justified by these results.

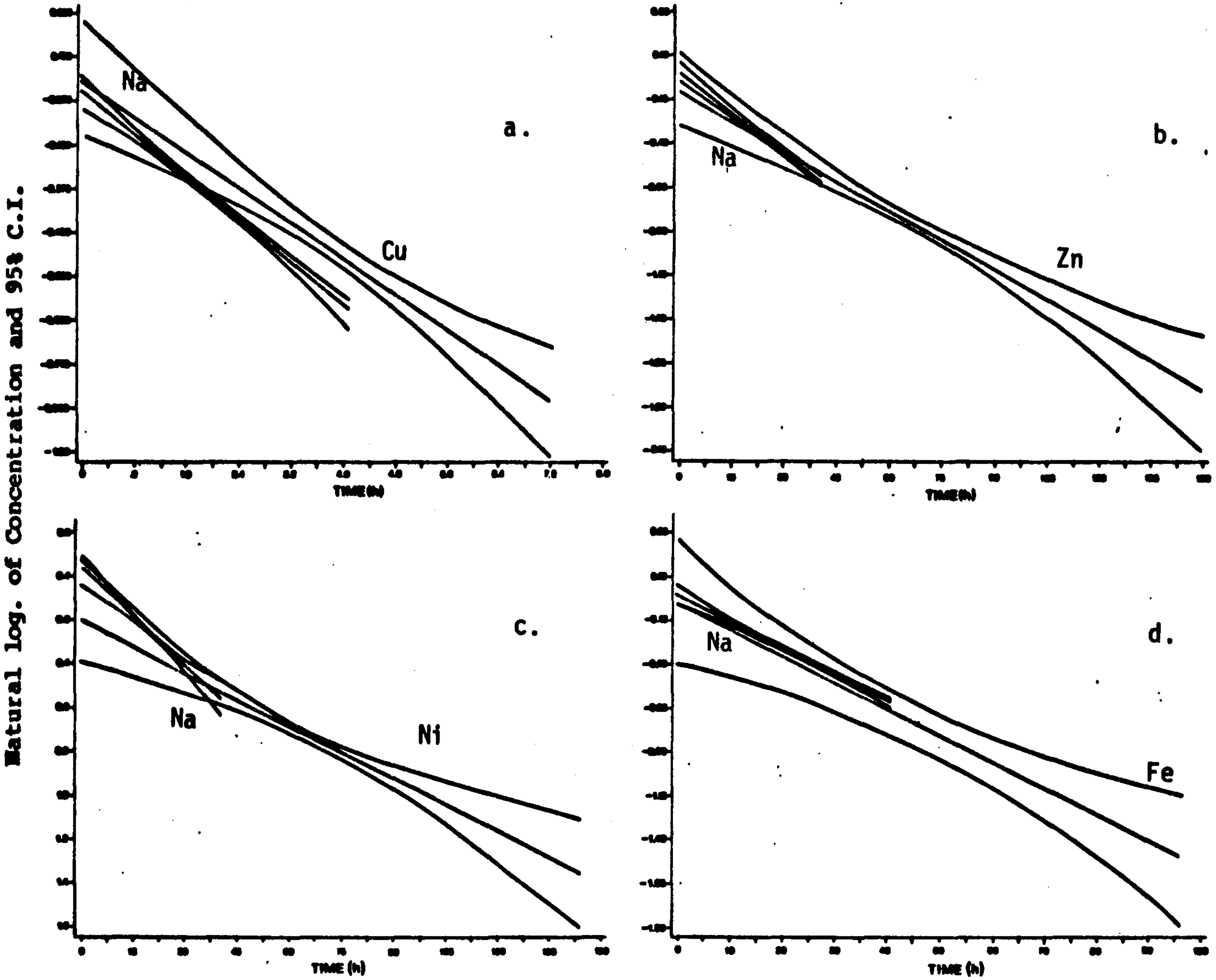

Figure 5.4 Typical Example for 95% C.I. on Part of the Degradation Curve Attributed to Volatilization - NaCN versus Cu (a), Zn (b), Ni (c), Fe (d)

6 ANALYSIS OF EXPERIMENTAL DESIGN

6.1 Introduction

The importance of each factor is determined by calculating its effect on the reaction. The effect of any factor is the change in response Y produced by a change in the level of the factor. When a factor is examined at two levels only, the effect is simply the difference between the average response of all trials carried out at the first level of the factor and that of all trials at the second level.

The effects were examined in three ways. They are:

i) Calculated effects.

ii) Half normal probability plots.

iii) Backward elimination procedure.

The theory about three ways is described in the following sections:

(i) Calculated effects - In these experiments the estimates of the main effects and the two and three factor interactions (see Table 5.1) were calculated by taking the sum of products between the response elements Y and the corresponding elements of the column (1 to k) and dividing this product by N/2 e.g.,

$$\text{Effect (1 to k)} = \frac{2}{N} \sum_{i=1}^{k} Y_i \qquad (6.1)$$

where $\{1 \text{ to } k\}$ stands for the elements of the 1 to k columns and the summation is taken over all N products (Draper and Smith, 1966).

ii) <u>Half normal probability plots</u> - Each estimated effect has a variance defined as:

$$\text{Var (effect)} = (x'x)^{-1} \sigma^2$$

where σ^2 is the variance of the individual observations and x and x' represent the design matrix and the transpose design matrix, respectively (Shaw, 1983).

No replicate runs were conducted because of the large number of experimental runs carried out (7 solutions times 8 conditions = 56) and the length of time required for each run. Therefore, the σ^2 value was determined by analyzing the half-normal probability plots. The value of the variance was estimated from the plots by considering the effects which lie close to the straight line joining the response points. The variables with effects that deviated most from the straight line are considered the most significant (Daniel, 1959). The confidence interval at the $\alpha/2$ level of significance for the best estimated individual effect β_i was calculated as:

$$\hat{\beta}_i \pm t_{\nu}, \alpha/2 \sqrt{\text{Var (effect)}}$$

where ν represents the degrees of freedom and $\alpha/2 = 0.025$, i.e., a 5% level of significance.

iii) Backward elimination procedure - The backward elimination procedure (Draper and Smith, 1966) was used as another way of verifying the results by separating significant from non-significant variables. This method first performs a complete linear regression using all variables i.e., finds the least squares equation on all independent variables, $\hat{y} = f(x_1, x_2, x_3)$. In order to be able to eliminate the non-significant variables the contribution of each of the variables to the regression sum of squares is determined. The partial F test values, calculated for every variable treated as though each one were the last to enter the equation, provide a measure of these contributions. The lowest partial F test value (F_L) is always compared with a preselected significance level F_o. If F_L is found to be less than F_o, the variable which gave rise to F_L is removed from consideration and the calculation carried out again, until all the variables that remain exceed the significance level F_o.

6.2 Results

i) Calculated effects - For metallo-cyanide single solutions and two mixes the response variables in the factorial design were the reaction rate constants (k_1's) (see Table 6.1), estimated as explained in Section 5.4.2, by using linear regression on the second portion of the curve which was attributed to metal cyanide decay.

The response variable for sodium cyanide solution was the reaction rate constant, k, estimated for the whole length of the curve, which was attributed to the removal of free cyanide (Table 6.1). Some variability was observed at the end of this degradation process (see the degradation curve in Figure 5.1 after 80 hours).

The main effects and the two and three factor interactions were determined by using Eq. 6.1 in the computer program FACT presented in the Appendix G.1 (example calculation in Appendix G.2). The values of the calculated effects are given in Table 6.2.

From the results in Table 6.2, temperature (C) seems to be the largest main effect in the majority of cases. The exceptions are Fe and low mix where UV light ("A") is the main effect.

ii) Half normal probability plots - To confirm the findings of the "calculated results", half normal probability plots were constructed using the values from Table 6.2. The effects were arranged in ascending order and plotted against $Pi(\%) = 100\ (i-1/2)/m$ where i is order number and m is the total number of effects. The plots are given as Figures G.3.1 to G.3.7 in Appendix G.3. Typical plots are presented in Figure 6.1.

When the half normal probability plots were visually inspected the temperature seemed to be the main effect for NaCN, Zn and Ni

TABLE 6.1. REACTION RATE CONSTANT AS THE RESPONSE VARIABLE

Test Code	Cyanide Solutions	Response Variables						
		Na	Cu	Zn	Ni	Fe	Low Mix	High Mix
I		0.0050	0.0033	0.0045	0.0027	0.0007	0.0046	0.0017
A		0.0139	0.0031	0.0096	0.0041	0.0040	0.0052	0.0011
B		0.0074	0.0038	0.0068	0.0030	0.0012	0.0046	0.0013
AB		0.0234	0.0036	0.0137	0.0042	0.0051	0.0087	0.0016
C		0.0238	0.0071	0.0194	0.0008	0.0026	0.0056	0.0025
AC		0.0253	0.0024	0.0181	0.0015	0.0222	0.0060	0.0022
BC		0.0394	0.0207	0.0062	0.0027	0.0016	0.0047	0.0026
ABC		0.0389	0.0153	0.0448	0.0008	0.0068	0.0075	0.0027

TABLE 6.2. RESULTS OF 2^3 FACTORIAL DESIGN IN TERMS OF RELATIVE EFFECTS

	Cyanide Solutions						
Factors*	Na	Cu	Zn	Ni	Fe	Low Mix	High Mix
A	0.0057	-0.0025	0.0123	0.0003	0.0079	0.0019	-0.0001
B	0.0088	0.0034	0.0049	0.0004	-0.0037	0.0010	0.0002
C	0.0180	0.0078	0.0135	-0.0020	0.0055	0.0002	0.0011
AB	0.0006	0.0032	0.0104	-0.0007	-0.0034	0.0015	0.0003
AC	-0.0068	-0.0023	0.0063	-0.0009	0.0044	-0.0004	0.0000
BC	0.0029	0.0029	0.0018	0.0002	-0.0045	-0.0007	0.0001
ABC	-0.0031	0.0032	0.0095	-0.0006	-0.0038	-0.0003	-0.0001

* A - UV light.
B - Aeration.
C - Temperature.
Single letters represent one factor effects and multiple letters represent interaction effects.

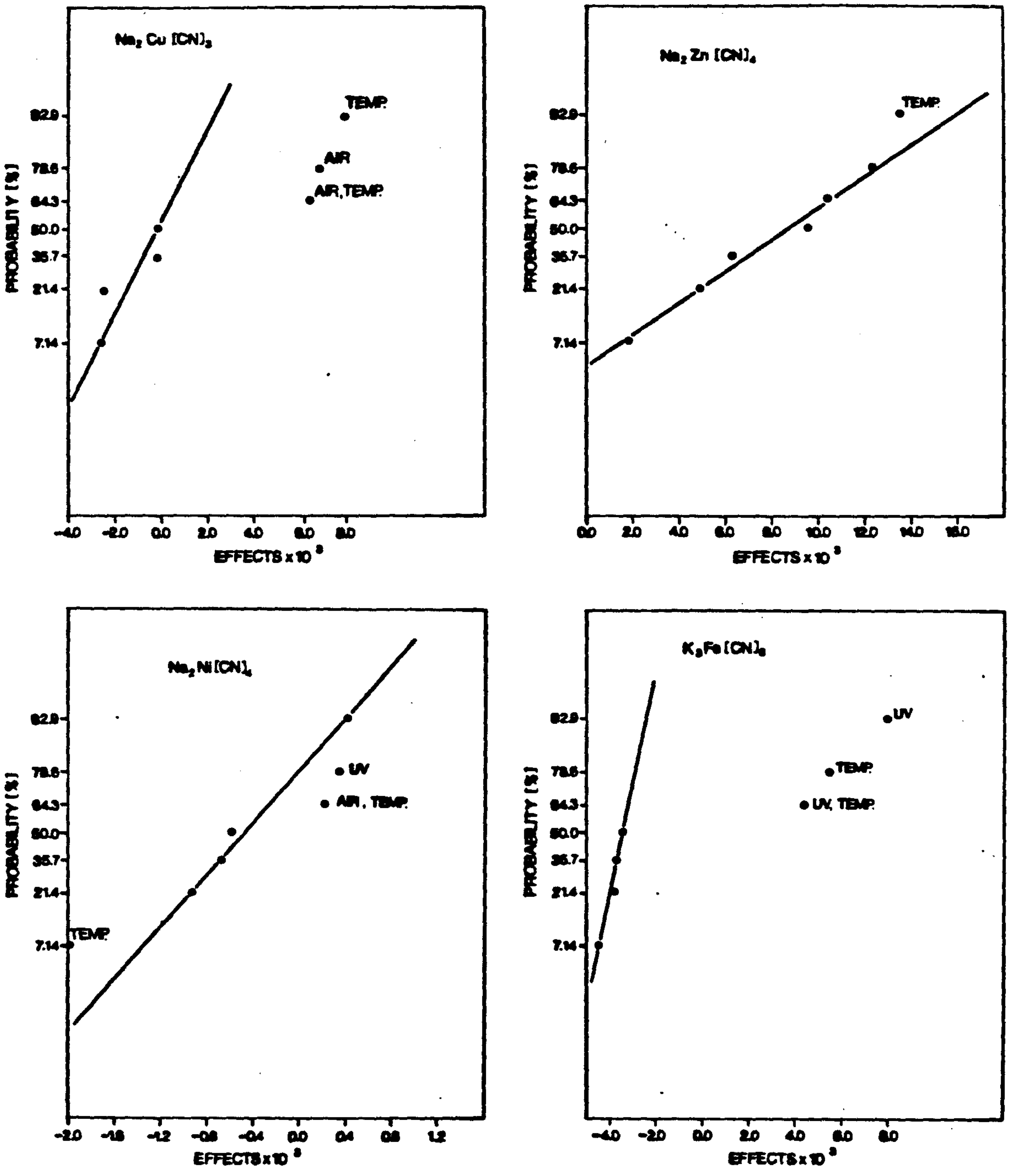

Figure 6.1 Half Normal Probability Plots (Cu, Zn, Ni and Fe Cyanide Solutions)

cyanide solutions and the high mix. Temperature combined with air, had some effect on Cu cyanide solution, while UV light combined with air affected the low mix. UV light showed a large effect on the iron cyanide solution and low mix. By taking the probability transform* as X and the effects that lie close to the straight line section as Y and applying a linear regression analyses, the estimates for the variances and the 95% confidence intervals on random effects were determined (Appendix G.4). Most factors found by visual inspection to have high effects, were proven significant at 95% CI. Only factors having an effect on zinc cyanide solutions were not significant at 95% significance level.

iii) Backward elimination procedure - The results of the backward elimination procedure are presented in Table 6.3. In order to carry out the backward elimination calculations the highest order interaction (three factor interaction) was taken as the estimate of error variance, due to the fact that there were no repeated runs in these experiments, and used for testing the significance of the other mean squares. The computer program LJUB7, using the backward elimination procedure as explained in Section 6.1, is applied and with the

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* "Probability transform" term used in this thesis refers to the linear units (mm) read off the probability graph in order to be able to perform linear regression calculations.

TABLE 6.3. COMPLETE RESULTS OF THE FULL 2^3 FACTORIAL DESIGN

Type of Cyanide Solution	The Highest Calculated Effect	Half Normal Probability Plots: Results of the Visual Inspection	Half Normal Probability Plots: Significant Effects (95% CI)	Results of Backward Elimination
NaCN	C	C	C	C
Cu-CN	C	C,B,BC	C,B,BC	C,B,BC
Zn-CN	C	C	-	C (non-signif.)
Ni-CN	C	C,BC	C	C
Fe-CN	A	A,C,AC	A,C,AC	A (non-signif.)
Low Mix	A	A,AB,B	A,AB,B	A,AB,B
High Mix	C	C	C	C

A - UV light
B - Aeration
C - Temperature

output of the example calculation, presented in the Appendix G.5. The calculations were carried out at one degree of freedom which affected the sensitivity of the F test, therefore, the results were considered slightly inferior to the methods outlined in Sections (i) and (ii).

The summarized results of the full 2^3 factorial design are presented in Table 6.3.

The temperature (C) is the largest main effect for most solutions (Na, Cu, Ni and high mix cyanide), while UV light (A) is the largest main effect for Fe and low mix. There is some effect of temperature on zinc cyanide removal but it is not significant.

6.3 The Effect of Aeration on NaCN Degradation

To assess the effect of air, UV light and temperature on the removal of cyanide in NaCN solution it was assumed that the whole NaCN curve represented the removal of free cyanide. However, neither the effects of aeration nor UV light are significant for the NaCN solution at the 5% level. This lack of significance is somewhat surprising.

Therefore, the reaction rate constant for NaCN was recalculated assuming that a cut-off point existed. The linear regression was carried out forward and backward on every set of data. The average residual sum of squares (RSS) values were compared (see computer program BACKRAT in Appendix D explained in Section 5.4.2). There was no sudden, but a small gradual change in these values, hence there were some difficulties in estimating the cut-off point. In the case of metallo-cyanide complex solutions, when there was a definite change in the cyanide removal mechanisms (from volatilization to metal cyanide decay), the sudden change in the average RSS values occurred.

The reaction rate constant k_v established for the first part of the curve did not differ significantly from estimates for the whole curve. When applied as the response variable for the estimation of the largest effects, the results presented in Table 6.4 were obtained.

These effects are arranged in ascending order (see Table 6.5) and a half normal probability plot prepared (Figure 6.2). The effects of temperature, air and their interaction were observed.

In order to check the significance of these effects the 95% confidence interval was calculated and it was found to be between -6.86×10^{-3} and 5.46×10^{-3}. Therefore the effects of temperature (C), air-temperature (BC) and air (B) were determined to be significant at the 95% confidence level (Figure 6.2).

This confirmed that the air played an important role in removal of free cyanide together with temperature within the first 48 to 72 hours.

The way the "second part" of the NaCN degradation curve can be explained is that with the decrease in the concentration of total cyanide the volatilization rate of HCN in the aerated solutions decreases too and the variability in the data at the end of the experiment was noted. In the non-aerated samples the variability occurred too, probably due to a change in thickness of the cyanide concentration gradient with time.

TABLE 6.4. THE RESPONSE VARIABLES AND EFFECTS - NaCN

Test Code	Response $k_v(h^{-1})$	Effects
I	0.0164	-
A	0.0193	-0.0018
B	0.0176	0.0169
AB	0.0159	-0.0004
C	0.0263	0.0235
AC	0.0205	-0.0024
BC	0.0597	0.0180
ABC	0.0569	0.0019

TABLE 6.5. PROBABILITY (%) AND EFFECTS ARRANGED IN ASCENDING ORDER (NaCN)

Order Number	1	2	3	4	5	6	7
Effect x 10^3	−2.45	−1.85	−0.4	1.9	16.9	18.0	23.5
Identity of effect	ac	a	ab	abc	b	bc	c
P = 100 (i-1/2)/7	7.14	21.4	35.7	50.0	64.3	78.6	92.9

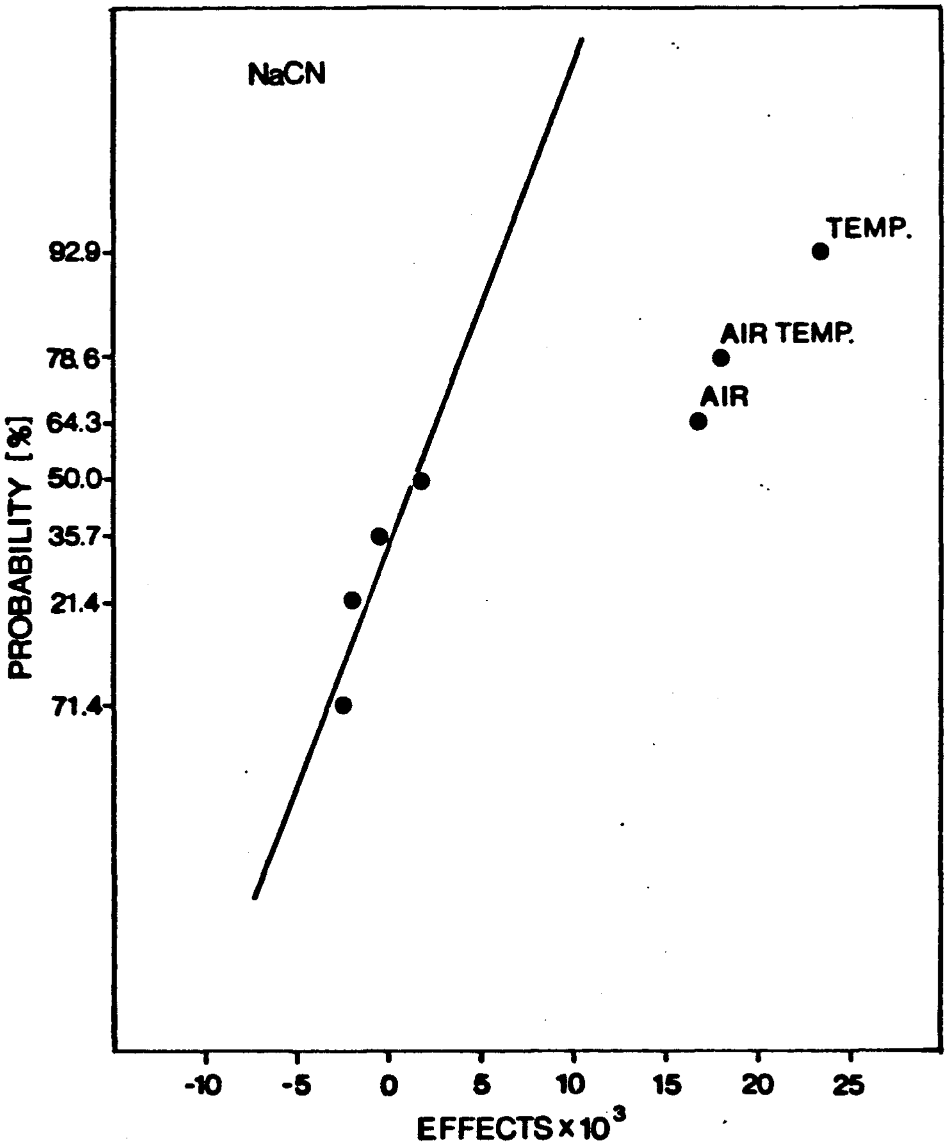

Figure 6.2 Half Normal Probability Plot for k_v for NaCN

7 MODEL DEVELOPMENT AND CALIBRATION

According to the results obtained from the experimental design, it was concluded that volatilization and metal cyanide decay are the two predominant mechanisms for cyanide removal from the synthetic solutions.

The results of the dot diagram analyses on the factors affecting volatilization of free cyanide suggest temperature as the main factor, followed by air and UV (see Table 5.2).

The experimental design results on the factors affecting the degradation of metal cyanide shows that the temperature is the largest main effect for all cyanide solutions except iron cyanide and the low mix (Table 6.3).

Such a strong influence of temperature on the reaction rates and the results of the calculations of the energy of activation for NaCN of 21 to 70 kJ/mol, suggest molecular diffusion and chemical reaction controlled processes.*

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* Stumm and Morgan (1981). For a very rapid diffusion controlled reaction, E has a range of 12.6 to 21 kJ/mol and for slow reactions controlled by chemical steps, E of about 70 kJ/mol (a pseudo-first order rate constant). Moore (1962) - for unimolecular gas phase decomposition E = 54.4 kJ/mol.

The reaction rate constants for the two predominant mechanisms for cyanide removal, and the important factors affecting these constants, will be taken into consideration for the development of a model.

7.1 Model Development

It is desirable to develop a mathematical model which is a fairly general expression of the mechanisms underlying a real process. The evidence found in the literature and the results obtained in this study suggest that this model should be based upon the following observations:

1. Metal cyanide complexes dissociate into metal and cyanide ions.
2. Cyanide ion, in a hydrolytic reaction with hydrogen from water, produces HCN and is in equilibrium with it.
3. The dominant form of free cyanide at pH 7.0 is molecular HCN. Molecular HCN is the species that volatilizes.
4. Temperature influences the rate of the dissociation of all metallo-cyanides. UV irradiation may affect the dissociation for a few metals.
5. The only parameter that was measured in the experiments is total cyanide $[TCN]_0$, which is the summation of all the different cyanides that exist in aqueous solution (i.e., $TCN = MCN + CN^- + HCN$).

6. HCN can oxidize chemically to cyanate. But measurements of cyanate made during the experimental runs showed that there was no CNO^- present, suggesting that chemical oxidation is not an important mechanism.

In order to develop a model for a single metallo-cyanide complex solution, each chemical species containing cyanide forms was considered as a separate component, as given in Figure 7.1.

The first component is the metal cyanide complex denoted as MCN, the second is the cyanide ion and the third is molecular HCN. If the second and third are taken together they represent free cyanide. Each arrow between the components represents a transformation of mass. The assumption was that one metal complex and free cyanide can explain the observed characteristics of cyanide loss from solution in the single metallo-cyanide solutions.

The coefficients k_1, k_2, k_3 are the rate constants (h^{-1}); k_V is the volatilization (aeration) mass transfer coefficient (cm/h), while k_{uv} is the additional effect upon k_1 due to ultraviolet irradiation (h^{-1}). For a batch reactor, taking into consideration the law of conservation of mass, the mass balance equations for each compartment are:

$$\frac{d[MCN]}{dt} V = - k_1 [MCN]V - k_{uv}[MCN]V \tag{7.1}$$

$$\frac{d[CN^-]}{dt} V = k_1 [MCN]V + k_{uv} [MCN]V - k_2 [CN^-]V + k_3[HCN]V \tag{7.2}$$

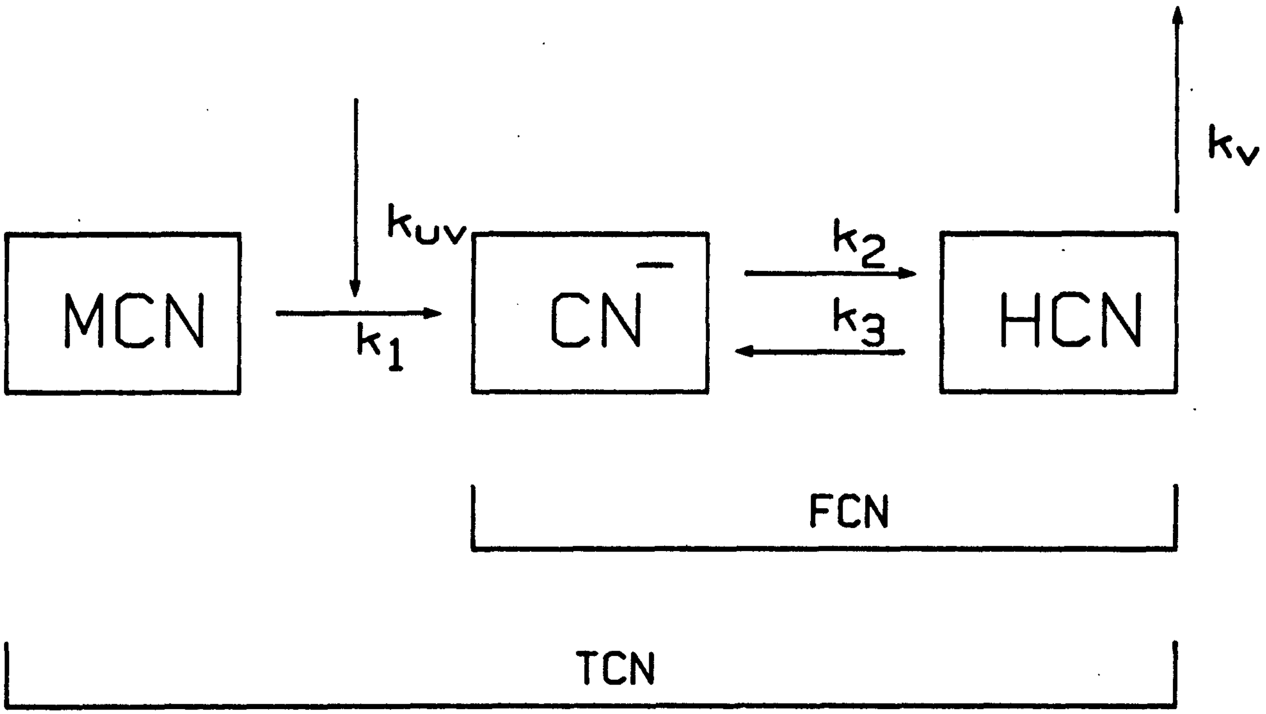

Figure 7.1 Cyanide Degradation Model

$$\frac{d[HCN]}{dt} V = k_2 [CN^-]V - k_3 [HCN]V + k_v As (C_s - [HCN]) \qquad (7.3)$$

The total cyanide is the sum of Equations 7.1, 7.2 and 7.3:

$$\frac{d[TCN]}{dt} V = -k_v A_s [HCN] \qquad (7.4)$$

Here A_s (cm^2) is the area of the air-water interface across which volatilization occurs, C_s is the saturation concentration of cyanide (mol/L) corresponding to the atmospheric partial pressure of cyanide (approximately equal to zero for natural conditions) and V is the reactor volume (cm^3).

Rearranging the equations yield:

- for metal cyanide

$$\frac{d[MCN]}{dt} = - k_1 [MCN] - k_{uv} [MCN] \qquad (7.5)$$

- for free cyanide (sum of CN^- and HCN)

$$\frac{d[FCN]}{dt} = k_1 [MCN] + k_{uv} [MCN] - \frac{k_v}{Z_h} [HCN] \qquad (7.6)$$

where $Z_h = V/A_s$. If the UV irradiation effect is insignificant, k_{uv} becomes zero.

Summing these two equations produces one for total cyanide

$$\frac{d[TCN]}{dt} = -\frac{k_v}{Z_h}[HCN] \tag{7.7}$$

Hence the model is equaions 7.5, 7.6 and 7.7.

Evidently the controlling steps are the rate of volatilization of the HCN form and the rate of dissociation of the MCN. Since the kinetics of HCN formation from CN^- and its dissociation to CN^- are fast (Eq. 2.1), it is not rate limiting. This allows one to treat HCN and CN^- as being constantly in equilibrium relative to other processes. The model thus derived represents a two compartment reaction-in-series model.

7.2 Parameter Estimation Method

The differential equations (7.5 to 7.7) were solved by numerical integration using the Runge-Kutta-Verner fifth and sixth order method (DVERK) available from the International Mathematical and Statistical Libraries Inc. for CYBER systems. This method uses given initial conditions and calculates the change of concentration over time for total, metal and free cyanides using ten-hour time increments.

To obtain the best estimates of the parameters for this model, an iterative, nonlinear least squares parameter estimation subroutine was used (GAUSHAUS*). It is based on Marquardt's method which combines the Gauss method (Taylor series) and the method of steepest descent (Meeter and Wolfe, 1965).

A starting estimate for the initial concentration of metal-cyanide $[MCN]_o$ was calculated from the initial metal concentration and stoichiometric relationship of the particular complexes formed from dissociation of the stock salt namely: $Cu(CN)_3^{2-}$, $Zn(CN)_4^{2-}$, $Ni(CN)_4^{2-}$, and $Fe(CN)_6^{3-}$. The estimate for initial free cyanide concentration $[FCN]_o$ was obtained by subtracting $[MCN]_o$ from the measured initial concentration of total cyanide, $[TCN]_o$. An example calculation is given in Appendix H.1.

In this case there were three parameters that needed to be estimated:the overall metal decay coefficient $(k_l + k_{uv})$, the volatilization coefficient (k_v) and $[FCN]_o$. However, the UWHAUS parameter estimation procedure allows for estimation of the initial metal cyanide concentration. Treating initial metal and initial free cyanide concentrations as parameters to be estimated creates a four-parameter estimation problem which was first evaluated herein.

The results of the four parameter estimation problem are described in Section 8.1. Three and two parameter estimation problems

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* GAUSHAUS now called UWHAUS.

are also carried out in this study and the results are presented in Sections 8.2 and 8.3, respectively. The parameters estimated by the three parameter estimation model specifying the MCN/TCN ratio to be equal to 0.17 are presented in Section 8.4.

A verification study concentrates on the simulations of low mixes (Section 9.1.1.) and attempts the simulations of high mixes (Section 9.1.2). Model calibration was evaluated by carrying out simulations on actual barren solutions (Section 9.2).

8 EVALUATION OF SINGLE METALLO-CYANIDE SOLUTIONS - RESULTS AND DISCUSSION

8.1 Four Parameter Estimation Model

A sample graph of the results obtained using four parameter estimation for a single metal cyanide solution, Zn-CN, is given in Figure 8.1. It appears that a good fit of the model to the data is obtained. This implies that, as postulated, volatilization of free cyanide controls the initial steep slope of the curve and that metal cyanide decay controls the lower part of the curve (the slower rate of degradation).

The estimated metal cyanide decay coefficients using four parameter estimation are presented in Table 8.1 with respect to temperature. There is some variability in these estimates. The calculated values of R^2, the multiple correlation coefficient, indicates that 93 to 99% of the total variability in the observed data is explained by the model (Eq. 7.5 to 7.7).

The estimated volatilization mass transfer coefficients k_v are given in Table 8.2. In reviewing these results, it was noted that although most were quite close, between some of them there was a difference of two orders of magnitude. The extent of this range was difficult to accept. A possible explanation was that the metal

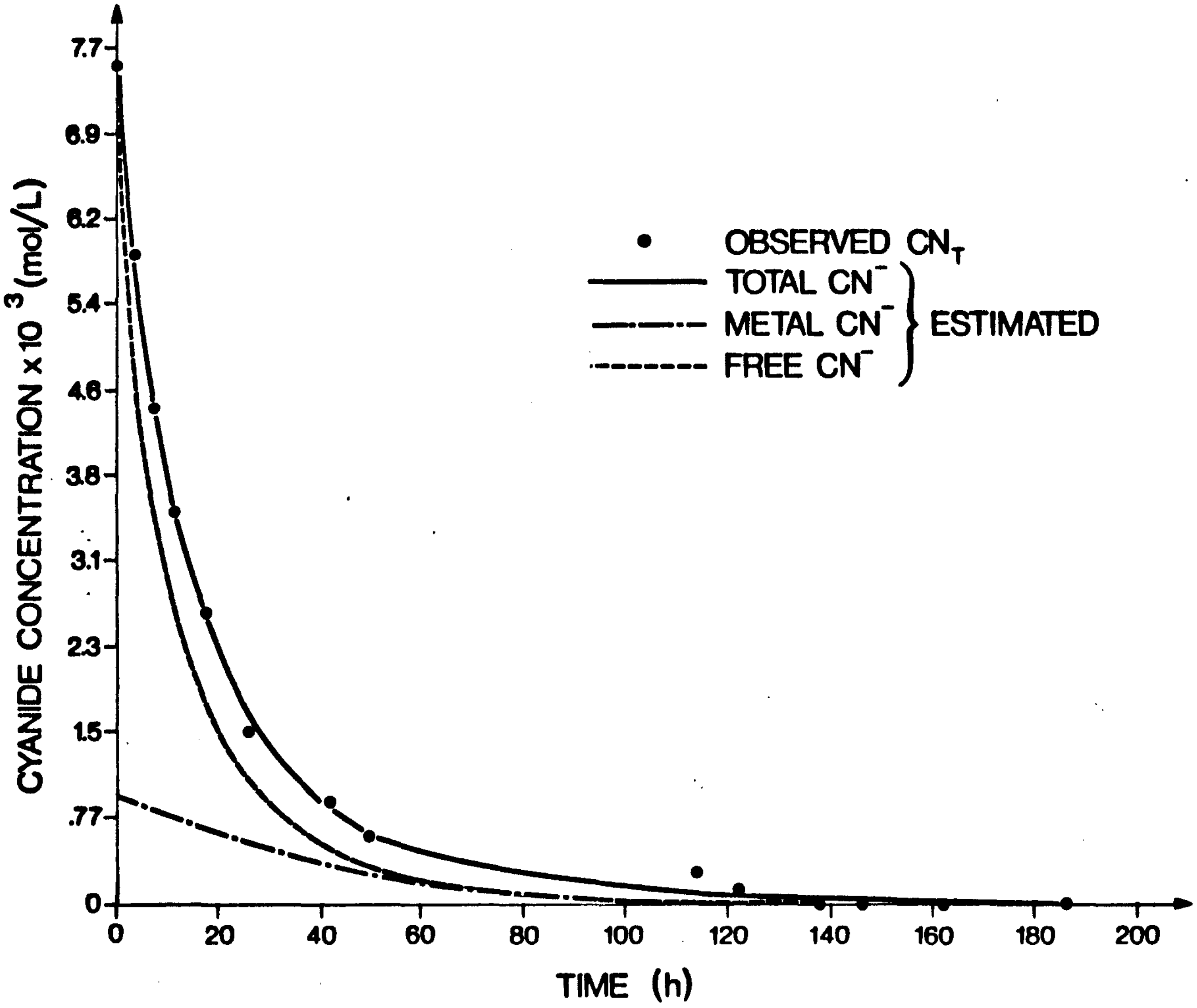

Figure 8.1 Four-Parameter Estimation Model - Typical Fit of Predicted Values to Observed Data (Zn-CN 20°C, AIR, UV)

TABLE 8.1. ESTIMATED METAL CYANIDE DECAY COEFFICIENTS k_1 [h^{-1}] FOR SINGLE METALLO-CYANIDE SOLUTIONS (FOUR-PARAMETER ESTIMATION MODEL)

			TEMPERATURE			
	AIR	UV	k_1 at 4°C	R^2[%]	k_1 at 20°C	R^2[%]
Cu						
	+	+	4.7×10^{-9}	98	8.9×10^{-3}	99
	+	-	1.0×10^{-9}	94	5.2×10^{-3}	98
	-	+	5.8×10^{-3}	98	1.5×10^{-9}*	98
	-	-	3.2×10^{-3}	99	1.4×10^{-1}**	98
Zn						
	+	+	7.0×10^{-2}	94	1.8×10^{-2}*	99
	+	-	7.9×10^{-3}	96	5.7×10^{-2}	99
	-	+	9.3×10^{-3}	98	7.9×10^{-2}	98
	-	-	4.4×10^{-3}	98	6.5×10^{-2}	98
Ni						
	+	+	4.5×10^{-9}	98	1.1×10^{-3}	99
	+	-	1.1×10^{-3}	94	3.6×10^{-3}	99
	-	+	3.2×10^{-3}	96	1.1×10^{-3}	93
	-	-	1.7×10^{-3}	96	4.2×10^{-5}*	99
Fe						
	+	+	5.9×10^{-5}	99	4.8×10^{-3}	99
	+	-	5.6×10^{-9}	98	4.9×10^{-3}	98
	-	+	4.9×10^{-3}	99	1.2×10^{-2}	99
	-	-	8.6×10^{-4}	99	1.6×10^{-3}	99

* Inconsistencies because k_1 at 20°C is less than k_1 at 4°C.

** Time of observation was too short to allow for adequate estimation of parameters.

TABLE 8.2. ESTIMATED VALUES OF VOLATILIZATION MASS TRANSFER COEFFICIENTS k_v [cm/h] (FOUR-PARAMETER ESTIMATION MODEL)

	AIR	UV	TEMPERATURE	
			k_v at 4°C	k_v at 20°C
Cu				
	+	+	0.56	139.12*
	+	-	0.46	2.02
	-	+	7.85*	0.55
	-	-	2.85*	0.53
Zn				
	+	+	0.74	0.08*
	+	-	2.14	29.73*
	-	+	1.66	0.74
	-	-	0.75	0.70
Ni				
	+	+	0.55	2.97
	+	-	0.91	0.77
	-	+	1.78	0.74
	-	-	1.11	3.33
Fe				
	+	+	0.29	3.69
	+	-	0.84	0.56
	-	+	428.06*	1.43
	-	-	1.55	0.71

* Inconsistencies.

complexes, in a somewhat random fashion acted as surfactants and were able to change the mass transfer characteristics of the volatilization coefficient. This was judged not to be probable. Another possible explanation was that the parameter estimation procedure had difficulty resolving parameter values for certain experiments, due to large correlations between parameters.

In all the runs, even when the model fit appeared to be satisfactory, some parameters were moderately correlated. A very high negative correlation existed between several parameters (FCN, MCN and k_1) for data sets which were termed inconsistent in Table 8.1 (Example in Appendix H.2; program TST used for four-parameter estimation and the output showing correlation matrix element value of -0.99). This means that an increase in one parameter is accompanied with a decrease in the other and that a unique set of estimates is difficult to obtain.

Considering the fact that the temperature had such a strong effect on the cyanide removal kinetics, the sodium cyanide volatilization mass transfer coefficients, used for the k_v initial values, were averaged for 4°C and 20°C ($k_{4°C}$ = 0.52 cm/h and $k_{20°C}$ = 1.33 cm/h) and the same four parameters (FCN, MCN, k_v, k_1) were reestimated. There was no noticeable improvement, in either the model fit within correlation matrix elements.

Another way of examining the estimated values is to compare the estimated ratio MCN/TCN from the four-parameter estimation model to the initially set ratio of 0.17, i.e., based on how the solutions were made. In 12 out of 32 cases, the MCN/TCN ratio is greater than 0.17 (Table 8.3). For these experiments the estimated FCN concentration was much smaller than originally calculated (based upon stoichiometry of the single metal complex). The estimated MCN concentration was much greater and metal decay appears to be controlling the cyanide degradation processes most of the time. Despite some difficulties, the overall fit of the model to the data for most experiments was good.

8.2 Three-Parameter Estimation Model

Decreasing the number of parameters in a given model usually decreases the incidence of high correlation but can also decrease the ability of the model to accurately predict observed phenomena.

Metal decay coefficients (k_1), and initial concentrations were reestimated for all four metals by fixing k_v at the global average value* of all the volatilization coefficients, k_v of 0.93 (cm/h). This reduced the problem to a three-parameter estimation (FCN_o, MCN_o and k_1). Contrary to the other metals, the estimates for metal decay coefficients for Cu were more consistent in the three than in the four parameter estimation model (See Table 8.4).

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* The Arrhenius' equation for the temperature effect on the rate constant was considered in the individual k values for 4°C and 20°C but not in calculating the global average value.

TABLE 8.3. METAL CYANIDE TO TOTAL CYANIDE RATIO - FOUR PARAMETER ESTIMATION MODEL

			MCN/TCN Ratio			MCN/TCN Ratio	
AIR	UV		4°C	20°C		4°C	20°C
+	+	Cu	0.09	0.27	Zn	0.30	0.13
+	-		0.17	0.09		0.60*	0.74*
-	+		0.58*	0.04		0.47*	0.18
-	-		0.69*	0.90*		0.69*	0.40*
+	+	Ni	0.12	0.17	Fe	0.08	0.18
+	-		0.30	0.21		0.16	0.30
-	+		0.34*	0.26		0.97*	0.35*
-	-		0.50*	0.13		0.25	0.25

* The MCN/TCN ratio is greater than 0.17.

TABLE 8.4. THE ESTIMATED METAL CYANIDE DECAY COEFFICIENT $k_1[h^{-1}]$ AT $k_v = 0.93$ [cm/h]

			TEMPERATURE	
	AIR	UV	4°C	20°C
Cu				
	+	+	0.6×10^{-2}	8.7×10^{-8}*
	+	-	0.4×10^{-2}	$0.2 \times 10^{+1}$*
	-	+	0.2×10^{-2}	0.6×10^{-2}
	-	-	0.2×10^{-2}	1.9×10^{-2}

* Inconsistency.

The problem common for the estimation with the overall average k_v was that all the estimates for MCN (except for ten conditions out of 32) were substantially higher than the theoretical initial concentrations $[MCN]_o$ (Tables 8.5a and b). The reason for this was that the volatilization coefficients were faster than the volatilization process in these experiments, forcing the model to treat the entire curve as one rate limiting process, metal decay, and thus the MCN concentrations appeared greater.

Typical model fits for these conditions are shown in Figures 8.2 and 8.3. For total cyanide in Figure 8.2, the model fits the data well; volatilization of free cyanide controls the initial portion of the curve while metal cyanide decay controls the plateau over a longer time period. The total cyanide in Figure 8.3 also shows a good fit, but the metal cyanide complex is estimated by the model to control the decay process over much more of the whole curve than is shown in Figure 8.2.

Additional analyses were performed with a three parameter estimation model on twelve data sets in which the four parameter estimation model gave a MCN/TCN ratio greater than 0.34 (Table 8.3). In these analyses a fixed stoichiometry of 0.17 was used and the three parameters to be estimated were initial free cyanide concentration and the two decay coefficients. There was apparent improvement. The estimated values for FCN and the metal decay coefficient were closer to the initial values and the correlation between all the parameters

TABLE 8.5a. THREE PARAMETER ESTIMATION MODEL - Cu AND Zn CYANIDE AT k_v AVERAGE

k_v = 0.93 (cm/h) - overall average			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Cu-CN	GIVEN	$[FCN]_o \times 10^2$ (mol/L)	0.632	0.667	0.651	0.629	0.647	0.628	0.620	0.655
		$[MCN]_o$ (mol/L)	0.13×10^{-2}							
		$k_{Cu} \times 10^2$ (h^{-1})	2.07	0.71	0.37	0.33	1.53	0.24	0.36	0.31
		FCN $\times 10^2$ UWHAUS	0.601	0.442	0.473	0.312	0.572	0.597	0.545	0.497
		MCN UWHAUS	0.41×10^{-5}*	0.38×10^{-2}	0.32×10^{-2}	0.39×10^{-2}	0.89×10^{-4}*	0.22×10^{-2}	0.25×10^{-2}	0.19×10^{-2}
		k_{Cu} UWHAUS	2.3	1.59×10^{-2}	0.38×10^{-2}	0.23×10^{-2}	0.87×10^{-7}	0.64×10^{-2}	0.60×10^{-2}	0.17×10^{-2}
Zn-CN	GIVEN	$[FCN]_o \times 10^2$ (mol/L)	0.584	0.518	0.620	0.502	0.624	0.639	0.628	0.601
		$[MCN]_o$ (mol/L)	0.13×10^{-2}							
		$k_{Zn} \times 10^2$ (h^{-1})	0.62	1.94	0.68	0.45	4.48	1.82	1.37	0.95
		FCN UWHAUS	0.56×10^{-2}	0.45×10^{-2}	0.51×10^{-2}	0.19×10^{-2}	NC	0.18×10^{-2}	0.94×10^{-8}	0.56×10^{-2}
		MCN UWHAUS	0.18×10^{-4}*	0.19×10^{-2}	0.24×10^{-2}	0.45×10^{-2}	NC	0.59×10^{-2}	0.77×10^{-2}	0.13×10^{-2}
		k_{Zn} UWHAUS	2.79	2.45×10^{-2}	0.60×10^{-2}	0.44×10^{-2}	NC	4.30×10^{-2}	8.97×10^{-2}	0.50×10^{-2}

NC - estimation routine was not converging.
* [MCN] lower than observed.

TABLE 8.5b. THREE PARAMETER ESTIMATION MODEL - NI AND Fe CYANIDE AT k_v AVERAGE

k_v = 0.93 (cm/h) - overall average			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
NI-CN	GIVEN	$[FCN]_o \times 10^2$ (mol/L)	0.753	0.635	0.667	0.522	0.636	0.632	0.639	0.547
		$[MCN]_o$ (mol/L)			0.13×10^{-2}					
		$k_{NI} \times 10^2$ (h^{-1})	0.27	0.08	0.30	0.27	0.08	0.15	0.42	0.41
		FCN $\times 10^2$ UWHAUS	0.572	0.541	0.541	0.362	0.534	0.590	0.534	0.502
		MCN $\times 10^2$ UWHAUS	0.279	0.063*	0.223	0.301	0.077*	0.192	0.283	0.111*
		k_{NI} UWHAUS	0.43×10^{-2}	0.42×10^{-8}	0.59×10^{-3}	0.12×10^{-2}	0.34×10^{-8}	0.18×10^{-2}	0.52×10^{-2}	0.32×10^{-8}
Fe-CN	GIVEN	$[FCN]_o \times 10^2$ (mol/L)	0.644	0.624	0.590	0.409	0.574	0.574	0.613	0.574
		$[MCN]_o$ (mol/L)			0.13×10^{-2}					
		$k_{Fe} \times 10^2$ (h^{-1})	0.16	0.26	0.12	0.07	0.68	2.22	0.51	0.40
		FCN $\times 10^2$ UWHAUS	0.410	0.532	0.615	0.379	0.467	0.623	0.264	0.178
		MCN $\times 10^2$ UWHAUS	0.387	0.242	0.119*	0.100*	0.021*	0.064*	0.473	0.505
		k_{Fe} UWHAUS	0.65×10^{-2}	0.25×10^{-2}	0.35×10^{-8}	0.18×10^{-9}	0.57×10^{-7}	0.54×10^{-2}	0.64×10^{-2}	0.46×10^{-2}

* [MCN] lower than observed.

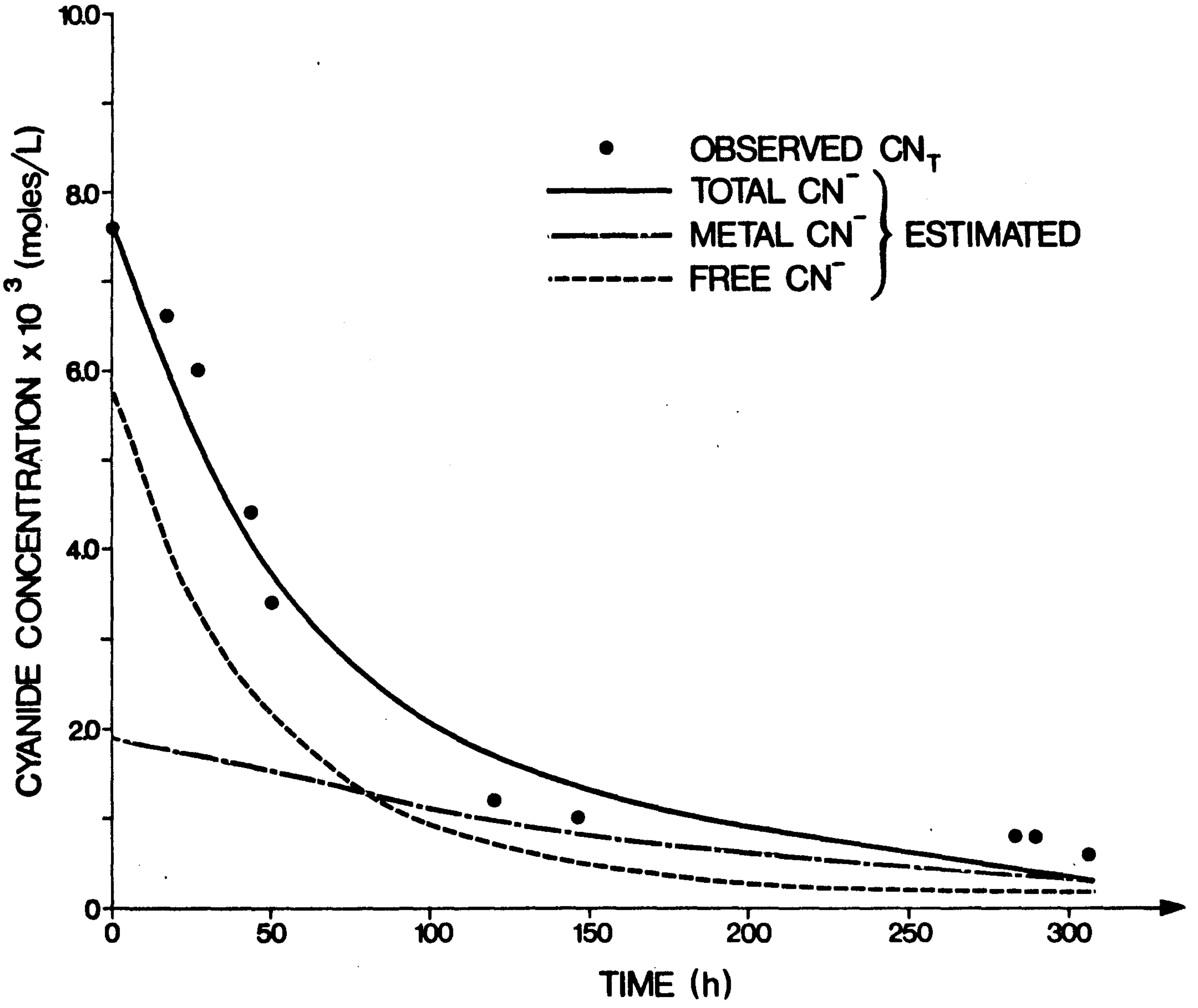

Figure 8.2 Three-Parameter Estimation Model - FCN > MCN (Cu 20°C, NO AIR, UV)

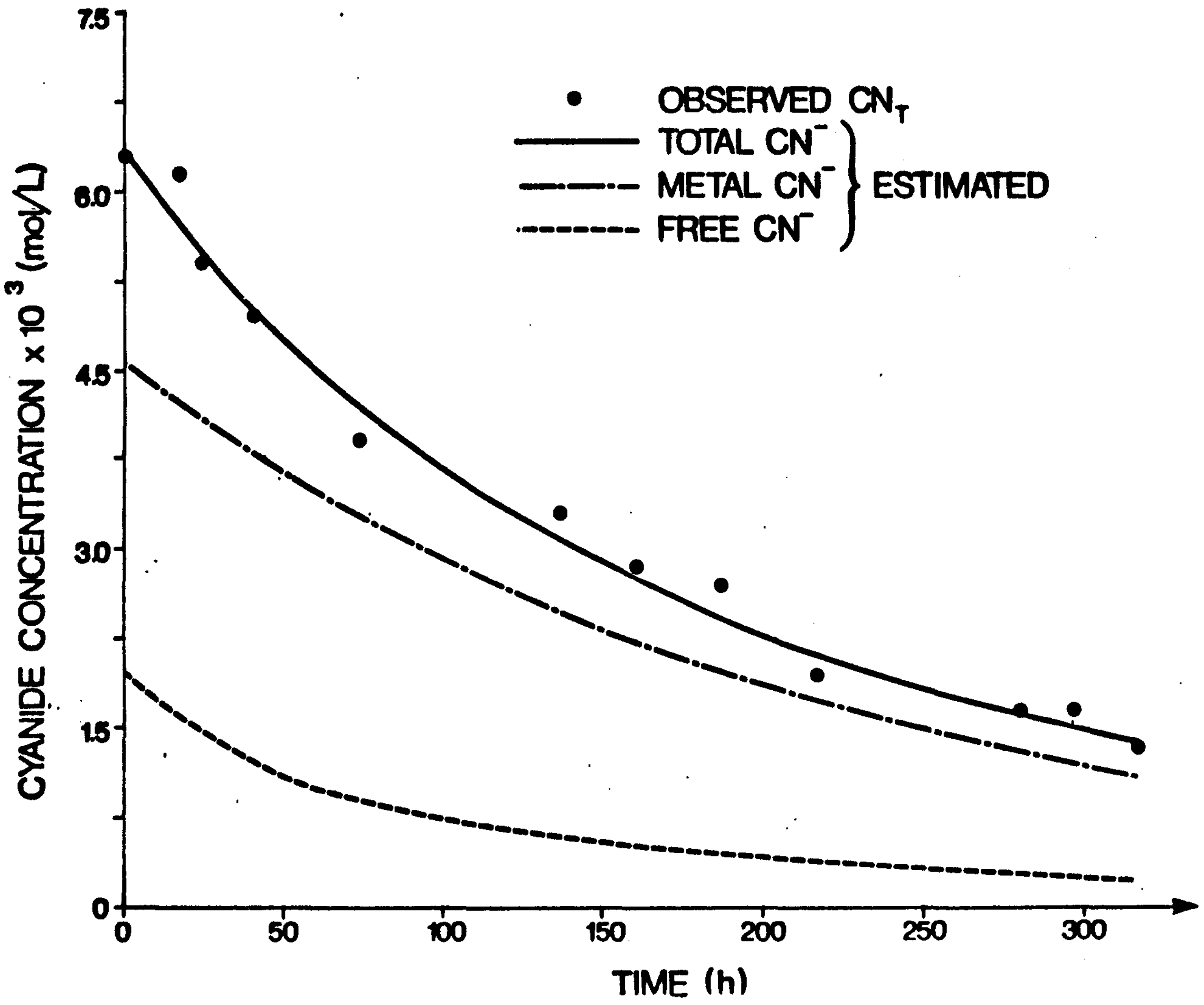

Figure 8.3 Three-Parameter Estimation Model - MCN > FCN (Zn 4°C, NO AIR, NO UV)

decreased, e.g., the correlation between FCN and k_1 decreased from 0.99 to 0.43 for Fe at 4°C, NO AIR, UV.

One other problem was that for some experiments the time period of observations was too short. Accordingly, because the data base was not sufficiently extensive, the lower portion of the curve did not adequately define the values of the coefficients. For such curves, there was a high correlation between estimated parameters in both the four-parameter problem format and in the three-parameter format.

In a few experiments which ran sufficiently long, the total cyanide concentration plateaued at a non-zero value whereas the model predicted that the concentration should decrease to zero. It was hypothesized that an additional metallo-cyanide complex existed in these solutions whose decay characteristics were much slower than those of the first complex.

Consequently, it was decided to perform the three parameter estimation (three parameters being MCN, k_v and k_1) with the volatilization mass transfer coefficient initial values equal to the value recorded for NaCN under each individual condition. This was possible since it was proven earlier that volatilization coefficients for metallo-cyanide complex solutions were within the 95% confidence interval of k_v for NaCN (k_{NaCN}). The computer program was adjusted so that the first predicted TCN value was equal to the initial observed TCN concentration and initial MCN was estimated. This resulted in FCN being equal to the difference between TCN and MCN. The results of this estimation process are presented in Appendix H.3, Tables 1 to 4.

There were three incidents (Cu 20°C, NO AIR, NO UV; Zn 4°C, AIR, UV; Zn 20°C, NO AIR, UV) where the estimated MCN value was much greater than the theoretical metal cyanide concentration or was even greater than the observed TCN concentration. One experiment (Cu 20°C, NO AIR, NO UV) was extremely short in time, 169 hours. Only four data points were available to use for the calculation of the metal decay coefficient and this was not a large enough data base to define adequately the values of the parameters. The correlation between MCN and k_1 for Cu (or k_{Cu}) was unity.

For Zn at 4°C, AIR, UV the values of k_1 and k_v were very close (0.019 and 0.014 h^{-1}, respectively) forcing the model to treat the entire curve as one process, and consequently giving too high an estimate for the MCN concentration and at the same time a negative value for the FCN concentration (since TCN = MCN+FCN). As expected there was a high negative correlation of -0.94 between k_v and k_1 for Zn (or k_{Zn}).

In the third case, Zn at 20°C, NO AIR, UV the same problem occurred, i.e., k_v and k_1 values determined for Zn were very close (0.021 and 0.018 h^{-1} respectively). In addition it was calculated that 93% of cyanide was removed during the volatilization process (from Time 0 to the cut-off point) and only 7% was due to metal decay (from the cut-off point to the end of the experiment). The observation time for metal decay was only 150 h long, and the change in cyanide concentration was not significant enough to give a good estimate for the metal decay rate. The high correlation of 1.0 found between MCN and k_{Zn} was not surprising.

The inability of the model to estimate adequate MCN concentration for these three cases was observed also when the values were plotted with their individual 95% confidence intervals, based on the linear hypothesis calculated by UWHAUS, Figure 8.3a and Appendix H.3, (Figures 1 to 3). The three conditions analyzed previously were characterized with very large confidence limits.

In spite of the difference between the original MCN/TCN = 0.17 and the MCN/TCN estimated values, ranging from 0.07 to 0.74, the calculated multiple correlation coefficient, R^2, indicated that 96 to 99% of the total variability in the data was explained by the model (Appendix H.3, Tables 1 to 4).

Generally, the estimated values for the parameters in the three-parameter estimation model improved and resulted in a better model fit compared to the estimates and model fit in the four-parameter estimation model. The correlation between parameters generally stayed high in the case of copper and zinc and decreased for iron and nickel. The reason for this was that the k_v and k_1 values determined for copper and zinc cyanide solutions were very close and that created a difficulty in estimating all the parameters.

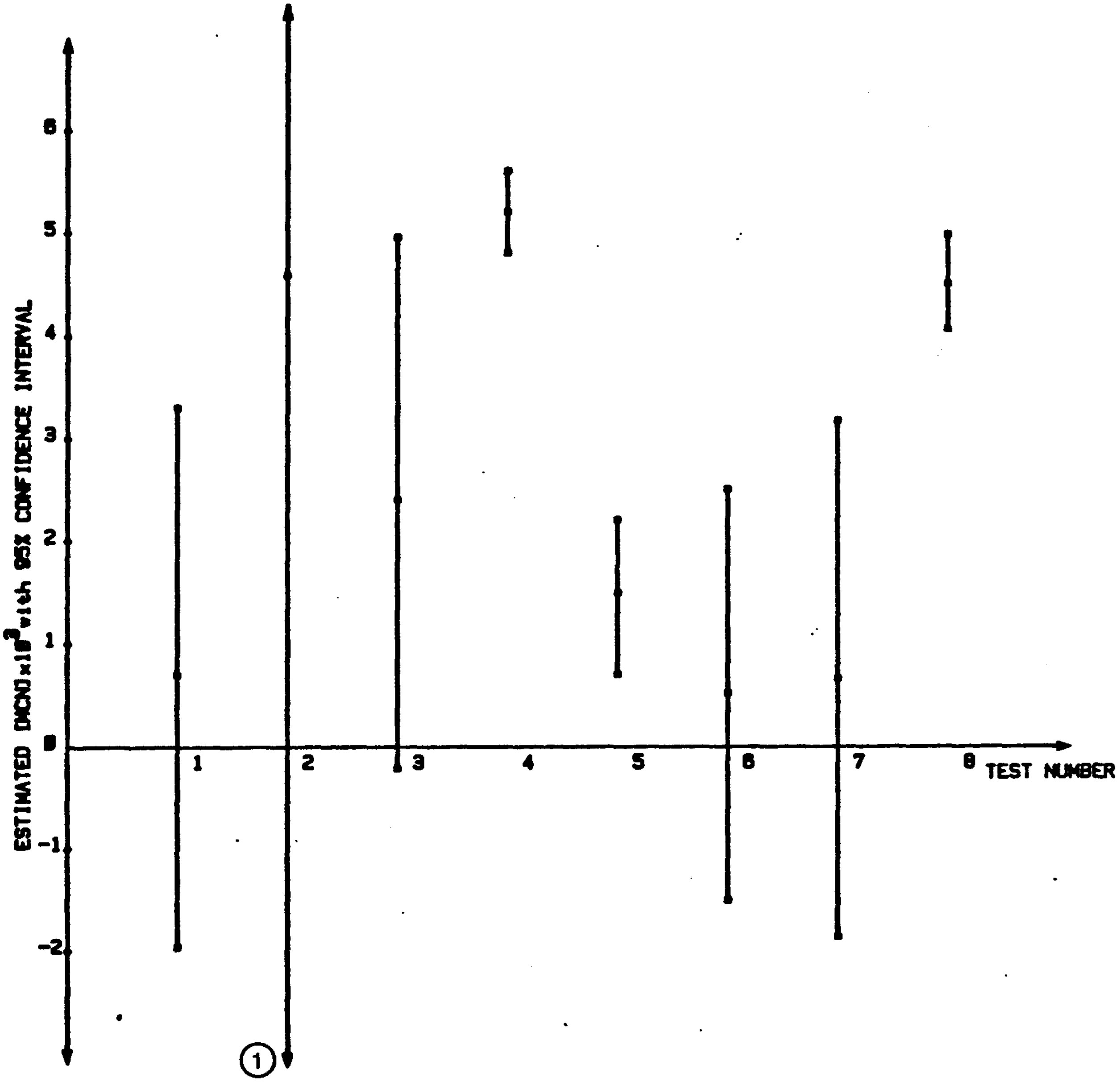

Figure 8.3 a Three-Parameter Estimation Model - Estimated MCN values with 95% Confidence Intervals - Cu.

More data which covered the complete range of variation would be the only way to significantly decouple the correlation among the parameters.

8.3 Two Parameter Estimation Model

By specifying the value of the volatilization mass transfer coefficient as equal to that estimated for NaCN solutions, and total cyanide concentration as equal to initial observed value, the only two parameters which need to be estimated are the metal decay coefficient and metal cyanide concentration. Free cyanide is thus equal to the difference between total cyanide and metal cyanide. The computer program used in two parameter estimation modelling is presented in the Appendix H.4 (see TSTOL2).

In this estimation process, the correlation between these two parameters (k_1 and MCN) decreased but the model fit was poorer. When the residual sum of squares (RSS) was compared between three and two parameter estimation problems the RSS in the two parameter estimation problem generally increased (Table 8.6).

The conclusion at the end of two parameter estimation modelling was that by decreasing the number of estimation parameters to two the ability of a model to predict them accurately also decreased substantially.

TABLE 8.6. RESULTS ON RESIDUAL SUMS OF SQUARES IN TWO AND THREE PARAMETER ESTIMATION MODELS (PEM)

Metallo-Cyanide Complex Solution		20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Cu-CN	Two PEM RSS x 10^6	2.8	1.3	1.1	2.6	16.3	2.3	2.2	10.6
	Three PEM RSS x 10^6	0.98	0.97	1.1	0.43	0.65	1.6	1.8	0.72
Zn-CN	Two PEM RSS x 10^6	13.1	0.73	0.72	0.42	1.1	0.81	1.7	4.8
	Three PEM RSS x 10^6	0.05	0.72	0.72	0.42	0.16	0.80	1.3	1.2
Ni-CN	Two PEM RSS x 10^6	0.49	39.5	2.4	1.8	8.6	1.1	1.6	10.7
	Three PEM RSS x 10^6	0.49	0.37	0.32	1.2	0.08	1.0	1.2	1.6
Fe-CN	Two PEM RSS x 10^6	2.2	0.36	1.4	6.7	8.6	0.62	0.33	0.64
	Three PEM RSS x 10^6	1.3	0.28	0.86	0.21	0.02	0.42	0.26	0.64

8.4 Parameter Estimation with Fixed MCN/TCN Ratio

As indicated earlier all the metallo-cyanide synthetic solutions examined were made based on the calculated value of MCN/TCN = 0.17, i.e., 17% of the available cyanide was in a complex with the metal(s) present. After completing four, three and two parameter estimation using the earlier defined model equations (7.5, 7.6 and 7.7), the three parameter estimation model seemed to give the best estimated values for all the parameters (MCN, k_v and k_1) but there were some discrepancies from the original MCN/TCN ratio of 0.17.

In order to see whether these estimated values were statistically different from the estimates obtained by presetting the MCN/TCN ratio to 0.17, an extensive set of calculations were carried out. A series of different MCN/TCN ratios were stipulated and used in the three parameter estimation problem for all four metals. MCN/TCN values used were 0.0425, 0.085, 0.17, 0.34 and 0.68. These values represent lower, equal and higher values than the theoretical MCN/TCN value of 0.17.

The complete results from this estimation process are presented in Appendix H.5 Tables 1 to 4, together with the example program "TSRATIO" used for the calculations. The residual sums of squares (RSS) were recorded for all estimation runs (the four metals under all eight experimental conditions). In 14 of 32 cases the MCN/TCN = 0.17 had the lowest RSS. Only under two conditions at MCN/TCN$<$0.17, RSS were the lowest, and all the others with the minimum RSS (16 of 32) happened to be with MCN/TCN $>$0.17 (Table 8.7). The RSS values were plotted versus the five MCN/TCN ratios (see Appendix H.5, Figures 1 to 4) to visualize better the minimum RSS conditions.

In order to determine the statistical significance in these results an F test was performed between two models, one using the RSS at MCN/TCN = 0.17, and the other for the MCN/TCN ratio having the minimum RSS of all five ratios examined. The total sum of squares (TSS) values for both models are identical, as is the number of parameters and degrees of freedom for the RSS being compared.

The results of the F test are given in Table 8.8. These F tests performed on the individual conditions prove that only five conditions (5 out of 32) are significantly different from the MCN/TCN ratio of 0.17. These conditions are mostly experimental data for which we have had estimation problems before: either too short experimental runs, or experiments with NO AIR where stratification probably occurred.

The general conclusion from these statistical tests is that the model fit obtained in 27 out of 32 conditions with the defined three parameter estimation model (using $k_v = k_{NaCN}$) was not significantly different (5% level of significance) from the fit made with the three parameter estimation model under preset MCN/TCN ratio of 0.17. The values of the three parameters estimated for the different experiments at fixed MCN/TCN = 0.17 are given in Table 8.9. Whenever there was a case where volatilization occurred extremely rapidly (e.g., as observed

TABLE 8.7. NUMBER OF MINIMUM RSS VALUES AT THE PARTICULAR MCN/TCN RATIO

Metallo-Cyanide Complex Solution	MCN/TCN				
	0.0425	0.085	0.17	0.34	0.68
Cu - CN	-	2	2	2	2
Zn - CN	-	-	3	1	4
Ni - CN	-	-	4	4	-
Fe - CN	-	-	5	3	-
Number of cases with the lowest RSS		2	14	10	6

TABLE 8.8. RESULTS OF THE F TEST

	$F = \frac{RSS(MCN/TCN = 0.17)/df}{RSS(MCN/TCN)/df}$	20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Cu-CN	RSS x 10^6 MCN/TCN=0.17	1.02	1.26	1.27	16.04		1.57		4.34
	MCN/TCN min	0.098	1.18	1.15	0.43		1.36		1.42
	df UWHAUS	11	6	11	14	NA	11	NA	10
	F test (ν_1,ν_2)	1.04	0.72	1.10	36.9*		1.16		3.06
	F test (5%) theoretical	2.83	4.28	2.83	2.50		2.83		2.98
Zn-CN	RSS x 10^6 MCN/TCN=0.17	0.63			0.44		1.40	2.93	1.4
	MCN/TCN min	0.05			0.39		0.98	2.00	1.3
	df UWHAUS	9	NA	NA	13	NA	14	12	11
	F test (ν_1,ν_2)	12.6*			1.13		1.43	1.46	1.08
	F test (5%) theoretical	3.18			2.57		2.50	2.69	2.83
Ni-CN	RSS x 10^6 MCN/TCN=0.17	0.29		4.42	14.93				3.40
	MCN/TCN min	0.26		0.41	1.79				1.50
	df UWHAUS	14	NA	13	13	NA	NA	NA	11
	F test (ν_1,ν_2)	1.11		10.78*	8.34*				2.27
	F test (5%) theoretical	2.50		2.57	2.57				2.83
Fe-CN	RSS x 10^6 MCN/TCN=0.17		0.63		3.16		0.49		
	MCN/TCN min		0.31		0.43		0.41		
	df UWHAUS	NA	12	NA	9	NA	15	NA	NA
	F test (σ_1,σ_2)		2.03		7.35*		1.19		
	F test (5%) theoretical		2.69		3.18		2.40		

NA - not applicable because the minimum RSS is at MCN/TCN = 0.17.
* - significant difference.

TABLE 8.9. THE RESULTS OF THREE PARAMETER ESTIMATION MODEL - MCN/TCN = 0.17

Metallo-Cyanide Complex Solution	Estimated Parameters	20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Cu-CN	FCN (mol/L)	0.0064	0.0069	0.0065	0.0062	0.0065	0.0067	0.0065	0.0059
	k_v (h^{-1})	0.0709	0.0148	0.0151	0.0147	0.1014*	0.0196	0.0184	0.0168
	k_{Cu} (h^{-1})	0.0119	0.0741	0.49×10^{-9}**	0.47×10^{-9}**	0.0066	0.0042	0.0029	0.28×10^{-9}**
Zn-CN	FCN (mol/L)	0.0056	0.0053	0.0062	0.0053	0.0063	0.0067	0.0067	0.0058
	k_v (h^{-1})	0.1062*	0.0192	0.0183	0.0069	0.0840	0.0222	0.0212	0.0242
	k_{Zn} (h^{-1})	0.0280	0.0671	0.0032	0.0014	0.0219	0.0629	0.0622	0.0045
Ni-CN	FCN (mol/L)	0.0070	0.0063	0.0066	0.0053	0.0064	0.0064	0.0067	0.0049
	k_v (h^{-1})	0.0177	0.1045*	0.0190	0.0153	0.0876	0.0196	0.0171	0.0192
	k_{Ni} (h^{-1})	0.87×10^{-3}	0.0017	0.30×10^{-9}**	0.63×10^{-10}**	0.0012	0.59×10^{-4}**	0.0017	0.12×10^{-9}**
Fe-CN	FCN (mol/L)	0.0066	0.0063	0.0061	0.0040	0.0058	0.0059	0.0061	0.0056
	k_v (h^{-1})	0.0140	0.0187	0.0249	0.0183	0.1142*	0.0297	0.0098	0.0069
	k_{Fe} (h^{-1})	0.0013	0.24×10^{-9}*	0.21×10^{-3}	0.89×10^{-9}*	0.0052	0.0078	0.0027	0.0014

* High estimated k_v value as a result of a fast volatilization process.

** Low estimated k_1 value, the result of either long volatilization process and short time of observation for metal decay, during which not much change in cyanide concentration occurred, or short volatilization process and plateaued value of cyanide decay.

in Figures 5.1 and 5.2) the estimated value for the volatilization mass transfer coefficient was an order of magnitude higher than the value experimentally determined. On the other hand some metal decay coefficients are estimated to have extremely low values (in the range of 0.6×10^{-4} to 0.6×10^{-10}); these low values generally occur when the metal decay rate plateaued for a substantial period of time (e.g. Ni) or when the volatilization process dominates most of the curve or when the experimental data is too short to give an adequate definition of the metal decay rate.

The estimated values of the metal decay rate coefficient were plotted on dot diagrams with respect to the three factors: UV light, air and temperature (Appendix H.6, Figures 1 to 3). Temperature has an effect on the decay rate of all four metals. There is no observed effect of either UV or air on nickel decay. There is some relationship between UV light and iron cyanide decay, and some relationship between air and copper cyanide decay.

When considering these results in connection with the actual cyanide-bearing solution in the tailings pond, the implication is that the worst condition for the degradation of cyanide is the cold weather, particularly ice covered ponds when the air and UV in addition to temperature have a minimum effect on cyanide degradation.

The results of this modelling excerise have, therefore, proven to be very realistic and in agreement with the similar information that can be found stated in the literature (Ingles, 1981a).

Contrary to this, it can be concluded that the best conditions for cyanide degradation would be warm weather, high temperatures, sunshine and wind (or some other mechanical source of aeration, Freeman (1983)).

9 VERIFICATION STUDIES

9.1 Simulation on the Synthetic Mixes

The parameters estimated by the three parameter estimation model specifying MCN/TCN = 0.17 were used to simulate the results from the low and high synthetic mix solutions.

As observed from the experimental and estimated values only temperature had a consistent effect on metal cyanide decay coefficients of all four metallo-cyanide solutions. Therefore the metal cyanide decay coefficients were averaged at 4°C and at 20°C and used in the simulations for the mixes (see Table 9.1). The parameter values that were judged as inconsistent were rejected before averaging the decay rates. The three criteria used to specify inconsistency were the following:

(i) The three values of k_1 for Cu (k_{Cu}) at 4°C estimated as extremely low, would signify almost a zero rate of reaction, while in reality the reaction was still going on (cyanide removal over that period averaged about 24%). Therefore, the assumption was that the more realistic value of 0.0029 (h^{-1}) was more representative of k_{Cu} at 4°C.

(ii) The value of 7.41×10^{-2} (h^{-1}) for k_{Cu} at 20°C was estimated as too high ($k_{Cu} > k_v$) because the estimation routine

TABLE 9.1. ESTIMATED METAL DECAY COEFFICIENT VALUES k_1 (h^{-1}) AT MCN/TCN = 0.17 (AVERAGED WITH RESPECT TO TEMPERATURE)

Metallo-Cyanide Complex Solution	AIR	UV	k_1 at 4°C	k_1 at 20°C
Cu-CN	+	-	0.49×10^{-9}*	0.0118
	-	-	0.47×10^{-9}*	0.0741*
	+	+	0.00295	0.0066
	-	+	0.28×10^{-9}*	0.0043
	Accepted Average $\bar{k}_{Cu}$ =		0.00295	0.00753
Zn-CN	+	-	0.0032	0.0280
	-	-	0.0014	0.0671
	+	+	0.0622	0.0219
	-	+	0.0045	0.0629
	Accepted Average $\bar{k}_{Zn}$ =		0.01783	0.04496
Ni-CN	+	-	0.30×10^{-9}	0.0009
	-	-	0.63×10^{-10}	0.0017
	+	+	0.0017	0.0012
	-	+	0.12×10^{-9}	0.59×10^{-4}
	Accepted Average $\bar{k}_{Ni}$ =		0.00044	0.00095
Fe-CN	+	-	0.0002	0.0013
	-	-	0.89×10^{-9}*	0.24×10^{-9}*
	+	+	0.0027	0.0052
	-	+	0.0014	0.0077
	Accepted Average $\bar{k}_{Fe}$ =		0.00143	0.00473

* Rejected as inconsistent.

did not have enough information due to the limited data base (total experimental time only 169 h). Therefore, the other three k_1's for Cu at 20°C (Table 9.1) were used to obtain the average k_{Cu} at 20°C.

(iii) The k_1 for Fe (k_{Fe}) for two conditions had very low estimated values (10^{-9} h^{-1}) and if they were included in the calculation for the average value they would change k_{Fe} drastically for the other six conditions, therefore they were also rejected as non-representative.

The energy of activation was calculated using Eq. 5.6 for the average k_1 values at 4°C and 20°C. The values obtained are listed in Table 9.2. The activation energy permits one to ascertain that values used for averaging are plausible and consistent with the idea that the activation energy for aqueous solution reactions are typically within a range of 10 to 100 kJ/mol*.

These energy of activation values are at the low end of such a scale. They seem to be on a border where diffusion control ends and chemical reaction control starts.

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* Stumm and Morgan (1981) - For very rapid diffusion controlled reactions they found E to have a range of 12.6 to 21 kJ/mol and a slow reaction controlled by chemical steps to have E = 70 kJ/mol (for a psuedo-first-order rate constant). On the same subject, Moore (1962) referred to a unimolecular gas phase decomposition with E = 54.4 kJ/mol.

TABLE 9.2. ENERGY OF ACTIVATION FOR k_1 BETWEEN 4°C and 20°C

Metallo-Cyanide Complex Solution	Estimated k_1 (h^{-1}) at 4°C	Estimated k_1 (h^{-1}) at 20°C	E kJ/mol
Cu - CN	0.00295	0.00753	39.4
Zn - CN	0.01783	0.04496	39.0
Ni - CN	0.00044	0.00095	33.0
Fe - CN	0.00143	0.00473	50.4

9.1.1 Low mix

The values of all the initial parameters necessary to carry out the simulation on the low mix cyanide solution are presented in Table 9.3. An example calculation is given in Appendix I.1. An example calculation for the rate constant due to ultraviolet irradiation is presented in Appendix I.2.

The initial metal cyanide concentration $[MCN]_o$ was calculated taking theoretical stoichiometry of cyanide complexes into consideration. The initial free cyanide concentration for all eight experimental conditions was calculated by subtracting $[MCN]_o$ from the measured $[TCN]_o$ value.

A typical example for the low mix model fit simulation is presented in Figure 9.1 for the conditions of 20°C, NO AIR, UV. The results of the model simulations on the low mix solutions under the other seven experimental conditions (Figures I.3.1 to I.3.7) and the sample program used for simulations are presented in Appendix I.3.

Predicted cyanide values are compared with observed values near the end of each low mix experiment in Table 9.4. Generally, the predicted TCN values are close to the observed values with one exception which is the 4°C, NO AIR, UV condition. The lack of agreement is obvious when the graph is inspected (Figure I.3.2, Appendix I.3). In order to illustrate the difficulty that the model encountered, the experimental results of the degradation process of single metallocyanide solutions and the low mix (concentration versus time) under the

TABLE 9.3. INITIAL PARAMETERS USED FOR THE MODEL SIMULATION OF THE LOW MIX

Parameters	20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
FCN = TH (1) (mol/L)	0.00638	0.00631	0.00615	0.00692	0.00592	0.00635	0.00631	0.00581
MCN = TH (2) (mol/L)				0.0013				
k_v = TH (3) (h^{-1})	0.0394	0.0238	0.0074	0.0050	0.0389	0.0253	0.0234	0.0139
[Cu-CN] = TH (4) (mol/L)				0.00033				
[Zn-CN] = TH (5) (mol/L)				0.00062				
[Ni-CN] = TH (6) (mol/L)				0.00014				
[Fe-CN] = TH (7) (mol/L)				0.00022				
k_{Cu} = TH (8) (h^{-1})	0.00753	0.00753	0.00295	0.00295	0.00753	0.00753	0.00295	0.00295
k_{Zn} = TH (9) (h^{-1})	0.04496	0.04496	0.01783	0.01783	0.04496	0.04496	0.01783	0.01783
k_{Ni} = TH (10) (h^{-1})	0.00095	0.00095	0.00044	0.00044	0.00095	0.00095	0.00044	0.00044
k_{Fe} = TH (11) (h^{-1})	0.00473	0.00473	0.00143	0.00143	0.00473	0.00473	0.00143	0.00143
k_{uv} = TH (12) (h^{-1})	-	-	-	-	0.00025	0.00025	0.00025	0.00025

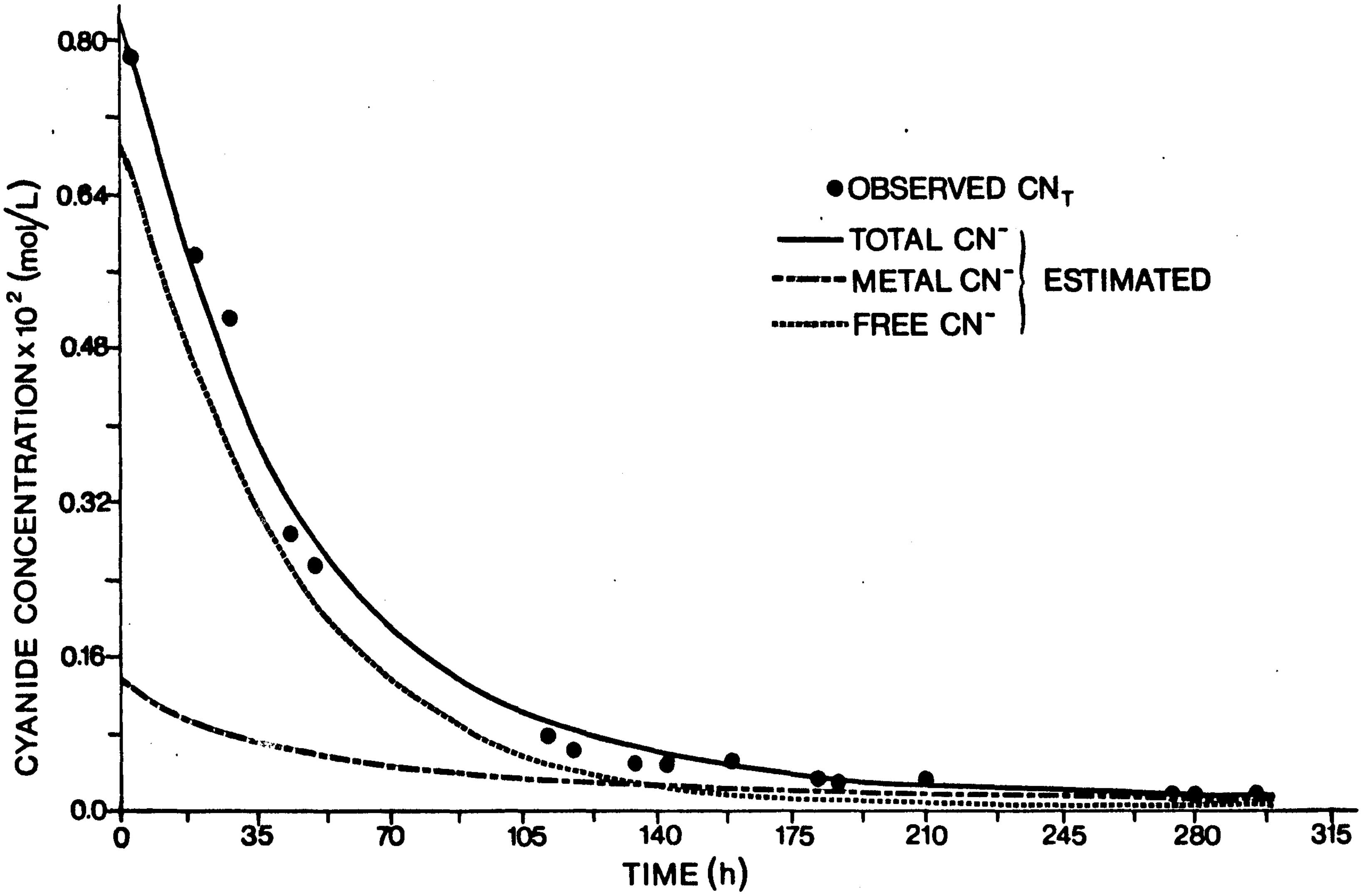

Figure 9.1 Low Mix Simulation - 20°C, NO AIR, UV

TABLE 9.4. TOTAL CYANIDE VALUES (OBSERVED AND ESTIMATED) FOR LOW MIX CYANIDE SOLUTION

Observed TCN versus Predicted TCN		20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Experimentally Observed Values	Exper. Time (h)	312	312	317	312	306	306	288	264
	TCN exp. (mol/L)	0.0004	0.0004	0.0015	0.0021	0.0001	0.0002	0.0004	0.00015*
Model Simulation Values	Simulated Time (h)	310	310	320	310	310	310	290	260
	TCN predic. (mol/L)	0.0002	0.0002	0.0012	0.0021	0.0002	0.0002	0.0004	0.00068

* Model estimation value considered more accurate than experimentally obtained value because of the discrepancies observed in this low mix experimental run.

same conditions were plotted on the same graph (Figure 9.2). The difference in the slope for the initial volatilization process is obvious. This is an extreme case, i.e., the volatilization process in the low mix happens so fast that it gives the definite indication that some of the assumed complexes do not form, instead that the free cyanide is released as soon as the process starts. This would explain a sudden decrease in total cyanide concentration for which the model could not account. Therefore, the low mix model simulation under 4°C, NO AIR, UV condition was assumed correct and the experimental observation of the low mix under the same condition incorrect.

Under the three conditions: 4°C, AIR, UV; 4°C, NO AIR, NO UV and 20°C, AIR, NO UV there seems to be a delay in the initial degradation of cyanide in the low mix. However, when compared to the range of variations observed in single solutions under these conditions, the "delay" was within the 95% confidence interval of the single solutions. Although this slowed down the process in the beginning, after 230 hours the concentration estimated by the model was similar to the observed values. Generally, it was observed that the conditions with NO UV would require a longer reaction time than that allowed, in order to have the model fit the data better. This was not surprising, since UV light was found earlier to have an effect on the rate of degradation of the low mix.

In order to check if the model was within the 95% confidence level of the observed data, a "modified F" test was used. According to

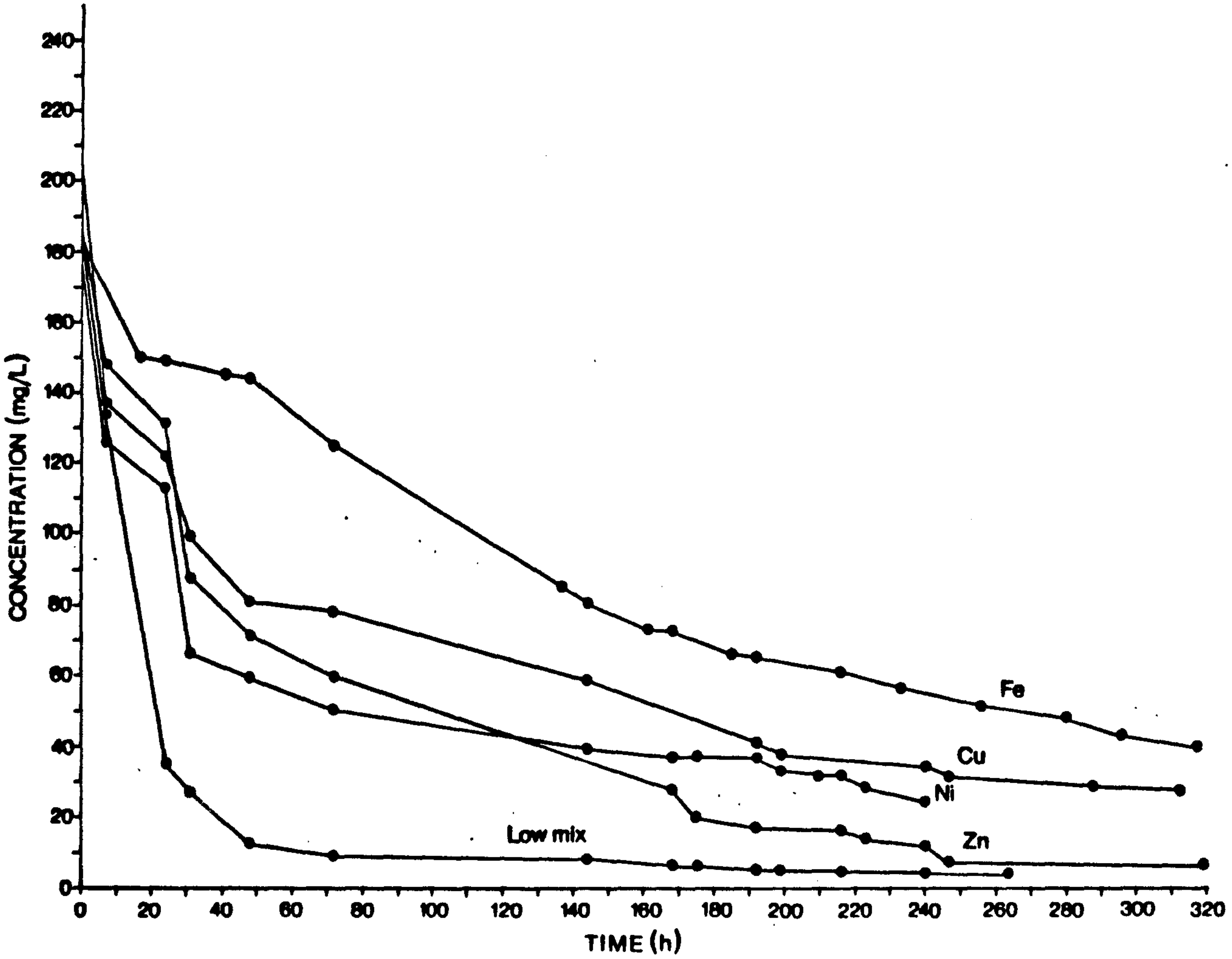

Figure 9.2 Total Cyanide Degradation - Single Metallo-Cyanide Complex Solutions and Low Mix Cyanide Solution (4°C, NO AIR, UV)

Bard (1974), it is possible to calculate the likelihood ratio test for two models with nonlinear coefficients by using the following simplified equation:

$$\text{Modified F test} = \frac{L_{(1)}}{L_{(2)}} = \left(\frac{\text{Model}_2 \text{ RSS}}{\text{Model}_1 \text{ RSS}}\right)^{\frac{n}{2}}$$

In this case, Model_1 is based on the mean; Model_2 is the low mix simulation, while n is the number of experiments. For $L_{(1)}/L_{(2)} \leq B$ hypothesis H_2 is accepted (Model_2 is correct), and for $L_{(1)}/L_{(2)} \geq A$ hypothesis H_1 is accepted (Model_1 is correct), and if $A > L_{(1)} / L_{(2)} > B$ the experimentation should continue. The A and B constants are determined depending upon the confidence we desire to place on the results. If $\alpha = \beta = 0.05$ the values of A and B are $A \approx \frac{1-\beta}{\alpha} = 19$ and $B \approx \frac{\beta}{1-\alpha} = 0.053$.

From the results of these calculations presented in Table 9.4a, the experiments under 20°C, NO AIR, NO UV and 4°C, AIR, UV conditions should be continued ($A > 4.14$ and $A > 1.69$) and for the condition of 20°C, AIR, NO UV, Model_1 is correct. Therefore, for five of the eight test conditions, the model fits the data at the 95% confidence level (identified with two asterisks in Table 9.4a).

When the calculated values are compared to the standard F test, only the model fits under two conditions (20°C, AIR, NO UV and 20°C, NO AIR, NO UV) are not acceptable.

TABLE 9.4a. VERIFICATION OF THE LOW MIX MODEL SIMULATION - STANDARD F TEST (5%) VERSUS MODIFIED F TEST*

	20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
d_f	13	14	18	17	12	12	4	8
Model_1 RSS	1.034	0.867	0.053	0.145	2.542	0.707	0.356	5.158
Model_2 RSS	2.571	1.035	0.006	0.0002	0.735	0.273	0.432	0.066
F Test	2.57	2.50	2.23	2.27	2.27	2.69	6.39	3.44
Modified F Test	926.5	4.14	$1.6\text{x}10^{-10}$**	$8.1\text{x}10^{-29}$**	$1.7\text{x}10^{-4}$**	$1.3\text{x}10^{-3}$**	1.69	$3.4\text{x}10^{-10}$**

* "Modified F Test" is a modified version of an F test for the model with nonlinear coefficients - See Ref. Y Bard, 1974. Chapter X.

** The model fits the data at the 95% confidence level.

9.1.2 High mix

The metal decay coefficients applied in the high mix model simulations were the same used for the low mix. These were the average values of the metal decay coefficients determined by the three-parameter estimation model carried out on the single metallo-cyanide complex solutions (preset MCN/TCN ratio of 0.17).

The initial values for cyanide concentrations in the high mix were obtained as explained in Appendix J.1 (i) and (ii). Because the high mix cyanide solution contained an excess of metals, some adjustments in cyanide concentrations had to be made before the model simulation process. The adjustments made for the first model simulation consisted in reducing all MCN concentrations by 15 to 23.1% in order to reach FCN = 0.0 mol/L. The initial values for all the parameters required for the simulation are presented in Table 9.5.

A typical example of the first model simulation and its fit are presented in Figure 9.3a. The model fit of Figure 9.3a is not satisfactory, throughout the whole domain. But final predictions for TCN were not too far from those observed (see Table 9.6). In this first simulation, either the original assumptions made were not warranted or the estimates of the metal decay coefficients made for the single metallo-cyanide solutions were not suitable for the high mix conditions.

A second set of model simulations on the high mix data were carried out after some adjustments were made on metallo-cyanide

TABLE 9.5. THE INITIAL PARAMETER VALUES FOR HIGH MIX CYANIDE SOLUTION (FIRST SIMULATION)

(i) High Mix Simulation	20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
FCN=TH(1) (mol/L)	0.0000							
MCN = TCN = TH(2)	0.0076	0.0075	0.0076	0.0076	0.0074	0.0073	0.0069	0.0074
k_v = TH(3) (h^{-1})	0.0394	0.0238	0.0074	0.0050	0.0389	0.0253	0.0234	0.0139
[Cu-CN] = TH(4) (mol/L)	0.0019	0.0019	0.0019	0.0019	0.0019	0.0019	0.0018	0.0019
[Zn-CN] = TH(5)	0.0036	0.0036	0.0036	0.0036	0.0035	0.0035	0.0033	0.0035
[Ni-CN] = TH(6)	0.0008	0.0008	0.0008	0.0008	0.0007	0.0008	0.0007	0.0008
[Fe-CN] = TH(7)	0.0013	0.0012	0.0012	0.0012	0.0012	0.0012	0.0015	0.0012
k_{Cu}= TH(8) (h^{-1})	0.0075	0.0075	0.0029	0.0029	0.0075	0.0075	0.0029	0.0029
k_{Zn}= TH(9)	0.0449	0.0449	0.0178	0.0178	0.0449	0.0449	0.0178	0.0178
k_{Ni}= TH(10)	0.0009	0.0009	0.0004	0.0004	0.0009	0.0009	0.0004	0.0004
k_{Fe}= TH(11)	0.0048	0.0048	0.0014	0.0014	0.0048	0.0048	0.0014	0.0014
k_{uv}= TH(12)	-	-	-	-	0.0002	0.0002	0.0002	0.0002

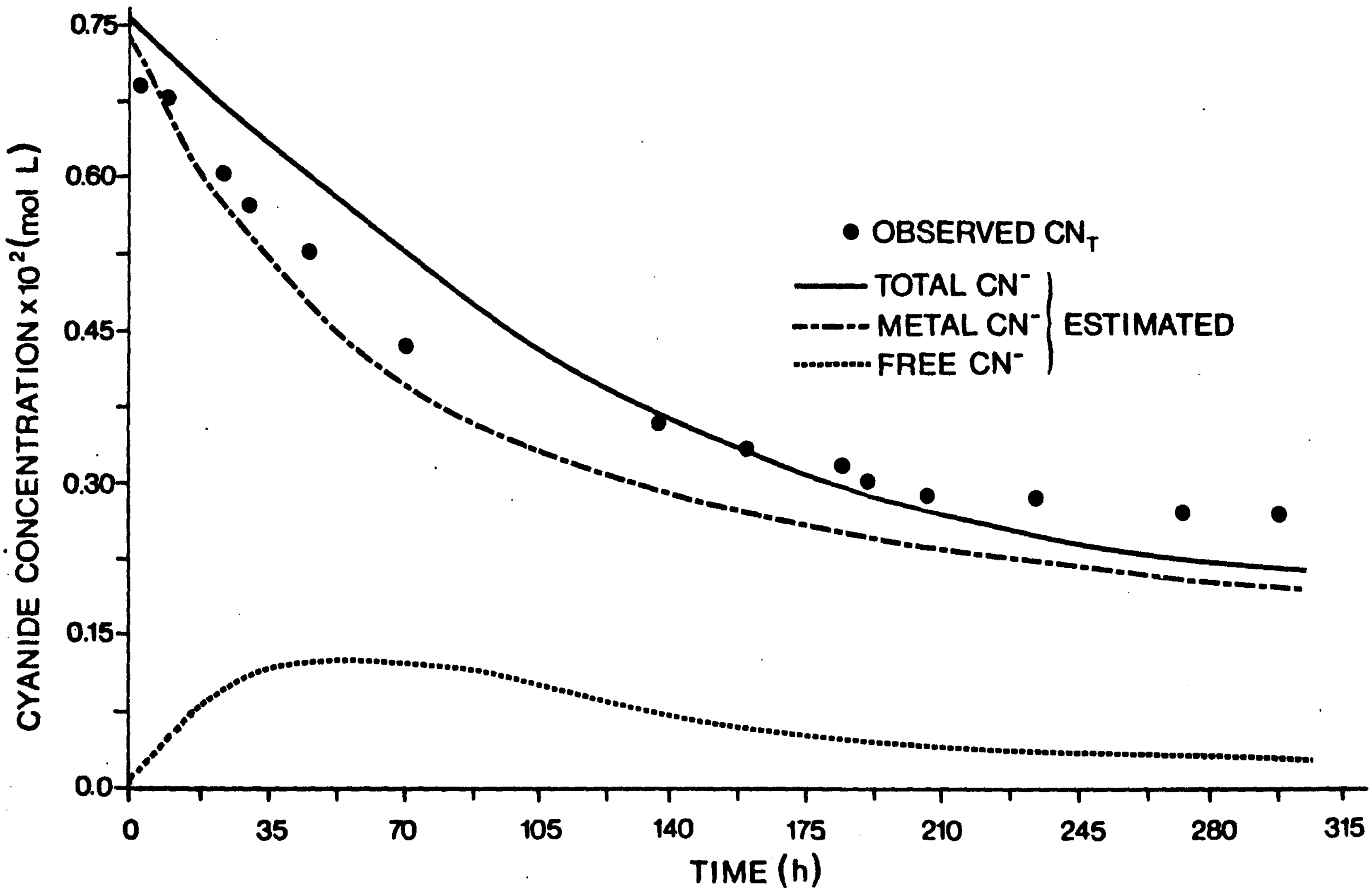

Figure 9.3a High Mix - First Simulation (4°C, NO AIR, NO UV)

TABLE 9.6. TOTAL CYANIDE VALUES, OBSERVED AND ESTIMATED FOR HIGH MIX CYANIDE SOLUTION (TWO ATTEMPTS)

High Mix Observed TCN vs Est. TCN		20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Experimentally observed values	Exper. Time (h)	266	266	312	306	306	306	312	317
	TCN exp. (mol/L)	0.0015	0.0022	0.0032	0.0031	0.0013	0.0019	0.0026	0.0032
Model simulation (i)	Simulated time (h)	270	270	310	310	310	310	310	320
	TCN predicted (mol/L)	0.0014	0.0015	0.0035	0.0044	0.0012	0.0011	0.0021	0.0026
Model simulation (ii)	Simulated time (h)	270	270	310	310	310	310	310	320
	TCN predicted (mol/L)	0.0015	0.0016	0.0034	0.0041	0.0010	0.0013	0.0024	0.0025

concentrations (Appendix J.1(ii)). The adjustments involved reduction of Cu and Zn metal concentrations in a complex with cyanide. The values of all the initial parameters are presented in Table 9.7. The assumption in this case was that Cu and Zn cyanide complexes were easily dissociated and cyanide became available for volatilization or further complexation, while metals could precipitate, adsorb or complex again.

According to Figure 9.3b cyanide was complexed again as part of a slow-decaying metallo-cyanide complex, because the model fit substantially improved in the metal decaying area. Model predictions agree much more closely with observations near the end of the experiments in this simulation (see Table 9.6 and Figure 9.3b).

The obvious observation concerning the high mix model fit in both Figures (9.3a and b) was that the model predicted a slower rate of volatilization and more rapid rate of metal decay than actually occurred. The problem in the volatilization area could be that the complexes assumed to be formed had not formed in the time available therefore, some free cyanide escaped initially, and once the cyanide did complex with the metals present, the decay rate slowed down. When dealing with a solution such as the high mix which has an excess of metals, the possible competition between metals and ligands (CN^-, OH^- and PO_4^{3-}) has to be suspected, which in itself could slow down the complexation process. According to the program REDEQL2 (McDuff and Morel, 1974) used for finding the equilibrium compositions of complex

TABLE 9.7. THE INITIAL PARAMETER VALUES FOR HIGH MIX CYANIDE SOLUTION (SECOND SIMULATION)

(ii) High Mix Simulation	20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
FCN=TH(1) (mol/L)	0.0000							
MCN = TCN = TH(2)	0.0076	0.0075	0.0076	0.0076	0.0074	0.0073	0.0069	0.0074
k_v = TH(3) (h^{-1})	0.0394	0.0238	0.0074	0.0050	0.0389	0.0253	0.0234	0.0139
[Cu-CN] = TH(4) (mol/L)	0.0015	0.0015	0.0015	0.0015	0.0019	0.0014	0.0013	0.0019
[Zn-CN] = TH(5)	0.0037	0.0036	0.0037	0.0037	0.0035	0.0035	0.0032	0.0035
[Ni-CN] = TH(6)	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009	0.0009
[Fe-CN] = TH(7)	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015	0.0015
k_{Cu}= TH(8) (h^{-1})	0.0075	0.0075	0.0029	0.0029	0.0075	0.0075	0.0029	0.0029
k_{Zn}= TH(9)	0.0449	0.0449	0.0178	0.0178	0.0449	0.0449	0.0178	0.0178
k_{Ni}= TH(10)	0.0009	0.0009	0.0004	0.0004	0.0009	0.0009	0.0004	0.0004
k_{Fe}= TH(11)	0.0048	0.0048	0.0014	0.0014	0.0048	0.0048	0.0014	0.0014
k_{uv}= TH(12)	-	-	-	-	0.0002	0.0002	0.0002	0.0002

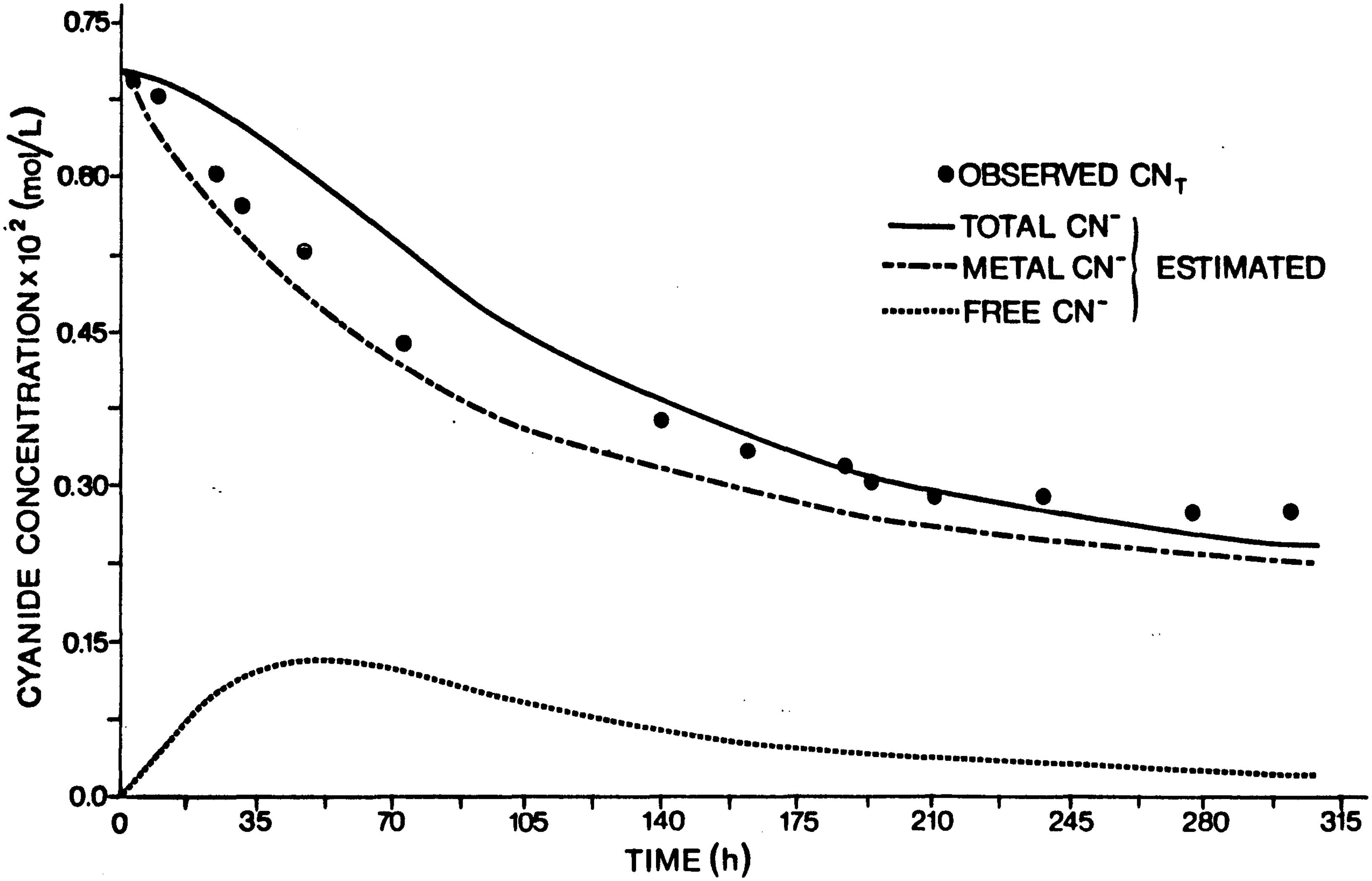

Figure 9.3b High Mix - Second Simulation (4°C, NO AIR, NO UV)

aqueous systems, assuming equilibrium in this system at pH 7.0, zinc can be found in solid form with a PO_4^{3-} ligand.

The general conclusion from the simulation attempts on high mix is that the estimated k_1 values for the single metallo-cyanide solutions are suitable for the mixes relatively low in metal concentration but when it comes to the solutions oversaturated with metals, the metal decay coefficient values may need reevaluation.

9.2 Evaluation of Model Calibration with Barren Solutions

9.2.1 Introduction

Three barren solutions were obtained from the well known gold mines in Canada. The apparatus used for these experiments was the same as the one used for synthetic solutions (Figure 4.1). Experiments were conducted under what was considered to be the best conditions for the natural degradation of cyanide to occur under a controlled environment, i.e., 20°C, AIR and UV.

The initial cyanide and metal concentrations in all three barren solutions were compared to the final concentrations recorded at the end of the experiment (see Table 9.8). It was difficult to compare values obtained after different times of observation, (968 h vs 1320 h) but since the concentrations of metals were not available <u>during</u> the experiments, only at the beginning and the end, these values had to be sufficient.

TABLE 9.8. BARREN SOLUTION PARAMETERS

Barren Solutions	TCN (mg/L)		Cu (mg/L)		Zn (mg/L)		Ni (mg/L)		Fe (mg/L)		pH	
	I	F	I	F	I	F	I	F	I	F	I	F
#1 (t_F = 1320h)	145	2.3	7.8	7.8	31	21(0.37)	1.5	1.5	0.1	0.1	11.5	8.2
#2 (t_F = 1320h)	295	7.2	15.0	13.0	131	128(0.24)	0.7	0.6	5.7	3.3(0.1)	12.0	9.0
#3 (t_F = 968h)	128	6.3	7.7	2.4(2.3)	1.1	.1	0.5	0.1	10.0	0.6 (0.5)	11.6	8.0

Values in parenthesis are metal concentrations in a filtered sample. All other metal values are total concentrations.
I - Initial time.
F - Final time.

Zinc and copper were the metals with the highest concentrations common for #1 and #2 barren solutions, while the #3 barren had the highest concentration of iron, followed by copper.

The cyanide removal in all of them was $>$95%. The concentration of metals generally decreased (all except Ni). It is suspected that with a change of pH from a high of 11.0 to 9.0 or 8.0, the metals precipitated in the form of hydroxides or were adsorbed on the walls of the container.

9.2.2 Simulations with the original k_1 values

At this point it was considered that the only differences between the barrens and synthetic solutions, were the cyanide and metal contents, and the pH of the solutions. From that aspect two adjustments had to be made to the model. The first adjustment (Appendix J.2) involved the assumption that barren solutions only contained the same metallo-cyanide complexes as the synthetic solutions. The theoretical stoichiometry for each complex was used in the calculations for $[MCN]_o$, which was subtracted from the analytically determined $[TCN]_o$ in order to obtain $[FCN]_o$. Since the model equations were derived for synthetic solutions at pH 7.0, the effects of pH on the volatilization of HCN had to be taken into consideration when modelling barren solutions. Hence the appropriate adjustments made on the model based on the equilibrium equation between HCN and CN^- were explained in

Appendix J3. The calculated values of all initial parameters required for the model simulation are presented in Table 9.9.

The results of the model simulation on barren solutions were very similar to the results of high mix simulation. The model volatilized cyanide too slowly and decayed metal cyanide too quickly (Figures 9.4, 9.6a and 9.7a). The reason for this may be the original assumption that the pH effect on metallo-cyanide complexes is insignificant and that only pH effect on HCN and CN^- ratio is important. From another viewpoint, if metal cyanide in barren solution was simply dissociating, as assumed, and releasing CN^-, the high pH would prevent formation of HCN. The released CN^- ion may complex with other metals, or form thiocyanate and precipitate, or oxidize into CNO^-, etc. There are many possibilities but not all of them could be covered in the model obtained for synthetic solutions.

The final estimated TCN is compared to the experimental TCN (Table 9.10). The observed and predicted TCN values for #1 barren solution were at least within the same order of magnitude, but the TCN predictions for #2 and #3 barrens were an order of magnitude lower than experimental TCN values.

9.2.3 Analyses of barren solutions' parameters

In order to find some explanation for the discrepancies in the model fit, other chemical characteristics of the barren solutions were examined. Pertinent data are given in Table 9.11.

TABLE 9.9. THE INITIAL PARAMETERS REQUIRED FOR THE MODEL SIMULATION OF BARREN SOLUTIONS

	#1	#2	#3
FCN=TH(1) (mol/L)	0.0032	0.0022	0.0034
MCN = TH(2)	0.0024	0.0091	0.0015
k_v = TH(3) (h^{-1})	0.0389	0.0389	0.0389
[Cu-CN] = TH(4) (mol/L)	0.0004	0.0007	0.0004
[Zn-CN] = TH(5)	0.0019	0.0078	0.0001
[Ni-CN] = TH(6)	0.0001	0.00005	0.00003
[Fe-CN] = TH(7)	0.00001	0.0006	0.0011
k_{Cu} = TH(8) (h^{-1})	0.0075	0.0075	0.0075
k_{Zn} = TH(9)	0.0449	0.0449	0.0449
k_{Ni} = TH(10)	0.0009	0.0009	0.0009
k_{Fe} = TH(11)	0.0048	0.0048	0.0048
k_{uv} = TH(12)	0.0002	0.0002	0.0002

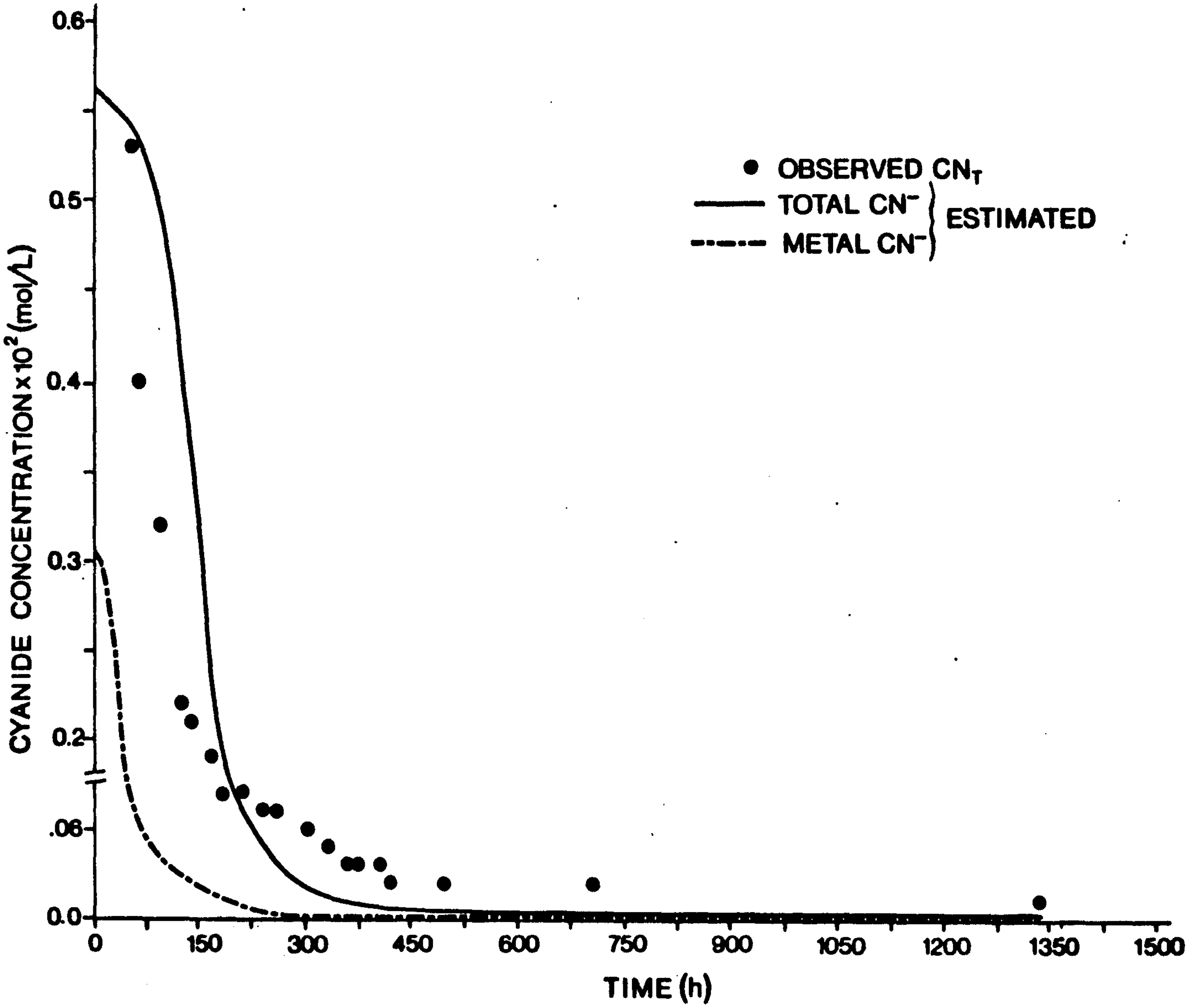

Figure 9.4 Barren Solution #1 - Original

TABLE 9.10. ORIGINAL SIMULATIONS ON BARREN SOLUTION

	Time (h)		TCN (mol/L)	
Barren Solutions	Exper.	Simulated	Exper.	Predicted
#1	1320	1320	0.88×10^{-4}	0.29×10^{-4}
#2	1320	1320	2.8×10^{-4}	1.6×10^{-5}
#3	968	970	2.4×10^{-4}	2.4×10^{-5}

TABLE 9.11. ADDITIONAL BARREN SOLUTIONS' PARAMETERS

Barren Solutions	CNS^- (mg/L)		CNO^- (mg/L)		TCN (mg/L)		CN_W (mg/L)		Total Alkalinity (mg/L as $CaCO_3$)		Phenolphthalein Alkalinity (mg/L as $CaCO_3$)		Ca (mg/L)		pH	
	I	F	I	F	I	F	I	F	I	F	I	F	I	F	I	F
#1	51	57	23	0	145	8.2	145	2.1	398	42.5	263	-	116	43	11.5	8.2
#2	428	412	125	72	295	7.2	286	4.7	1,309	757	890	115	176	105	12.0	9.0
#3	1090	1074	56	23	128	6.3	96.5	4.6	338	292	239	-	116	31.5	11.6	8.0

CN_W - Weak acid dissociable cyanide.

I = Initial time.

F = Final time.

Initially, most of the total cyanide measured in the first two barrens was equal to the weak acid dissociable cyanide (compare TCN and CN_W). This meant that cyanide was tied up in any other complex but iron cyanide, i.e., susceptible to natural degradation even without UV light present. The difference between TCN and CN_W in the third barren solution was assumed to be mostly the cyanide complexed with the iron present in the solution.

The thiocyanate CNS^- fluctuated slightly in all three barren solutions, but generally it did not change significantly. There was no noticeable production of cyanate (oxidation of CN^- to CNO^-) but the initial CNO^- gradually decomposed, probably into CO_2 and ammonium ion, which were lost in the atmosphere.

The total alkalinity was extremely high in the second solution. This was probably the reason that slowed down the decrease of its pH value (high buffering capacity). All three solutions had an OH^- alkalinity at the beginning, which became CO_3^{2-} and HCO_3^- alkalinity at the end of the experiments. In all barren solutions, some precipitation of $CaCO_3$ also occurred during the experiment (see Table 9.11).

9.2.4 Simulations with the adjusted k_1 values

Taking into consideration the high concentrations of Zn and Cu in two out of three barren solutions and the fact that these are the metals with the highest decay coefficients, (k_{Cu} = 0.0075 and

k_{Zn} = 0.0449 h^{-1}) it was postulated that these must control the rapid metal decay rate produced in the model simulation. Therefore, the k_1 values for these two metals were recalibrated using data from the first barren solution. The values obtained, k_{Cu} = 0.0022 h^{-1} and k_{Zn} = 0.003 h^{-1} gave a good model to data fit (see Figure 9.5). Then the recalibrated values were used to simulate the other two barrens. Simulation of the #2 barren's data was just as good as for #1 (Figure 9.6b) but the model fit in the case of the third barren solution while improved was still poor (Figure 9.7b). There was a significant improvement in the part of the degradation curve attributed to the metal decay process in the first two barrens. This validates the theory that Cu and Zn control this part of the curve. There was some improvement in the model fit for the third barren solution (compare Tables 9.10 and 9.12) but not significant enough. The estimated TCN values are compared to the experimentally obtained TCN in Table 9.12. The final values estimated for TCN are almost equal to the experimental TCN concentration for #1 and #2 barren solutions.

In a way the minimal change in #3 barren solution simulation was expected since this solution contained a higher Fe concentration than Cu and Zn, therefore the changes in k_{Cu} and k_{Zn} would not have much effect on the rapid metal decay rate in this particular case. But, when k_{Fe} was recalibrated from 0.0048 (h^{-1}) to 0.001 (h^{-1}) the model simulation on #3 barren changed and the fit improved significantly (Figure 9.8a and b). All curves still showed discrepancies

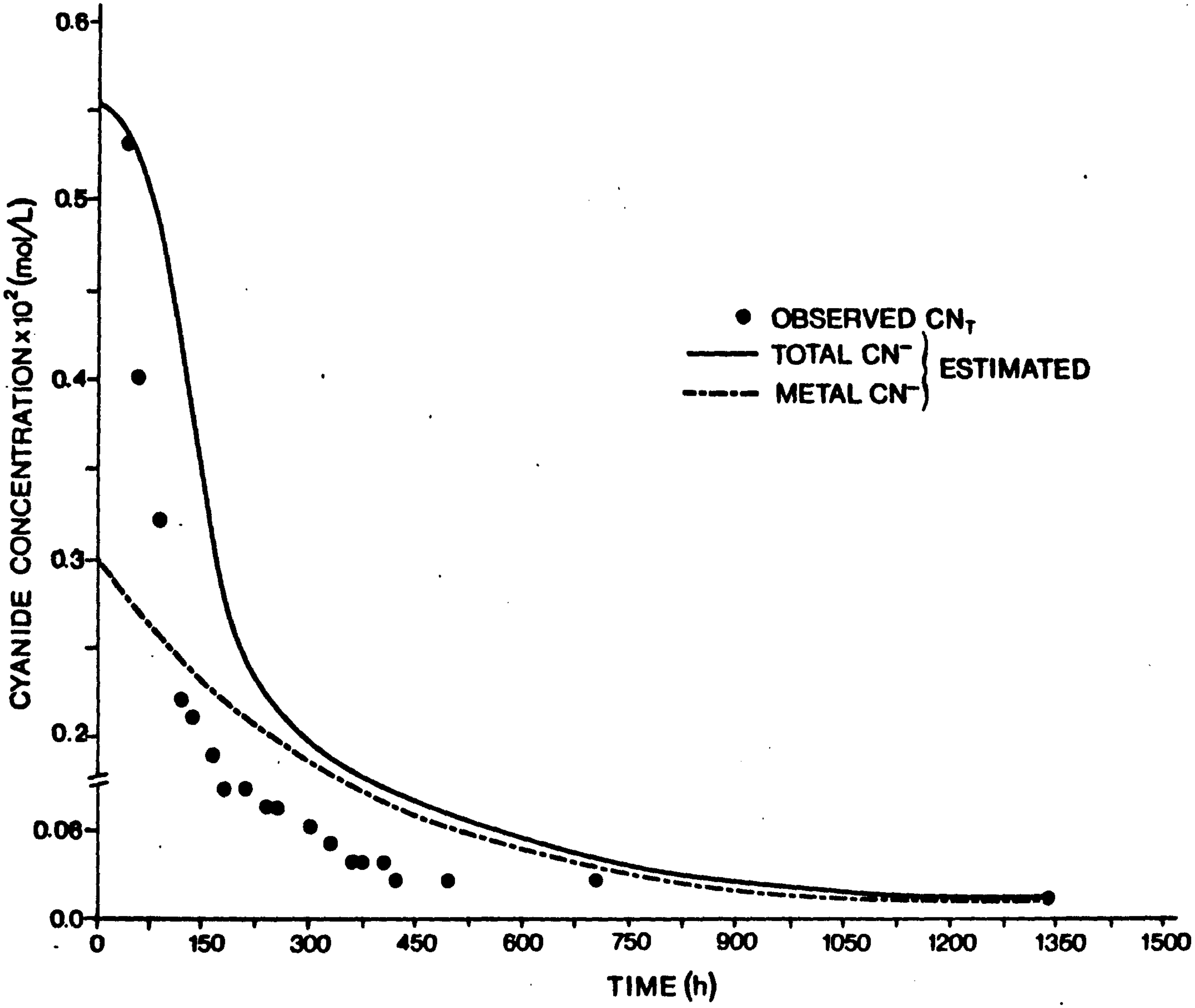

Figure 9.5 Barren Solution #1 - Adjusted k_{Cu} and k_{Zn}

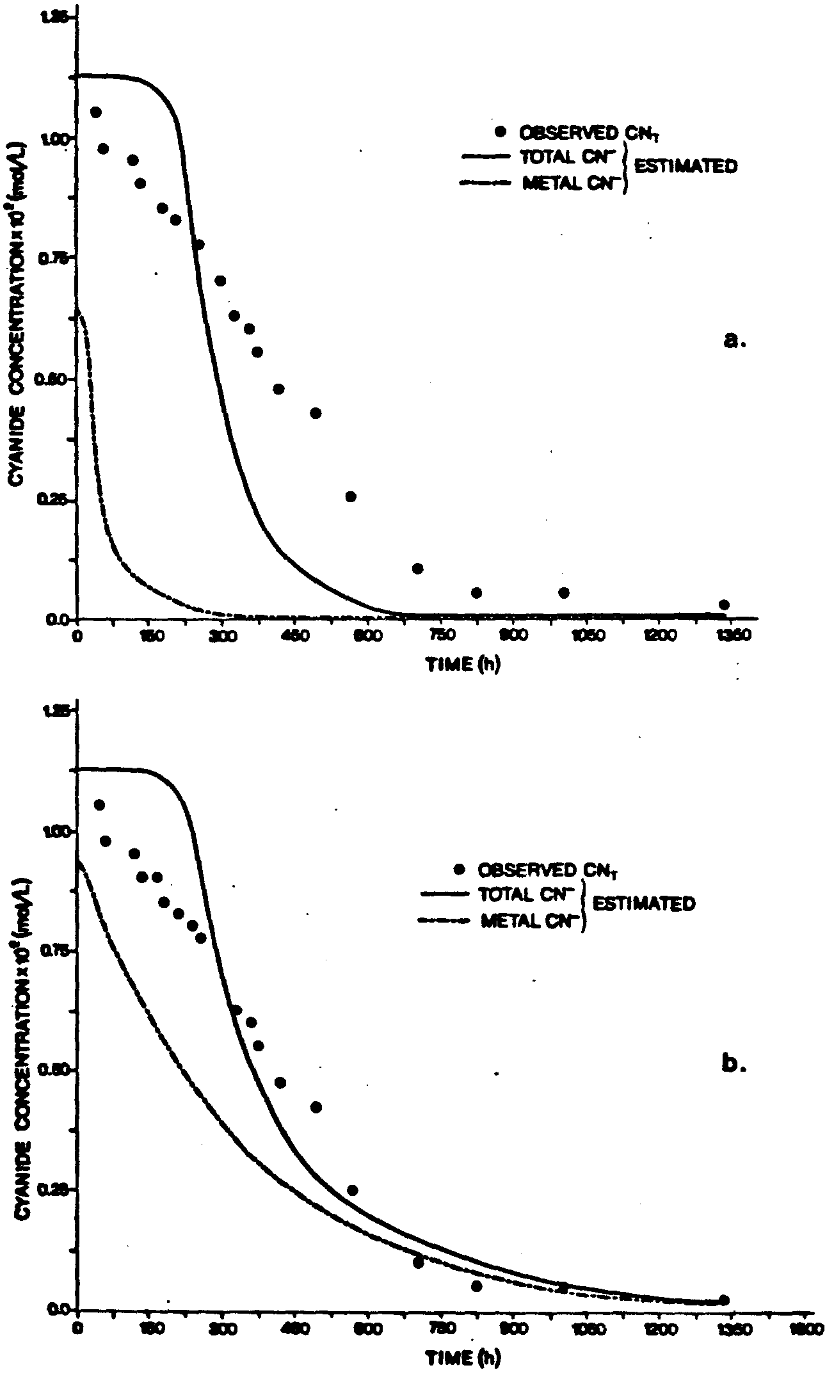

Figure 9.6 Barren Solution #2 – a) Original; b) Adjusted k_{Cu} and k_{Zn}

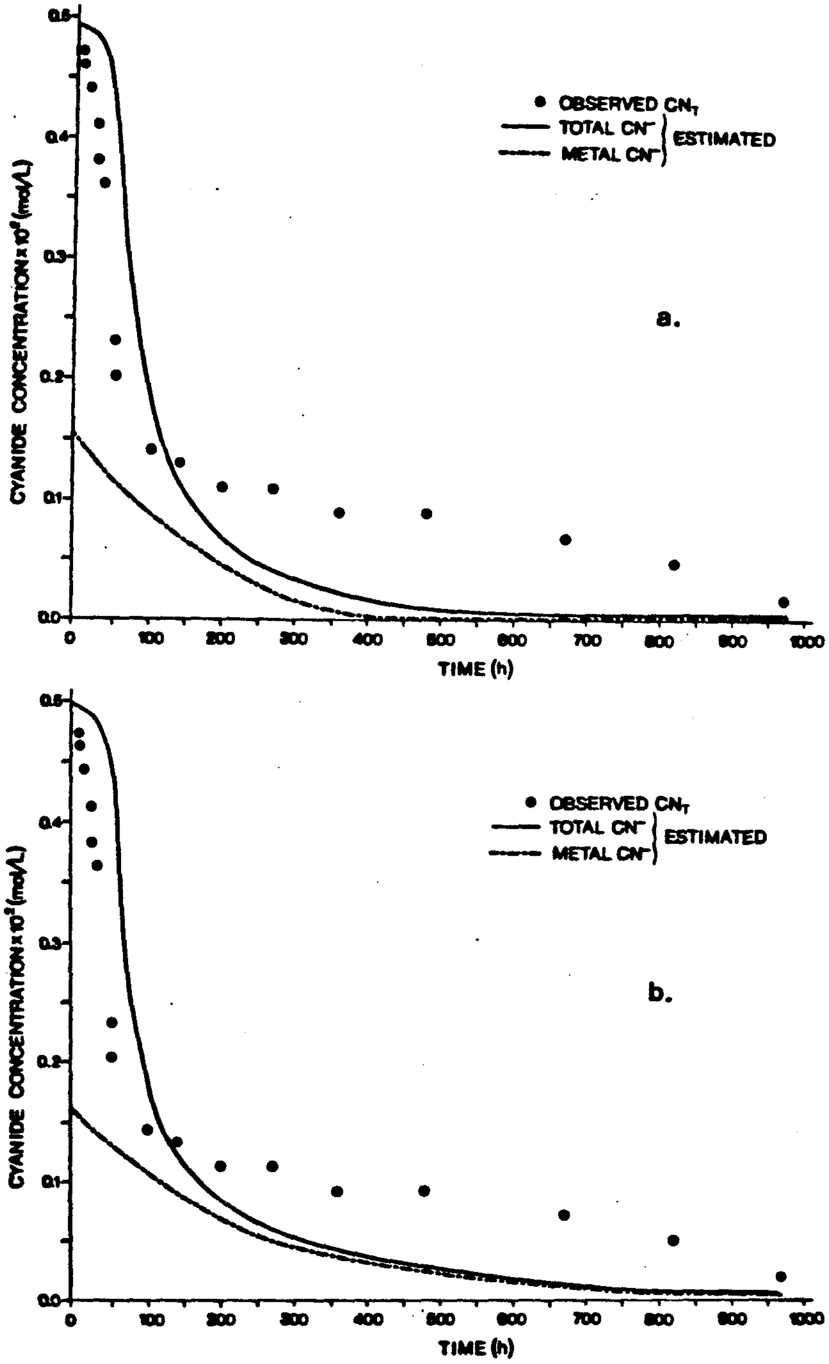

Figure 9.7 Barren Solution #3 - a) Original; b) Adjusted k_{Cu} and k_{Zn}

TABLE 9.12. MODIFIED SIMULATION ON BARREN SOLUTIONS

	Time (h)		TCN (mol/L)	
Barren Solutions	Exper.	Simulated	Exper.	Predicted
#1	1320	1320	0.88×10^{-4}	0.9×10^{-4}
#2	1320	1320	2.8×10^{-4}	2.4×10^{-4}
#3	968	970	2.4×10^{-4}	0.7×10^{-4}

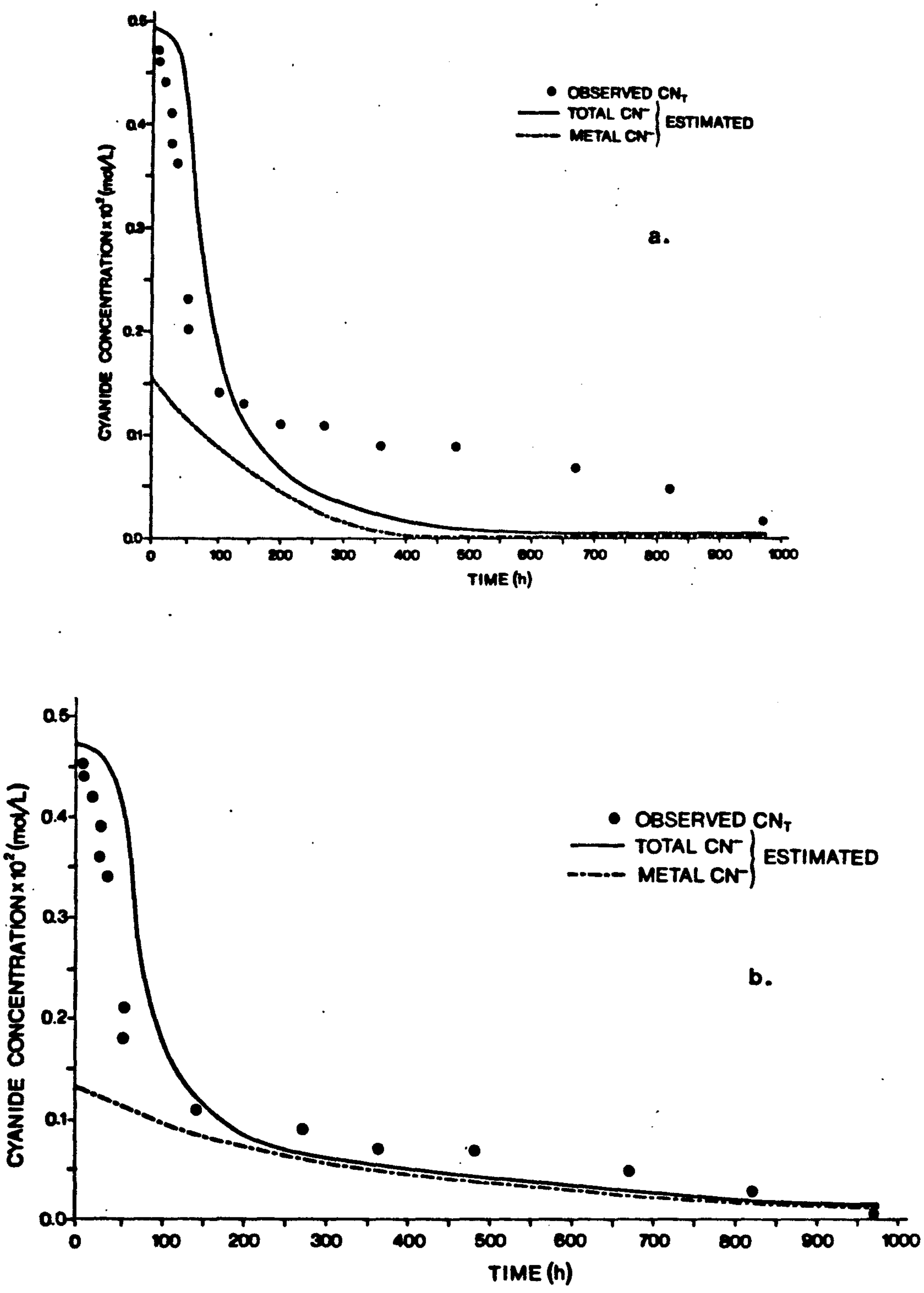

Figure 9.8 Barren Solution #3 - a) Original; b) Adjusted k_{Fe}

during volatilization process (the first part of the curve). This is suspected to be due to a change in pK value, and the increase in ionic strength of the solution. Ionic strength correction would change the effect of pK by a small amount; this change would not significantly influence the curve predicted by the model.

The general conclusion from the model simulations is that the volatilization mass transfer coefficient and the values obtained for metal decay rate for single metallo-cyanide complex solutions, were very good for these particular solutions and to some extent for a low mix. However, in order to be used for high mix and barren solutions, more observation and some recalibration of the parameters is necessary.

10 CONCLUSIONS

The long-term objective of this work is to model the kinetics of removal of cyanide from tailings ponds containing gold mill effluents. The approach in this research was to emulate the general characteristics of the actual systems and by creating a synthetic solutions, examine them under controlled conditions and then compare the results with observations on the actual systems.

The thesis describes the experimental design used in the laboratory to delineate major factors affecting cyanide removal in the synthetic solutions and modelling the results of the synthetic and actual barren solutions.

The general conclusions from the experiments are the following:

1) Volatilization and metal cyanide decay are the controlling mechanisms for removal of cyanide from solution; volatilization is a very rapid process, therefore metal cyanide decay is the rate limiting mechanism.

2) Analysis of the results from the full 2^3 factorial design show that temperature has the most significant effect on the volatilization coefficients of all cyanide solutions examined, including NaCN solution. The aeration effect on the volatilization coefficient is

significant combined with temperature, but only for the first 48 to 72 hours of the volatilization process.

3) Temperature has a large main effect upon the metal cyanide decay in most of the solutions. UV light has an effect on Fe-CN and low mix solutions.

4) A model was derived to describe cyanide removal from solution. It assumes that the volatilization of HCN and the decay rate of one metallo-cyanide complex control the disappearance of total cyanide from single metallo-cyanide solutions.

5) The rate of volatilization of HCN (k_v) from the single metallo-cyanide solutions was determined to be within 95% confidence interval of the volatilization rate of HCN in sodium cyanide solutions. The means and standard deviations for k_v values at 4°C and 20°C were: 0.0124 ± 0.008 and 0.0318 ± 0.008, respectively. The metal decay rates varied among different metals and at different test conditions.

6) The best estimates of the metal decay coefficients from single metallo-cyanide complex solutions and their energy of activation using Arrhenius's equation were determined:

Metallo-Cyanide Complex Solutions	k_1 at 4°C (h^{-1})	k_1 at 20°C (h^{-1})	E (kJ/mol)
$Na_2Cu(CN)_3$	0.00295	0.00753	39.4
$Na_2Zn(CN)_4$	0.01783	0.04496	39.0
$Na_2Ni(CN)_4$	0.00044	0.00095	33.0
$K_3Fe(CN)_6$	0.00143	0.00473	50.4

These energy of activation values seem to point out that the reactions occurring are on a border where molecular diffusion control ends and chemical reaction control starts.

7) These metal decay coefficients were used to simulate the experimental data of the mixed metallo-cyanide solutions. They produced a good fit for the low mixes. The model fits the data at the 95% confidence level for five of the eight test conditions.

8) The model, calibrated using the rate coefficients from the single synthetic solutions was applied to the high mix and the actual gold mill effluents (barren solutions). For the high mixes and barren solutions the results showed that the model can be used for the basic estimate of the cyanide degradation rate. For the more precise results the recalibration of the parameters is necessary as a function of the solution's metal content.

11 RECOMMENDATIONS

The following are recommended for future modelling work:

1. Experiments with the solutions containing single metallo-cyanide complexes with the high concentration of metal, in order to determine the metal cyanide decay rate that could be used for modelling high mixes.
2. Recalibration of the metal decay rates for at least 10 to 15 different barren solutions, to determine the best values that could be used for modelling other similar solutions.
3. Examine the possibility of the formation of more than one metallo-cyanide complexes in the high mixes and barren solutions.
4. To develop a model for dynamic systems that could be applied to cyanide removal from the tailings pond that is continuously being filled.

The recommendations that could be applied to any future study concerning cyanide in gold mill effluents, are the following:

1. Detailed characterization of the individual gold mill effluents is required before treatment.
2. Investigate techniques for obtaining and preserving mine process samples containing particulates.

3. Investigate the possibility of refining existing methods and/or devising better methods for quantifying cyanide species in process effluents.
4. Study microbial degradation of cyanide in mine tailings ponds over long retention times.
5. Develop a model with which to predict the equilibrium chemical species of all interactive inorganic and organic chemicals in mill effluents.
6. Devise a method to accelerate natural degradation of cyanide and metallo-cyanide compounds in tailings impoundments.

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APPENDIX A

Cyanide Terminology

A CYANIDE TERMINOLOGY

Cyanide ion refers to the free cyanide ion CN^-.

Molecular HCN - the cyanide in form of an uncharged intact molecule in aqueous solution. Therefore the terms hydrogen cyanide, hydrocyanic acid and HCN all refer to cyanide as molecular HCN.

Free cyanide - the summation of molecular HCN and the cyanide ion ($HCN + CN^-$) in aqueous solution.

Simple cyanide refers to a cyanide compound which dissociates directly in water to a cation and the cyanide ion with no soluble intermediates.

Complex cyanide - cyanide compound which dissociates in water to a cation and a negative ligand which may be subject to further dissociation.

Weak-acid dissociable cyanides (CN_W) - all forms of cyanide excluding iron recovered by the chemical analysis.

Total cyanide (TCN) includes free cyanide, and all the simple and complex cyanides.

APPENDIX B

Determination of Cyanide by
Picric Acid and Distillation Methods

B.1 DETERMINATION OF CYANIDE BY PICRIC ACID METHOD

Principle

Cyanide ion and simple cyanides react with picric acid at a pH of 10 at elevated temperature to form a stable coloured complex. The complex obeys Beer's law from 0 to at least 500 µg of CN^- (Kolthoff et al., 1969). With a 5 cm cell, in the spectrophotometer, the detection limit is 1.3 µg.

Interferences

Thiocyanates and cyanates in concentrations up to 50 mg/L do not interfere. Sulphide ion causes the most interference, 0.1 mg of sulphide being equivalent to 0.025 mg of cyanide ion. Sulphite ion interferes at levels in the microgram range.

Precautions

Picric acid is also known as trinitrophenol, and is explosive. It is not readily detonated and is not particularly hazardous to use, but all spills should be wiped up and solutions should be disposed of by washing down a sink with copious amounts of water. Aqueous and organic solutions act as dyes and stain many materials, including the skin. Most of the stain can be removed from working surfaces and glassware by means of acetone, but the hands should be protected with rubber gloves.

Storage

Samples should be preserved by adding enough NaOH (either 50% w/w or pellets) to raise the pH to 12.

Apparatus

Regular laboratory glassware, a hotplate capable of heating samples at 90-95°C, and a spectrophotometer for measuring optical density at 490 nm.

Reagents

1. Stock cyanide solution (1 mL ≡ 1000 μg CN^-)

Dissolve 1.884 g NaCN in distilled water and dilute to 1000 mL. Adjust the pH to 12 with NaOH. Standardize as follows: Dilute 5.0 mL aliquot of stock solution in 100 mL of distilled water at pH 11 or higher, add 15 drops of rhodanine indicator solution and titrate with standard $AgNO_3$ solution to a salmon-pink end point.

2. Working cyanide solution

Prepare daily by appropriate dilution of stock solution.

3. Rhodanine indicator solution

Dissolve 1.632 g $AgNO_3$ in distilled water and dilute to 1000 mL. 1 mL ≡ 500 μg CN^-.

4. Standard silver nitrate solution

Dissolve 1.632 g $AgNO_3$ in distilled water and dilute to 1000 mL. 1 mL ≡ 500 μg CN^-.

5. Picric acid solution

- 1% aqueous.

6. 0.1M EDTA (37.22 g/L of EDTA - disodium salt)

7. EDTA - Na_2CO_3 solution

- 15 g/L EDTA (disodium salt)
- 52 g/L Na_2CO_3

Preparation of Calibration Curve

1. Into a series of 250 mL volumetric flasks, pipet appropriate amounts of cyanide working solution to cover the working range up to 500 µg CN^-.
2. Add enough distilled water to bring the volume to approximately 100 mL.
3. Include a flask containing no cyanide as a blank.
4. Continue from the beginning of step 2 under "Analysis of Samples".

Analysis of Samples

1. Pipet an appropriate aliquot of sample up to 10 mL* into a 250 mL volumetric flask. The aliquot should not contain more than 500 µg CN^-. Bulk to about 100 mL.
2. Add 2 mL of 0.1 EDTA solution, 10 mL of the EDTA - Na_2CO_3 solution and 15 mL of the 1% picric acid solution.
3. Heat on the hotplate at 90 to 95°C for 20 min.
4. Cool to room temperature with cold water; and dilute to 250 mL with distilled water.
5. Measure the absorbance in a spectrophotometer at 490 nm with a 5 cm cell.
6. Construct a calibration graph by plotting the absorbence vs µg of cyanide.

Note: *Volumes larger than 10 mL may be taken provided that the pH is adjusted to 10 with pH meter and buffer.

7. From the calibration graph, read the number of μg of cyanide in sample and blank solutions.

8. Calculate the concentration of CN^- in the sample:

$$CN^- \text{ (mg/L)} = \frac{a}{b}$$

where a = μg of CN^- in sample aliquot

b = volume of sample taken for analysis

B.2. CYANIDE DETERMINATION BY DISTILLATION METHOD

Principles

Most complex cyanides (except gold and cobalt complexes) can be coverted to molecular HCN gas by boiling with hydrochloric acid and hydroxylamine hydrochloride. The HCN gas is liberated under reduced pressure, absorbed in a solution of 1N sodium hydroxide and determined either titrimetrically or colorimetrically, depending on the amount of cyanide present. Sulphides are removed from the sample by treatment of the sample with lead carbonate. Sulphides originating from the sample as either sulphide or thiocyanate are precipitated in the absorbing solution as cadmium sulphide using cadmium chloride.

Using the titration (for samples above 5 mg/L CN^-), an aliquot of the sodium hydroxide absorbing solution is titrated with silver nitrate until an excess of silver ion is detected with a special silver ion indicator. In the colorimetric test (for samples below 5 mg/L CN^-), cyanide ion is first converted to cyanogen chloride (ClCN) using chloramine T. This in turn forms a blue complex with a sodium isonicotinate-sodium barbiturate reagent. Absorbence of this complex, measured at 600 nm, is proportional to the amount of cyanide present in the aliquot of sodium hydroxide taken for analysis.

Using the described procedure, this method has been used on samples with a minimum reportable value of 0.01 mg/L cyanide.

Storage

Samples must be preserved by adding enough sodium hydroxide (either pellets or 50% w/w) to raise the pH to 12. For samples containing high levels of soluble sulphides, one precipitates the sulphides first using lead carbonate, filter, before raising the pH to 12.

Apparatus

The distillation system (Figure B.1) consists of: (1) 3-neck one litre distilling flask, (2) Friedricks condenser (315 mm), (3) Thistle tube with ground glass joint to fit flask (the tube must extend below the level of liquid in the flask), (4) 125 mL gas absorbing bottle (impinger) with ground glass joint and fritted disc, and (5) low vacuum system. The tube joining the condenser (2) to the gas washing bottle (4) should be glass as far as possible. The air entering the thistle tube should be scrubbed with 1N NaOH to remove any airborn HCN.

Heating Mantle

Spectrophotometer capable of measuring at 600 nm

Reagents

1. Sodium hydroxide - 1N. Dissolve 40 g NaOH in distilled water and dilute to 1 L.
2. Acetic acid - Glacial.
3. Acetic acid - 1:4. Slowly add 100 mL glacial acetic acid to 400 mL distilled water.
4. Chloramine-T solution - Dissolve 1 g chloramine-T in distilled water and dilute to 100 mL. Prepare daily.
5. Isonicotinic acid - barbituric acid reagent. In 1000 mL of distilled water at 60 to 70°C dissolve 12 g of NaOH, 20 g of isonicotinic acid and 10 g of barbituric acid. After cooling, adjust the pH to 8.0 with acetic acide.

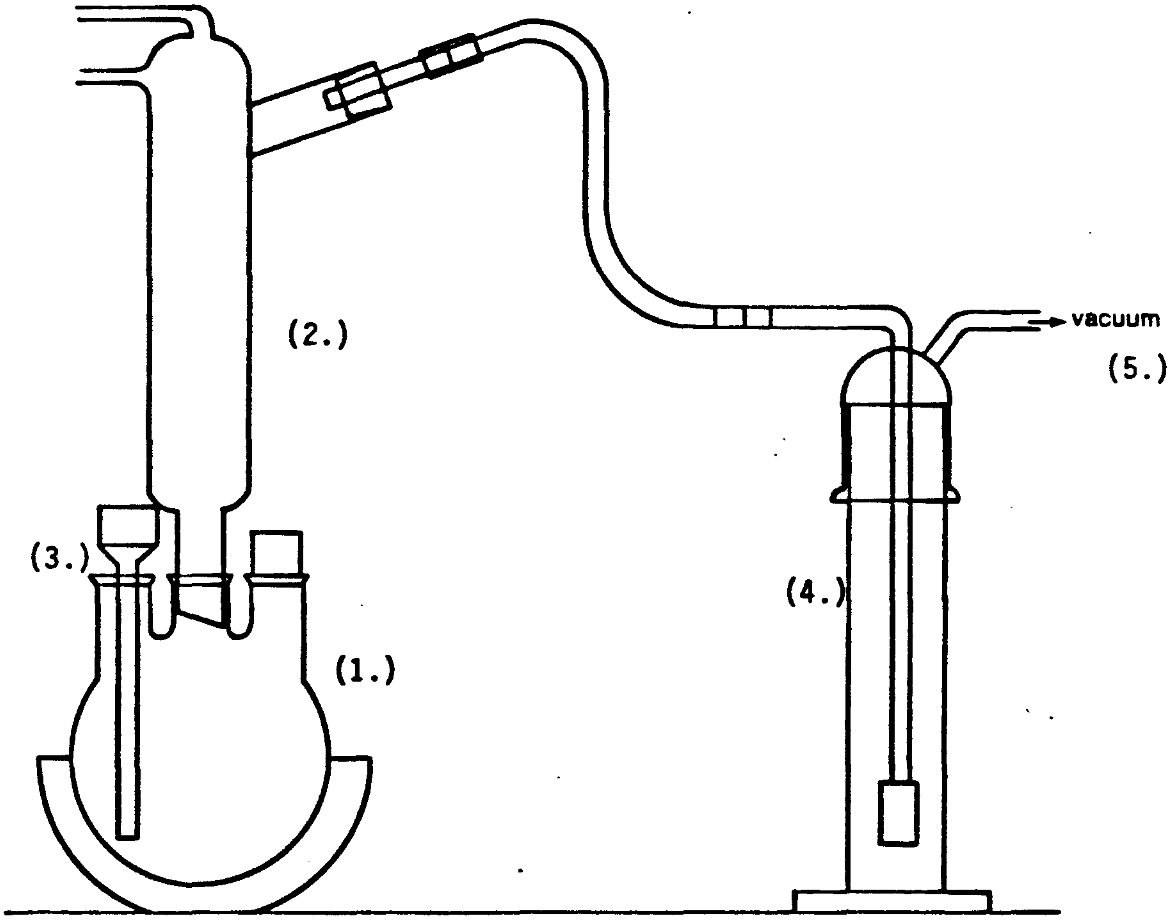


Figure B.1 The Distillation System

6. p-Nitrophenol Indicator - 0.1% W/V solution in ethanol.
7. Standard Silver Nitrate Solution. Dissolve 1.632 g $AgNO_3$ in distilled water and dilute to 1000 mL. 1 mL = 500 μg CN^-.
8. Rhodanine Indicator Solution. Dissolve 0.02 g p = dimethyl-amino-benzal-rhodanine in 100 mL acetone.
9. Stock Cyanide Solution (1 mL = 1 mg CN^-). Dissolve 1.884 g NaCN in distilled water and dilute to 1000 mL. Adjust pH to at least 12. Standardize every day as follows: Dilute 1.0 mL aliquot of stock solution in 100 mL of distilled water at pH 11 or higher, add 0.5 mL of rhodanine indicator solution and titrate with standard $AgNO_3$ solution, to a salmon pink end point.
10. Working Cyanide Solution (1 mL = 1 μg CN^-). Prepare daily. Dilute 1 mL of stock and 10 mL of 1N NaOH to 1000 mL with distilled water.
11. Hydrochloric Acid - hydroxylamine hydrochloride reagent 50% (V/V) - 10% (W/V) - Dissolve 100 g $NH_2OH \cdot HCl$ in 300 mL of distilled water. Add 500 mL of hydrochloric acid and dilute to 1000 mL.
12. Cadmium Chloride. Powder.

Procedure

1. Place 400 mL of distilled water into the 1L boiling flask. Insert the thistle tube and rinse the diffuser with distilled water.

2. Add 100 mL 1N NaOH, 0.2 to 0.3 g cadmium chloride powder to the gas absorbing bottle (Note 2). Turn on the vacuum, and insert the diffuser into the gas absorbing bottle.
3. Close the system by making the connection between the condenser and the gas absorbing bottle. Into the boiling flask through the thistle tube add 25 mL of HCl - HH, rinse with distilled water, add 100 mL of sample (see Note 1).
4. Turn on the heat and cold water and allow the mixture to boil for 45 min.
5. After boiling, turn off the heat and allow the vacuum to operate for 15 to 20 min.
6. Disconnect the condenser from the gas absorbing bottle, turn off pump and water, disconnect and reconnect the vacuum a couple of times to transfer any cyanide from inside the air diffuser out to the solution in the bottle.
7. Remove the diffuser from the absorbing solution while the vacuum is operating. Also rinse the diffuser with 25% HCl and turn off the vacuum. Filter the absorbing solution through acid washed #40 Whatman paper (see Note 3) into a polyethylene bottle.
8. Clean the entire system thoroughly between samples using 25% hydrochloric acid (V/V). Rinse the boiling flask with distilled water.

Notes

1. For samples containing high levels of sulphide, ensure that they have been treated for sulphide removal as soon as possible after sampling. Add sufficient lead carbonate to remove all sulphide, filter and raise the pH to 12.
2. Cadmium chloride is added to the gas absorbing bottles when samples are known or suspected to contain sulphide, thiocyanate, or thiosulphate.
3. Before filtering the absorbing solution through #40 Whatman paper, rinse the paper once with 25% HCl and twice with distilled water.

A. Titrimetric Method - to be used on samples containing 5.0 mg/L cyanide or greater.

1. Treat sample by distillation procedure.
2. Pipet an aliquot (up to 50 mL) of the 1N Sodium hydroxide absorbing solution into a 300 mL Erlenmeyer flask. Dilute to about 100 mL. Ensure that the pH is at least 11. Add 0.5 mL of rhodanine indicator.
3. Titrate with silver nitrate working solution to a salmon pink end point.
4. Calculations

$$\text{mg/L Cyanide as } CN^- = \frac{(A-B)500}{C} \times \frac{100}{D}$$

where:

A = mL of silver nitrate required to titrate sample aliquot

B = mL of silver nitrate required to titrate blank

C = mL of sodium hydroxide absorbing solution taken for titration

D = mL of distilled sample

B. <u>Colorimetric Method</u> - to be used when cyanide concentration is below 5.0 mg/L CN.

1. Treat sample by distillation procedure.
2. Pipet either 1 mL or 10 mL of absorbing solution (depending on cyanide concentration being measured) into a 25 mL volumetric flask. For samples in the range 0 to 1.0 mg/L CN^-, use 10 mL.
3. Adjust the volume to about 15 mL with distilled water, add 2 drops of p-nitrophenol indicator and neutralize to a colorless end point using 1:4 acetic acid.
4. Repeat for a blank and standards (1 mL or 10 mL 1N NaOH), depending on the level of cyanide being measured.
5. To each flask, add 1.0 mL of chloramine T solution (1%) and mix. Allow to stand for 2 to 5 min.
6. Add 5.0 mL of the sodium isonicotinate - sodium barbiturate reagent, dilute to volume and mix.
7. After 30 min read the absorbence at 600 nm (1 cm cells) using the prepared blank as a reference. If working in the 0 to 1.0 mg/L range, use the 10 mL blank; if working in the 0 to 10 mg/L range use the 1 mL blank.

8. Construct a graph of recorded absorbences for standards and corresponding μg of cyanide present. One graph each for 0 to 1.0 mg/L range and one graph for 0 to 10 mg/L range.

9. Calculation:

$$\text{mg/L Cyanide as } CN^- = \frac{A \times B}{C \times D}$$

where:

A = μg of cyanide ion from graph

B = volume of absorbing solution (usually 100 mL)

C = original aliquot of sample taken for distillation (usually 100 mL)

D = volume of absorbing solution taken for colorimetric analyses (1 or 10 mL).

APPENDIX C

Experimental Results

TABLE C.1. EXPERIMENTAL RESULTS FOR SODIUM CYANIDE AT 4°C

	4°C AIR UV			4°C NO AIR UV			4°C AIR NO UV			4°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
NaCN	0	203.0	0.0	0	200.0	0.0	0	202.0	0.0	0	225.0	0.0
	7	176.4	13.1	7	119.0	40.5	19	148.0	26.6	17	158.9	29.4
	24	129.9	36.0	24	111.6	44.2	24	140.7	30.4	24	105.7	53.0
	48	104.8	48.4	31	88.8	55.6	41	108.2	46.4	41	98.2	56.3
	54	76.9	62.1	48	73.3	63.4	48	82.1	59.3	48	91.9	59.1
	72	38.4	81.0	72	48.3	75.9	65	(90.0)	55.4	65	(88.3)	60.7
	79	29.2	85.6	144	17.2	91.4	72	53.0	73.8	72	65.8	70.7
	144	10.6	94.8	168	13.3	93.4	113	(58.3)	71.1	137	63.6	71.7
	151	(10.6)*	94.8	175	11.3	94.4	144	41.4	79.5	144	62.5	72.2
	168	6.9	96.6	192	10.9	94.5	151	44.1	78.2	161	60.2	73.2
	175	5.0	97.5	199	(11.9)	94.0	168	37.1	81.6	168	58.5	74.0
	192	3.3	98.4	216	5.3	97.3	175	36.3	82.0	185	56.1	75.1
	216	1.2	99.4	223	4.6	97.7	192	36.1	82.1	192	(45.4)	79.8
	240	0.5	99.7	240	4.0	98.0	199	(37.6)	81.4	209	46.8	79.2
	312	(0.5)	99.7	288	2.9	98.5	216	33.1	83.6	216	(39.1)	82.6
				312	2.6	98.7	223	24.5	87.9	233	39.3	82.5
				319	2.4	98.8	241	23.2	88.5	256	38.3	83.0
							247	21.8	89.2	280	36.3	83.9
							312	20.4	89.9	296	35.1	84.4
										317	28.6	87.3

$k_v(h^{-1})$	0.0159 (0.665 cm/h)	0.0193 (0.808 cm/h)	0.0176 (0.728 cm/h)	0.0164 (0.686 cm/h)
$k\ (h^{-1})$	0.0234 (0.979 cm/h)	0.0139 (0.588 cm/h)	0.0074 (0.318 cm/h)	0.0050 (0.209 cm/h)
t 1/2 (h)	30	50	94	139

* Values in parenthesis were not used for modelling purposes.
\- The cut-off point.

TABLE C.2. EXPERIMENTAL RESULTS FOR SODIUM CYANIDE AT 20°C

	20°C AIR UV			20°C NO AIR UV			20°C AIR NO UV			20°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
NaCN	0	189.0	0.0	0	190.0	0.0	0	200.0	0.0	0	196.0	0.0
	18	61.0	67.7	18	140.0	26.3	6	113.7	43.1	6	140.3	28.4
	25	33.0	82.5	25	(168.0)*	11.6	23	56.9	71.5	23	110.0	43.9
	42	17.0	91.0	42	120.0	36.8	29	29.8	85.1	29	74.7	61.9
	49	11.0	94.2	114	20.0	89.5	47	11.2	94.4	47	54.7	72.1
	114	6.8	96.4	121	17.4	90.8	53	1.4	99.3	53	23.5	88.0
	121	1.2	99.4	138	14.9	92.2	119	1.2	99.4	119	9.8	95.0
	138	0.6	99.7	145	4.8	97.5	126	1.0	99.5	126	9.1	95.4
	145	0.15	99.9	162	2.8	98.5	143	0.6	99.7	143	5.4	97.2
				169	2.4	98.7	167	0.1	99.9	150	4.9	97.5
				186	2.0	98.9				174	3.7	98.1
				193	1.8	99.0				197	2.3	98.2
				210	1.2	99.4				285	1.1	99.4
				216	0.7	99.6						
				306	0.28	99.9						
$k_v(h^{-1})$	0.0569 (2.382 cm/h)			0.0205 (0.858 cm/h)			0.0597 (2.499 cm/h)			0.0263 (1.101 cm/h)		
$k\ (h^{-1})$	0.0389 (1.628 cm/h)			0.0253 (1.059 cm/h)			0.0394 (1.649 cm/h)			0.0238 (1.003 cm/h)		
t 1/2 (h)	18			27			18			29		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.3. EXPERIMENTAL RESULTS FOR COPPER-CYANIDE COMPLEX AT 4°C

Synthetic Cyanide Solution	4°C AIR UV			4°C NO AIR UV			4°C AIR NO UV			4°C NO AIR NO UV		
	t(h)	CN (mg/L) T	% Removed	t(h)	CN (mg/L) T	% Removed	t(h)	CN (mg/L) T	% Removed	t(h)	CN (mg/L) T	% Removed
$Na_2Cu(CN)_3$	0	195.0	0.0	0	204.0	0.0	0	203.0	0.0	0	197.3	0.0
	7	185.6	4.8	7	137.0	32.8	19	(62.4)	69.3	17	149.2	24.4
	24	172.4	11.6	24	121.9	40.2	24	148.5	26.8	24	136.9	30.6
	48	103.4	46.9	31	99.1	51.4	41	135.3	33.3	41	136.0	31.1
	54	87.5	55.1	48	80.9	60.3	48	126.7	37.8	48	114.6	41.9
	72	68.9	64.7	72	78.2	61.6	65	100.6	50.4	65	112.5	43.0
	79	67.6	65.3	144	58.6	71.2	72	71.5	64.8	72	111.3	43.6
	144	36.9	81.1	168	30.2	85.2	113	55.6	72.6	137	93.1	52.8
	151	37.1	81.0	175	35.8	82.4	144	66.2	67.4	161	90.9	53.9
	168	31.0	84.1	192	41.1	79.8	151	59.6	70.6	168	84.7	57.1
	175	29.7	84.8	199	37.8	81.5	168	49.2	75.8	185	85.9	56.5
	192	(26.5)	86.4	216	33.8	83.4	175	51.8	74.5	192	74.0	62.5
	216	27.6	85.9	223	34.4	83.1	192	77.8	61.7	209	70.7	64.2
	240	23.7	87.8	240	34.4	83.1	199	37.6	81.5	216	68.9	65.1
	312	19.7	89.9	247	31.8	84.4	216	44.3	78.2	233	70.1	64.5
				288	23.9	88.3	223	35.4	82.6	256	60.3	69.4
				312	22.8	86.3	241	36.8	81.9	280	58.9	70.1
				319	28.5	86.0	247	34.7	82.9	296	51.5	73.9
							312	34.3	83.1	317	50.2	74.5
k_v (h^{-1})	0.0148	(0.62 cm/h)		0.0174	(0.73 cm/h)		0.0126	(0.53 cm/h)		0.0073	(0.30 cm/h)	
k_1 (h^{-1})	0.0036			0.0031			0.0037			0.0033		
t 1/2 (h)	192			220			187			210		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

Table C.4. EXPERIMENTAL RESULTS FOR COPPER-CYANIDE COMPLEX AT 20°C

	20°C AIR UV			20°C NO AIR UV			20°C AIR NO UV			20°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
$Na_2Cu(CN)_3$	0	202.0	0.0	0	197.0	0.0	0	198.0	0.0	0	207.0	0.0
	11	106.5	47.3	18	172.0	12.7	18	94.3	52.4	18	192.5	7.0
	14	73.0	63.9	25	156.0	20.8	24	39.8	79.9	24	144.4	30.2
	18	46.4	77.0	42	115.0	41.6	42	32.3	83.7	42	124.4	39.9
	25	45.0	77.7	49	85.9	56.4	48	29.0	85.3	48	99.6	51.9
	42	38.0	81.2	114	47.3	76.0	114	12.1	93.9	114	42.7	79.4
	114	24.0	88.1	121	32.4	83.5	121	9.7	95.1	121	36.6	82.3
	121	15.5	92.3	138	(23.7)	88.1	138	9.1	95.4	138	28.8	86.1
	145	14.7	92.7	145	24.2	87.7	169	7.3	95.4	169	28.1	86.4
	162	13.7	93.2	162	24.2	87.7	186	7.0	96.3			
	193	9.3	95.4	169	(27.8)	85.9	192	4.7	96.5			
	210	9.1	95.5	186	22.7	88.5	210	2.3	97.6			
	217	8.5	95.8	192	23.6	88.0	265	0.7	98.8			
	282	2.4	98.8	210	22.4	88.6	282	0.3	99.7			
	316	0.7	99.6	216	21.3	89.2			99.8			
				282	20.0	89.9						
				289	19.0	90.4						
				306	15.1	92.3						
k_v (h^{-1})	0.0392 (1.64 cm/h)			0.0146 (0.61 cm/h)			0.0402 (1.68 (cm/h)			0.0150 (0.63 cm/h)		
k_l (h^{-1})	0.0153			0.0024			0.0207			0.0071		
t 1/2 (h)	45			289			34			98		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.5. EXPERIMENTAL RESULTS FOR ZINC-CYANIDE COMPLEX AT 4°C

Synthetic Cyanide Solution	4°C AIR UV			4°C NO AIR UV			4°C AIR NO UV			4°C NO AIR NO UV		
	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
$Na_2Zn(CN)_4$	0	197.0	0.0	0	190.0	0.0	0	195.0	0.0	0	164.2	0.0
	7	188.3	4.4	7	148.0	22.1	19	140.7	27.8	17	158.9	3.2
	24	171.1	13.1	24	131.2	30.9	24	(108.2)	44.5	24	141.6	13.8
	48	79.6	59.6	31	87.5	53.9	41	121.8	37.5	41	129.6	21.1
	54	54.4	72.4	48	71.7	62.3	48	103.3	47.0	48	125.6	23.5
	72	49.1	75.1	72	59.9	68.4	65	79.4	59.3	65	124.6	24.1
	79	37.1	81.1	144	(27.6)	85.5	72	58.3	70.1	72	100.0	39.1
	144	9.0	95.4	168	27.8	85.3	113	(47.7)	75.5	137	84.1	48.8
	151	8.5	95.7	175	20.0	89.5	144	58.3	70.1	144	(68.2)	58.5
	168	8.2	95.8	192	16.9	91.1	151	57.0	70.8	161	72.7	55.7
	175	5.6	97.2	199	15.9	91.6	168	(24.6)	87.4	168	71.6	56.4
	192	3.9	98.0	216	(16.4)	91.4	175	31.1	84.0	185	69.2	57.9
	216	3.8	98.0	223	13.9	92.7	192	29.3	85.0	192	69.2	57.9
	240	2.9	98.5	240	11.9	93.7	199	27.0	86.1	209	66.3	59.6
	312	2.6	98.7	247	7.3	96.2	216	23.2	88.1	216	50.5	69.2
				288	7.3	96.2	223	22.5	88.5	233	50.1	69.5
				312	7.3	96.2	241	20.4	89.5	256	44.9	72.7
				319	6.4	96.6	247	18.4	90.6	280	43.5	73.5
							312	12.6	93.5	296	42.1	74.4
										317	33.8	79.4
k_v (h^{-1})	0.01873 (0.78 cm/h)			0.01622 (0.68 cm/h)			0.01517 (0.63 cm/h)			0.00602 (0.25 cm/h)		
k_l (h^{-1})	0.01366			0.0095			0.00682			0.00446		
t 1/2 (h)	51			73			102			155		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.6. EXPERIMENTAL RESULTS FOR ZINC-CYANIDE COMPLEX AT 20°C

	20°C AIR UV			20°C NO AIR UV			20°C AIR NO UV			20°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
$Na_2Zn(CN)_4$	0	196.0	0.0	0	200.0	0.0	0	185.6	0.0	0	168.4	0.0
	18	68.3	65.1	18	168.0	16.0	2	139.2	25.0	2	(159.1)	5.5
	25	41.0	79.1	25	126.0	37.0	5	117.2	36.8	5	160.4	4.7
	42	25.0	87.2	42	98.0	51.0	7	106.1	42.8	7	145.9	13.4
	49	15.7	92.0	49	62.3	68.8	24	38.4	79.3	24	115.6	31.3
	114	9.7	95.0	114	16.2	91.9	27	34.1	81.6	27	107.4	36.2
	121	2.4	98.8	121	15.7	92.1	30.5	29.9	83.8	30.5	(118.0)	29.9
	138	1.2	99.4	138	14.3	92.8	48	(5.3)	97.1	48	79.6	52.8
	145	0.6	99.7	145	3.6	98.2	51	7.4	96.0	51	70.3	58.3
	162	0.2	99.9	162	2.9	98.5	54.7	5.8	96.9	54.7	47.7	71.6
	186	0.1	99.9	169	2.1	98.9	72	.8	99.6	72	45.3	73.1
				186	2.0	99.0	75	.7	99.6	75	43.8	74.0
				192	1.8	99.1	102.5	.6	99.7	78.5	32.9	80.5
				210	1.2	99.4				96	31.6	81.3
				216	1.4	99.3				102.5	26.5	84.2
				281	0.6	99.7				168	10.3	93.9
				289	0.1	99.9				174.5	8.2	95.1
										192	5.0	97.0
										198.5	3.3	98.0
										216	2.1	98.7
										240	1.3	99.2

k_v (h^{-1})	0.0494 (2.07 cm/h)	0.02101 (0.88 cm/h)	0.0607 (2.54 cm/h)	0.01884 (0.79 cm/h)
k_1 (h^{-1})	0.0448	0.01815	0.0062	0.01944
t 1/2 (h)	15	38	111	36

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.7. EXPERIMENTAL RESULTS FOR NICKEL-CYANIDE COMPLEX AT 4°C

Synthetic Cyanide Solution	4°C AIR UV t(h)	CN_T(mg/L)	% Removed	4°C NO AIR UV t(h)	CN_T(mg/L)	% Removed	4°C AIR NO UV t(h)	CN_T(mg/L)	% Removed	4°C NO AIR NO UV t(h)	CN_T(mg/L)	% Removed
$Na_2Ni(CN)_4$	0	200.0	0.0	0	176.0	0.0	0	207.0	0.0	0	169.5	0.0
	7	198.3	1.0	7	125.9	28.5	19	(196.2)	5.2	17	153.6	9.4
	24	169.7	15.1	24	112.7	36.0	24	121.8	41.2	24	140.2	17.3
	48	107.4	46.3	31	66.3	62.3	41	112.0	45.9	41	98.2	42.1
	54	104.8	47.6	48	59.4	66.2	48	100.6	51.4	48	95.7	43.5
	72	(67.6)	66.2	72	50.4	71.4	65	87.9	57.5	65	90.3	46.7
	79	68.9	65.5	144	39.5	77.5	72	82.2	60.3	72	88.6	47.7
	144	39.2	80.4	168	37.1	78.9	113	62.2	69.9	137	84.1	50.4
	151	40.0	80.0	175	37.0	78.9	144	62.1	70.0	144	(73.8)	56.5
	168	41.6	79.2	192	36.7	79.1	151	(58.3)	71.8	161	78.1	53.9
	175	36.6	81.7	199	33.1	81.2	168	57.0	72.5	168	(66.8)	60.6
	192	34.5	82.8	216	31.8	81.9	175	59.6	71.2	185	71.6	57.8
	216	(36.8)	81.6	223	28.5	83.8	192	59.2	71.4	192	69.2	59.2
	240	28.9	85.5	240	24.5	86.0	199	57.8	72.1	209	(60.9)	64.1
	312	26.3	86.9				216	55.9	73.0	216	64.5	61.9
							223	55.2	73.3	233	(64.5)	61.9
							241	53.1	74.3	256	61.7	63.6
							247	49.0	76.3	280	56.1	66.9
							312	40.4	80.5	296	54.7	67.7
										317	50.0	70.5
k_v (h^{-1})	0.01400 (0.59 cm/h)			0.01633 (0.68 cm/h)			0.01000 (0.42 cm/h)			0.01014 (0.42 cm/h)		
k_l (h^{-1})	0.00416			0.00406			0.002978			0.00269		
t 1/2 (h)	167			171			233			258		

* Values in parenthesis were not used for modelling purposes.

- The cut-off point.

TABLE C.8. EXPERIMENTAL RESULTS FOR NICKEL-CYANIDE COMPLEX AT 20°C

	20°C AIR UV			20°C NO AIR UV			20°C AIR NO UV			20°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
$Na_2Ni(CN)_4$	0	199.0	0.0	0	198.0	0.0	0	229.4	0.0	0	198.9	0.0
	18	65.9	66.9	18	158.0	20.2	2	212.2	7.5	2	159.1	20.0
	25	55.0	72.4	25	140.0	29.3	5	202.9	11.5	5	144.5	27.3
	42	42.0	78.9	42	106.0	46.5	7	197.6	13.9	7	132.6	33.3
	49	30.9	84.5	49	83.4	57.9	24	(196.2)	14.5	24	41.1	79.3
	114	29.7	85.1	114	69.8	64.7	27	151.2	34.1	27	35.8	82.0
	121	(28.5)	85.7	121	(49.8)	74.8	30.5	143.2	37.6	30	31.6	84.1
	138	28.6	85.6	138	49.8)	74.8	48	116.7	49.1	48	30.0	84.9
	145	28.4	85.7	145	39.0	80.3	51	110.6	51.8	51	29.4	85.2
	162	28.0	85.9	162	37.5	81.1	55	104.2	54.6	54	29.2	85.3
	210	26.6	86.6	169	37.0)	81.3	75	85.4	62.8	72	28.2	85.8
	289	25.6	87.1	186	(37.0)	81.3	78.5	84.9	63.0	75	27.9	85.9
				192	37.2	81.2	102.5	72.4	68.4	78	(27.9)	85.9
				210	36.8	81.4	168	43.0	81.3	96	27.8	86.0
				216	36.0	81.8	174.5	40.1	82.5	102	27.3	86.3
				282	35.0	82.3	192	39.3	82.9	168	27.2	86.3
				289	34.2	82.7	198.5	39.2	82.9	174	27.0	86.4
				306	32.1	83.8	222.7	35.0	84.7	192	26.0	86.9
							240	(35.0)	84.7	198	25.7	87.1
							252	33.9	85.2	216	24.9	87.5
k_v (h^{-1})	0.03480 (1.46 cm/h)			0.01713 (0.72 cm/h)			0.01264 (0.53 cm/h)			0.06212 (2.6 cm/h)		
k_1 (h^{-1})	0.00082			0.001487			0.00268			0.000814		
t 1/2 (h)	845			466			259			851		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.9. EXPERIMENTAL RESULTS FOR IRON-CYANIDE COMPLEX AT 4°C

	4°C AIR UV			4°C NO AIR UV			4°C AIR NO UV			4°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
$K_3Fe(CN)_6$	0	193.0	0.0	0	183.0	0.0	0	187.0	0.0	0	140.0	0.0
	19	160.0	17.1	17	150.0	18.0	24	138.0	26.2	10	108.0	22.9
	24	155.0	19.7	24	149.0	18.6	48	66.0	64.7	24	62.0	55.7
	41	143.0	25.9	41	145.0	21.0	72	57.3	69.4	40	54.0	61.4
	48	133.0	31.1	48	144.0	21.3	96	46.0	75.4	48	50.0	64.3
	65	120.0	37.8	72	125.0	31.7	168	34.8	81.4	60	42.0	70.0
	72	116.0	39.9	137	85.2	53.4	192	33.3	82.2	72	34.0	75.7
	113	76.6	60.3	144	80.6	55.9	216	33.0	82.3	96	33.0	76.4
	144	63.3	67.2	161	72.9	60.2	240	32.8	82.5	168	32.0	77.1
	151	62.6	67.6	168	72.6	60.3	264	30.4	83.7	192	29.7	78.8
	168	55.0	71.5	185	66.2	63.8				216	31.0	77.9
	175	54.0	72.0	192	65.3	64.3				240	30.0	78.6
	192	48.6	74.8	209	(58.9)	67.8				264	29.0	79.3
	199	46.5	75.9	216	61.1	66.6						
	216	43.9	77.2	233	56.6	69.1						
	223	42.1	78.2	256	51.5	71.8						
	241	38.4	80.1	280	48.0	73.8						
	247	37.1	80.8	296	43.2	76.4						
	312	27.8	85.6	317	39.7	78.3						
k_v (h^{-1})	0.00682 (0.28 cm/h)			0.00915 (0.38 cm/h)			0.01535 (0.64 cm/h)			0.01527 (0.64 cm/h)		
k_1 (h^{-1})	0.00510			0.00399			0.001189			0.00074		
t 1/2 (h)	136			174			583			937		

* Values in parenthesis were not used for modelling purposes.
\- The cut-off point.

TABLE C.10. EXPERIMENTAL RESULTS FOR IRON-CYANIDE COMPLEX AT 20°C

Synthetic Cyanide Solution	20°C AIR UV			20°C NO AIR UV			20°C AIR NO UV			20°C NO AIR NO UV		
	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
$K_3Fe(CN)_6$	0	183.0	0.0	0	183.0	0.0	0	201.0	0.0	0	196.0	0.0
	18	49.8	72.8	18	130.0	29.0	7	190.0	5.5	7	184.0	6.1
	25	37.9	79.3	25	94.1	48.6	24	165.0	17.9	24	150.0	23.5
	42	24.8	86.4	42	69.2	62.2	48	134.0	33.3	31	130.0	33.7
	49	24.7	86.5	49	62.4	65.9	54	132.0	34.3	48	97.0	50.5
	114	(18.3)	90.0	114	26.2	85.7	72	85.8	57.3	72	80.9	58.7
	121	18.8	89.7	121	24.5	86.6	79	84.8	57.8	144	53.4	72.8
	138	16.4	91.0	138	21.0	88.5	144	45.8	77.2	168	48.5	75.3
	145	16.7	90.9	145	18.7	89.8	151	44.5	77.9	192	45.0	77.0
	162	15.0	91.8	162	14.7	92.0	168	44.1	78.1	199	42.8	78.2
	169	14.4	92.1	169	13.0	92.9	175	(41.1)	79.5	216	38.9	80.1
	186	12.5	93.2	186	10.2	94.4	192	42.2	79.0	223	(40.3)	79.4
	193	11.6	93.7	192	8.7	95.2	216	36.5	81.8	240	38.7	80.3
	210	11.1	93.9	210	6.5	96.4	240	(36.5)	81.8	247	38.1	80.6
	217	10.3	94.4	216	6.0	96.7	312	35.5	82.3	288	35.4	81.9
	282	6.6	96.4	282	0.9	99.5				312	33.8	82.8
	289	6.1	96.7	289	0.7	99.6						
	306	5.5	97.0	306	0.4	99.8						
k_v (h^{-1})	0.03976(1.66 cm/h)			0.02263 (0.95 cm/h)			0.01042 (0.44 cm/h)			0.01306 (0.55 cm/h)		
k_1 (h^{-1})	0.00679			0.0222			0.00163			0.00264		
t 1/2 (h)	102			31			425			262		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.11. EXPERIMENTAL RESULTS FOR LOW MIX AT 4°C

	4°C AIR UV			4°C NO AIR UV			4°C AIR NO UV			4°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
Low Mix	0	198.0	0.0	0	185.0	0.0	0	194.0	0.0	0	214.0	0.0
	7	197.3	0.3	7	133.5	27.8	17	145.0	25.2	19	211.0	1.4
	24	175.0	11.6	24	35.0	81.1	24	143.0	26.3	24	207.0	3.3
	31	173.0	12.6	31	27.3	85.2	41	140.0	27.8	41	195.0	8.9
	48	120.5	39.1	48	12.8	93.1	48	130.0	33.0	48	193.0	9.8
	72	63.0	68.2	72	9.2	95.0	65	124.0	36.1	65	(189.0)	11.7
	120	35.0	82.3	120	(8.1)	95.6	72	121.0	37.6	72	172.0	19.6
	144	34.8	82.4	144	8.3	95.5	137	83.8	56.8	113	148.0	30.8
	168	(35.1)	82.3	168	6.3	96.6	144	78.1	59.7	144	152.0	29.0
	175	34.3	82.7	175	6.2	96.6	161	74.8	61.4	151	144.0	32.7
	192	31.0	84.3	192	5.2	97.2	168	72.0	62.9	168	127.0	40.6
	199	31.3	84.2	199	5.0	97.3	185	68.6	64.6	175	118.0	44.9
	216	26.6	86.6	216	4.9	97.3	192	66.8	65.6	192	92.2	56.9
	240	11.1	94.4	240	4.5	97.6	209	65.6	66.2	199	93.3	56.4
	247	10.7	94.6	264	3.9	97.9	216	58.5	69.8	216	84.6	60.5
	288	10.5	94.7				233	59.4	69.4	223	83.7	60.9
							256	48.7	74.9	241	73.2	65.8
							280	46.7	75.9	247	72.6	66.1
							296	41.9	78.4	312	55.1	74.2
							317	38.0	80.4			
k_v (h^{-1})	0.00974 (0.41 cm/h)			0.06566 (2.75 cm/h)			0.00603 (0.25 cm/h)			0.00292 (0.12 cm/h)		
k_l (h^{-1})	0.00868			0.00523			0.00460			0.00464		
t 1/2 (h)	80			132			151			149		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.12. EXPERIMENTAL RESULTS FOR LOW MIX AT 20°C

	20°C AIR UV			20°C NO AIR UV			20°C AIR NO UV			20°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
Low Mix	0	188.0	0.0	0	199.0	0.0	0	200.0	0.0	0	198.0	0.0
	18	55.3	70.6	18	147.0	26.1	7	197.0	1.5	7	187.0	5.6
	25	39.3	79.1	25	129.0	35.2	24	147.0	26.5	24	181.0	8.6
	42	18.9	89.0	42	74.1	62.8	48	108.0	46.0	31	122.0	38.4
	49	15.5	91.8	49	67.5	66.1	54	93.2	53.4	48	79.4	59.9
	114	8.7	95.4	114	19.5	90.2	72	66.8	66.6	72	58.3	70.6
	121	7.6	95.9	121	17.5	91.2	79	62.1	68.9	144	28.2	85.8
	138	6.4	96.6	138	14.1	92.9	144	23.4	88.3	168	23.0	88.4
	145	6.2	96.7	145	13.2	93.4	151	(23.8)	88.1	192	19.0	90.4
	162	(5.1)	97.3	162	11.3	94.3	168	19.4	90.3	199	18.2	90.8
	169	5.5	97.1	169	10.6	94.7	175	17.4	91.3	216	16.3	91.8
	184	4.6	97.5	186	9.5	95.2	192	17.3	91.3	223	15.7	92.1
	193	(3.9)	97.9	192	8.7	95.6	216	14.7	92.6	240	15.1	92.4
	210	4.5	97.6	210	(9.5)	95.2	240	12.8	93.6	247	14.4	92.7
	217	4.3	97.7	216	7.5	96.2	312	10.4	94.8	288	11.8	94.0
	282	2.3	98.8	282	6.2	96.9				312	10.5	94.7
	289	2.3	98.8	289	6.1	96.9						
	306	1.8	99.0	306	5.6	97.2						
k_v (h^{-1})	0.05039 (2.11 cm/h)			0.02336 (0.98 cm/h)			0.01532 (0.64 cm/h)			0.01788 (0.75 cm/h)		
k_l (h^{-1})	0.00749			0.00599			0.00468			0.00562		
t 1/2 (h)	92			116			148			123		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.13. EXPERIMENTAL RESULTS FOR HIGH MIX at 4°C

	4°C AIR UV			4°C NO AIR UV			4°C AIR NO UV			4°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed
High Mix	0	180.0	0.0	0	192.0	0.0	0	198.0	0.0	0	198.0	0.0
	7	175.0	2.8	17	163.0	15.1	19	185.0	6.6	18	181.0	8.6
	24	156.0	13.3	24	(153.0)	20.3	24	175.0	11.6	25	175.0	11.6
	31	148.0	17.8	41	165.0	14.1	41	(158.0)	20.2	42	164.0	17.2
	48	135.0	25.0	48	152.0	20.8	48	160.0	19.2	49	155.0	21.7
	72	115.0	36.1	65	147.0	23.4	65	150.0	24.2	114	138.0	30.3
	144	93.0	48.3	72	140.0)	27.1	72	(150.0)	24.2	121	139.0	29.8
	168	84.7	52.9	137	125.0	34.9	113	127.0	35.9	138	132.0	33.3
	192	81.8	54.6	144	123.0	35.9	144	(120.0)	39.4	145	133.0	32.8
	199	76.8	57.3	161	119.0	38.0	151	125.0	36.9	162	(134.0)	32.3
	216	74.5	58.6	168	117.0	39.1	168	117.0	40.9	169	126.0	36.4
	223	(76.3)	57.6	185	112.0	41.7	175	99.9	49.5	186	(126.0)	36.4
	240	(77.7)	56.8	192	(115.0)	40.1	192	98.0	50.5	192	120.0	39.4
	247	74.3	58.7	209	109.0	43.2	199	96.7	51.2	210	(120.0)	39.4
	288	71.4	60.3	216	92.7	51.7	216	(94.0)	52.5	216	93.0	53.0
	312	68.7	61.8	233	91.0	52.6	223	95.4	51.8	282	82.2	58.5
				256	89.9	53.2	241	92.4	53.3	289	81.1	59.0
				280	88.8	53.7	247	89.4	54.8	306	80.9	59.1
				296	83.6	56.5	312	83.8	57.7			
				317	83.1	56.7						
k_v (h^{-1})	0.00628 (0.26 cm/h)			0.00246 (0.10 cm/h)			0.00391 (0.16 cm/h)			0.00231 (0.09 cm/h)		
k_l (h^{-1})	0.00159			0.00112			0.00223			0.00167		
t 1/2 (h)	435			619			311			415		

* Values in parenthesis were not used for modelling purposes.

\- The cut-off point.

TABLE C.14. EXPERIMENTAL RESULTS FOR HIGH MIX AT 20°C

	20°C AIR UV			20°C NO AIR UV			20°C AIR NO UV			20°C NO AIR NO UV		
Synthetic Cyanide Solution	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN_T(mg/L)	% Removed	t(h)	CN (mg/L)	% Removed
High Mix	0	193.0	0.0	0	191.0	0.0	0	199.0	0.0	0	196.0	0.0
	18	92.4	52.1	18	153.0	19.9	19	92.9	53.3	19	162.0	17.3
	25	87.0	54.9	25	146.0	23.6	26	81.0	59.3	26	150.0	23.5
	42	70.3	63.6	42	99.5	47.9	43	(67.7)	66.0	43	99.0	49.5
	49	66.0	65.8	49	97.2	49.1	50	68.8	65.4	50	95.6	51.2
	114	(54.5)	71.8	114	70.1	63.3	67	63.3	68.2	67	87.4	55.4
	121	56.0	70.9	121	70.6	63.0	74	(58.4)	70.6	74	(76.9)	60.8
	138	53.5	72.3	138	66.7	65.1	91	59.3	70.2	91	77.9	60.3
	145	53.9	72.1	145	63.2	66.9	98	54.4	72.7	98	75.1	61.7
	162	(46.9)	75.7	162	(63.9)	66.5	163	48.8	75.5	163	65.7	66.5
	169	50.9	73.6	169	63.0	67.0	170	48.1	75.8	170	64.1	67.3
	186	48.8	74.7	186	59.0	69.1	187	45.5	77.1	187	(62.1)	68.3
	193	(43.6)	77.4	192	58.2	69.5	194	45.6	77.1	194	62.1	68.3
	210	45.2	76.6	210	56.9	70.2	211	43.4	78.2	211	59.5	69.6
	217	43.6	77.4	216	55.4	71.0	218	42.2	78.8	218	58.7	70.0
	282	36.9	80.9	282	(52.0)	72.8	235	40.3	79.7	235	(59.5)	69.6
	289	35.2	81.8	289	53.0	72.2	242	38.7	80.5	242	58.2	70.3
	306	33.2	82.8	306	50.2	73.7	266	38.4	80.7	266	57.4	70.7
k_v (h^{-1})	0.03366(1.41 cm/h)			0.01106 (0.46 cm/h)			0.03570 (1.49 cm/h)			0.01023(0.43 cm/h)		
k_1 (h^{-1})	0.00268			0.00224			0.00264			0.00247		
t 1/2 (h)	256			309			262			281		

* Values in parenthesis were not used for modelling purposes.
\- The cut-off point.

APPENDIX D

The Cut-off Point Determination by Using Linear Regression

(Example: Ni-CN at 4°C, NO AIR, NO UV)

```
      PROGRAM BACKRAT(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      REAL T(100),C1(100),C(100),CX(100), CHAT(100), R(100), RS(100),
     +PX(100),CHATM(100),CHATP(100),TREV(100),CREV(100)
    1 CONTINUE
C ***************************************************************
C
C     THIS PROGRAM CALCULATES RATE(S) FROM TOP TO BOTTOM
C     AND VICE VERSA
C
C  **************************************************************
      READ*,N
      WRITE(*,200)N
      IF(N.GT.100)GO TO 777
  200 FORMAT(1X,+N=+,I3)
C
C     CHECK IF IT IS OK TO PROCEED
C
      IF ((N.GT.0).AND.(N.LT.100))THEN
      WRITE(*,300)
  300 FORMAT(1X,≠OK TO PROCEED≠)
      ENDIF
      READ*,C0
      WRITE(*,400)
  400 FORMAT(1X,≠TIME T IN HRS ≠,5X,≠CN CONC IN MG/L≠,)
      DO 10  I=1,N
C
C     CHECK IF N IS WITHIN SPFCIFIED DIMENSION RANGE
C
      IF (N.EQ.0) STOP
      IF ((N.LT.0).OR.(N.GT.100)) THEN
      WRITE(*,500)
  500 FORMAT(1X,+N MUST BE GREATER THAN ZERO ANC LESS THAN 100+)
      ENDIF
C
C     READ IN GIVEN SETS OF DATA
C
      READ*,T(I),C1(I)

C        ************************************************************

C     T HOLDS INDEPENDENT VARIABLES
C     C HOLDS DEPENCENT VARIABLES
C     I   HOLDS NUMBER OF ELEMENTS IN ARRAY
C     ST IS SUM OF INDEPFNDENT VARIABLES
C     SC IS SUM OF DEPENDENT VARIABLES
C     STC IS SUM OF PRODUCT OF T AND C
C     STT IS SUM OF SQUARED T
C     SCC IS SUM OF SQUARED C
C     A IS COFFFICIENT REPRESENTING SLOPE OF THE STRAIGHT LINE
C     B IS COEFFICIENT  REPPESENTING INTERCEPT OF THE STRAIGHT LINE
```

```
C         CORR IS CORRELATION COEFFICIENT
C         CHAT REPRESENTS PREDICTED DEPENDENT VARIABLE
C         SCHAT HOLDS THE SUM OF PREDICTED DEP. VARIABLES
C         R HOLDS RESIDUALS
C         SR HOLDS SUM OF RESIDUALS
C         RS HOLDS SQUARED RESIDUALS
C         RSS HOLDS SUM OF SQUARED RESIDUALS
C         SEE REPRESENTS STANDARD ERROR OF ESTIMATION
C
C       ***********************************************************
C
          CX(I)=C1(I)/C0
          C(I)=ALOG(CX(I))
          WRITE(*,600) T(I),C1(I)
  600     FORMAT(1X,F10.5,5X,F10.5,)
 10       CONTINUE
          RFLAG=0
          NUMDAT=N
 650      CONTINUE
          NTOTAL=N
          IF(NTOTAL.GT.15)NTOTAL=15
          DO 5000 N=3,NTOTAL
C
C         COMPUTE SUMMATIONS FOR LEAST SQUARS
C
          ST=0.0
          SC=0.0
          STC=0.0
          STT=0.0
          SCC=0.0
          DO 20 I=1,N
C
C         ADD THE VALUES OF T AND C TO THE ACCUMULATING VALUES
C         IN SUMMATIONS
C
          ST=ST+T(I)
          SC=SC+C(I)
          STC=STC+(T(I)*C(I))
          STT=STT+(T(I)**2)
          SCC=SCC+(C(I)**2)
 20       CONTINUE
C
C         COMPUTE COEFFICIENTS ≠A≠ AND ≠B≠
C
          A1=STC-((ST*SC)/N)
          A2=STT-((ST*ST)/N)
          A=A1/A2
          B1=SC-(A*ST)
          B=B1/N
C
C         COMPUTE CORRELATION COEFFICIENT ≠CORR≠
C
          A3=SCC-((SC*SC)/N)
          CORR=A1/(SQRT(A2)*SQRT(A3))
C
C         USE THESE A AND B COEFFICIENTS TO CALCULATE PREDICTED
```

```
C         DEPENDENT VARIABLE ≠CHAT≠
C
          SR=0.0
          SCHAT=0.0
          RSS=0.0
          DO 30 I=1,N
          CHAT(I)=A*T(I)+B
          SCHAT=SCHAT+CHAT(I)
C
C         COMPUTE THE PREDICTED ERRORS I.E.RESIDUALS
C
          R(I)=C(I)-CHAT(I)
          SR=SR+R(I)
          RS(I)=R(I)**2
          RSS=   RSS+RS(I)
   30     CONTINUE
C
C        COMPUTE RESIDUAL VARIANCE
C
          RV=RSS/(N-2)
          SIGMAS=(A3-(A*A1))/(N-2)
C
C         COMPUTE STANDARD ERROR OF ESTIMATION
C
          SEE=SQRT(RV)
C
C         WRITE ALL CALCULATED VALUES
C
          WRITE(*,1100)
 1100     FORMAT(//,≠***********************************≠,)
          DO 40 I=1,N
          WRITE(*,1200)T(I),C1(I)
 1200     FORMAT(3X,F10.5,20X,F10.5,)
  40      CONTINUE
          WRITE (*,1400) A,B,CORR,RSS
  1400    FORMAT(/,5X,≠SLOPE A=≠,F12.9,5X,≠INTERC.B=≠,F12.9,5X,≠CORR=
     +    ≠,F10.5,5X, ≠RSS= ≠,F10.5,/)
          RSSAVG=RSS/N
          WRITE(*,1500)N,RSSAVG
 1500     FORMAT(/,3X,≠AVERAGE RSS    FOR≠,I2,≠POINTS=≠,F8.5,//,≠*****
     +    ***********************************************≠)
  5000    CONTINUE
C     **********************************************
C     DO REGRESSION ON OUR DATA BACKWARDS FROM LAST TO FIRST
C     ***********************************************
          N=NUMDAT
          DO 50 I=1,N
          TREV(I)=T(N-I+1)
 50       CREV(I)=C(N-I+1)
          DO 60 I=1,N
          T(I)=TREV(I)
 60       C(I)=CREV(I)
          RFLAG= RFLAG+1
          IF(RFLAG.EQ.1)THEN
          WRITE(*,1700)
```

```
          1700      FORMAT(///,3X,≠BACKWARDS REGRESSION≠,///)
                    ENDIF
                    IF(RFLAG.EQ.1)GO TO 650
                    GO TO 1
           777      CONTINUE
                    STOP
                    END
N= 16
OK TO PROCEED
TIME T IN HRS       CN CONC IN MG/L
   0.00000       169.50000
  17.00000       153.60000
  24.00000       140.20000
  41.00000        98.20000
  48.00000        95.70000
  65.00000        90.30000
  72.00000        88.60000
 137.00000        84.10000
 161.00000        78.10000
 185.00000        71.60000
 192.00000        69.20000
 216.00000        64.50000
 256.00000        61.70000
 280.00000        56.10000
 296.00000        54.70000
 317.00000        50.00000


*****************************
     0.00000                    169.50000
    17.00000                    153.60000
    24.00000                    140.20000

    SLOPE A= -.007514532     INTERC.B=  .006603923     CORR=            -.97716     RSS=     .00081

  AVERAGE RSS    FOR 3POINTS=  .00027

*******   ****************************************************


*****************************
     0.00000                    169.50000
    17.00000                    153.60000
```

```
    24.00000                          140.20000
    41.00000                           98.20000

    SLOPE A= -.013305600     INTERC.B=  .064232109     CORR=            -.94988     RSS=      .01659

  AVERAGE RSS    FOR 4POINTS=  .00415

*******   *****************************************************


****************************
     0.00000                          169.50000
    17.00000                          153.60000
    24.00000                          140.20000
    41.00000                           98.20000
    48.00000                           95.70000

    SLOPE A= -.013263664     INTERC.B=  .063702194     CORR=            -.96939     RSS=      .01659

  AVERAGE RSS    FOR 5POINTS=  .00332

*******   *****************************************************


****************************
     0.00000                          169.50000
    17.00000                          153.60000
    24.00000                          140.20000
    41.00000                           98.20000
    48.00000                           95.70000
    65.00000                           90.30000

    SLOPE A= -.011260590     INTERC.B=  .026722353     CORR=            -.96026     RSS=      .02933

  AVERAGE RSS    FOR 6POINTS=  .00489

*******   *****************************************************
```

```
*****************************
    0.00000                    169.50000
   17.00000                    153.60000
   24.00000                    140.20000
   41.00000                     98.20000
   48.00000                     95.70000
   65.00000                     90.30000
   72.00000                     88.60000

   SLOPE A= -.010136252     INTERC.B=  .003168188     CORR=           -.95553     RSS=      .03987

  AVERAGE RSS     FOR 7POINTS=  .00570

*******   ******************************************************

*****************************
    0.00000                    169.50000
   17.00000                    153.60000
   24.00000                    140.20000
   41.00000                     98.20000
   48.00000                     95.70000
   65.00000                     90.30000
   72.00000                     88.60000
  137.00000                     84.10000

   SLOPE A= -.005445741     INTERC.B= -.148121133     CORR=           -.82760     RSS=      .17224

  AVERAGE RSS     FOR 8POINTS=  .02153

*******   ******************************************************

*****************************
    0.00000                    169.50000
   17.00000                    153.60000
   24.00000                    140.20000
   41.00000                     98.20000
```

```
    48.00000                    95.70000
    65.00000                    90.30000
    72.00000                    88.60000
   137.00000                    84.10000
   161.00000                    78.10000

    SLOPE A= -.004399819     INTERC.B= -.186001467     CORR=          -.83198     RSS=     .20212

  AVERAGE RSS    FOR 9POINTS=  .02246

*******   ***************************************************


***************************
     0.00000                   169.50000
    17.00000                   153.60000
    24.00000                   140.20000
    41.00000                    98.20000
    48.00000                    95.70000
    65.00000                    90.30000
    72.00000                    88.60000
   137.00000                    84.10000
   161.00000                    78.10000
   185.00000                    71.60000

    SLOPE A= -.003988078     INTERC.B= -.203061017     CORR=          -.85661     RSS=     .21306

  AVERAGE RSS    FOR10POINTS=  .02131

*******   ***************************************************


***************************
     0.00000                   169.50000
    17.00000                   153.60000
    24.00000                   140.20000
    41.00000                    98.20000
    48.00000                    95.70000
    65.00000                    90.30000
```

```
     72.00000                        88.60000
    137.00000                        84.10000
    161.00000                        78.10000
    185.00000                        71.60000
    192.00000                        69.20000

     SLOPE A= -.003830974      INTERC.B= -.209885813      CORR=              -.87738      RSS=      .21667

   AVERAGE RSS     FOR11POINTS=  .01970

*******   ********************************************************


*****************************
      0.00000                       169.50000
     17.00000                       153.60000
     24.00000                       140.20000
     41.00000                        98.20000
     48.00000                        95.70000
     65.00000                        90.30000
     72.00000                        88.60000
    137.00000                        84.10000
    161.00000                        78.10000
    185.00000                        71.60000
    192.00000                        69.20000
    216.00000                        64.50000

     SLOPE A= -.003699990      INTERC.B= -.216593397      CORR=              -.89526      RSS=      .22020

   AVERAGE RSS     FOR12POINTS=  .01835

*******   ********************************************************


*****************************
      0.00000                       169.50000
     17.00000                       153.60000
     24.00000                       140.20000
     41.00000                        98.20000
     48.00000                        95.70000
```

```
   65.00000                         90.30000
   72.00000                         88.60000
  137.00000                         84.10000
  161.00000                         78.10000
  185.00000                         71.60000
  192.00000                         69.20000
  216.00000                         64.50000
  256.00000                         61.70000

   SLOPE A= -.003444885     INTERC.B= -.232554613     CORR=           -.90351     RSS=      .23612

 AVERAGE RSS    FOR13POINTS=  .01816

*******   *******************************************************


*****************************
    0.00000                        169.50000
   17.00000                        153.60000
   24.00000                        140.20000
   41.00000                         98.20000
   48.00000                         95.70000
   65.00000                         90.30000
   72.00000                         88.60000
  137.00000                         84.10000
  161.00000                         78.10000
  185.00000                         71.60000
  192.00000                         69.20000
  216.00000                         64.50000
  256.00000                         61.70000
  280.00000                         56.10000

   SLOPE A= -.003319224     INTERC.B= -.241230645     CORR=           -.91671     RSS=      .24205

 AVERAGE RSS    FOR14POINTS=  .01729

*******   *******************************************************
```

```
******************************
    0.00000                      169.50000
   17.00000                      153.60000
   24.00000                      140.20000
   41.00000                       98.20000
   48.00000                       95.70000
   65.00000                       90.30000
   72.00000                       88.60000
  137.00000                       84.10000
  161.00000                       78.10000
  185.00000                       71.60000
  192.00000                       69.20000
  216.00000                       64.50000
  256.00000                       61.70000
  280.00000                       56.10000
  296.00000                       54.70000

    SLOPE A= -.003214217     INTERC.B= -.248979504     CORR=           -.92579     RSS=      .24849

  AVERAGE RSS    FOR15POINTS=  .01657

*******  **************************************************


  BACKWARDS REGRESSION



******************************
  317.00000                      169.50000
  296.00000                      153.60000
  280.00000                      140.20000

    SLOPE A= -.003170466     INTERC.B= -.208770105     CORR=           -.97244     RSS=      .00040

  AVERAGE RSS    FOR 3POINTS=  .00013
```

```
   317.00000                     169.50000
   296.00000                     153.60000
   280.00000                     140.20000
   256.00000                      98.20000

    SLOPE A= -.003324936     INTERC.B= -.161938551     CORR=          -.99052     RSS=     .00042

  AVERAGE RSS    FOR 4POINTS=  .00011

*******  *******************************************************


*****************************
   317.00000                     169.50000
   296.00000                     153.60000
   280.00000                     140.20000
   256.00000                      98.20000
   216.00000                      95.70000

    SLOPE A= -.002514362     INTERC.B= -.400437877     CORR=          -.97037     RSS=     .00237



  AVERAGE RSS    FOR 5POINTS=  .00047

*******  *******************************************************


*****************************
   317.00000                     169.50000
   296.00000                     153.60000
   280.00000                     140.20000
   256.00000                      98.20000
   216.00000                      95.70000
   192.00000                      90.30000

    SLOPE A= -.002440198     INTERC.B= -.421792879     CORR=          -.98266     RSS=     .00244

  AVERAGE RSS    FOR 6POINTS=  .00041
```

```
******************************
   317.00000                      169.50000
   296.00000                      153.60000
   280.00000                      140.20000
   256.00000                       98.20000
   216.00000                       95.70000
   192.00000                       90.30000
   185.00000                       88.60000

    SLOPE A= -.002485203     INTERC.B= -.408954217     CORR=              -.98769     RSS=      .00252

  AVERAGE RSS    FOR 7POINTS=  .00036

*******   *********************************************************


******************************
   317.00000                      169.50000
   296.00000                      153.60000
   280.00000                      140.20000
   256.00000                       98.20000
   216.00000                       95.70000
   192.00000                       90.30000
   185.00000                       88.60000
   161.00000                       84.10000

    SLOPE A= -.002599389     INTERC.B= -.377515955     CORR=              -.98973     RSS=      .00325

  AVERAGE RSS    FOR 8POINTS=  .00041

*******   *********************************************************


******************************
   317.00000                      169.50000
   296.00000                      153.60000
   280.00000                      140.20000
   256.00000                       98.20000
   216.00000                       95.70000
```

```
   192.00000                      90.30000
   185.00000                      88.60000
   161.00000                      84.10000
   137.00000                      78.10000

    SLOPE A= -.002691041     INTERC.B= -.353098780     CORR=             -.99164     RSS=     .00393

  AVERAGE RSS     FOR 9POINTS=  .00044

*******   *********************************************************


******************************
   317.00000                     169.50000
   296.00000                     153.60000
   280.00000                     140.20000
   256.00000                      98.20000
   216.00000                      95.70000
   192.00000                      90.30000
   185.00000                      88.60000
   161.00000                      84.10000
   137.00000                      78.10000
    72.00000                      71.60000

    SLOPE A= -.002426517     INTERC.B= -.419152860     CORR=             -.98525     RSS=     .00952

  AVERAGE RSS     FOR10POINTS=  .00095

*******   *********************************************************


******************************
   317.00000                     169.50000
   296.00000                     153.60000
   280.00000                     140.20000
   256.00000                      98.20000
   216.00000                      95.70000
   192.00000                      90.30000
   185.00000                      88.60000
   161.00000                      84.10000
```

```
   137.00000                        78.10000
    72.00000                        71.60000
    65.00000                        69.20000

    SLOPE A= -.002330363      INTERC.B= -.442986127      CORR=              -.98595      RSS=      .01138

  AVERAGE RSS     FOR11POINTS=  .00103

*******   *******************************************************


*****************************
   317.00000                       169.50000
   296.00000                       153.60000
   280.00000                       140.20000
   256.00000                        98.20000
   216.00000                        95.70000
   192.00000                        90.30000
   185.00000                        88.60000
   161.00000                        84.10000
   137.00000                        78.10000
    72.00000                        71.60000
    65.00000                        69.20000
    48.00000                        64.50000
    SLOPE A= -.002305722      INTERC.B= -.448954360      CORR=              -.98856      RSS=      .01158

  AVERAGE RSS     FOR12POINTS=  .00097

*******   *******************************************************


*****************************
   317.00000                       169.50000
   296.00000                       153.60000
   280.00000                       140.20000
   256.00000                        98.20000
   216.00000                        95.70000
   192.00000                        90.30000
   185.00000                        88.60000
```

```
   161.00000                      84.10000
   137.00000                      78.10000
    72.00000                      71.60000
    65.00000                      69.20000
    48.00000                      64.50000
    41.00000                      61.70000

    SLOPE A= -.002302938     INTERC.B= -.449621037     CORR=           -.99046     RSS=     .01159

  AVERAGE RSS    FOR13POINTS=  .00089

*******   ******************************************************


*****************************
   317.00000                     169.50000
   296.00000                     153.60000
   280.00000                     140.20000
   256.00000                      98.20000
   216.00000                      95.70000
   192.00000                      90.30000
   185.00000                      88.60000
   161.00000                      84.10000
   137.00000                      78.10000
    72.00000                      71.60000
    65.00000                      69.20000
    48.00000                      64.50000
    41.00000                      61.70000
    24.00000                      56.10000
    SLOPE A= -.002631473     INTERC.B= -.373374317     CORR=           -.95504     RSS=     .08934

  AVERAGE RSS    FOR14POINTS=  .00638

*******   ******************************************************


*****************************
   317.00000                     169.50000
   296.00000                     153.60000
```

```
   280.00000                     140.20000
   256.00000                      98.20000
   216.00000                      95.70000
   192.00000                      90.30000
   185.00000                      88.60000
   161.00000                      84.10000
   137.00000                      78.10000
    72.00000                      71.60000
    65.00000                      69.20000
    48.00000                      64.50000
    41.00000                      61.70000
    24.00000                      56.10000
    17.00000                      54.70000

    SLOPE A= -.002915535     INTERC.B= -.308378326     CORR=          -.94003     RSS=     .17226

  AVERAGE RSS    FOR15POINTS=  .01148

*******   ***************************************************
N=500
```

Comparison of the Average Residual Sum of Squares

	Forward (from 0 to 317 h)	Backward (from 317 to 0 h)	
For first 3 points	0.00027	0.01148	
	0.00415	0.00638	
	0.00332	0.00089	
	0.00489	0.00097	
The cut-off point	0.00570	0.00103	
	0.02153	0.00095	
	0.02246	0.00044	
	0.02131	0.00041	
	0.01970	0.00036	
	0.01835	0.00041	
	0.01816	0.00042	
	0.01729	0.00011	
	0.01657	0.00013	For first 3 points

APPENDIX E

Calculation of the Reaction Rate Constant by Using Linear Regression

```
      PROGRAM RATE(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      REAL T(100),C1(100),C(100),CX(100), CHAT(100), R(100), RS(100),
C ********************************************************************
C
C     THIS PROGRAM CALCULATES RATE(S)
C
C  *******************************************************************
      READ*,N
      WRITE(*,100)N
      IF(N.GT.100)GO TO 777
 100  FORMAT(1X,'N=',I3)
C
C     CHECK IF IT IS OK TO PROCEED
C
      IF ((N.GT.0).AND.(N.LT.100))THEN
      WRITE(*,200)
 200  FORMAT(1X,"OK TO PROCEED")
      ENDIF
      READ*,C0
      WRITE(*,300)TESTT
 300  FORMAT(1X,"TESTT=",F10.5,)
      WRITE(*,400)
 400  FORMAT(1X,"CN CONC IN MG/L",5X,"CX=C1/C0",5X,"NAT.LOG.OF CX",)
      DO 10  I=1,N
C
C     CHECK IF N IS WITHIN SPECIFIED DIMENSION RANGE
C
      IF (N.EQ.0) STOP
      IF ((N.LT.0).OR.(N.GT.100)) THEN
      WRITE(*,500)
 500  FORMAT(1X,'N MUST BE GREATER THAN ZERO AND LESS THAN 100')
      ENDIF
C
C     READ IN GIVEN SETS OF DATA
C
      READ*,T(I),C1(I)

C    ***************************************************************

C     T HOLDS INDEPENDENT VARIABLES
C     C HOLDS DEPENDENT VARIABLES
C     I   HOLDS NUMBER OF ELEMENTS IN ARRAY
C     ST IS SUM OF INDEPENDENT VARIABLES
C     SC IS SUM OF DEPENDENT VARIABLES
C     STC IS SUM OF PRODUCT OF T AND C
C     STT IS SUM OF SQUARED T
C     SCC IS SUM OF SQUARED C
C     A IS COEFFICIENT REPRESENTING SLOPE OF THE STRAIGHT LINE
C     B IS COEFFICIENT  REPRESENTING INTERCEPT OF THE STRAIGHT LINE
C     CORR IS CORRELATION COEFFICIENT
C     CHAT REPRESENTS PREDICTED DEPENDENT VARIABLE
C     SCHAT HOLDS THE SUM OF PREDICTED DEP. VARIABLES
C     R HOLDS RESIDUALS
C     SR HOLDS SUM OF RESIDUALS
C     RS HOLDS SQUARED RESIDUALS
C     RSS HOLDS SUM OF SQUARED RESIDUALS
C     SEE REPRESENTS STANDARD ERROR OF ESTIMATION
C
C     **************************************************************
C
      CX(I)=C1(I)/C0
      C(I)=ALOG(CX(I))
      WRITE(*,600) C1(I),CX(I),C(I)
 600  FORMAT(1X,F10.5,5X,F10.5,5X,F10.5,)
 10   CONTINUE
```

```
C
C        COMPUTE SUMMATIONS FOR LEAST SQUARS
C
         ST=0.0
         SC=0.0
         STC=0.0
         STT=0.0
         SCC=0.0
C        WRITE(*,700)
C 700    FORMAT(" SUM T",9X,"SUM C",9X,"SUM TC",9X,"SUM TT",9X,
C    +   "SUM CC",)
         DO 20 I=1,N
C
C        ADD THE VALUES OF T ANC C TO THE ACCUMULATING VALUES
C        IN SUMMATIONS
C
         ST=ST+T(I)
         SC=SC+C(I)
         STC=STC+(T(I)*C(I))
         STT=STT+(T(I)**2)
         SCC=SCC+(C(I)**2)
 20      CONTINUE
C
C        COMPUTE COEFFICIENTS "A" AND "B"
C
         A1=STC-((ST*SC)/N)
         A2=STT-((ST*ST)/N)
         A=A1/A2
         B1=SC-(A*ST)
         B=B1/N
C
C        COMPUTE CORRELATION COEFFICIENT "CORR"
C
         A3=SCC-((SC*SC)/N)
         CORR=A1/(SQRT(A2)*SQRT(A3))
C
C        USE THESE A AND B COEFFICIENTS TO CALCULATE PREDICTED
C        DEPENDENT VARIABLE "CHAT"
C
         WRITE(*,900)
 900     FORMAT(" CHAT",12X,"SCHAT",)
         SR=0.0
         SCHAT=0.0
         RSS=0.0
         DO 30 I=1,N
         CHAT(I)=A*T(I)+B
         SCHAT=SCHAT+CHAT(I)
         WRITE(*,1000)CHAT(I),SCHAT
 1000    FORMAT(1X,2F10.5,)
C
C        COMPUTE THE PREDICTED ERRORS I.E.RESIDUALS
C
         R(I)=C(I)-CHAT(I)
         SR=SR+R(I)
         RS(I)=R(I)**2
         RSS=   RSS+RS(I)
  30     CONTINUE
C
C        COMPUTE RESIDUAL VARIANCE
```

```
      RV=RSS/(N-2)
      SIGMAS=(A3-(A*A1))/(N-2)
      WRITE(*,1050)RV,SIGMAS
 1050 FORMAT(1X,"RV=",F10.5,5X,"SIGMAS=",F10.5,)
C
C     COMPUTE STANDARD ERROR OF ESTIMATION
C
      SEE=SQRT(RV)
C
C     WRITE ALL CALCULATED VALUES
C
      WRITE(*,1100)
 1100 FORMAT("  TIME  T  IN  HOURS   ",12X,"CONCENTRATION C ",
     +3X,"RESIDUALS R=C-CHAT",9X,"CHATM",8X,"CHATP",)
      DO 40 I=1,N
      WRITE(*,1200)T(I),C(I),R(I),CHATM(I),CHATP(I)
 1200 FORMAT(8X,F10.5,20X,F10.5,15X,F10.5,5X,F10.5,5X,F10.5,)
      CALL PLOTPT (T(I),C(I),2)
      CALL PLOTPT(T(I),CHAT(I),20)
  40  CONTINUE
      WRITE(*,1300)ST,SC,SR
 1300 FORMAT(4X,"SUM OF T=",F10.5,4X,"SUM OF C=",F10.5,4X,"SUM OF
     +R=",F10.5/)
      WRITE (*,1400) A,B,CORR,RSS
 1400 FORMAT(/,5X,"SLOPE A=",F12.9,5X,"INTERC.B=",F12.9,5X,"CORR=
     +",F10.5,5X, "RSS= ",F10.5,/)
      CALL OUTPLT
      STOP
      END
```

APPENDIX F

Linear Regression and 95% Confidence Interval Calculations Performed on the Part of the Degradation Curve Attributed to Volatilization (NaCN and Cu-CN, Zn-CN, Ni-CN, Fe-CN Complexes)

```
      PROGRAM VOLCONF(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      REAL T(100),C1(100),C(100),CX(100), CHAT(100), R(100), RS(100),
     r PX(100),CHATM(100),CHATP(100)
 1    CONTINUE
C ********************************************************************
C
C     THIS PROGRAM CALCULATES RATE(S) PLOTS THE
C     GRAPH AND GIVES 95x CONF. INTERVAL
C
C  *******************************************************************
      WRITE(*,100)
  100 FORMAT("1 INPUT NUMBER OF DATA POINTS")
      READ*,N
      WRITE(*,200)N
      IF(N.GT.100)GO TO 777
  200 FORMAT(1X,'N=',I3)
C
C     CHECK IF IT IS OK TO PROCEED
C
      IF ((N.GT.0).AND.(N.LT.100))THEN
      WRITE(*,300)
  300 FORMAT(1X,"OK TO PROCEED")
      ENDIF
      READ*,C0
      READ*,TESTT
      WRITE(*,350)TESTT
 350  FORMAT(1X,"TESTT=",F10.5,)
      WRITE(*,400)
  400 FORMAT(1X,"CN CONC IN MG/L",5X,"CX=C1/C0",5X,"NAT.LOG.OF CX",)
      DO 10  I=1,N
C
C     CHECK IF N IS WITHIN SPECIFIED DIMENSION RANGE
C
      IF (N.EQ.0) STOP
      IF ((N.LT.0).OR.(N.GT.100)) THEN
      WRITE(*,500)
```

```
  500    FORMAT(1X,'N MUST BE GREATER THAN ZERO AND LESS THAN 100')
         ENDIF
C
C        READ IN GIVEN SETS OF DATA
C
         READ*,T(I),C1(I)

C     ****************************************************************

C        T HOLDS INDEPENDENT VARIABLES
C        C HOLDS DEPENDENT VARIABLES
C        I   HOLDS NUMBER OF ELEMENTS IN ARRAY
C        ST IS SUM OF INDEPENDENT VARIABLES
C        SC IS SUM OF DEPENDENT VARIABLES
C        STC IS SUM OF PRODUCT OF T AND C
C        STT IS SUM OF SQUARED T
C        SCC IS SUM OF SQUARED C
C        A IS COEFFICIENT REPRESENTING SLOPE OF THE STRAIGHT LINE
C        B IS COEFFICIENT  REPRESENTING INTERCEPT OF THE STRAIGHT LINE
C        CORR IS CORRELATION COEFFICIENT
C        CHAT REPRESENTS PREDICTED DEPENDENT VARIABLE
C        SCHAT HOLDS THE SUM OF PREDICTED DEP. VARIABLES
C        R HOLDS RESIDUALS
C        SR HOLDS SUM OF RESIDUALS
C        RS HOLDS SQUARED RESIDUALS
C        SRS HOLDS SUM OF SQUARED RESIDUALS
C        SEE REPRESENTS STANDARD ERROR OF ESTIMATION
C
C      ***************************************************************
C
         CX(I)=C1(I)/C0
         C(I)=ALOG(CX(I))
         WRITE(*,600) C1(I),CX(I),C(I)
  600    FORMAT(1X,F10.5,5X,F10.5,5X,F10.5,)
 10      CONTINUE
C
C        COMPUTE SUMMATIONS FOR LEAST SQUARS
C
         ST=0.0


         SC=0.0
         STC=0.0
```

```
      STT=0.0
      SCC=0.0
      WRITE(*,700)
  700 FORMAT(" SUM T",9X,"SUM C",9X,"SUM TC",9X,"SUM TT",9X,
     +"SUM CC",)
      DO 20 I=1,N
C
C     ADD THE VALUES OF T ANC C TO THE ACCUMULATING VALUES
C     IN SUMMATIONS
C
      ST=ST+T(I)
      SC=SC+C(I)
      STC=STC+(T(I)*C(I))
      STT=STT+(T(I)**2)
      SCC=SCC+(C(I)**2)
 20   CONTINUE
C
C     COMPUTE COEFFICIENTS "A" AND "B"
C
      A1=STC-((ST*SC)/N)
      A2=STT-((ST*ST)/N)
      A=A1/A2
      B1=SC-(A*ST)
      B=B1/N
C
C     COMPUTE CORRELATION COEFFICIENT "CORR"
C
      A3=SCC-((SC*SC)/N)
      CORR=A1/(SQRT(A2)*SQRT(A3))
C
C     USE THESE A AND B COEFFICIENTS TO CALCULATE PREDICTED
C     DEPENDENT VARIABLE "CHAT"
C
      WRITE(*,900)


 900  FORMAT(" CHAT",12X,"SCHAT",)
      SR=0.0
      SCHAT=0.0
      SRS=0.0
      DO 30 I=1,N
      CHAT(I)=A*T(I)+B
      SCHAT=SCHAT+CHAT(I)
      WRITE(*,1000)CHAT(I),SCHAT
```

```
 1000    FORMAT(1X,2F10.5,)
C
C        COMPUTE THE PREDICTED ERRORS I.E.RESIDUALS
C
         R(I)=C(I)-CHAT(I)
         SR=SR+R(I)
         RS(I)=R(I)**2
         SRS=   SRS+RS(I)
  30     CONTINUE
C
C       COMPUTE RESIDUAL VARIANCE
C
        RV=SRS/(N-2)
        SIGMAS=(A3-(A*A1))/(N-2)
        WRITE(*,1050)RV,SIGMAS
 1050   FORMAT(1X,"RV=",F10.5,5X,"SIGMAS=",F10.5,)
C
C        COMPUTE STANDARD ERROR OF ESTIMATION
C
         SEE=SQRT(RV)
C
C        COMPUTE 95% CONF.LIMITS FOR A
C
         AA2=SQRT(A2)
         ALPHAM=A-((TESTT*SEE)/AA2)
         ALPHAP=A+((TESTT*SEE)/AA2)
C
C        COMPUTE 95% CONF.LIMITS FOR B
C
         AN2=N*A2
         BETAM=B-((TESTT*SEE*SQRT(STT))/SQRT(AN2))


         BETAP=B+((TESTT*SEE*SQRT(STT))/SQRT(AN2))
C
C        COMPUTE 95% CONF.LIMITS FOR CHAT
C
         REVN=1/N
         TMEAN=ST/N
         CMEAN=SC/N
         DO 35 I=1,N
         PX(I)=(T(I)-TMEAN)**2
         CHATM(I)=CHAT(I)-(TESTT*SEE*SQRT(REVN+(PX(I)/A2)))
```

```
      CHATP(I)=CHAT(I)+(TESTT*SEE*SQRT(REVN+(PX(I)/A2)))
 35   CONTINUE
C
C     WRITE ALL CALCULATED VALUES
C
      WRITE(*,1100)
1100  FORMAT("  TIME  T  IN  HOURS    ",5X,"CONCENTRATION C ",
     +5X,"RESIDUALS R=C-CHAT",5X,"CHATM",10X,"CHATP",)
      DO 40 I=1,N
      WRITE(*,1200)T(I),C(I),R(I),CHATM(I),CHATP(I)
1200  FORMAT(8X,F10.5,20X,F10.5,15X,F10.5,5X,F10.5,5X,F10.5,)
      CALL PLOTPT (T(I),CHAT(I),2)
      CALL PLOTPT(T(I),CHATM(I),20)
      CALL PLOTPT(T(I),CHATP(I),20)
 40   CONTINUE
      WRITE(*,1300)ST,SC,SR
1300  FORMAT(4X,"SUM OF T=",F10.5,4X,"SUM OF C=",F10.5,4X,"SUM OF
     +R=",F10.5/)
      WRITE (*,1400) A,B,CORR,SRS
1400  FORMAT(/,5X,"SLOPE A=",F12.9,5X,"INTERC.B=",F12.9,5X,"CORR=
     +",F10.5,5X, "SRS= ",F10.5,/)
      WRITE(*,1500)ALPHAM,ALPHAP,BETAM,BETAP,TMEAN,CMEAN
1500  FORMAT(3X,"ALPHAM=",F12.9,5X,"ALPHAP=",
     +F12.9,5X,"BETAM=",F12.9,5X,"BETAP=",F12.9,5X,
     +"TMEAN=",F5.2,5X,"CMEAN=",F5.2,/)
      GO TO 1

777   CONTINUE
      CALL OUTPLT
      STOP
      END
```

APPENDIX G.1

The Computer Program for the Analysis of 2^3 Factorial Design Data - Calculation of the Effects by Using Matrix of Independent Variables and Equation 6.1

```
       PROGRAM FACT (INPUT,OUTPUT,FDAT,TAPE10=FDAT,TAPE30=OUTPUT)
************************************************************************
*                                                                      *
*             ANALYSIS OF FACTORIAL DESIGN DATA                        *
*                                                                      *
*  NOMENCLATURE:                                                       *
*        NF = NUMBER OF FACTORS                                        *
*        NT = NUMBER OF TESTS                                          *
*        TYPE = "FULL" FOR A FULL FACTORIAL DESIGN                     *
*             = "FRAC" FOR A FRACTIONAL DESIGN                         *
*             (TYPE IS A CHARACTER VARIABLE)                           *
*        TEST = ARRAY OF TEST CODES                                    *
*             (TEST IS A CHARACTER VARIABLE)                           *
*        R = ARRAY OF TEST RESULTS                                     *
*                                                                      *
* INPUT:                                                               *
*        INPUT ALL DATA USING A FILE CALLED "FDAT"                     *
*        IN THE FOLLOWING ORDER:                                       *
*        NF, NT, TYPE, TEST(1), R(1), TEST(2), R(2)... TEST(NT), R(NT) *
*         E.G. 3  8  'FULL' 'I'  .032  'A'  .054  'B'  .71  ....ETC    *
*  OUTPUT:                                                             *
*        INPUT DATA "TYPE", "NF", "TEST(NT)" AND "R(NT)" ARE REPEATED  *
*        FOR CONFIRMATION.  EFFECTS ARE LISTED IN THE FOLLOWING ORDER: *
*        MAIN, 2-FACTOR, 3-FACTOR.  THE 3-FACTOR EFFECTS ARE           *
*        CALCULATED ONLY FOR FULL FACTORIALS (TEMPORARY LIMITATION).   *
*                                                                      *
*  LIMITATIONS: THIS PROGRAM WILL ACCEPT TWO-LEVEL FULL OR FRACTIONAL  *
*               FACTORIAL DESIGN DATA IN ANY ORDER.  THE MAXIMUM       *
*               SIZE IS 2**8 (8 FACTORS).                              *
*                                                                      *
*  NOTE: THIS IS A FORTRAN-5 PROGRAM                                   *
*                                                                      *
************************************************************************
      DIMENSION  R(256)
      CHARACTER  TYPE*4,TEST(256)*8,E(3)*1,EFF1(8)*1
      READ (10,*) NF,NT,TYPE, (TEST(I),R(I),I=1,NT)
      WRITE (30,500)
      IF (TYPE.EQ.'FULL') GO TO 160
      WRITE (30,600) NF
      GO TO 170
  160 WRITE (30,700) NF
  170 WRITE (30,800) (TEST(I),R(I),I=1,NT)
      WRITE (30,900)
*
*     DEFINE EFFECT LABELS
*
      EFF1(1) = 'A'
      EFF1(2) = 'B'
      EFF1(3) = 'C'
      EFF1(4) = 'D'
      EFF1(5) = 'E'
      EFF1(6) = 'F'
      EFF1(7) = 'G'
      EFF1(8) = 'H'
*
*     DETERMINE MAIN EFFECTS
*
      DO 50 K=1,NF
      SUM=0.
      DO 40 I=1,NT
      L=1
```

```
   10 IF(TEST(I)(L:L).EQ.EFF1(K)) GO TO 20
      IF(L.EQ.8) GO TO 30
      L=L+1
      GO TO 10
   20 SUM = SUM + R(I)
      GO TO 40
   30 SUM = SUM - R(I)
   40 CONTINUE
      END = SUM/(NT/2)
   50 WRITE (30,1000) EFF1(K),END
*
*     DETERMINE TWO-FACTOR INTERACTIONS
*
      NF1 = NF-1
      DO 80 N=1,NF1
      N1 = N+1
      DO 80 M = N1,NF
      E(1) = EFF1(N)
      E(2) = EFF1(M)
      SUM = 0.
      DO 70 I=1,NT
      KT = 0
      DO 63 KL=1,2
      L = 1
   60 IF(TEST( I)(L:L).EQ.E(KL)) GO TO 61
      IF(L.EQ.8) GO TO 62
      L=L+1
      GO TO 60
   61 KT = KT+1
      GO TO 63
   62 KT = KT-1
   63 CONTINUE
      IF(KT.EQ.0) SUM = SUM - R(I)
      IF(KT.NE.0) SUM = SUM + R(I)
   70 CONTINUE
      END=SUM/(NT/2)
   80 WRITE (30,2000) E(1),E(2),END
*
*     DETERMINE THREE-FACTOR INTERACTIONS
*
      IF (TYPE.EQ.'FRAC') GO TO 98
      NF1 = NF-1
      NF2 = NF-2
      DO 96 N=1,NF2
      N1=N+1
      DO 96 M=N1,NF1
      M1=M+1
      DO 96 MN=M1,NF
      E(1) = EFF1(N)
      E(2) = EFF1(M)
      E(3) = EFF1(MN)
      SUM = 0.
      DO 95 I=1,NT
      KT = 0
      DO 94 IJK=1,3
      L = 1
   89 IF(TEST(I)(L:L).EQ.E(IJK)) GO TO 91
      IF(L.EQ.5) GO TO 93
      L =L+1
      GO TO 89
   91 KT=KT+1
      GO TO 94
   93 KT = KT-1
   94 CONTINUE
      IF(KT.EQ.3) SUM = SUM+R(I)
```

```
      IF(KT.EQ.-1) SUM = SUM+R(I)
      IF(KT.EQ.-3) SUM = SUM-R(I)
      IF(KT.EQ.1) SUM = SUM-R(I)
   95 CONTINUE
      END=SUM/(NT/2)
   96 WRITE(30,3000) E(1),E(2),E(3),END
   98 CONTINUE
*
*     FORMAT STATEMENTS
*
  500 FORMAT(///,10X,"ANALYSIS OF FACTORIAL DESIGN DATA",///
     +,5X,"PROJECT NUMBER 01", 10X,
     +"EXPERIMENTAL SOLUTION ..NACN...",//,5X,
     +"RESPONSE PARAMETER IS REACTION RATE CONSTANT K(1/H)")
*
  600 FORMAT(//,2X,"THIS EXPERIMENT IS A FRACTIONAL FACTORIAL OF",
     +1X,I2,1X,"FACTORS",//,5X,"TEST CODE",5X,"RESPONSE")
*
  700 FORMAT(//,2X,"THIS EXPERIMENT IS A FULL FACTORIAL OF",
     +1X,I2,1X,"FACTORS",//,5X,"TEST CODE",5X,"RESPONSE")
*
  800 FORMAT(/,7X,A8,3X,F10.6)
*
  900 FORMAT(///,5X, "EFFECTS")
*
 1000 FORMAT(/,5X,A1,1X,"=",1X,F10.6)
*
 2000 FORMAT(/,5X,2A1,1X,"=",1X,F10.6)
*
 3000 FORMAT(/,5X,3A1,1X,"=",1X,F10.6)
*
*
      STOP
      END
```

APPENDIX G.2

Examples for the Calculation of the Effects

G.2 CALCULATION OF THE EFFECTS

The following is an example calculation of the effects on nickel cyanide complex solution solved by using given matrix of independent variables and Equation 6.1 (applied in program FACT).

I	A	B	C	AB	AC	BC	ABC	$Y \times 10^{-3}$
+	-	-	-	+	+	+	-	2.69
+	+	-	-	-	-	+	+	4.06
+	-	+	-	-	+	-	+	2.98
+	+	+	-	+	-	-	-	4.16
+	-	-	+	+	-	-	+	0.81
+	+	-	+	-	+	-	-	1.49
+	-	+	+	-	-	+	-	2.68
+	+	+	+	+	+	+	+	0.83

$$\text{Effect of A} = \frac{(-2.69 + 4.06 - 2.98 + 4.16 - 0.81 + 1.49 - 2.68 + 0.83) \times 10^{-3}}{4}$$

$$= 0.34 \times 10^{-3}$$

$$\text{Effect of B} = \frac{(-2.69 - 4.06 + 2.98 + 4.16 - 0.81 - 1.49 + 2.68 + 0.83) \times 10^{-3}}{4}$$

$$= 0.40 \times 10^{-3}$$

$$\text{Effect of C} = \frac{(-2.69 - 4.06 - 2.98 - 4.16 + 0.81 + 1.49 + 2.68 + 0.83) \times 10^{-3}}{4}$$

$$= -2.02 \times 10^{-3}$$

Effect of AB = $\frac{(+2.69 -4.06 -2.98 +4.16 +0.81 -1.49 -2.68 +0.83)\times 10^{-3}}{4}$

$= -0.68 \times 10^{-3}$

Effect of AC = $\frac{(+2.69 -4.06 +2.98 -4.16 -0.81 +1.49 -2.68 +0.83)\times 10^{-3}}{4}$

$= 0.21 \times 10^{-3}$

Effect of ABC= $\frac{(-2.69 +4.06 +2.98 -4.16 +0.81 -1.49 -2.68 +0.83)\times 10^{-3}}{4}$

$= -0.59 \times 10^{-3}$

APPENDIX G.3

Half Normal Probability Plots

G.3 PROBABILITY (%) AND EFFECTS ORDERED IN ASCENDING MAGNITUDE - HALF NORMAL PROBABILITY PLOTS

NaCN

Order Number i	1	2	3	4	5	6	7
Effect $\times 10^3$	-6.78	-3.10	+0.58	+2.90	+5.68	+8.80	+18.04
Identity of effect	ac	abc	ab	bc	a	b	c
$P = 100\,(i-1/2)/7$	7.14	21.4	35.7	50.0	64.3	78.6	92.9

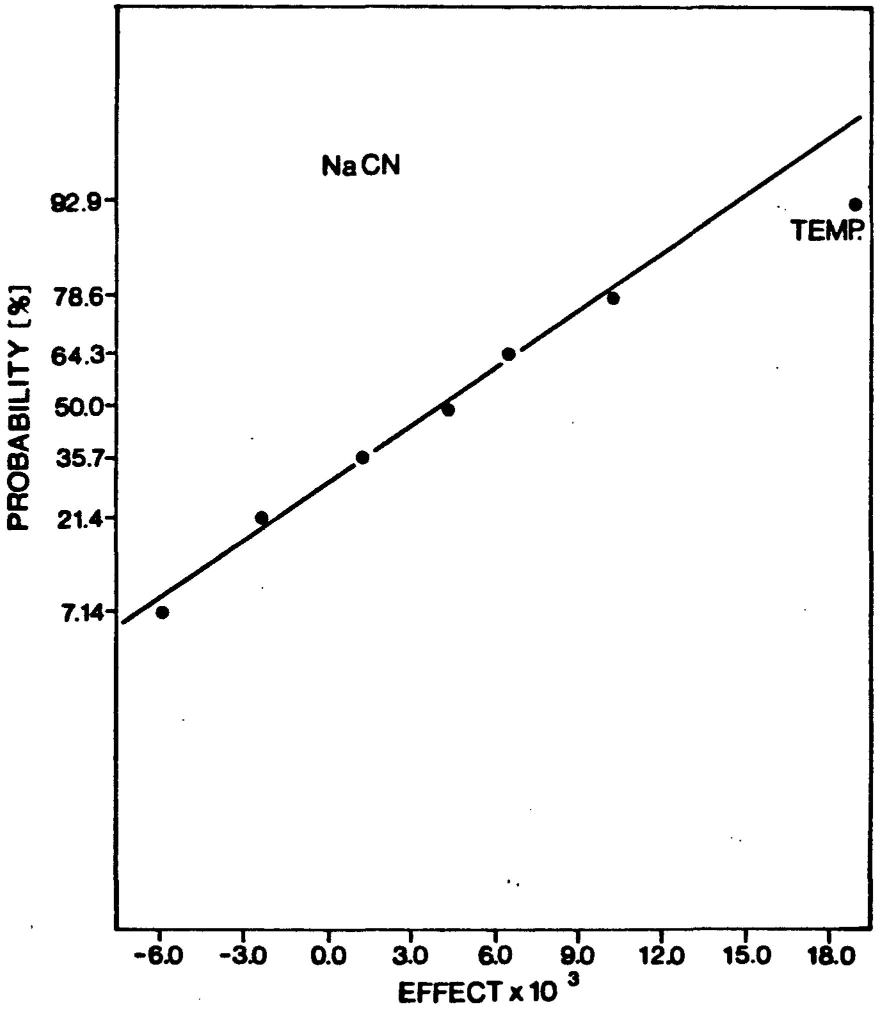


Figure G.1. Half normal probability plot for NaCN

$Na_2Cu(CN)_3$

Order Number i	1	2	3	4	5	6	7
Effect $x10^3$	-2.60	-2.44	-0.185	-0.175	+6.39	+6.85	+7.92
Identity of effect	a	ac	ab	abc	bc	b	c
P(%)	7.14	21.4	35.7	50.0	64.3	78.6	92.9

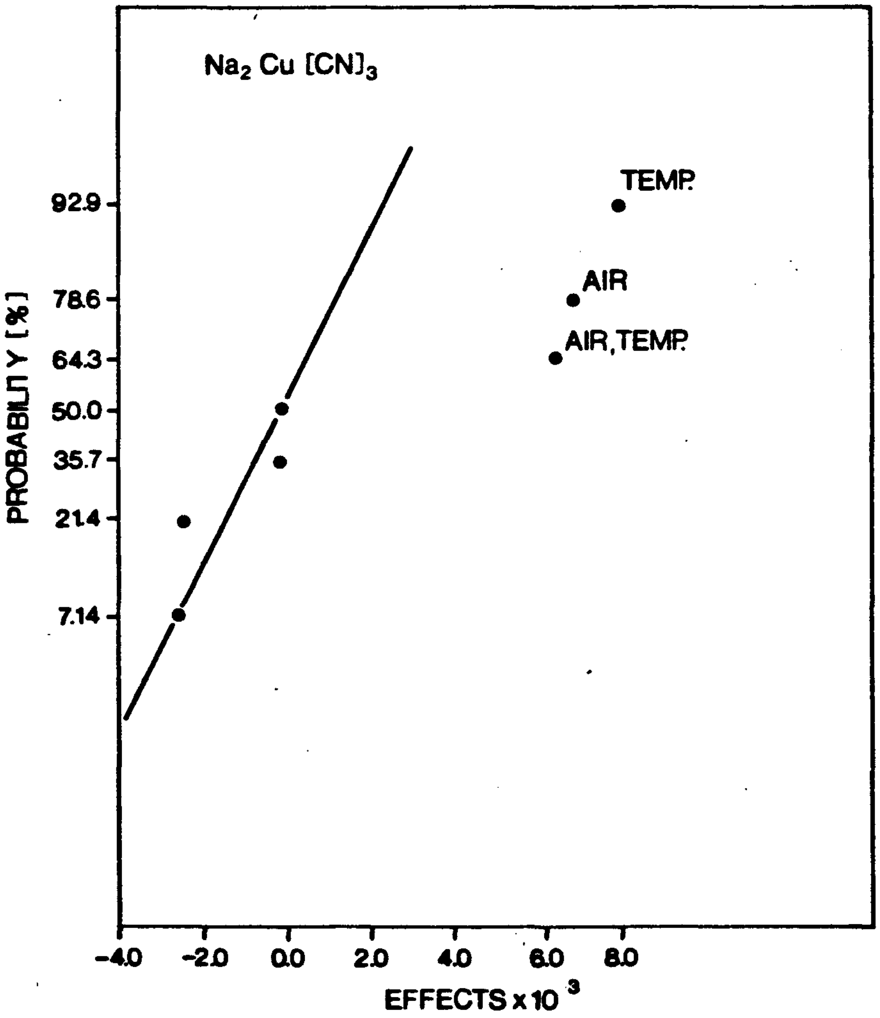


Figure G.2. Half normal probability plot for copper cyanate complex

$Na_2Zn(CN)_4$

Order number i	1	2	3	4	5	6	7
Effect $x10^3$	+1.78	+4.97	+6.33	+9.55	+10.39	+12.33	+13.52
Identity of effect	bc	b	ac	abc	ab	a	c
P(%)	7.14	21.4	35.7	50.0	64.3	78.6	92.9

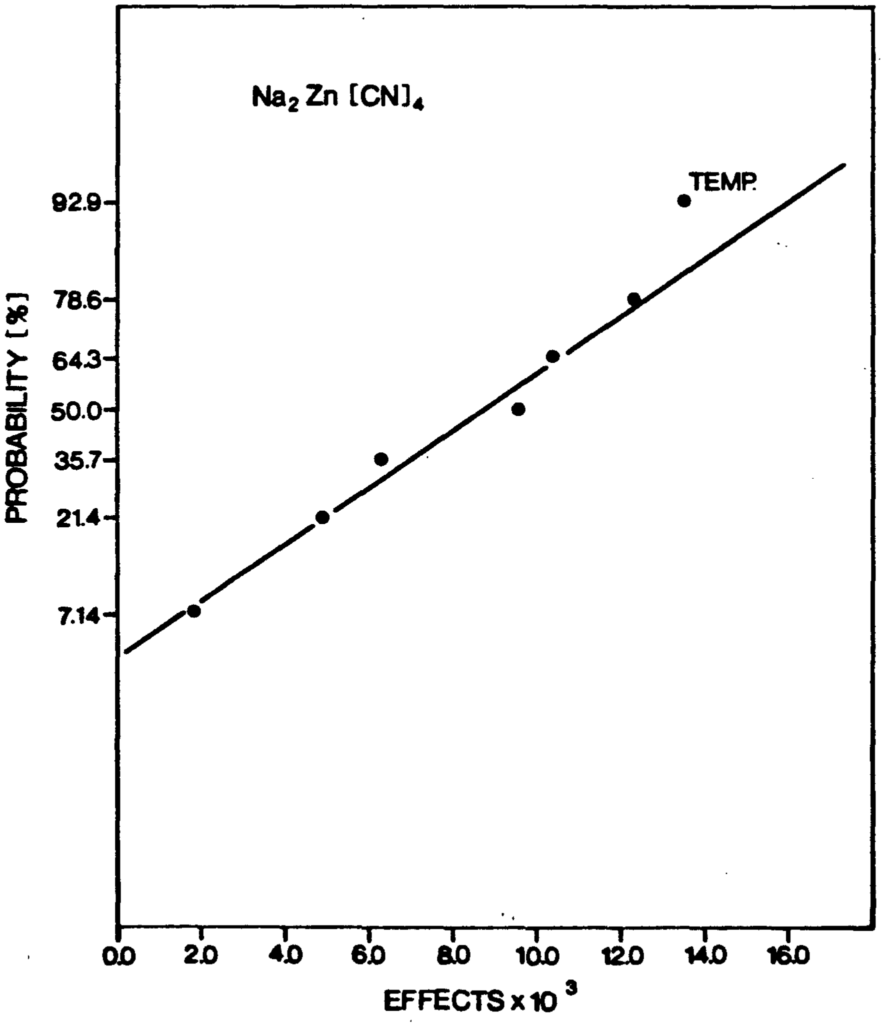


Figure G.3. Half normal probability plot for zinc cyanide complex

Na_2 $Ni(CN)_4$

Order number i	1	2	3	4	5	6	7
Effect $x10^3$	-2.02	-0.93	-0.68	-0.59	+0.21	+0.34	+0.40
Identity of effect	c	ac	ab	abc	bc	a	b
P(%)	7.14	21.4	35.7	50.0	64.3	78.6	92.9

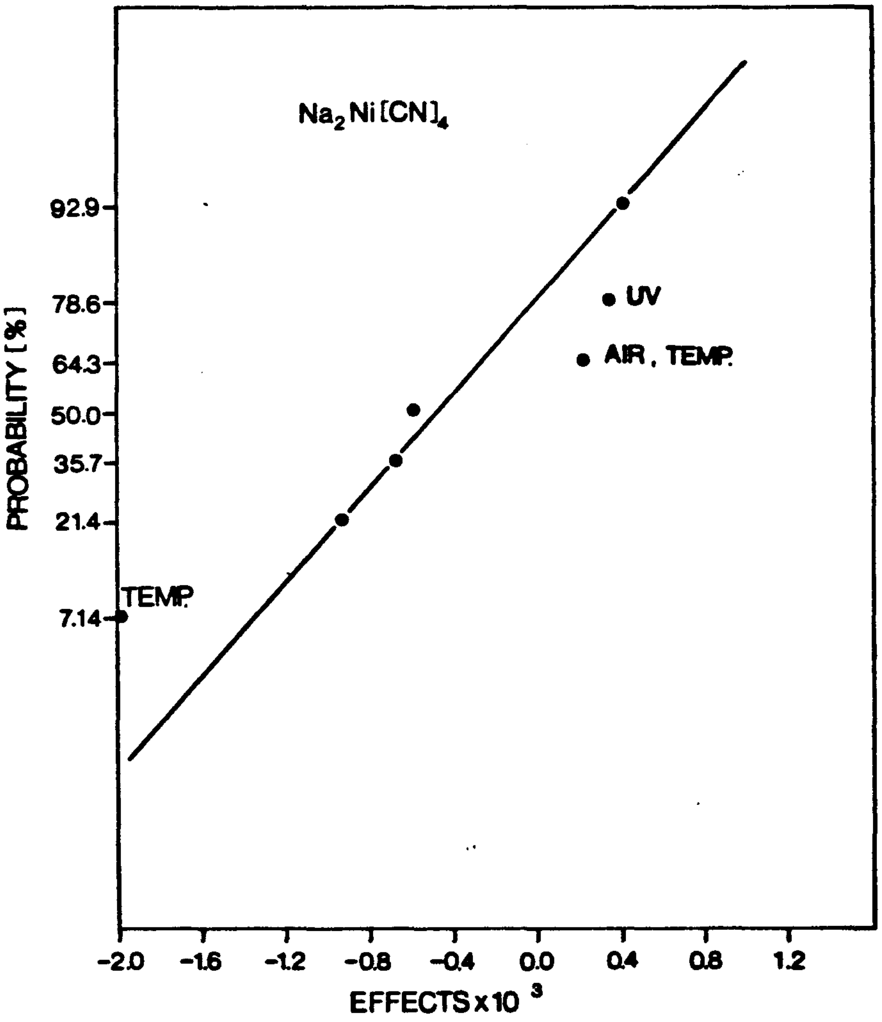


Figure G.4. Half normal probability plot for nickel cyanide complex

$K_3Fe(CN)_6$

Order Number i	1	2	3	4	5	6	7
Effect x10^3	-4.49	-3.76	-3.71	-3.43	+4.39	+5.56	+ 7.97
Identity of effect	bc	abc	b	ab	ac	c	a
P (%)	7.14	21.4	35.7	50.0	64.3	78.6	92.9

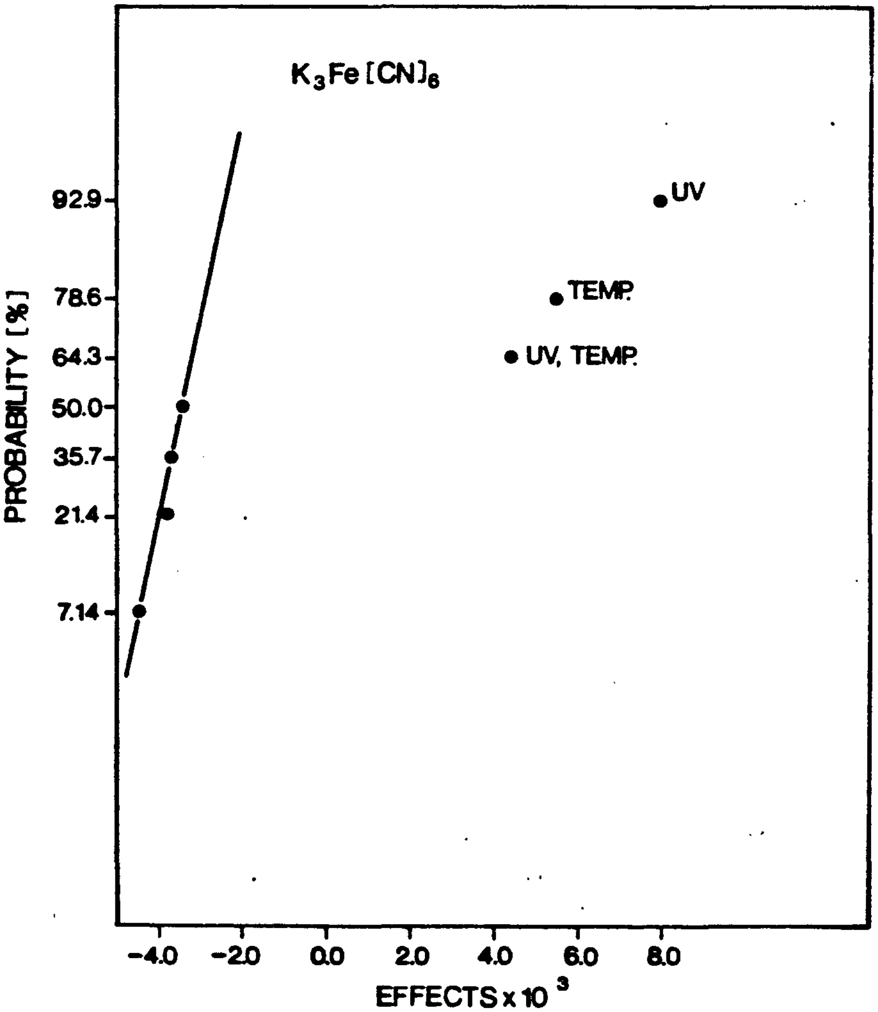


Figure G.5. Half normal probability plot for iron cyanide complex

Low Mix

Order number i	1	2	3	4	5	6	7
Effect x10^3	-0.71	-0.37	-0.26	+0.16	+0.99	+1.48	+1.96
Identity of effect	bc	ac	abc	c	b	ab	a
P(%)	7.14	21.4	35.7	50.0	64.3	78.6	92.9

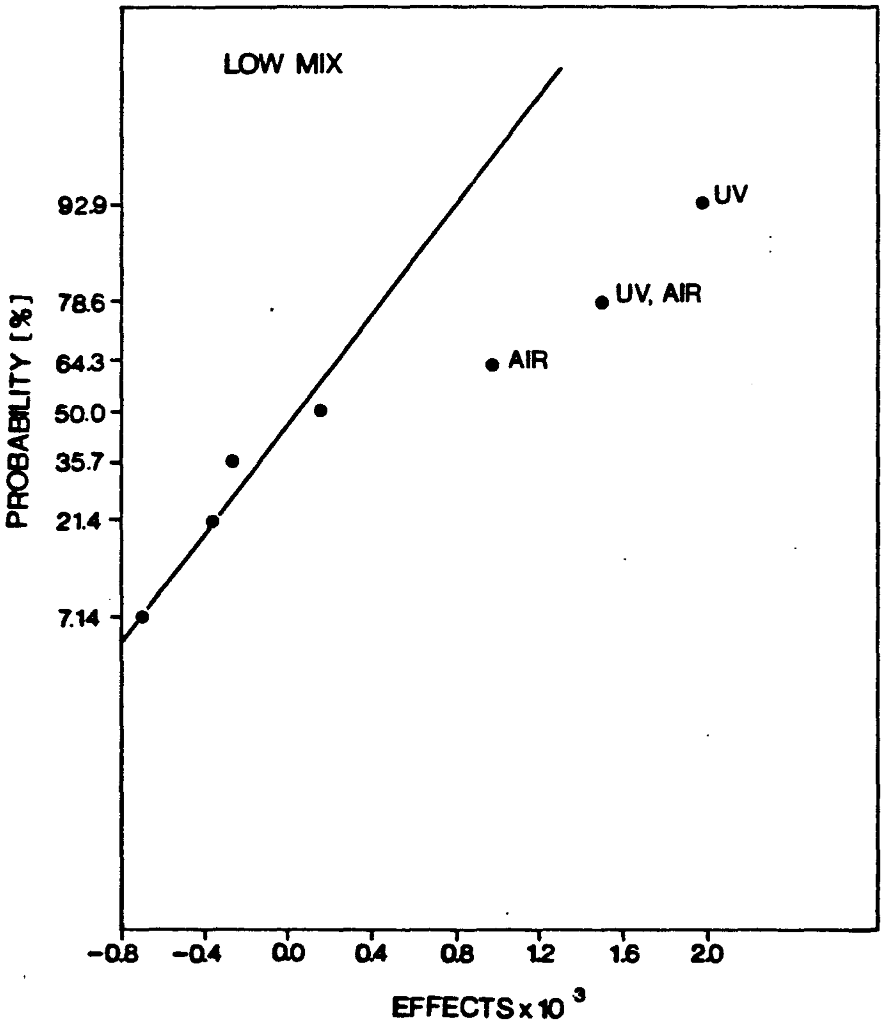


Figure G.6. Half normal probability plot for low mix cyanide solution

High Mix

Order number i	1	2	3	4	5	6	7
Effect x10^3	−0.135	−0.12	+0.025	+0.12	+0.185	+0.27	+1.08
Identity of effect	abc	a	ac	bc	b	ab	c
P(%)	7.14	21.4	35.7	50.0	64.3	78.6	92.9

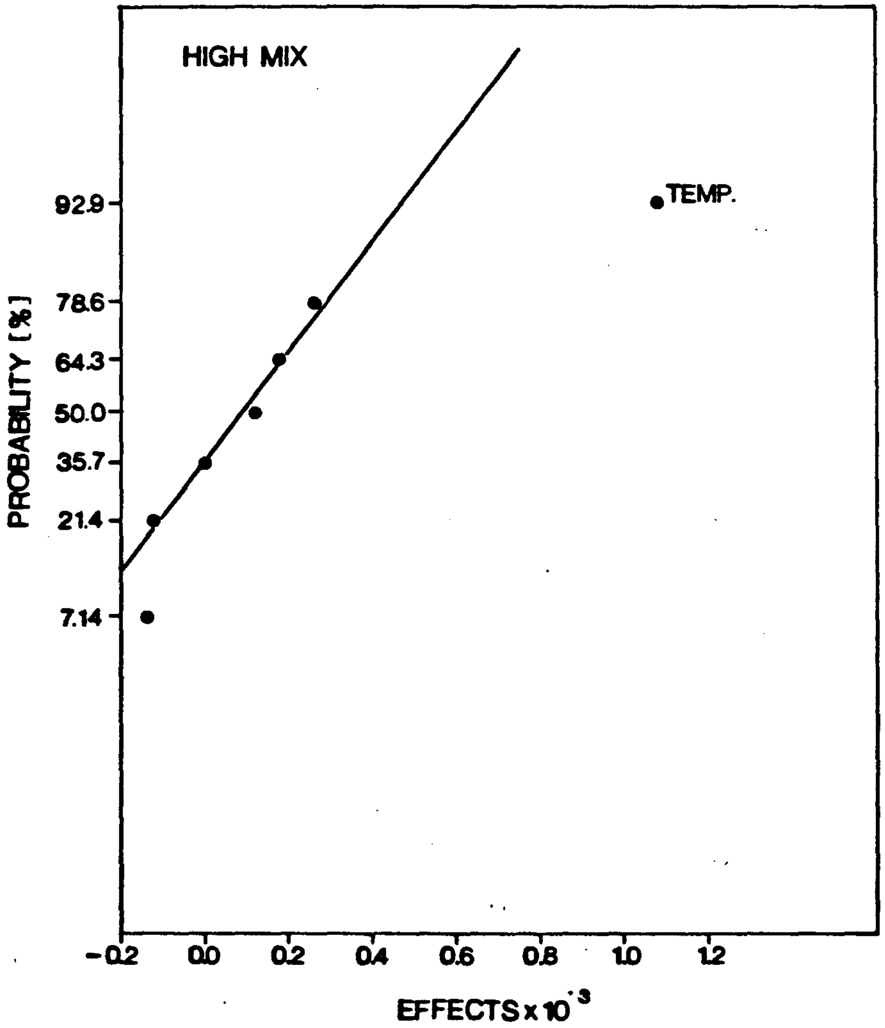


Figure G.7. Half normal probability plot for high mix cyanide solution

APPENDIX G.4

Calculation of 95% Confidence Intervals from the Half Normal Probability Plots

G.4. THE DETERMINATION OF SIGNIFICANT EFFECTS BY CALCULATING 95% CONFIDENCE INTERVAL (CI)

NaCN (See Fig. G.1)

Probability Transform* X	Effects $Y \times 10^3$
7.14	-5.97
9.40	-2.27
10.80	1.27
11.95	4.32
13.15	6.47
14.50	10.27

$$\text{Mean} = 2.35 \times 10^{-3}$$

$$\sigma = 5.92 \times 10^{-3}$$

$$t_5^{0.025} = 2.571$$

Therefore 95% CI on random effects $= \text{Mean} \pm t_{\upsilon}^{0.025}\,\sigma$

$$= 2.35 \times 10^{-3} \pm 2.571\ (5.92 \times 10^{-3})$$

$$= (-12.9 \times 10^{-3},\ 17.5 \times 10^{-3})$$

The temperature effect is significant at 95% confidence level.

---

* "Probability transform" term used in this thesis refers to the lower units (mm) read off the probability graph in order to be able to perform linear regression calculations.

Cu-CN (See Fig. G.2)

Probability Transform X	Effects $Y \times 10^3$
7.14	-2.600
9.40	-2.440
10.80	-0.185
11.95	-0.175

Mean = -1.35×10^{-3}

$\sigma = 1.353 \times 10^{-3}$

$t_3^{0.025} = 3.182$

The 95% CI is = $-1.35 \times 10^{-3} \pm 3.182\ (1.353 \times 10^{-3})$

= $(-5.65 \times 10^{-3},\ 2.95 \times 10^{-3})$

Therefore temperature, air and their interaction are significant at the 95% confidence level.

<u>Zn - CN (See Fig. G.3)</u>

Probability Transform X	Effects Y x 10^3
7.14	1.78
9.40	4.97
10.80	6.33
11.95	9.55
13.15	10.39
14.50	12.33

Mean = 7.56×10^{-3}

$\sigma = 3.91 \times 10^{-3}$

$t_5^{0.025} = 2.571$

95% CI = $7.56 \times 10^{-3} \pm 2.571\ (3.91 \times 10^{-3})$

$= (-2.49 \times 10^{-3},\ \ 17.6 \times 10^{-3})$

Therefore, none of the effects are significant at the 95% confidence level.

Ni - CN (See Fig. G.4)

Probability Transform X	Effects Y x 10^3
9.40	-0.93
10.80	-0.68
11.95	-0.59
13.15	0.21
14.50	0.34
16.60	0.40

Mean = -2.08×10^{-3}

$\sigma = 5.89 \times 10^{-4}$

$t_5^{0.025} = 2.571$

95% CI is = $-2.08 \times 10^{-3} \pm 2.571\ (5.89 \times 10^{-4})$

$= (1.31 \times 10^{-3}, -1.72 \times 10^{-3})$

The effect of temperature is significant at 95% CI.

Fe - CN (See Fig. G.5)

Probability Transform X	Effects $Y \times 10^3$
7.14	-4.49
9.40	-3.76
10.80	-3.71
11.95	3.43

Mean = -3.85×10^{-3}

$\sigma = 4.5 \times 10^{-4}$

$t_3^{0.025} = 3.182$

95% CI = $-3.85 \times 10^{-3} \pm 3.182\ (4.5 \times 10^{-4})$

= $(-5.29 \times 10^{-3}, -2.41 \times 10^{-3})$

Therefore, UV, temperature and their interaction are significant at 95% confidence level.

Low Mix (See Fig. G.6)

Probability Transform X	Effects $Y \times 10^3$
7.14	-0.71
9.40	-0.37
10.80	-0.26
11.95	0.16

Mean = -0.295×10^{-3}

σ = 0.36×10^{-3}

$t_3^{0.0025}$ = 3.182

$$95\%\ \text{CI} = -0.295 \times 10^{-3} \pm 3.182\ (0.36 \times 10^{-3})$$

$$= (-1.43 \times 10^{-3},\ 0.84 \times 10^{-3})$$

Therefore UV, air and their interaction are significant at 95% confidence level.

High Mix (See Fig. G.7)

Probability Transform X	Effects Y x 10^3
9.40	-0.12
10.80	0.02
11.95	0.12
13.15	0.18
14.50	0.27

Mean $= 9.6 \times 10^{-5}$

$\sigma = 1.50 \times 10^{-4}$

$t_4^{0.025} = 2.776$

95% CI $= 9.6 \times 10^{-5} \pm 2.776\ (1.5 \times 10^{-4})$

$= (0.51 \times 10^{-3}, -0.32 \times 10^{-3})$

Therefore, temperature is significant at 95% confidence level.

APPENDIX G.5

Backward Elimination Procedure for the Determination of Significant Effects - Linear Regression with Sequential F-tests

```
****************************************************************
PROGRAM LJUB7
****************************************************************

PROGRAM TO FACILITATE BACKWORD ELIMINATION PROCEDURE: REFERENCES:
    1.) BACKWARD ELIMINATION PROCEDURE: DRAPER & SMITH P. 167-169.
    2.) SEQUENTIAL F-TESTS:- DRAPER & SMITH, P. 72-72.
    3.) EXTRA SUM OF SQUARES:- DRAPER & SMITH, P. 67-68.
    4.) LINEAR REGRESSION USING MATRICES:- DRAPER & SMITH, P. 58-64.
    5.) SUM OF SQUARES FOR LACK OF FIT:- DRAPER & SMITH, P. 30-31.
    6.) COMPUTATIONAL PROCEDURE FOR CORRELATION MATRIX:-
                                             DRPAER & SMITH, P. 178-179.
-----------------------------------------------------------------
INFORMATION TO BE SUPPLIED IN FILE AS FOLLOWING:
   <------- X MATRIX ----------> RESPONSES:
   1  X11  X12  X13  X14 ...X1K      Y1
   1  X21  X22  X23  X24 ...X2K      Y2
   1  X31  X32 .............X3K      Y3
   .   .    .                .        .
   .   .    .                .        .
   .   .    .                .        .
   1  XN1  XN2  XN3  XN4 ...XNK      YN
-----------------------------------------------------------------
INSTRUCTIONS FOR RUNNING PROGRAM:
RU,BAKLM,LU,N,N1,NC,NR     WHERE:
             LU=READ LOGICAL UNIT NO.
             LL=LIST LOGICAL UNIT NO.=6 ('HARDCODED' IN PROGRAM)
             N=NO. OF RUNS=NO. OF ROWS IN X MATRIX
             N1=NO. OF COLS. IN INPUT X-MATRIX
             NC=NO. OF COLS. IN CONSTRUCTED X-MATRIX  FOR:
                NC>0: USER READS IN X-MATRIX AS A (N1,N) MATRIX &
                      THEN MASSAGES INPUT MATRIX TO OBTAIN A (NC,NI
                      MATRIX;  SEE PROGRAM CODE, LINE 139 & BELOW.
                 NC<0 : INPUT MATRIX IS USED AS IS.
             NR=DETERMINES TYPE OF OUTPUT AS FOLLOWS:
                NR>0 : REPICATES:EXPANDED ANOVA TABLE &
                       EXTRA SUM OF SQUARES CALCULATIONS.
                NR=0 : NO REPS: BASIC ANOVA TABLE &
                       EXTRA SUM OF SQUARES CALCULATIONS.
                NR<0 : NO REPS: BASIC ANOVA TABLE ONLY.
             (SEE DRAPER & SMITH P. 62 FOR COMMENT ON REPLICATES)
-----------------------------------------------------------------
USER MUST SUPPLY IN ADDITION:
1.) NAME OF FILE CONTAINING X MATRIX & Y RESPONSE VECTOR,
2.) FROM TABLE: t(n-np,95%), FOR b-VALUE CONFIDENCE LEVELS,
3.) FOR RUNS WHICH INCLUDE REPICATES: SUM OF SQUARES FOR PURE
        ERROR (SSPE) & DEGREES OF FREEDOM ASSOCIATED WITH
        PURE ERROR (DFPE),
4.) FROM TABLES: F(n-np-ne,ne,95%), FOR LACK OF FIT TEST, &
5.) FROM TABLES: F(1,n-np,95%), FOR TESTING PARTIAL F-VALUES.
-----------------------------------------------------------------
```

```
TO LOAD BAKLM:
     LOADR: LI,$HLIB1
     LOADR: LI,$HLIB2
     LOADR: RE,%BAKLM
     LOADR: SL
     LOADR: EN
IF SIZE OF INPUT MATRIX IS GREATER THAN 22 PAGES USE:
     LOADR: OP,LB
     --------------------------------------------------------------------
     INITIALIZE
     IMPLICIT DOUBLE PRECISION (A-H,P-Z)
     DOUBLE PRECISION DSQRT
     VECTORS FOR COL. MEANS & STD. DEV.: CMEAN(NC),CSTD(NC)
     DIMENSION CMEAN(7),CSTD(7)
     MATRICES NECESSARY FOR CARRYING OUT LINEAR REGRESSION:
     X-MATRIX MANIPULATION: X(N,NC),XT(NC,N),XTX(NC,NC),XTY(NC,1)
     DIMENSION X(8,7),XT(7,8),XTX(7,7),XTY(7,1)
     Y-VECTOR MANIPULATION: Y(N,1),YT(1,N)
     DIMENSION Y(8,1),YT(1,8)
     CORRELATION MATRIX: XC(N,NC),XCT(NC,N),XCTXC(NC,NC),COR(NC,NC)
     DIMENSION XC(8,7),XCT(7,8),XCTXC(7,7),COR(7,7)
     B-VECTOR MANIPULATION: B(NC,1),BT(1,NC)
     DIMENSION B(7,1),BT(1,7)
     FOR SUM OF SQUARES:
     DIMENSION SSYM(1,1),SSM(1,1)
     MISCELLANEOUS: IR(NC),IC(NC),E(N,1)
     DIMENSION IR(7),IC(7),E(8,1)
     DIMENSION NAME(5),IP(5),IDBC1(144),IBUF(50)

     MATRICES NECESSARY FOR CALCULATING EXTRA SUM OF SQUARES:
     XD MATRIX MANIPULATION: XD(N,NC-1),XDT(NC-1,N),XDXDT(NC-1,NC-1),XDTY(NC-1,1)
     DIMENSION XD(8,6),XDT(6,8),XDTXD(6,6),XDTY(6,1)
     BD VECTOR MANIPULATION: BD(NC-1,1),BDT(1,NC-1)
     DIMENSION BD(6,1),BDT(1,6)
     FOR SUM OF SQUARES: SSMD(1,1)
     DIMENSION SSMD(1,1)
     MISCELLANEOUS: IDR(NC-1),IDC(NC-1)
     DIMENSION IDR(6),IDC(6)
     --------------------------------------------------------------------
     CALL RMPAR(IP)
     LU=IP(1)
     N=IP(2)
     NI=IP(3)
     NC=IP(4)
     NR=IP(5)
     LL=6
     WRITE(LL,311)LU,LL,N,NI,NC,NR
11   FORMAT(2X,"LU=",I2,5X,"LL=",I2,5X,"N=",I2,5X,
    ("NI=",I2,5X,"NC=",I2,5X,"NR=",I2)

     --------------------------------------------------------------------
```

```
     READ IN AND WRITE OUT NAME OF FILE:
     WRITE(LU,300)
00   FORMAT(2X,"ENTER FILE NAME CONTAINING X MATRIX & Y VECTOR")
     READ(LU,301)NAME
01   FORMAT(3A2)
     WRITE(LL,302)NAME
02   FORMAT(//,2X,"FILE CONTAINING CALIBRATION DATA:",2X,3A2)
     ------------------------------------------------------------------
     OPEN FILE CONTAINING CALIBRATION DATA & READ IN & WRITE OUT DATA:
      CALL OPEN(IDBC1,IERR,NAME)
     IF(IERR.GE.0)GO TO 303
     WRITE(LU,304)
04   FORMAT(2X,"FILE FAILED TO OPEN")
      GO TO 1000
03   CONTINUE
      I1=1
05   CONTINUE
     IL=50
     CALL READF(IDBC1,IERR,IBUF,IL,LEN)
     IF(LEN.EQ.-1)GO TO 306
     CALL CODE
     READ(IBUF,*)(X(I1,J),J=1,N1),Y(I1)
     IF(I1.GE.N)GO TO 306
     I1=I1+1
     GO TO 305
06   CALL CLOSE(IDBC1,IERR)
---------------------------------------------------------------------
     CONVERT FLOWS IN L/MIN TO FLOWS IN L/SEC.
     DO 370 I1=1,N
     CONVERT CLARIFER INFLOWS
     X(I1,3)=X(I1,3)/6.0D1
     CLARIFIER UNDERFLOWS:
     X(I1,4)=X(I1,4)/6.0D1
370   CONTINUE
-------------------------------------------------------------
     IF(NC.LT.0)GO TO 391
-------------------------------------------------------------
     MANIPULATION OF INPUT MATRIX IN ORDER TO EXAMINE INTERATIONS
     DO 390 I1=1,N
     DO 777 K1=3,5
     K2=K1+1
     X(I1,K1)=X(I1,K2)
777  CONTINUE
     X(I1,6)=X(I1,3)*X(I1,5)
     DO 777 K1=4,6
     K2=K1+1
     X(I1,K1)=X(I1,K2)
777  CONTINUE
90   CONTINUE
     NP=NC
     GO TO 724
```

```
91   NP=NI
24   WRITE(LL,901)
01   FORMAT(//,10X,"********** LINEAR LEAST SQUARES **********")
     WRITE(LL,310)
10   FORMAT(//,10X,"---------------X MATRIX & Y VECTOR---------------")
     DO 11 I=1,N
     IM=10
     IF(NP.LT.10)IM=NP
     WRITE(LL,990)(X(I,J),J=1,IM),Y(I)
     IF(NP.LE.10)GO TO 11
     WRITE(LL,723)(X(I,J),J=11,NP)
1    CONTINUE
90   FORMAT(/,1X,11(D10.3,1X))
23   FORMAT(5X,30(D10.3,1X))
     DETERMINE COLUMN MEANS & STANDARD DEVIATIONS:
     DO 701 J=2,NP
     JJ=J-1
     CSUM=0.0D0
     DO 702 I=1,N
02   CSUM=CSUM+X(I,J)
     CMEAN(JJ)=CSUM/N
01   CONTINUE
     YSUM=0.0D0
     DO 703 I=1,N
03   YSUM=YSUM+Y(I)
     CMEAN(NP)=YSUM/N
     YMEAN=CMEAN(NP)
     WRITE OUT THE COLUMN MEANS:
     WRITE(LL,50)
0    FORMAT(//,11X,"COLUMN MEANS:")
     NX=NP-1
     WRITE(LL,51)(CMEAN(J),J=1,NX),CMEAN(NP)
1    FORMAT(11X,20(D10.3,1X))
     DETERMINE COLUMN STANDARD DEVIATIONS:
     DO 706 J=2,NP
     JJ=J-1
     CSUM=0.0D0
     DO 707 I=1,N
07   CSUM=CSUM+((X(I,J)-CMEAN(JJ))**2)
     CSTD(J)=DSQRT(CSUM/(N-1.0D0))
06   CONTINUE
     YSUM=0.0D0
     DO 708 I=1,N
08   YSUM=YSUM+((Y(I)-YMEAN)**2)
     YSTD=DSQRT(YSUM/(N-1.0D0))
     WRITE OUT THE COLUMN STANDARD DEVIATIONS:
     WRITE(LL,52)
2    FORMAT(//,11X,"COLUMN STANDARD DEVIATIONS")
     WRITE(LL,51)(CSTD(J),J=2,NP),YSTD
     DETERMINE TRANSPOSE OF X MATRIX
```

```
      DO 13 I=1,N
      DO 12 J=1,NP
  12  XT(J,I)=X(I,J)
  13  CONTINUE
      WRITE(LL,991)
991   FORMAT(//,5X," X TRANSPOSE")
      DO 14 I=1,NP
  14  WRITE(LL,990)(XT(I,J),J=1,N)
      CARRY OUT MATRIX MULTIPLICATION: XTX=XT*X
      CALL MUT(XT,X,XTX,NP,N,N,NP,NP,NP)
      WRITE(LL,992)
992   FORMAT(//,5X," X PRIME X MATRIX ")
      DO 15 I=1,NP
  15  WRITE(LL,990)(XTX(I,J),J=1,NP)
      COMPUTE & WRITE OUT CORRELATION MATRIX:
      DO 811 I=1,N
      NXX=NP-1
      DO 810 J=1,NXX
      JJ=J+1
10    XC(I,J)=X(I,JJ)
      XC(I,NP)=Y(I)
11    CONTINUE
      WRITE(LL,812)
812   FORMAT(//,5X,"XC MATIX:")
      DO 817 I=1,N
817   WRITE(LL,990)(XC(I,J),J=1,NP)
      DETERMINE TRANSPOSE OF XC MATRIX:
      DO 813 I=1,N
      DO 814 J=1,NP
14    XCT(J,I)=XC(I,J)
13    CONTINUE
      WRITE(LL,815)
815   FORMAT(//,5X,"XCT MATRIX:")
      DO 816 I=1,NP
816   WRITE(LL,990)(XCT(I,J),J=1,N)
      CARRY OUT MATRIX MULT.: XCTXC=XCT*XC
      CALL MUT(XCT,XC,XCTXC,NP,N,N,NP,NP,NP)
      WRITE(LL,804)
804   FORMAT(//,1X,"XCTXC MATRIX:")
      DO 800 I=1,NP
      CSUMI=N*CMEAN(I)
      DO 801 J=1,NP
      CSUMJ=N*CMEAN(J)
01    XCTXC(I,J)=XCTXC(I,J)-((CSUMI*CSUMJ)/N)
      WRITE(LL,990)(XCTXC(I,J),J=1,NP)
00    CONTINUE
      WRITE(LL,805)
05    FORMAT(//,1X,"CORRELATION MATRIX:")
      DO 802 I=1,NP
      DO 803 J=1,NP
```

```
      ZITER=XCTXC(I,I)*XCTXC(J,J)
03    COR(I,J)=XCTXC(I,J)/DSQRT(ZITER)
      IM=10
      IF(NP.LT.10)IM=NP
      WRITE(LL,880)(COR(I,J),J=1,IM)
      IF(NP.LE.10)GO TO 802
      WRITE(LL,881)(COR(I,J),J=11,NP)
80    FORMAT(/,1X,10(F5.2,5X))
81    FORMAT(5X,30(F5.2,5X))
02    CONTINUE
      CARRY OUT INVERSION OF XTX MATRIX:
      CALL GBSIN(XTX,NP,NP,DETA,IER,IR,IC)
      WRITE(LL,994)
994   FORMAT(//,5X,"X TRANSPOSE X-INVERSE")
      DO 16 I=1,NP
 16   WRITE(LL,990)(XTX(I,J),J=1,NP)
      CARRY OUR MATRIX MULTIPLICATION: XTY=XT*Y
      CALL MUT(XT,Y,XTY,NP,N,N,1,NP,1)
      WRITE(LL,220)
20    FORMAT(//,5X,"XTY MATRIX:")
      DO 221 I=1,NP
221   WRITE(LL,990)XTY(I,1)
      CARRY OUT MATRIX MULTIPLICATION: B=XTX-1*XTY
      CALL MUT(XTX,XTY,B,NP,NP,NP,1,NP,1)
      DETERMINE TRANSPOSE OF B MATRIX:
      DO 18 I=1,NP
 18   BT(1,I)=B(I,1)
      DETERMINE TRANSPOSE OF Y MATRIX:
      DO 17 I=1,N
 19   YT(1,I)=Y(I,1)
      CARRY OUT MATRIX MULTIPLICATION: SSYM=YT*Y:
      CALL MUT(YT,Y,SSYM,1,N,N,1,1,1)
      TSSU=SSYM(1,1)
      BSS=N*(YMEAN**2)
      TSSC=TSSU-BSS
      CARRY OUT MATRIX MULTIPLICATION: SSM=BT*XTY
      CALL MUT(BT,XTY,SSM,1,NP,NP,1,1,1)
      XMSS=SSM(1,1)-BSS
      CALCULATE RESIDUAL SUM OF SQUARES:
      RSS=TSSC-XMSS
      DFTU=N
      DFTC=N-1.0D0
      DFM=NP-1.0D0
      DFR=DFTC-DFM
      DFB=1.0D0
      XMSM=XMSS/DFM
      XMSR=RSS/DFR
      F=XMSM/XMSR
      WRITE(LU,783)
83    FORMAT(1X,"ENTER t(n-p,95%) TO DETERMINE CONFIDENCE LIMITS")
      READ(LU,*)STUDE
```

```
      CALCULATE CONFIDENCE LIMITS FOR B's:
      WRITE(LL,780)
80    FORMAT(//,1X,"b-ESTIMATES WITH 95% CONFIDENCE LIMITS")
      DO 781 I=1,NP
      ZA=XTX(I,I)
      ZB=STUDE*DSQRT(XMSR*ZA)
      BPLUS=B(I,1)+ZB
      BMINS=B(I,1)-ZB
      WRITE(LL,785)STUDE,ZA,ZB
785   FORMAT(10X,"t-VALUE=",F15.3,"ZA=",F15.3,"ZB=",F15.3)
      WRITE(LL,782)B(I,1),BMINS,BPLUS
B2    FORMAT(1X,F20.5,10X,F20.5,"-",F20.5)
81    CONTINUE
      DETERMINE COEFFICIENT OF MULTIPLE DETERMINATION
      CMDET=(XMSS/TSSC)*1.0D2
      WRITE(LL,784)CMDET
84    FORMAT(//,1X,"COEFFICIENT OF MULTIPLE DETERMINATION=",
     (1X,F4.1,"%")
      DETERMINE PREDICTED Y'S & RESIDUALS:
      CARRY OF MATRIX MULTIPLICATION: E=X*B
      WRITE(LL,788)
88    FORMAT(//,8X,"PREDICTED VALUES:",15X,"RESIDUALS:")
      CALL MUT(X,B,E,N,NP,NP,1,N,1)
      DO 786 I=1,N
      RES=Y(I)-E(I,1)
      WRITE(LL,787)E(I,1),RES
87    FORMAT(1X,F20.5,5X,F20.5)
86    CONTINUE
      IF(NR.GT.0)GO TO 250
      WRITE(LL,230)
30    FORMAT(//,5X,"********** BASIC ANOVA TABLE **********")
      WRITE(LL,231)
31    FORMAT(//,3X,"SOURCE:",15X,"SS:",15X,"DF:",17X,
     ("MS",17X,"F:")
      WRITE(LL,232)XMSS,DFM,XMSM,F
32    FORMAT(//,3X,"MODEL:",12X,F10.5,7X,F8.0,10X,F10.5,10X,F10.5)
      WRITE(LL,233)RSS,DFR,XMSR
33    FORMAT(//,3X,"RESIDUAL",10X,F10.5,7X,F8.0,10X,F10.5)
      WRITE(LL,54)BSS,DFB
4     FORMAT(//,3X,"MEAN (B0)",9X,F10.5,7X,F8.0)
      WRITE(LL,55)TSSC,DFTC
5     FORMAT(//,3X,"TOTAL (CORR)",6X,F10.5,7X,F8.0)
      WRITE(LL,234)TSSU,DFTU
34    FORMAT(//,3X,"TOTAL (UNCORR)",3X,F10.5,7X,F8.0)
      IF(NR.LT.0)GO TO 3000
      GO TO 264
50    CONTINUE
      READ IN SUM OF SQUARES FOR PURE ERROR (REPEATS) & DEGREES OF FREEDOM:
      WRITE(LU,251)
51    FORMAT(1X,"ENTER SS(p.e.) & DF(p.e), ie. SSPE,DF")
```

```
      READ(LU,*)SSPE,DFPE
      SSLF=RSS-SSPE
      DFLF=DFR-DFPE
      XMSLF=SSLF/DFLF
      XMSPE=SSPE/DFPE
      FLF=XMSLF/XMSPE
      WRITE(LL,253)
53    FORMAT(//,10X,"********** EXPANDED ANOVA TABLE **********")
      WRITE(LL,254)
54    FORMAT(//,3X,"SOURCE:",15X,"SS:",15X,"DF:",
     (15X,"MS:",15X,"F:")
      WRITE(LL,770)XMSS,DFM,XMSM,F
70    FORMAT(//,3X,"MODEL:",12X,F10.5,7X,F8.0,10X,F10.5,10X,F10.5)
      WRITE(LL,771)RSS,DFR,XMSR
71    FORMAT(//,3X,"RESIDUAL",10X,F10.5,7X,F8.0,10X,F10.5)
      WRITE(LL,772)SSLF,DFLF,XMSLF,FLF
72    FORMAT(//,5X,"LACK OF FIT",5X,F10.5,7X,F8.0,
     (10X,F10.5,10X,F10.5)
      WRITE(LL,773)SSPE,DFPE,XMSPE
73    FORMAT(//,5X,"PURE ERROR",6X,F10.5,7X,F8.0,10X,F10.5)
      WRITE(LL,774)BSS,DFB
74    FORMAT(//,3X,"MEAN (B0)",9X,F10.5,7X,F8.0)
      WRITE(LL,775)TSSC,DFTC
75    FORMAT(//,3X,"TOTAL (CORR)",6X,F10.5,7X,F8.0)
      WRITE(LL,776)TSSU,DFTU
76    FORMAT(//,3X,"TOTAL (UNCORR)",4X,F10.5,7X,F8.0)
64    CONTINUE
      DETERMINE EXTRA SUM OF SQUARES FOR EACH B:
      WRITE(LL,402)
02    FORMAT(//,10X,"********** EXTRA SUM OF SQUARES **********")
      NPD=NP-1
      DO 2000 IK=2,NP
      DETERMINE DUMMY MATRIX, XD, USED IN EXTRA SUM OF SQUARES CALCULATIONS:
      JJ=1
      DO 401 J=1,NP
      IF(J.EQ.IK)JJ=JJ+1
      DO 400 II=1,N
00    XD(II,J)=X(II,JJ)
      JJ=JJ+1
01    CONTINUE
      WRITE(LL,403)
403   FORMAT(//,10X,"---------- XD MATRIX & YD VECTOR ---------")
      DO 404 I=1,N
404   WRITE(LL,990)(XD(I,J),J=1,NPD),Y(I)
      DETERMINE TRANSPOSE OF XD MATRIX
      DO 405 I=1,N
      DO 406 J=1,NPD
06    XDT(J,I)=XD(I,J)
05    CONTINUE
      WRITE(LL,407)
```

```
07   FORMAT(//,5X," XD TRANSPOSE")
     DO 408 I=1,NPD
408  WRITE(LL,990)(XDT(1,J),J=1,N)
     CARRY OUT MATRIX MULTIPLICATION: XXTXD=XDT*XD
     CALL MUT(XDT,XD,XDTXD,NPD,N,N,NPD,NPD,NPD)
     WRITE(LL,409)
409  FORMAT(//,5X," XD PRIME XD MATRIX ")
     DO 410 I=1,NPD
410  WRITE(LL,990)(XDTXD(1,J),J=1,NPD)
     CARRY OUT INVERSION OF XDTXD MATRIX:
     CALL GBSIN(XDTXD,NPD,NPD,DETA,IER,IDR,IDC)
     WRITE(LL,411)
11   FORMAT(//,5X,"XD TRANSPOSE XD-INVERSE")
     DO 412 I=1,NPD
412  WRITE(LL,990)(XDTXD(1,J),J=1,NPD)
     CARRY OUT MATRIX MULTIPLICATION: XDTY=XDT*Y
     CALL MUT(XDT,Y,XDTY,NPD,N,N,1,NPD,1)
     WRITE(LL.413)
13   FORMAT(//,5X,"XDTY MATRIX:")
     DO 414 I=1,NPD
414  WRITE(LL,990)XDTY(I,1)
     CARRY OUT MATRIX MULTIPLICATION: BD=XDTXD-1*XDTY
     CALL MUT(XDTXD,XDTY,BD,NPD,NPD,NPD,1,NPD,1)
     WRITE(LL,415)
415  FORMAT(//,5X,"LLAST SQUARES ESTIMATES--BD-VALUES")
     DO 416 I=1,NPD
416  WRITE(LL,990) BD(1,1)
     DETERMINE TRANSPOSE OF BD MATRIX:
     DO 417 I=1,NPD
17   BDT(1,I)=BD(I,1)
     CARRY OUT MATRIX MULTIPLICATION: SSMD=BDT*XDTY
     CALL MUT(BDT,XDTY,SSMD,1,NPD,NPD,1,1,1)
     XMDSS=SSMD(1,1)-BSS
     WRITE(LL,710)XMDSS
710  FORMAT(//,7X,"MODEL SUM OF SQUARES=",1X,F20.5)
     EXSS=XMSS-XMDSS
     DFXS=1.0D0
     FXS=EXSS/XMSR
     III=IK-1
     IF(III.GT.1)GO TO 419
     WRITE(LL,420)
20   FORMAT(//,3X,"ADDED LAST:",11X,"SS:",15X,"DF:",17X,
    ("MS:",17X,"F:")
19   WRITE(LL,421)III,EXSS,DFXS,EXSS,FXS
21   FORMAT(//,3X,"B(",I2,")",13X,F10.5,7X,F8.0,
    (10X,F10.5,10X,F10.5)
000  CONTINUE
000  CONTINUE
```

```
000  STOP
     END
     SUBROUTINE GBSIN(A,IA,MA,DETA,IER,IR,IC)
      IMPLICIT DOUBLE PRECISION (A-H,P-Z)
     DIMENSION A(IA,IA),IR(MA),IC(MA)

     CCIW MATRIX INVERSION

      IF(IA-MA) 1,2,2
   1 WRITE(6,13)
      IER=1
     RETURN
   2 IER=0
     DO 3 I=1,MA
      IR(I)=0
   3 IC(I)=0
      DETA=1.
     DO 8 IJKL=1,MA
     CALL GBS99(A,IA,IA,MA,MA,IR,IC,I,J)
      PIV=A(I,J)
     DETA=PIV*DETA
      IF(PIV.EQ.0.0) GO TO 12
     IR(I)=J
      IC(J)=I
     PIV=1./PIV
      DO 4 K=1,MA
   4 A(I,K)=A(I,K)*PIV
      A(I,J)=PIV
     DO 6 K=1,MA
      IF(K.EQ.I) GO TO 6
     PIV1=A(K,J)
      DO 5 L=1,MA
   5 A(K,L)=A(K,L)-PIV1*A(I,L)
      A(K,J)=PIV1
   6 CONTINUE
      PIV1=A(I,J)
     DO 7 K=1,MA
   7 A(K,J)=-PIV*A(K,J)
     A(I,J)=PIV1
   8 CONTINUE
     DO 11 I=1,MA
     K=IC(I)
     M=IR(I)
     IF(K.EQ.I) GO TO 11
      DETA=-DETA
     DO 9 L=1,MA
      TEMP=A(K,L)
     A(K,L)=A(I,L)
   9 A(I,L)=TEMP
     DO 10 L=1,MA
```

```
      TEMP=A(L,M)
      A(L,M)=A(L,I)
   10 A(L,I)=TEMP
      IC(M)=K
      IR(K)=M
   11 CONTINUE
      RETURN
   12 IER=1
      RETURN
   13 FORMAT(1H ,"ERROR - DIMENSION OF WORK VECTOR IS < DIMENSION OF M
     *ATRIX ")
      END
      SUBROUTINE GBS99(A,IA,JA,MA,NA,IR,IC,I,J)
      IMPLICIT DOUBLE PRECISION (A-H,P-Z)
      DOUBLE PRECISION DABS
      DIMENSION A(IA,JA),IR(MA),IC(NA)

      THIS SUBR IS CALLED BY THE MAT INVERSION SUBR

      I=0
      J=0
      TEST=0.0
      DO 2 K=1,MA
      IF(IR(K).NE.0) GO TO 2
      DO 1 L=1,NA
      IF(IC(L).NE.0) GO TO 1
      X=DABS(A(K,L))
      IF(X.LT.TEST) GO TO 1
      I=K
      J=L
      TEST=X
    1 CONTINUE
    2 CONTINUE
      RETURN
      END
      SUBROUTINE ADD(A,B,C,M,N,X)
      IMPLICIT DOUBLE PRECISION (A-H,P-Z)
      DIMENSION A(M,N),B(M,N),C(M,N)
      DO 1 I=1,M
      DO 1 J=1,N
1     C(I,J)=A(I,J)+X*B(I,J)
      RETURN
      END
      SUBROUTINE MUT(A,B,C,MA,NA,MB,NB,MC,NC)
      IMPLICIT DOUBLE PRECISION (A-H,P-Z)
      DIMENSION A(MA,NA),B(MB,NB),C(MC,NC)
      DO 1 J=1,NB
      DO 2 I=1,MA
      SUM=0.
      DO 3 K=1,NA
```

```
      SUM=SUM+A(I,K)*B(K,J)
3     CONTINUE
      C(I,J)=SUM
2     CONTINUE
1     CONTINUE
      RETURN
      END
      SUBROUTINE MUTS(X,A,C,M,N)
      IMPLICIT DOUBLE PRECISION (A-H,P-Z)
      DIMENSION A(M,N),C(M,N)
      DO 1 I=1,M
      DO 1 J=1,N
1     C(I,J)=X*A(I,J)
      RETURN
      END
```

The Output from the Backward Elimination Program

(LJUB7)

```
LU= 1     LL= 6     N= 8     NI= 7     NC=-1     NR= 0

FILF CONTAINING CALIBRATION DATA:  SD07

FILE CONTAINING CALIBRATION DATA:

       ********** LINEAR LEAST SQUARES **********

       ----------------X MATRIX & Y VECTOR----------------

 .100D+01  -.100D+01  -.100D+01  -.100D+01   .100D+01   .100D+01   .100D+01   .503D-02

 .100D+01   .100D+01  -.100D+01  -.100D+01  -.100D+01  -.100D+01   .100D+01   .139D-01

 .100D+01  -.100D+01   .100D+01  -.100D+01  -.100D+01   .100D+01  -.100D+01   .740D-02

 .100D+01   .100D+01   .100D+01  -.100D+01   .100D+01  -.100D+01  -.100D+01   .234D-01

 .100D+01  -.100D+01  -.100D+01   .100D+01   .100D+01  -.100D+01  -.100D+01   .238D-01

 .100D+01   .100D+01  -.100D+01   .100D+01  -.100D+01   .100D+01  -.100D+01   .253D-01

 .100D+01  -.100D+01   .100D+01   .100D+01  -.100D+01  -.100D+01   .100D+01   .394D-01

 .100D+01   .100D+01   .100D+01   .100D+01   .100D+01   .100D+01   .100D+01   .389D-01

        COLUMN MEANS:
          .000D+00   .000D+00   .000D+00   .000D+00   .000D+00   .000D+00   .221D-01

        COLUMN STANDARD DEVIATIONS
          .107D+01   .107D+01   .107D+01   .107D+01   .107D+01   .107D+01   .129D-01

CORRELATION MATRIX:

 1.00      0.00      0.00      0.00      0.00      0.00       .27

 0.00      1.00      0.00      0.00      0.00      0.00       .42

 0.00      0.00      1.00      0.00      0.00      0.00       .80

 0.00      0.00      0.00      1.00      0.00      0.00       .05

 0.00      0.00      0.00      0.00      1.00      0.00      -.25
```

```
0.00      0.00      0.00      0.00      0.00      1.00      .18

 .27       .42       .80       .05      -.25       .18      1.00


b-ESTIMATES WITH 95% CONFIDENCE LIMITS
             .02214                         .01935-            .02493
             .00323                         .00044-            .00603
             .00513                         .00234-            .00793
             .00971                         .00692-            .01254
             .00064                        -.00215-            .00343
            -.00298                        -.00578-           -.00019
             .00217                        -.00063-            .00496


COEFFICIENT OF MULTIPLE DETERMINATION= 99.1%


       PREDICTED VALUES:              RESIDUALS:
             .00389                    .00114
             .01504                   -.00114
             .00854                   -.00114
             .02226                    .00114
             .02494                   -.00114
             .02416                    .00114
             .03826                    .00114
             .04004                   -.00114


    ********** BASIC ANOVA TABLE **********


  SOURCE:             SS:            DF:            MS               F:


  MODEL:              .00116          6.            .00019          18.56486


  RESIDUAL            .00001          1.            .00001


  MEAN (B0)           .00392          1.


  TOTAL (CORR)        .00117          7.


  TOTAL (UNCORR)     .00509          8.
```

```
          ********** EXTRA SUM OF SQUARES **********

ADDED LAST:        SS:           DF:             MS:            F:

B( 1)             .00008          1.            .00008        8.02081

B( 2)             .00021          1.            .00021       20.23522

B( 3)             .00075          1.            .00075       72.37109

B( 4)             .00000          1.            .00000         .31571

B( 5)             .00007          1.            .00007        6.83539

B( 6)             .00004          1.            .00004        3.60293
```

APPENDIX H.1

Example Calculation of the Initial Theoretical Metal Cyanide Concentration

H.1 CALCULATION OF THEORETICAL METAL CYANIDE CONCENTRATION AT THE BEGINNING OF EXPERIMENT (EXAMPLE CALCULATION FOR Fe-CN at 4°C, AIR, UV)

Measured total cyanide $[\mathrm{TCN}]_o$ = 193 mg/L = 0.00742 mol/L. Analytically determined metal concentration $[\mathrm{Fe}^{3+}]$ = 12.04 mg/L. The stoichiometric relationship for ferricyanide is

$$\frac{[(\mathrm{CN})_6^{3-}]}{[\mathrm{Fe}^{3+}]} = 2.795$$

where molecular weight for cyanide is MW_{CN^-} = 26.02 g/mol and molecular weight for iron is $MW_{Fe^{3+}}$ = 55.85 g/mol. Therefore, the initial cyanide concentration tied up with iron present will be: $[\mathrm{MCN}]_o$ = 2.795 x 12.04 = 33.65 mg/L = 0.00129 mol/L and the initial free-cyanide value will be:

$$[\mathrm{FCN}]_o = [\mathrm{TCN}]_o - [\mathrm{MCN}]_o = 0.00742 - 0.00129 = 0.00613 \text{ mol/L}.$$

APPENDIX H.2

Computer Program Used for Four-Parameter Estimation Model

(FCN, MCN, k_v, k_l)

(Example: Synthenic Iron-Cyanide at 4°C, AIR, UV)

```
      PROGRAM TST(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,
     +DEBUG=OUTPUT,TAPE11)
      DIMENSION Y(25),TH(4),DIFF(4),SIGNS(4),SCRAT(6000)
C*********************************************************
C     FOUR PARAMETER MODEL
C*********************************************************
      COMMON /B/ X(25),YP(6,61),DELT,NTSTEP,TT(61),NT1,YINIT
      EXTERNAL MODEL
      DATA NP,MIT/4,15/
      DATA NOB/15/
      DATA NPROB/1/
      DATA EPS1,EPS2,FLAM,FNU/1.E-6,1.E-6,0.01,10./
      READ(5,*) (TH(I),I=1,NP)
      WRITE(6,100) (TH(I),I=1,NP)
 100  FORMAT(4F12.9)
      READ(5,*) (X(I),Y(I),I=1,NOB)
      WRITE(6,*) (X(I),Y(I),I=1,NOB)
      YAV=0.
      DO 30 I=1,NOB
 30   YAV=YAV+Y(I)
      YAV=YAV/FLOAT(NOB)
      TSS=0.
      DO 35 I=1,NOB
 35   TSS=TSS+(Y(I)-YAV)**2
      TSOS=TSS/(26000.**2)
      WRITE(6,200)TSOS
 200  FORMAT(1X,"TOTAL SUM OF SQUARES IS"E14.7)
      DO 40 J=1,NOB
      Y1=Y(J)/26000.
      Y(J)=Y1
      CALL PLOTPT(X(J),Y1,5)
  40  CONTINUE
      YINIT=Y(1)
      DELT=2.
      NTSTEP=X(NOB)/DELT
      DO 45 I=1,NP
      DIFF(I)=0.01
  45  SIGNS(I)=1.0
      CALL UWHAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT,
     +FLAM,FNU,SCRAT,6)
C     CALL MODEL (NPROB,TH,F,NOB,NP)
      DO 50 J=1,NT1
```

```
      T=TT(J)
      CALL PLOTPT (T,YP(1,J),4)
      CALL PLOTPT (T,YP(2,J),2)
      CALL PLOTPT (T,YP(3,J),20)
   50 CONTINUE
      CALL OUTPLT
      STOP
      END

      SUBROUTINE MODEL(NPROB,TH,F,NOB,NP)
      DIMENSION TH(4),F(25)
      COMMON /B/ X(25),YP(6,61),DELT,NTSTEP,TT(61),NT1,YINIT
      INTEGER  N,IND,NW,IER,K
      REAL IX,IY
      REAL    YY(3),C(24),W(3,9),XX,TOL,XEND
      COMMON /A/ RKC,VK,UVKN,XK,YK,IX,IY
      EXTERNAL FCN1
      NW=3
      N=3
      XX=0.0
      ITMAX=1
      IF(NTSTEP.GT.60)ITMAX=(NTSTEP/60.)+1
      YY(1)=TH(1)
      YY(2)=TH(2)
      F(1)=YINIT
C     CONSTANT DELT MUST BE LESS THAN OR EQUAL TO MINIMUM
C     TIME BETWEEN OBSERVATIONS
      T=0.
      JOBS=2
      VK=.0364340
      XK=TH(3)
      YK=TH(4)
      IX=5
      IY=4
      YY(3)=F(1)-(IX*YY(1)+IY*YY(2))
      TT(1)=T
      YP(1,1)=YY(3)
      YP(2,1)=IX*YY(1)+IY*YY(2)
      YP(3,1)=YP(1,1)+YP(2,1)
      TOL=0.0001
      IND=1
      DO 55 K=1,NTSTEP
```

```
      XEND=FLOAT(K)*DELT
      CALL DVERK (N,FCN1,XX,YY,XEND,TOL,IND,C,NW,W,IER)
      IF (IND.LT.0.OR.IER.GT.0)  GOTO 400
      T=T+DELT
      JPRED=(X(JOBS)/DELT)
      YYY=IX*YY(1)+IY*YY(2)+YY(3)
      IF(JPRED.EQ.K)F(JOBS)=YYY
      IF(JPRED.EQ.K)JOBS=JOBS+1
      IF(((K/ITMAX)*ITMAX).EQ.K)GO TO 300
      GO TO 55
300   KK=(K/ITMAX)
      TT(KK+1)=T
      YP(1,KK+1)=YY(3)
      YP(2,KK+1)=IX*YY(1)+IY*YY(2)
      YP(3,KK+1)=YY(3)+YP(2,KK+1)
  55  CONTINUE
400   CONTINUE
      NT1=KK+1
      RETURN
      END
      SUBROUTINE FCN1(N,XX,YY,YPRIME)
      COMMON /A/ RKC,UK,UUKN,XK,YK,IX,IY
      REAL      YY(N),YPRIME(N),XX,IX,IY
      YPRIME(1)=-XK*(YY(1))
      YPRIME(2)=(XK*(YY(1)))-(YK*(YY(2)))
      YPRIME(3)=(IX*XK*YY(1))-(IY*XK*YY(1))+(IY*YK*(YY(2)))-
     +(UK*.99*YY(3))
      RETURN
      END
      SUBROUTINE UWHAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,
     1  MIT, FLAM, FNU, SCRAT,LL)
      DIMENSION SCRAT(1)
      IA=1
      IB=IA+NP
      IC=IB+NP
      ID=IC+NP

      IF=IE+NP
      IG=IF+NOB
      IH=IG+NOB
      II = IH + NP * NOB
      IJ = IH
           CALL  HAUS9(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT
     1  ,FLAM,FNU,SCRAT(IA), SCRAT(IB), SCRAT(IC), SCRAT(ID),
```

```
     2 SCRAT(IE), SCRAT(IF), SCRAT(IG), SCRAT(IH), SCRAT(II),
     3 SCRAT(IJ),LL)
      RETURN
      END
      SUBROUTINE HAUS9(NPRBO, MODEL, NBO, Y,NQ,TH,DIFZ,SIGNS,EP1S,EP2S,
     1MIT,FLAM,FNU,    Q,P,E,PHI,TB,F,R,A,D,DELZ,LL)
C$    STORES(GA,Q,TEMP,A,P,SDEV,FNU,D,R,EPS,DELZ)
C
C     DIMENSION TH(NQ), DIFZ(NQ), SIGNS(NQ), Y(NBO)
C     DIMENSION Q(NQ), P(NQ), E(NQ), PHI(NQ), TB(NQ)
C     DIMENSION F(NBO), R(NBO)
C     DIMENSION A(NQ,NQ), D(NQ,NQ), DELZ(NBO,NQ)
C
      DIMENSION TH(1), DIFZ(1), SIGNS(1), Y(1), Q(1), P(1), E(1),
     1   PHI(1), TB(1), F(1), R(1), A(1), D(1), DELZ(1)
      ACOS(X) = ATAN(SQRT(1.0/X**2 - 1.0))
      NP = NQ
      NPROB = NPRBO
      NOB = NBO
      EPS1 = EP1S
      EPS2 = EP2S
      NPSQ = NP * NP
       NSCRAC = 5*NP+NPSQ +2*NOB+NP*NOB
       WRITE(LL,1000) NPROB, NOB, NP, NSCRAC
      WRITE(LL,1001)
       CALL GASS0(1, NP, TH, TEMP, TMEP,LL)
      WRITE(LL,1002)
       CALL GASS0(1, NP, DIFZ, TEMP, TEMP,LL)
      IF(MIN0(NP-1,50-NP,NOB-NP,MIT-1,999-MIT))99,15,15
 15   IF(FNU-1.0)99, 99, 16
 16   CONTINUE
      DO 19 I=1,NP
      TEMP = ABS(DIFZ(I))
      IF(AMIN1(1.0-TEMP, ABS(TH(I))))99, 99, 19
 19   CONTINUE
      GA = FLAM
      NIT = 1
      LAOS = 0
      IF(EPS1) 5,70,70
 5    EPS1 = 0
   70 SSQ = 0
      CALL MODEL(NPROB, TH, F, NOB, NP)
      DO 90 I = 1, NOB
```

```
      R(I) = Y(I) - F(I)
   90 SSQ=SSQ+R(I)*R(I)
      WRITE(LL,1003)SSQ
C
C                                                BEGIN ITERATION
C
  100 GA = GA / FNU
      INTCNT = 0
      WRITE(LL,1004)NIT
  101 JS = 1 - NOB
      DO 130 J=1,NP
      TEMP = TH(J)
      P(J)=DIFZ(J)*TH(J)
      TH(J)= TH(J)+P(J)
      Q(J)=0
      JS = JS + NOB
C     WRITE(6,10)J
   10 FORMAT(1H ,*$$$*,I5)
C***
      CALL MODEL(NPROB, TH, DELZ(JS), NOB, NP)
      IJ = JS-1
      DO 120 I = 1, NOB
      IJ = IJ + 1
      DELZ(IJ) = DELZ(IJ) - F(I)
  120 Q(J) = Q(J) + DELZ(IJ) * R(I)
      Q(J)= Q(J)/P(J)
C                                      Q=XT*R (STEEPEST DESCENT)
  130 TH(J) = TEMP
      IF(LAOS) 131,131,414
  131 DO 150 I = 1, NP
      DO 151 J=1,I
      SUM = 0
      KJ = NOB*(J-1)
      KI = NOB*(I-1)
      DO 160 K = 1, NOB
      KI = KI + 1
      KJ = KJ + 1
  160 SUM = SUM + DELZ(KI) * DELZ(KJ)
      TEMP= SUM/(P(I)*P(J))
      JI = J + NP*(I-1)
      D(JI) = TEMP
      IJ = I + NP*(J-1)
  151 D(IJ) = TEMP
```

```
 150  E(I) = SQRT(D(JI))
 666  CONTINUE
      DO 153  I = 1, NP
      IJ = I-NP
.0,TB(IO 153 J=1,I
, 221
 221  CONTINUE
      SUMB=0
      CALL MODEL(NPROB, TB, F, NOB, NP)
      DO 230 I=1,NOB
      R(I)=Y(I)-F(I)
230   SUMB=SUMB+R(I)*R(I)
      WRITE(LL,1043)SUMB
      IF(SUMB - (1.0+EPS1)*SSQ) 662, 662, 663
 663  IF( AMIN1(TEMP-30.0, GA)) 665, 665, 664
665   STEP=STEP/2.0
      INTCNT = INTCNT + 1
      IF(INTCNT - 36) 170, 2700, 2700
  664 GA=GA*FNU
      INTCNT = INTCNT + 1
      IF(INTCNT - 36) 666, 2700, 2700
 662  WRITE(LL,1007)
      DO 669 I=1,NP
669   TH(I)=TB(I)
       CALL GASS0(1, NP, TH, TEMP, TEMP,LL)
      WRITE(LL,1040) GA, SUMB
      IF(EPS2) 229,229,225
  229 IF(EPS1) 270,270,265
 225  DO 240 I = 1, NP
      IF(ABS(P(I))/(1.E-20+ABS(TH(I)))-EPS2) 240, 240, 241
  241 IF(EPS1) 270,270,265
  240 CONTINUE
      WRITE(LL,1009)EPS2
      GO TO 280
 265  IF(ABS(SUMB - SSQ) - EPS1*SSQ) 266, 266, 270
 266  WRITE(LL,1010) EPS1
      GO TO 280
270   SSQ=SUMB
      NIT=NIT+1
      IF(NIT - MIT) 100, 100, 280
 2700 WRITE(LL,2710)
 2710 FORMAT(//115H0**** THE SUM OF SQUARES CANNOT BE REDUCED TO THE SUM
     1OF SQUARES AT THE END OF THE LAST ITERATION - ITERATING STOPS   /)
```

```
C                                            END ITERATION
C
 200  WRITE(LL,1011)
      WRITE(LL,2001) (F(I), I = 1, NOB)
      WRITE(LL,1012)
      WRITE(LL,2001) (R(I), I = 1, NOB)
      WRITE(LL,1017)
 1017 FORMAT(////," X PRIME-X MATRIX")
      CALL GASS0(4,NP,TEMP,TEMP,D,LL)
      SSQ=SUMB
      IDF=NOB-NP
      WRITE(LL,1015)
      I=0
       CALL MATIN(D, NP, P, I, DET)
      DO 7692 I=1,NP
      II = I + NP*(I-1)
 7692 E(I) = SQRT(D(II))
      DO 340 I=1,NP
      JI = I + NP*(I-1) - 1
      IJ = I + NP*(I-2)
      DO 340 J = I, NP
      JI = JI + 1
      A(JI) = D(JI) / (E(I)*E(J))
      IJ = IJ + NP
 340   A(IJ) = A(JI)
       CALL GASS0(3, NP, TEMP, TEMP, A,LL)
      WRITE(LL,1016)
       CALL GASS0(1, NP, E, TEMP, TEMP,LL)
      IF(IDF) 341, 410, 341
 341  DEV = SSQ / IDF
      W14) SDEV, IDF
    DEV)
      DO 391 I=1,NP
      P(I)=TH(I)+2.0*E(I)*SD391   TB(I)=TH(I)-2.0       WRITE(LL,1039)
       CALL GASS0(2, NP, TB, P, TEMP,LL)
     LAOS = 1
      GO TO 101
 414  DO 415 K = 1, NOB
      TEMP = 0
      DO 420 I=1,NP
      DO 420 J=1,NP
      ISUB = K+N  DEBUG1 = DELZ(ISUB = DELZ(K + NOB*(I-1))
      ISUB = K+NOB*(J-1)
```

```
      DEBUG2 = DELZ(ISUB)
C     DEBUG2 = DELZ(K + NOB*(J-1))
      IJ = I + NP*(J-1)
      DEBUG3 = D(IJ)/(DIFZ(I)*THDIFZ(J)*TH(J))
+ DEBUG1 * DEBUG2 * TEMP = 2.0*SQRT(TEMP(K)=F(K)+TEMP
 415  F(K)=F(K)-TEMP
      WRITE(LL,1000)
      IE=0
      DO 425 I=1,NOB,5
      IE=IE+5
      IF(NOB-IE) 430,435,435
  430 IE=NOB
 435  WRITE(LL,2001) (R(J), J = I, IE)
 425  WRITE(LL,2006) (F(J), J = I, IE)
 410  WRITE(LL,1033) NPROB
      RETURN
 99   WRITE(LL,1034)
      GO TO 410
 1000 FORMAT(30H1NON-LINEAR ESTIMATION, PROBLEM NUMBER   I3,// I5,
     1  14H OBSERVATIONS, I5, 11H PARAMETERS  I7, 17H SCRATCH REQUIRED)
 1001 FORMAT(/25H0INITIAL PARAMETER VALUES   )
 1002 FORMAT(/54H0PROPORTIONS USED IN CALCULATING DIFFERENCE QUOTIENTS )
 1003 FORMAT(/25H0INITIAL SUM OF SQUARES =   E12.4)
 1004 FORMAT(/////45X,13HITERATION NO.  I4)
 1007 FORMAT(/32H0PARAMETER VALUES VIA REGRESSION  )
 1008 FORMAT(////54H0APPROXIMATE CONFIDENCE LIMITS FOR EACH FUNCTION VAL
     1UE    )
 1009 FORMAT(/62H0ITERATION STOPS - RELATIVE CHANGE IN EACH PARAMETER LE
     1SS THAN   E12.4)
 1010 FORMAT(/62H0ITERATION STOPS - RELATIVE CHANGE IN SUM OF SQUARES LE
     1SS THAN   E12.4)
 1011 FORMAT(22H1FINAL FUNCTION VALUES   )
 1012 FORMAT(////10H0RESIDUALS   )
 1014 FORMAT(//24H0VARIANCE OF RESIDUALS =    ,E12.4,1H,I4,
     120H DEGREES OF FREEDOM   )
 1015 FORMAT(////19H0CORRELATION MATRIX    )
 1016 FORMAT(////21H0NORMALIZING ELEMENTS    )
 1033 FORMAT(//19H0END OF PROBLEM NO.  I3)
 1034 FORMAT(/16H0PARAMETER ERROR  )
 1039 FORMAT(/71H0INDIVIDUAL CONFIDENCE LIMITS FOR EACH PARAMETER (ON LI
     1NEAR HYPOTHESIS)    )
 1040 FORMAT(/9H0LAMBDA =E10.3, 4X,33HSUM OF SQUARES AFTER REGRESSION =
     1E15.7)
```

```
 1041 FORMAT(14H DETERMINANT =  E12.4, 6X, 25H ANGLE IN SCALED COORD. =
     1  F5.2, 8HDEGREES   )
 1043 FORMAT(28H0TEST POINT SUM OF SQUARES =    E12.4)
 2001 FORMAT(/5E12.4)
 2006 FORMAT(5E12.4)
      END
      SUBROUTINE MATIN(A, NVAR, B, NB, DET)
      DIMENSION A(NVAR, 1), B(NVAR, 1)
       PIVOTM = A(1,1)
       DET = 1.0
      DO 550 ICOL = 1, NVAR
       PIVOT = A(ICOL, ICOL)
      PIVOTM = AMIN1(PIVOT, PIVOTM)
       DET = PIVOT * DET
C
C     DIVIDE PIVOT ROW BY PIVOT ELEMENT
C
       A(ICOL, ICOL) = 1.0

      PIVOT = AMAX1(PIVOT, 1.E-20)
       PIVOT = A(ICOL, ICOL)/PIVOT
      DO 350 L=1,NVAR
  350  A(ICOL, L) = A(ICOL, L)*PIVOT
      IF(NB .EQ. 0) GO TO 371
      DO 370 L=1,NB
  370  B(ICOL, L) = B(ICOL, L)*PIVOT
C
C     REDUCE NON-PIVOT ROWS
C
  371 DO 550 L1=1,NVAR
       IF(L1 .EQ. ICOL) GO TO 550
       T = A(L1, ICOL)
       A(L1, ICOL) = 0.
      DO 450 L=1,NVAR
  450  A(L1, L) = A(L1, L) - A(ICOL, L)*T
      IF(NB .EQ. 0) GO TO 550
      DO 500 L=1,NB
  500  B(L1, L) = B(L1, L)-B(ICOL,L)*T
  550 CONTINUE
      RETURN
      END
       SUBROUTINE GASS0(ITYPE, NQ, A, B, C,LL)
      DIMENSION A(NQ),B(NQ),C(NQ,NQ)
```

```
        NP = NQ
        NR = NP/10
        LOW = 1
        LUP = 10
10     IF( NR )15,20,30
15     RETURN
20     LUP=NP
       IF(LOW .GT. LUP) RETURN
30     WRITE(LL,500) (J,J=LOW,LUP)
       GO TO (40,60,80,80),ITYPE
40     WRITE(LL,600)(A(J),J=LOW,LUP)
       GO TO 100
60     WRITE(LL,600) (B(J),J=LOW,LUP)
       GO TO 40
80     DO 90 I=LOW,LUP
90     WRITE(LL,720)I,(C(J,I),J=LOW,I)
       LOW2=LUP+1
       IF(LOW2 .GT. NP) GO TO 100
       DO 95 I=LOW2,NP
95     WRITE(LL,720)I,(C(J,I),J=LOW,LUP)
100     LOW = LOW + 10
        LUP = LUP + 10
        NR = NR - 1
        GO TO 10
500    FORMAT(/5X,I7,9(5X,I7))
600    FORMAT(5E12.4)
720    FORMAT(1H0,I3,9(1X,F12.4))
       END
```

```
SUBROUTINE GASSO       73/171  OPT=1                        FTN 4.8+538        84/04/29. 22.40.43        PAGE      1

                 SUBROUTINE GASSO(ITYPE, NQ, A, B, C,LL)
                DIMENSION A(NQ),B(NQ),C(NQ,NQ)
                 NP = NQ
                 NR = NP/10
                 LOW = 1
                 LUP = 10
           10   IF( NR )15,20,30
           15   RETURN
           20   LUP=NP
                IF(LCW .GT. LUP) RETURN
           30   WRITE(LL,500) (J,J=LOW,LUP)
                GO TO (40,60,80,80),ITYPE
           40   WRITE(LL,600)(A(J),J=LOW,LUP)
                GO TO 100
           60   WRITE(LL,600) (B(J),J=LOW,LUP)
                GO TO 40
           80   DO 90 I=LOW,LUP
           90   WRITE(LL,720)I,(C(J,I),J=LOW,I)
                LOW2=LUP+1
                IF(LOW2 .GT. NP) GO TO 100
                DO 95 I=LOW2,NP
           95   WRITE(LL,720)I,(C(J,I),J=LOW,LUP)
          100    LOW = LOW + 10
                 LUP = LUP + 10
                 NR = NR - 1
                 GO TO 10
          500   FORMAT(/5X,I7,9(5X,I7))
          600   FORMAT(5E12.4)
          720   FORMAT(1H0,I3,9(1X,F12.4))
                END
  .0061287    .0012944     .0215182
  .0064800
0. 193. 19. 160. 24. 155. 41. 143. 48. 133. 65. 120. 72. 116. 113. 76.6 144. 63.3 151. 62.6 168. 55. 175. 54. 192. 48.6
199. 46.5 216. 43.9 223. 42.1 241. 38.4 247. 37.1 312. 27.8
TOTAL SUM OF SQUARES IS  .6955889E-04
```

```
NON-LINEAR ESTIMATION, PROBLEM NUMBER  1

  19 OBSERVATIONS,    4 PARAMETERS    150 SCRATCH REQUIRED


INITIAL PARAMETER VALUES

         1           2           3           4
  .6129E-02   .1294E-02   .2152E-01   .6480E-02


PROPORTIONS USED IN CALCULATING DIFFERENCE QUOTIENTS

         1           2           3           4
  .1000E-01   .1000E-01   .1000E-01   .1000E-01


INITIAL SUM OF SQUARES =   .3497E-04




                                                 ITERATION NO.   1
DETERMINANT =    .1678E-02       ANGLE IN SCALED COORD. =40.29DEGREES

TEST POINT PARAMETER VALUES
  .4852E-02   .2409E-02   .1189E-01  -.1821E-02
DETERMINANT =    .7674E-02       ANGLE IN SCALED COORD. =33.68DEGREES

TEST POINT PARAMETER VALUES
  .5291E-02   .1983E-02   .1015E-01  -.3453E-02
DETERMINANT =    .1023E+00       ANGLE IN SCALED COORD. =28.92DEGREES

TEST POINT PARAMETER VALUES
  .5631E-02   .1864E-02   .1125E-01  -.3783E-02

TEST POINT PARAMETER VALUES
  .5880E-02   .1579E-02   .1638E-01   .1349E-02

TEST POINT SUM OF SQUARES =   .5498E-05

PARAMETER VALUES VIA REGRESSION

         1           2           3           4
  .5880E-02   .1579E-02   .1638E-01   .1349E-02

LAMBDA =  .100E+00    SUM OF SQUARES AFTER REGRESSION =   .5498036E-05



                                                 ITERATION NO.   2
DETERMINANT =    .8736E-02       ANGLE IN SCALED COORD. =53.66DEGREES

TEST POINT PARAMETER VALUES
  .5597E-02   .1701E-02   .9553E-02   .2303E-02

TEST POINT SUM OF SQUARES =   .1870E-05
```

```
PARAMETER VALUES VIA REGRESSION

          1            2            3            4
  .5597E-02    .1701E-02    .9553E-02    .2303E-02


LAMBDA =  .100E-01     SUM OF SQUARES AFTER REGRESSION =    .1870273E-05




                                                 ITERATION NO.    3
DETERMINANT =     .2833E-03         ANGLE IN SCALED COORD. =73.14DEGREES

TEST POINT PARAMETER VALUES
  .6271E-02    .1092E-02    .9496E-02    .2256E-02

TEST POINT SUM OF SQUARES =    .2479E-06


PARAMETER VALUES VIA REGRESSION

          1            2            3            4
  .6271E-02    .1092E-02    .9496E-02    .2256E-02


LAMBDA =  .100E-02     SUM OF SQUARES AFTER REGRESSION =    .2478693E-06




                                                 ITERATION NO.    4
DETERMINANT =     .7924E-04         ANGLE IN SCALED COORD. =63.11DEGREES

TEST POINT PARAMETER VALUES
  .7951E-02  -.6375E-03   .6345E-02  -.3180E-02
DETERMINANT =     .3009E-03         ANGLE IN SCALED COORD. =62.97DEGREES

TEST POINT PARAMETER VALUES
  .6719E-02    .6322E-03   .8665E-02    .7854E-03

TEST POINT SUM OF SQUARES =    .2465E-06


PARAMETER VALUES VIA REGRESSION

          1            2            3            4
  .6719E-02    .6322E-03   .8665E-02    .7854E-03


LAMBDA =  .100E-02     SUM OF SQUARES AFTER REGRESSION =    .2464799E-06




                                                 ITERATION NO.    5
DETERMINANT =     .1181E-03         ANGLE IN SCALED COORD. =87.92DEGREES

TEST POINT PARAMETER VALUES
  .7706E-02  -.3940E-03   .7023E-02  -.5754E-02
DETERMINANT =     .3511E-03         ANGLE IN SCALED COORD. =86.09DEGREES
```

```
TEST POINT PARAMETER VALUES
  .7053E-02   .2862E-03   .8154E-02  -.1858E-02
DETERMINANT =   .2927E-02        ANGLE IN SCALED COORD. =71.11DEGREES

TEST POINT PARAMETER VALUES
  .6761E-02   .5897E-03   .8651E-02  -.9406E-04
DETERMINANT =   .5690E-01        ANGLE IN SCALED COORD. =47.21DEGREES

TEST POINT PARAMETER VALUES
  .6716E-02   .6306E-03   .8682E-02   .2925E-03

TEST POINT SUM OF SQUARES =   .2360E-06


PARAMETER VALUES VIA REGRESSION

          1           2           3           4
  .6716E-02   .6306E-03   .8682E-02   .2925E-03


LAMBDA =  .100E+00    SUM OF SQUARES AFTER REGRESSION =   .2360175E-06




                                               ITERATION NO.   6
DETERMINANT =   .3133E-02        ANGLE IN SCALED COORD. =64.38DEGREES

TEST POINT PARAMETER VALUES
  .6769E-02   .5817E-03   .8640E-02  -.1362E-03

TEST POINT SUM OF SQUARES =   .2342E-06


PARAMETER VALUES VIA REGRESSION

          1           2           3           4
  .6769E-02   .5817E-03   .8640E-02  -.1362E-03


LAMBDA =  .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2341554E-06




                                               ITERATION NO.   7
DETERMINANT =   .4533E-03        ANGLE IN SCALED CCORD. =67.59DEGREES

TEST POINT PARAMETER VALUES
  .7077E-02   .2572E-03   .8075E-02  -.2275E-02

TEST POINT SUM OF SQUARES =   .2628E-06
DETERMINANT =   .3293E-02        ANGLE IN SCALED CCORD. =66.72DEGREES

TEST POINT PARAMETER VALUES
  .6816E-02   .5333E-03   .8560E-02  -.4845E-03

TEST POINT SUM OF SQUARES =   .2327E-06


PARAMETER VALUES VIA REGRESSION
```

```
          1            2            3            4
  .6816E-02    .5333E-03    .8560E-02  -.4815E-03


LAMBDA =  .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2327138E-06



                                                  ITERATION NO.   8
DETERMINANT =    .4893E-03        ANGLE IN SCALED COORD. =63.54DEGREES

TEST POINT PARAMETER VALUES
  .7095E-02    .2362E-03    .8038E-02  -.2630E-02

TEST POINT SUM OF SQUARES =    .2613E-06
DETERMINANT =    .3402E-02        ANGLE IN SCALED COORD. =62.85DEGREES

TEST POINT PARAMETER VALUES
  .6860E-02    .4871E-03    .8482E-02  -.8414E-03

TEST POINT SUM OF SQUARES =    .2313E-06


PARAMETER VALUES VIA REGRESSION

          1            2            3            4
  .6860E-02    .4871E-03    .8482E-02  -.8414E-03


LAMBDA =  .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2313454E-06



                                                  ITERATION NO.   9
DETERMINANT =    .5299E-03        ANGLE IN SCALED COORD. =65.26DEGREES

TEST POINT PARAMETER VALUES
  .7110E-02    .2197E-03    .8007E-02  -.2970E-02

TEST POINT SUM OF SQUARES =    .2579E-06
DETERMINANT =    .3519E-02        ANGLE IN SCALED COORD. =64.57DEGREES

TEST POINT PARAMETER VALUES
  .6901E-02    .4437E-03    .8407E-02  -.1210E-02

TEST POINT SUM OF SQUARES =    .2301E-06


PARAMETER VALUES VIA REGRESSION

          1            2            3            4
  .6901E-02    .4437E-03    .8407E-02  -.1210E-02


LAMBDA =  .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2300657E-06
```

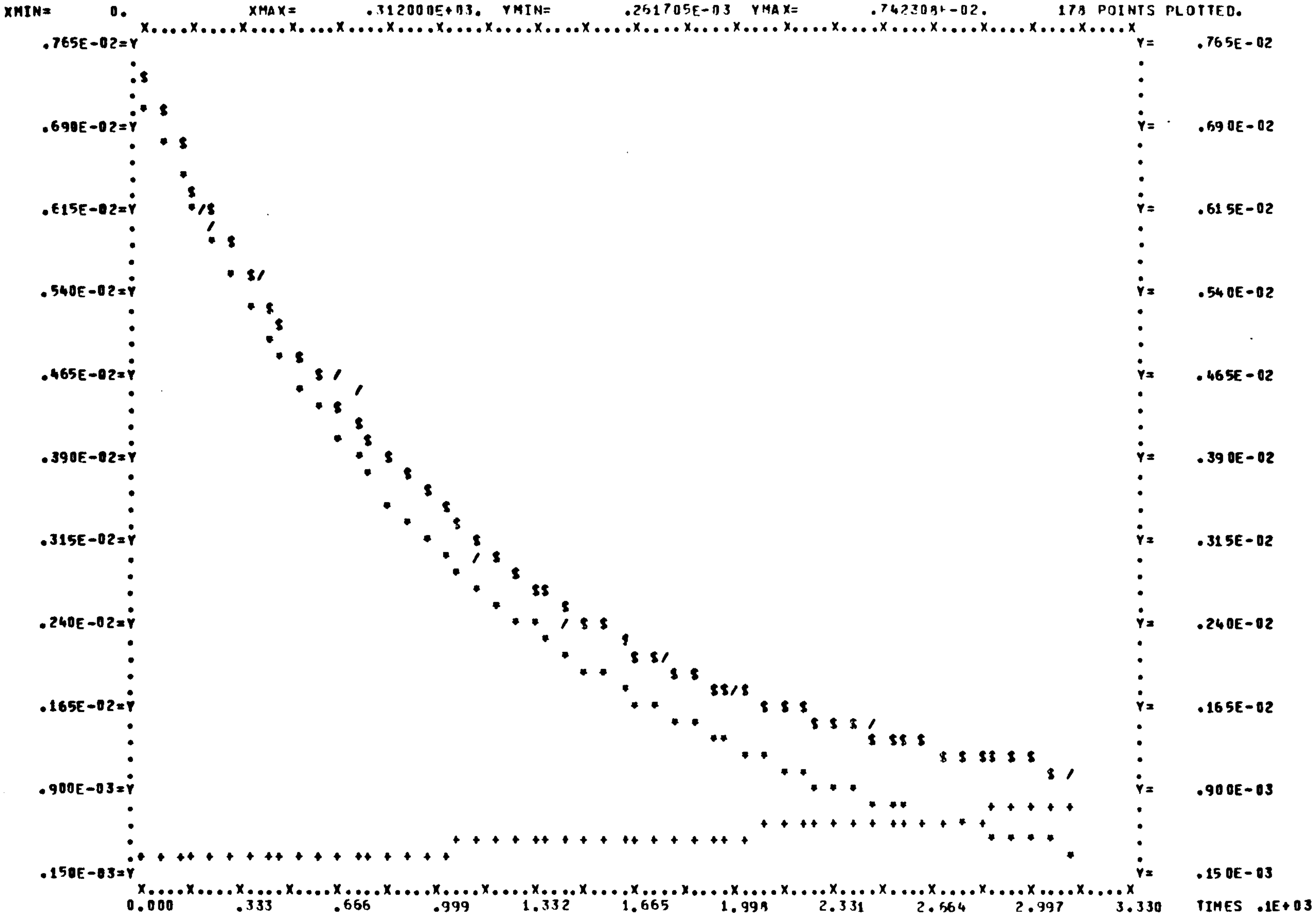
```
                                                 ITERATION NO.  10
DETERMINANT =    .5768E-03        ANGLE IN SCALED COORD. =67.09DEGREES

TEST POINT PARAMETER VALUES
  .7120E-02   .2075E-03   .7983E-02  -.3289E-02

TEST POINT SUM OF SQUARES =    .2528E-06
DETERMINANT =    .3648E-02        ANGLE IN SCALED COORD. =66.39DEGREES

TEST POINT PARAMETER VALUES
  .6938E-02   .4035E-03   .8337E-02  -.1587E-02

TEST POINT SUM OF SQUARES =    .2289E-06


PARAMETER VALUES VIA REGRESSION

         1           2           3          4
  .6938E-02   .4035E-03   .8337E-02  -.1587E-02


LAMBDA = .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2289004E-06




                                                 ITERATION NO.  11
DETERMINANT =    .6304E-03        ANGLE IN SCALED COORD. =68.54DEGREES

TEST POINT PARAMETER VALUES
  .7127E-02   .1990E-03   .7964E-02  -.3576E-02

TEST POINT SUM OF SQUARES =    .2464E-06
DETERMINANT =    .3791E-02        ANGLE IN SCALED COORD. =67.82DEGREES

TEST POINT PARAMETER VALUES
  .6972E-02   .3669E-03   .8272E-02  -.1965E-02

TEST POINT SUM OF SQUARES =    .2279E-06


PARAMETER VALUES VIA REGRESSION

         1           2           3          4
  .6972E-02   .3669E-03   .8272E-02  -.1965E-02


LAMBDA = .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2278730E-06




                                                 ITERATION NO.  12
DETERMINANT =    .6902E-03        ANGLE IN SCALED COORD. =69.55DEGREES

TEST POINT PARAMETER VALUES
  .7131E-02   .1935E-03   .7950E-02  -.3827E-02

TEST POINT SUM OF SQUARES =    .2400E-06
DETERMINANT =    .3944E-02        ANGLE IN SCALED COORD. =68.83DEGREES
```

```
TEST POINT PARAMETER VALUES
  .7002E-02   .3344E-03   .8213E-02  -.2335E-02

TEST POINT SUM OF SQUARES =   .2270E-06


PARAMETER VALUES VIA REGRESSION

         1           2           3           4
  .7002E-02   .3344E-03   .8213E-02  -.2335E-02


LAMBDA =  .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2270004E-06



                                                   ITERATION NO.  13
DETERMINANT =    .7550E-03        ANGLE IN SCALED COORD. =70.08DEGREES

TEST POINT PARAMETER VALUES
  .7133E-02   .1904E-03   .7940E-02  -.4038E-02

TEST POINT SUM OF SQUARES =   .2344E-06
DETERMINANT =    .4104E-02        ANGLE IN SCALED COORD. =69.36DEGREES

TEST POINT PARAMETER VALUES
  .7028E-02   .3061E-03   .8160E-02  -.2689E-02

TEST POINT SUM OF SQUARES =   .2263E-06


PARAMETER VALUES VIA REGRESSION

         1           2           3           4
  .7028E-02   .3061E-03   .6160E-02  -.2689E-02


LAMBDA =  .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2262893E-06



                                                   ITERATION NO.  14
DETERMINANT =    .8229E-03        ANGLE IN SCALED COORD. =70.09DEGREES

TEST POINT PARAMETER VALUES
  .7134E-02   .1887E-03   .7933E-02  -.4208E-02

TEST POINT SUM OF SQUARES =   .2302E-06
DETERMINANT =    .4267E-02        ANGLE IN SCALED COORD. =69.39DEGREES

TEST POINT PARAMETER VALUES
  .7050E-02   .2819E-03   .8114E-02  -.3018E-02

TEST POINT SUM OF SQUARES =   .2257E-06


PARAMETER VALUES VIA REGRESSION

         1           2           3           4
  .7050E-02   .2819E-03   .8114E-02  -.3018E-02
```

```
LAMBDA =  .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2257352E-06



                                                    ITERATION NO.  15
DETERMINANT =    .8915E-03       ANGLE IN SCALED COORD. =69.52DEGREES

TEST POINT PARAMETER VALUES
  .7134E-02   .1879E-03   .7928E-02  -.4341E-02

TEST POINT SUM OF SQUARES =   .2275E-06
DETERMINANT =    .4427E-02       ANGLE IN SCALED COORD. =68.86DEGREES

TEST POINT PARAMETER VALUES
  .7068E-02   .2617E-03   .8074E-02  -.3315E-02

TEST POINT SUM OF SQUARES =   .2253E-06


PARAMETER VALUES VIA REGRESSION

          1           2           3           4
  .7068E-02   .2617E-03   .8074E-02  -.3315E-02


LAMBDA =  .100E-01    SUM OF SQUARES AFTER REGRESSION =   .2253223E-06
```

```
FINAL FUNCTION VALUES

  .7330E-02   .6375E-02   .6087E-02   .5384E-02   .5067E-02

  .4491E-02   .4230E-02   .3161E-02   .2533E-02   .2433E-02

  .2164E-02   .2083E-02   .1867E-02   .1802E-02   .1629E-02

  .1577E-02   .1440E-02   .1400E-02   .1097E-02



RESIDUALS

  .9314E-04  -.2211E-03  -.1252E-03   .1156E-03   .4888E-04

  .1247E-03   .2312E-03  -.2150E-03  -.9809E-04  -.2539E-04

 -.4860E-04  -.6543E-05   .2599E-05  -.1352E-04   .5985E-04

  .4206E-04   .3689E-04   .2729E-04  -.2804E-04



X PRIME-X MATRIX

            1           2           3           4

  1       4.7290

  2       8.8171     31.3005

  3      -1.5559     -5.5953      1.1320

  4       -.1107      -.8885       .1422       .0367



CORRELATION MATRIX

            1           2           3           4

  1       1.0000

  2       -.9808      1.0000

  3       -.9197       .9712      1.0000

  4       -.9811       .9890       .9348      1.0000



NORMALIZING ELEMENTS

            1           2           3           4
  .3448E+01   .3808E+01   .7764E+01   .5338E+02
```

```
VARIANCE OF RESIDUALS =    .1502E-07,  15 DEGREES OF FREEDOM

INDIVIDUAL CONFIDENCE LIMITS FOR EACH PARAMETER (ON LINEAR HYPOTHESIS)

         1           2           3           4
  .7914E-02   .1195E-02   .9977E-02   .9769E-02
  .6223E-02  -.6716E-03   .6171E-02  -.1640E-01



APPROXIMATE CONFIDENCE LIMITS FOR EACH FUNCTION VALUE

  .7525E-02   .6489E-02   .6189E-02   .5481E-02   .5166E-02
  .7135E-02   .6261E-02   .5985E-02   .5288E-02   .4967E-02

  .4595E-02   .4336E-02   .3253E-02   .2623E-02   .2526E-02
  .4386E-02   .4125E-02   .3069E-02   .2442E-02   .2340E-02

  .2268E-02   .2192E-02   .1988E-02   .1928E-02   .1765E-02
  .2060E-02   .1975E-02   .1745E-02   .1676E-02   .1493E-02

  .1716E-02   .1584E-02   .1544E-02   .1285E-02
  .1439E-02   .1296E-02   .1255E-02   .9093E-03


END OF PROBLEM NO.  1
```


XMIN= 0. XMAX= .312000E+03, YMIN= .261705E-03 YMAX= .742308E-02. 178 POINTS PLOTTED.
.765E-02=Y
.690E-02=Y
.615E-02=Y
.540E-02=Y
.465E-02=Y
.390E-02=Y
.315E-02=Y
.240E-02=Y
.165E-02=Y
.900E-03=Y
.150E-03=Y
Y= .765E-02
Y= .690E-02
Y= .615E-02
Y= .540E-02
Y= .465E-02
Y= .390E-02
Y= .315E-02
Y= .240E-02
Y= .165E-02
Y= .900E-03
Y= .150E-03
0.000
.333
.666
.999
1.332
1.665
1.998
2.331
2.664
2.997
3.330
TIMES .1E+03

APPENDIX H.3

Results of Three-Parameter Estimation Model (Tables 1 to 4) and the Plots of Estimated MCN Values with their 95% Confidence Intervals (UWHAUS Estimation Based on the Linear Hypothesis)

- Parameters estimated: MCN, k_v, k_1.
- $[TCN]_o$ Equal Initial Measured Value that Changes in Time.

TABLE H.3.1. THREE PARAMETER ESTIMATION MODEL (MCN, k_v, k_1) - COPPER CYANIDE COMPLEX

$k_v = k_{NaCN}$			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
	G I	k_v (cm/h) (h^{-1})	1.65 (.0394)	1.00 (.0238)	0.31 (.0074)	0.21 (.0050)	1.63 (.0389)	1.06 (.0253)	0.98 (.0234)	0.58 (.0138)
Cu-CN	V E	$[MCN]_o$ (mole/L)				0.13 x 10^{-2}				
	N	k_{Cu} (h^{-1})	.0207	.0071	.0037	.0033	.0153	.0024	.0036	.0031
		k_v UWHAUS	.0635	.0154	.0187	.0829	.1049	.0153	.0148	.2259
		MCN x 10^2 UWHAUS	.092	5.67	.237	.523	.146	.052	.066	.451
		k_{Cu} (h^{-1}) UWHAUS	$.88 \times 10^{-2}$	.94	$.26 \times 10^{-2}$	$.32 \times 10^{-2}$	$.72 \times 10^{-2}$	$.61 \times 10^{-8}$	$.29 \times 10^{-7}$	$.53 \times 10^{-2}$
		TCN x 10^2 (mole/L)	.761	.796	.781	.759	.777	.758	.750	.785
		MCN/TCN	.12	NA	.30	.69	.19	.07	.09	.57
		TSS x 10^6	55.9	59.3	58.1	38.0	58.9	81.5	74.1	50.2
		RSS x 10^6	1.0	1.2	1.1	.43	.65	1.6	1.8	.72
		R^2 (%)	98	98	98	99	99	98	97	98

NA - not acceptable

TABLE H.3.2 THREE PARAMETER ESTIMATION MODEL (MCN, k_v, k_1) - ZINC CYANIDE COMPLEX

$k_v = k_{NaCN}$			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
	G	k_v (cm/h)	1.65	1.00	0.31	0.21	1.63	1.06	0.98	0.58
	I	(h^{-1})	(.0394)	(.0238)	(.0074)	(.0050)	(.0389)	(.0253)	(.0234)	(.0138)
Zn-CN	V	$[MCN]_o$								
	E	(mol/L)	0.13×10^{-2}							
	N	k_{Zn} (h^{-1})	.0062	.0194	.0068	.0045	.0448	.0181	.0137	.0095
		k_v UWHAUS	.8323	.0195	.0194	.0172	.0770	.0257	.0314	.0613
		MCN UWHAUS	$.53 \times 10^{-2}$	$.11 \times 10^{-2}$	$.15 \times 10^{-2}$	$.40 \times 10^{-2}$	$.95 \times 10^{-3}$	$.87 \times 10^{-1}$	$.10 \times 10^{-1}$	$.38 \times 10^{-2}$
		k_{Zn} UWHAUS	.0559	.0612	.0039	.0043	.0181	1.10	.0698	.0096
		TCN x 10^2 (mole/L)	.714	.648	.750	.631	.754	.769	.758	.731
		MCN/TCN	.74	.17	.20	.63	.12	NA	NA	.52
		TSS x 10^6	67.3	97.8	62.9	43.7	50.2	100.9	106.5	69.5
		RSS x 10^6	.03	.72	.72	.42	.16	.80	1.3	1.2
		R^2 (%)	99	99	98	99	99	99	98	98

NA - not acceptable

TABLE H.3.3. THREE PARAMETER ESTIMATION MODEL (MCN, k_v, k_1) - NICKEL CYANIDE COMPLEX

$k_v = k_{NaCN}$			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
	G	k_v (cm/h)	1.65	1.00	0.31	0.21	1.63	1.06	0.98	0.58
	I	(h^{-1})	(.0394)	(.0238)	(.0074)	(.0050)	(.0389)	(.0253)	(.0234)	(.0138)
Ni-CN	V	$[MCN]_o$								
	E	(mol/L)	0.13×10^{-2}							
	N	k_{Ni} (h^{-1})	.0027	.0008	.0030	.0027	.0008	.0015	.0042	.0041
		k_v UWHAUS	.0382	.0972	.0395	.0304	.0873	.0204	.0139	.0581
		MCN x 10^2 UWHAUS	.419	.103	.322	.345	.129	.153	.083	.239
		k_{Ni} UWHAUS	$.615 \times 10^{-2}$	$.603 \times 10^{-4}$	$.232 \times 10^{-2}$	$.179 \times 10^{-2}$	$.116 \times 10^{-2}$	$.80 \times 10^{-3}$	$.87 \times 10^{-9}$	$.36 \times 10^{-2}$
		TCN x 10^2 (mol/L)	.882	.765	.796	.652	.765	.761	.769	.677
		MCN/TCN	.47	.13	.40	.53	.17	.20	.11	.35
		TSS x 10^6	106.9	82.4	38.2	28.6	38.2	59.3	69.7	39.1
		RSS x 10^6	.49	.37	.32	1.2	.07	1.0	1.2	1.6
		R^2 (%)	99	99	99	96	99	98	98	96

NA - not acceptable

TABLE H.3.4. THREE PARAMETER ESTIMATION MODEL (MCN, k_v, k_l) - IRON CYANIDE PROCESS

$k_v = k_{NaCN}$			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
	G	k_v (cm/h)	1.65	1.00	0.31	0.21	1.63	1.06	0.98	0.58
	I	(h^{-1})	(.0394)	(.0238)	(.0074)	(.0050)	(.0389)	(.0253)	(.0234)	(.0138)
Fe-CN	V	$[MCN]_o$ (mol/L)	0.13×10^{-2}							
	E									
	N	k_{Fe} (h^{-1})	.0016	.0026	.0012	.0007	.0068	.0222	.0051	.0039
		k_v UWHAUS	.0123	.0194	.0235	.0438	.1098	.0391	.0099	.0111
		MCN x 10^2 UWHAUS	.094	.185	.118	.129	.113	.233	.123	.289
		k_{Fe} UWHAUS	$.48 \times 10^{-9}$	$.13 \times 10^{-2}$	$.63 \times 10^{-8}$	$.51 \times 10^{-3}$	$.49 \times 10^{-2}$	$.11 \times 10^{-1}$	$.24 \times 10^{-2}$	$.32 \times 10^{-2}$
		TCN x 10^2 (mol/L)	.773	.754	.719	.539	.704	.704	.742	.704
		MCN/TCN	.12	.24	.16	.24	.16	.33	.17	.41
		TSS x 10^6	67.4	67.3	38.2	20.1	41.0	65.4	69.5	51.3
		RSS x 10^6	1.3	.28	.86	.21	.02	.42	.26	.64
		R^2 (%)	98	99	98	.99	99	99	99	99

NA - not acceptable

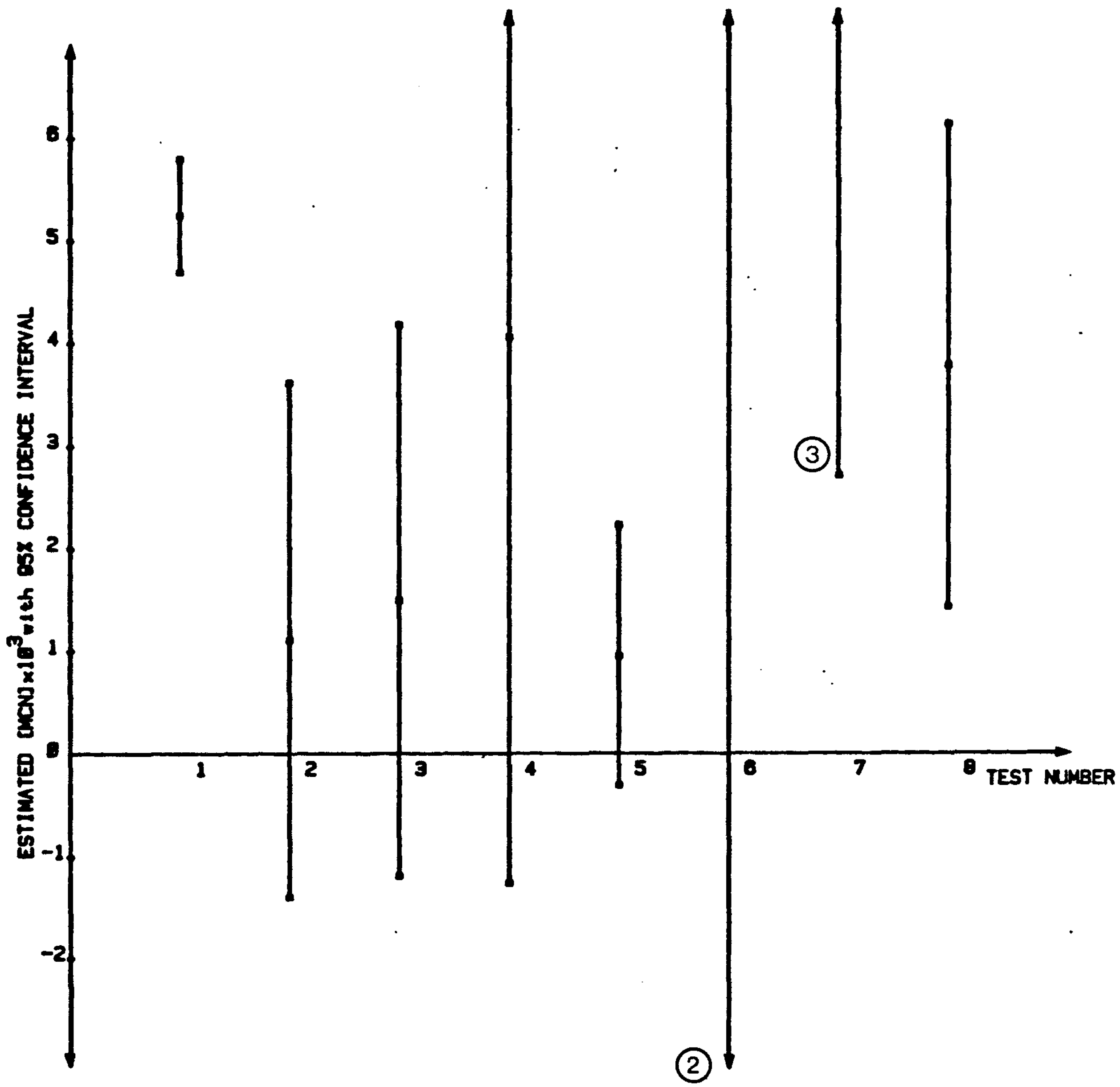


Figure H.3.1 Three-Parameter Estimation Model - Estimated MCN Values with 95% Confidence Intervals - Zn

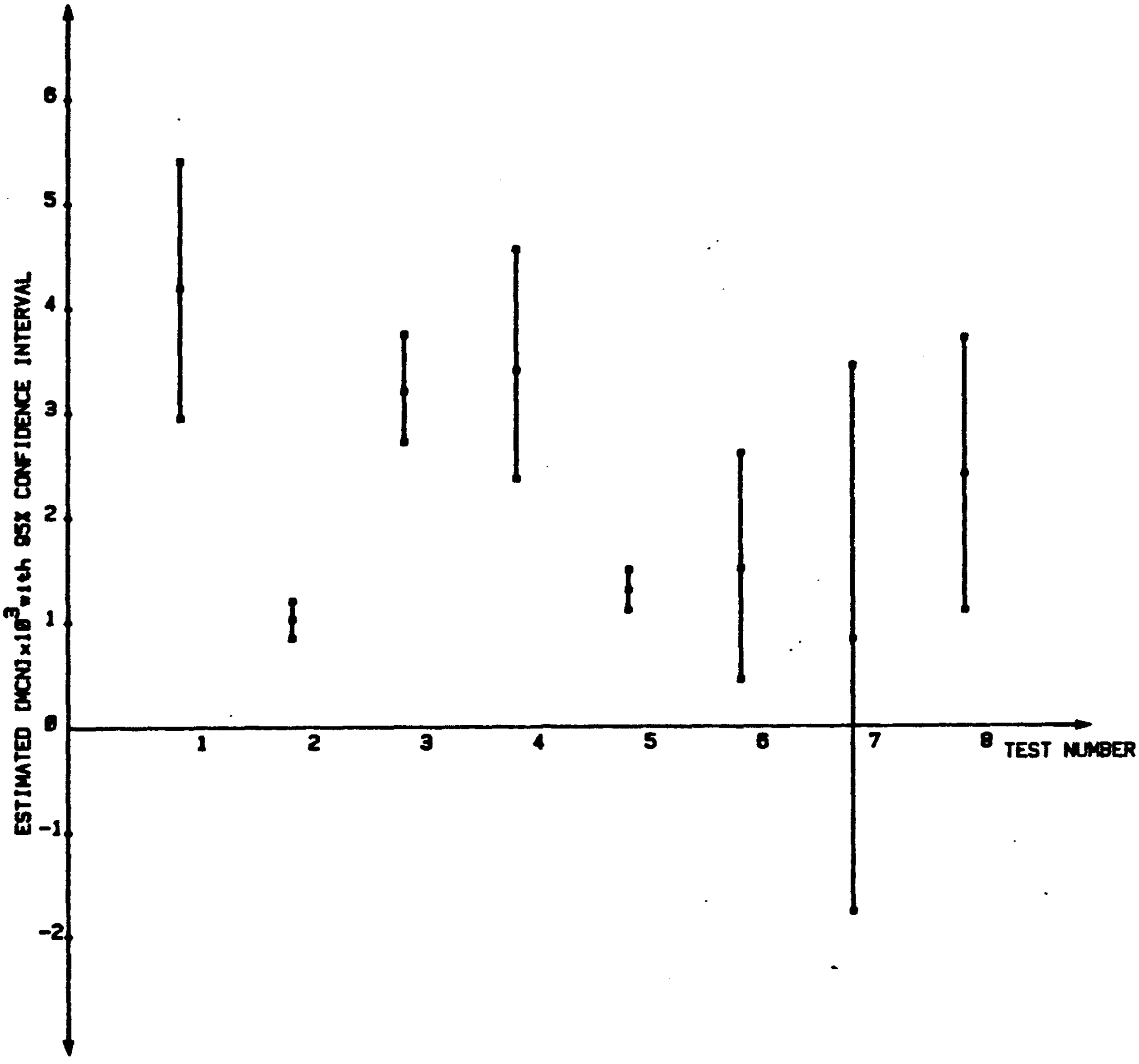


Figure H.3.2 Three-Parameter Estimation Model - Estimated MCN Values with 95% Confidence Intervals - Ni

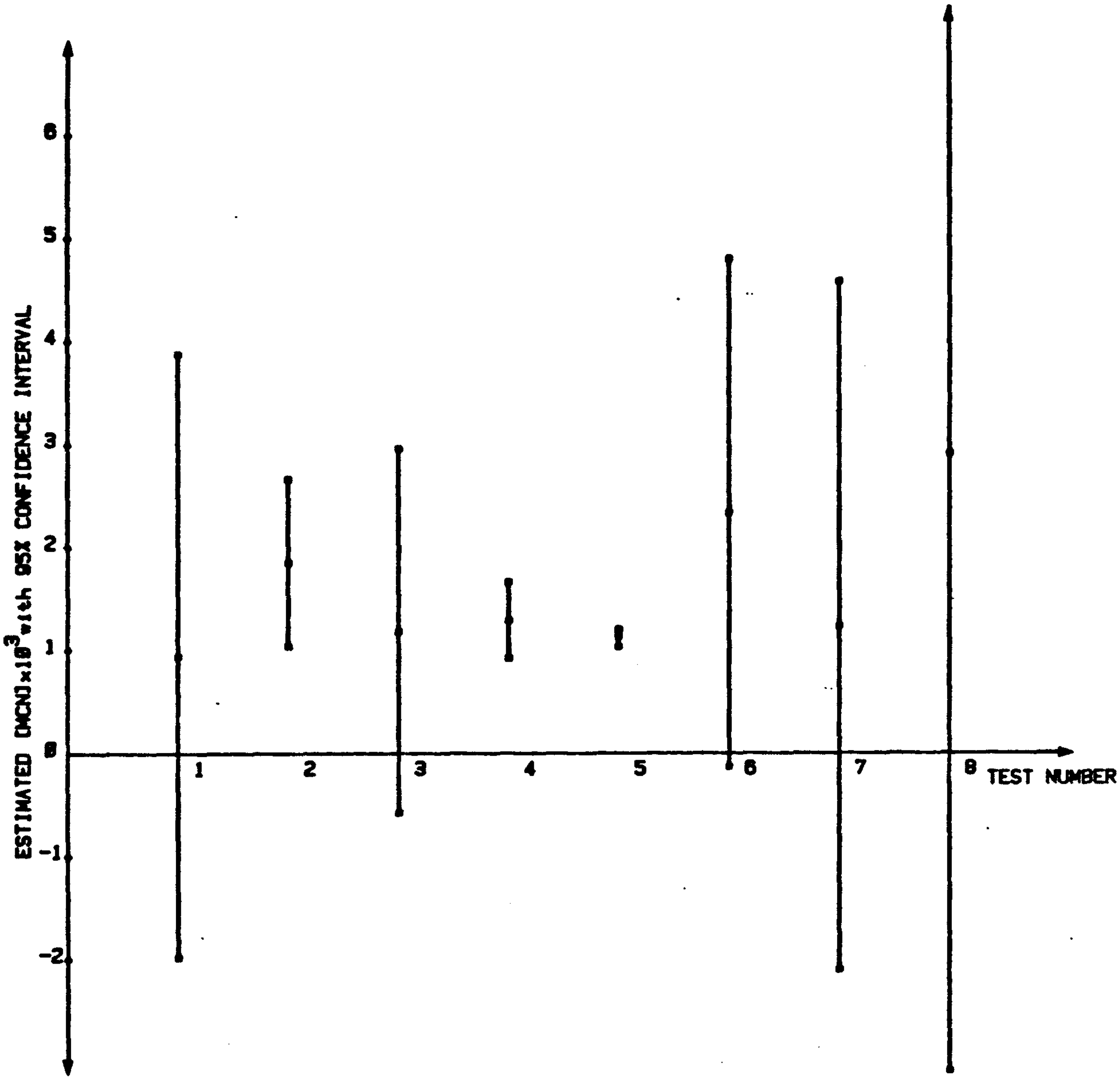


Figure H.3.3 Three-Parameter Estimation Model - Estimated MCN Values with 95% Confidence Intervals - Fe

APPENDIX H.4

Example Program for Two-Parameter Estimation Model

- MCN, k_1-parameters to be estimated.
- $[TCN]_o$ Equal Initial Measured Value which Changes in Time.
- $[FCN] = [TCN] - [MCN]$.

```
      PROGRAM TSTOL2(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,
     +DEBUG=OUTPUT,TAPE11)
      DIMENSION Y(25),TH(2),DIFF(3),SIGNS(3),SCRAT(6000)
      COMMON /B/ X(25),YP(7,61),DELT,NTSTEP,IT(61),NT1,YINIT
C
C     TWO PARAMETER ESTIMATION MODEL
C
C
      EXTERNAL MODEL
      DATA NP,MIT/2,15/
      DATA NOB/14/
      DATA NPROB/1/
      DATA EPS1,EPS2,FLAM,FNU/1.E-6,1.E-6,0.01,10./
      READ(5,*) (TH(I),I=1,NP)
      WRITE(6,100) (TH(I),I=1,NP)
  100 FORMAT(3F12.7)
      READ(5,*) (X(I),Y(I),I=1,NOB)
      WRITE(6,*) (X(I),Y(I),I=1,NOB)
      YAV=0.
      DO 30 I=1,NOB
   30 YAV=YAV+Y(I)
      YAV=YAV/FLOAT(NOB)
      TSS=0.
      DO 35 I=1,NOB
   35 TSS=TSS+(Y(I)-YAV)**2
      TSOS=TSS/(26000.**2)
      WRITE(6,200)TSOS
  200 FORMAT(1X,≠TOTAL SUM OF SQUARES IS≠E14.7)
      DO 40 J=1,NOB
      Y1=Y(J)/26000.
      Y(J)=Y1
      CALL PLOTPT(X(J),Y1,5)
   40 CONTINUE
      YINIT=Y(1)
      DELT=2.
      NTSTEP=X(NOB)/DELT
      DO 45 I=1,NP
      DIFF(I)=0.01
   45 SIGNS(I)=1.0
      CALL UWHAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT,
     +FLAM,FNU,SCRAT,6)
C     CALL MODEL (NPROB,TH,F,NOB,NP)
      DO 50 J=1,NT1
      T=IT(J)
      CALL PLOTPT (T,YP(1,J),4)
      CALL PLOTPT (T,YP(2,J),2)
      CALL PLOTPT (T,YP(3,J),20)
   50 CONTINUE
      CALL OUTPLT
      STOP
      END
```

```
      SUBROUTINE MODEL(NPROB,TH,F,NOB,NP)
      DIMENSION TH(2),F(25)
      COMMON /B/ X(25),YP(7,61),DELT,NTSTEP,TT(61),NT1,YINIT
      REAL    YY(3),C(24),W(3,9),XX,TOL,XEND
      COMMON /A/ RKC,VK,UVKN
      EXTERNAL FCN1
      NW=3
      N=3
      XX=0.0
      ITMAX=1
      IF(NTSTEP.GT.60)ITMAX=(NTSTEP/60.)+1
      YY(2)=TH(2)
      YY(3)=YINIT
      YY(1)=YY(3)-YY(2)
      F(1)=YINIT
C     CONSTANT DELT MUST BE LESS THAN OR EQUAL TO MINIMUM
C     TIME BETWEEN OBSERVATIONS
      T=0.
      JOBS=2
      VK=.0138080
      RKC=TH(1)
C     AS=.04778
      TT(1)=T
C     V=2.
      YP(1,1)=YY(1)
      YP(2,1)=YY(2)
      YP(3,1)=YY(3)
      TOL=0.0001
      IND=1
      DO 55 K=1,NTSTEP
        XEND=FLOAT(K)*DELT
        CALL DVERK (N,FCN1,XX,YY,XEND,TOL,IND,C,NW,W,IER)
         IF (IND.LT.0.OR.IER.GT.0)  GOTO 400
      T=T+DELT
      JPRED=(X(JOBS)/DELT)
      IF(JPRED.EQ.K)F(JOBS)=YY(3)
      IF(JPRED.EQ.K)JOBS=JOBS+1
      IF(((K/ITMAX)*ITMAX).EQ.K)GO TO 300
      GO TO 55
  300 KK=(K/ITMAX)
      TT(KK+1)=T
      YP(1,KK+1)=YY(1)
      YP(2,KK+1)=YY(2)
      YP(3,KK+1)=YY(3)
   55 CONTINUE
  400 CONTINUE
      NT1=KK+1
      RETURN
      END
```

```
      SUBROUTINE FCN1(N,XX,YY,YPRIME)
      COMMON /A/ RKC,VK,UVKN,AS,V
      REAL       YY(N),YPRIME(N),XX
      YPRIME(1)=(RKC*YY(2))-(VK*YY(1))
      YPRIME(2)=YY(2)*(-RKC)
      YPRIME(3)=-VK*YY(1)
      RETURN
      END
```

```
      SUBROUTINE UNHAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,
     1  MIT, FLAM, FNU, SCRAT,LL)
      DIMENSION SCRAT(1)
      IA=1
      IB=IA+NP
      IC=IB+NP
      ID=IC+NP
      IE=ID+NP
      IF=IE+NP
      IG=IF+NOB
      IH=IG+NOB
      II = IH + NP * NOB
      IJ = IH
           CALL  HAUS9(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT
     1  ,FLAM,FNU,SCRAT(IA), SCRAT(IB), SCRAT(IC), SCRAT(ID),
     2  SCRAT(IE), SCRAT(IF), SCRAT(IG), SCRAT(IH), SCRAT(II),
     3  SCRAT(IJ),LL)
      RETURN
      END
```

```
      SUBROUTINE HAUS9(NPRBO, MODEL, NBO, Y,NQ,TH,DIFZ,SIGNS,EP1S,EP2S,
     1MIT,FLAM,FNU,    Q,P,E,PHI,TB,F,R,A,D,DELZ,LL)
C$    STORES(GA,Q,TEMP,A,P,SDEV,FNU,D,R,EPS,DELZ)
C
C     DIMENSION TH(NQ), DIFZ(NQ), SIGNS(NQ), Y(NBO)
C     DIMENSION Q(NQ), P(NQ), E(NQ), PHI(NQ), TB(NQ)
C     DIMENSION F(NBO), R(NBO)
C     DIMENSION A(NQ,NQ), D(NQ,NQ), DELZ(NBO,NQ)
C
      DIMENSION TH(1), DIFZ(1), SIGNS(1), Y(1), Q(1), P(1), E(1),
     1  PHI(1), TB(1), F(1), R(1), A(1), D(1), DELZ(1)
      ACOS(X) = ATAN(SQRT(1.0/X**2 - 1.0))
      NP = NQ
      NPROB = NPRBO
      NOB = NBO
      EPS1 = EP1S
      EPS2 = EP2S
      NPSQ = NP * NP
       NSCRAC = 5*NP+NPSQ +2*NOB+NP*NOB
       WRITE(LL,1000) NPROB, NOB, NP, NSCRAC
      WRITE(LL,1001)
       CALL GASSO(1, NP, TH, TEMP, THEP,LL)
      WRITE(LL,1002)
       CALL GASSO(1, NP, DIFZ, TEMP, TEMP,LL)
      IF(MIN0(NP-1,50-NP,NOB-NP,MIT-1,999-MIT))99,15,15
 15   IF(FNU-1.0)99, 99, 16
 16   CONTINUE
      DO 19 I=1,NP
      TEMP = ABS(DIFZ(I))
      IF(AMIN1(1.0-TEMP, ABS(TH(I))))99, 99, 19
 19   CONTINUE
      GA = FLAM
      NIT = 1
      LAOS = 0
      IF(EPS1) 5,70,70
 5    EPS1 = 0
   70 SSQ = 0
      CALL MODEL(NPROB, TH, F, NOB, NP)
      DO 90 I = 1, NOB
      R(I) = Y(I) - F(I)
   90 SSQ=SSQ+R(I)*R(I)
      WRITE(LL,1003)SSQ
C
C                                                     BEGIN ITERATION
C
 100  GA = GA / FNU
      INTCNT = 0
      WRITE(LL,1004)NIT
 101  JS = 1 - NOB
      DO 130 J=1,NP
      TEMP = TH(J)
      P(J)=DIFZ(J)*TH(J)
      TH(J)= TH(J)+P(J)
      Q(J)=0
      JS = JS + NOB
```

```
C     WRITE(6,10)J
   10 FORMAT(1H ,*$$$*,I5)
C***
      CALL MCOEL(NPROB, TH, DELZ(JS), NOB, NP)
      IJ = JS-1
      DO 120 I = 1, NOB
      IJ = IJ + 1
      DELZ(IJ) = DELZ(IJ) - F(I)
  120 Q(J) = Q(J) + DELZ(IJ) * R(I)
      Q(J)= Q(J)/P(J)
C                                       Q=XT*R (STEEPEST DESCENT)
  130 TH(J) = TEMP
      IF(LAOS) 131,131,414
  131 DO 150 I = 1, NP
      DO 151 J=1,I
      SUM = 0
      KJ = NOB*(J-1)
      KI = NOB*(I-1)
      DO 160 K = 1, NOB
      KI = KI + 1
      KJ = KJ + 1
  160 SUM = SUM + DELZ(KI) * DELZ(KJ)
      TEMP= SUM/(P(I)*P(J))
      JI = J + NP*(I-1)
      D(JI) = TEMP
      IJ = I + NP*(J-1)
  151 D(IJ) = TEMP
  150 E(I) = SQRT(D(JI))
  666 CONTINUE
      DO 153  I = 1, NP
      IJ = I-NP
      DO 153 J=1,I
      IJ = IJ + NP
      A(IJ) = D(IJ) / (E(I)*E(J))
      JI = J + NP*(I-1)
  153 A(JI) = A(IJ)
C                                       A= SCALED MOMENT MATRIX
      II = - NP
      DO 155 I=1,NP
      P(I)=Q(I)/E(I)
      PHI(I)=P(I)
      II = NP + 1 + II
  155 A(II) = A(II) + GA
C
      I=1
       CALL MATIN(A, NP, P, I, DET)
C                                       P/E = CORRECTION VECTOR
       STEP=1.0
      SUM1=0.
      SUM2=0.
      SUM3=0.
      DO 231 I=1,NP
      SUM1=P(I)*PHI(I)+SUM1
      SUM2=P(I)*P(I)+SUM2
      SUM3= PHI(I) * PHI(I) + SUM3
  231 PHI(I) = P(I)
       TEMP = SUM1/SQRT(SUM2*SUM3)
```

```
      TEMP = AMIN1(TEMP, 1.0)
      TEMP = 57.295*ACOS(TEMP)
      WRITE(LL,1041) DET, TEMP
  170 DO 220 I = 1, NP
      P(I) = PHI(I) *STEP / E(I)
      TB(I) = TH(I) + P(I)
  220 CONTINUE
      WRITE(LL,7000)
 7000 FORMAT(30H0TEST POINT PARAMETER VALUES      )
      WRITE(LL,2006) (TB(I), I = 1, NP)
      DO 221 I = 1, NP
      IF(SIGNS(I)) 221, 221, 222
  222 IF(SIGN(1.0,TH(I))*SIGN(1.0,TB(I))) 663, 221, 221
  221 CONTINUE
      SUMB=0
      CALL MODEL(NPROB, TB, F, NOB, NP)
      DO 230 I=1,NOB
      R(I)=Y(I)-F(I)
230   SUMB=SUMB+R(I)*R(I)
      WRITE(LL,1043)SUMB
      IF(SUMB - (1.0+EPS1)*SSQ) 662, 662, 663
  663 IF( AMIN1(TEMP-30.0, GA)) 665, 665, 664
665   STEP=STEP/2.0
      INTCNT = INTCNT + 1
      IF(INTCNT - 36) 170, 2700, 2700
   664 GA=GA*FNU
      INTCNT = INTCNT + 1
      IF(INTCNT - 36) 666, 2700, 2700
  662 WRITE(LL,1007)
      DO 669 I=1,NP
669   TH(I)=TB(I)
       CALL GASS0(1, NP, TH, TEMP, TEMP,LL)
      WRITE(LL,1040) GA, SUMB
      IF(EPS2) 229,229,225
   229 IF(EPS1) 270,270,265
  225 DO 240 I = 1, NP
      IF(ABS(P(I))/(1.E-20+ABS(TH(I)))-EPS2) 240, 240, 241
   241 IF(EPS1) 270,270,265
   240 CONTINUE
      WRITE(LL,1009)EPS2
      GO TO 280
  265 IF(ABS(SUMB - SSQ) - EPS1*SSQ) 266, 266, 270
  266 WRITE(LL,1010) EPS1
      GO TO 280
270   SSQ=SUMB
      NIT=NIT+1
      IF(NIT - MIT) 100, 100, 280
 2700 WRITE(LL,2710)
 2710 FORMAT(//115H0**** THE SUM OF SQUARES CANNOT BE REDUCED TO THE SUM
     1OF SQUARES AT THE END OF THE LAST ITERATION - ITERATING STOPS   /)
C
C                                                    END ITERATION
C
  280 WRITE(LL,1011)
      WRITE(LL,2001) (F(I), I = 1, NOB)
      WRITE(LL,1012)
      WRITE(LL,2001) (R(I), I = 1, NOB)
```

```
      WRITE(LL,1017)
 1017 FORMAT(////,≠ X PRIME-X MATRIX≠)
      CALL GASSO(4,NP,TEMP,TEMP,D,LL)
      SSQ=SUMB
      IDF=NOB-NP
      WRITE(LL,1015)
      I=0
       CALL MATIN(D, NP, P, I, DET)
      DO 7692 I=1,NP
      II = I + NP*(I-1)
 7692 E(I) = SQRT(D(II))
      DO 340 I=1,NP
      JI = I + NP*(I-1) - 1
      IJ = I + NP*(I-2)
      DO 340 J = I, NP
      JI = JI + 1
      A(JI) = D(JI) / (E(I)*E(J))
      IJ = IJ + NP
 340   A(IJ) = A(JI)
       CALL GASSO(3, NP, TEMP, TEMP, A,LL)
      WRITE(LL,1016)
       CALL GASSO(1, NP, E, TEMP, TEMP,LL)
      IF(IDF) 341, 410, 341
 341  SDEV = SSQ / IDF
      WRITE(LL,1014) SDEV, IDF
       SDEV = SQRT(SDEV)
      DO 391 I=1,NP
      P(I)=TH(I)+2.0*E(I)*SDEV
391   TB(I)=TH(I)-2.0*E(I)*SDEV
      WRITE(LL,1039)
       CALL GASSO(2, NP, TB, P, TEMP,LL)
      LAOS = 1
      GO TO 101
 414  DO 415 K = 1, NOB
      TEMP = 0
      DO 420 I=1,NP
      DO 420 J=1,NP
      ISUB = K+NOB*(I-1)
      DEBUG1 = DELZ(ISUB)
C     DEBUG1 = DELZ(K + NOB*(I-1))
      ISUB = K+NOB*(J-1)
      DEBUG2 = DELZ(ISUB)
C     DEBUG2 = DELZ(K + NOB*(J-1))
      IJ = I + NP*(J-1)
      DEBUG3 = D(IJ)/(DIFZ(I)*TH(I)*DIFZ(J)*TH(J))
 420  TEMP = TEMP + DEBUG1 * DEBUG2 * DEBUG3
       TEMP = 2.0*SQRT(TEMP)*SDEV
      P(K)=F(K)+TEMP
 415  F(K)=F(K)-TEMP
      WRITE(LL,1008)
      IE=0
      DO 425 I=1,NOB,5
      IE=IE+5
      IF(NOB-IE) 430,435,435
  430 IE=NOB
 435  WRITE(LL,2001) (P(J), J = I, IE)
 425  WRITE(LL,2005) (F(J), J = I, IE)
 410  WRITE(LL,1033) NPROB
```

```
      RETURN
99    WRITE(LL,1034)
      GO TO 41J
1000 FORMAT(38H1NON-LINEAR ESTIMATION, PROBLEM NUMBER    I3,// I5,
    1  14H OBSERVATIONS, I5, 11H PARAMETERS  I7, 17H SCRATCH REQUIRED)
1001 FORMAT(/25H0INITIAL PARAMETER VALUES   )
1002 FORMAT(/54H0PROPORTIONS USED IN CALCULATING DIFFERENCE QUOTIENTS )
1003 FORMAT(/25H0INITIAL SUM OF SQUARES =   E12.4)
1004 FORMAT(/////45X,13HITERATION NO.  I4)
1007 FORMAT(/32H0PARAMETER VALUES VIA REGRESSION  )
1008 FORMAT(////54H0APPROXIMATE CONFIDENCE LIMITS FOR EACH FUNCTION VAL
    1UE      )
1009 FORMAT(/52H0ITERATION STOPS - RELATIVE CHANGE IN EACH PARAMETER LE
    1SS THAN    E12.4)
1010 FORMAT(/52H0ITERATION STOPS - RELATIVE CHANGE IN SUM OF SQUARES LE
    1SS THAN    E12.4)
1011 FORMAT(22H1FINAL FUNCTION VALUES   )
1012 FORMAT(////10H0RESIDUALS   )
1014 FORMAT(//24H0VARIANCE OF RESIDUALS =      ,E12.4,1H,I4,
    120H DEGREES OF FREEDOM    )
1015 FORMAT(////19H0CORRELATION MATRIX    )
1016 FORMAT(////21H0NORMALIZING ELEMENTS    )
1033 FORMAT(//14H0END OF PROBLEM NO.  I3)
1034 FORMAT(/16H0PARAMETER ERROR   )
1039 FORMAT(/71H0INDIVIDUAL CONFIDENCE LIMITS FOR EACH PARAMETER (ON LI
    1NEAR HYPOTHESIS)     )
1040 FORMAT(/9H0LAMBDA =E10.3, 4X,33HSUM OF SQUARES AFTER REGRESSION =
    1E15.7)
1041 FORMAT(14H DETERMINANT =  F12.4, 6X, 25H ANGLE IN SCALED COORD. =
    1  F5.2, 8HDEGREES    )
1043 FORMAT(28H0TEST POINT SUM OF SQUARES =     E12.4)
2001 FORMAT(/5E12.4)
2006 FORMAT(5E12.4)
      END
```

```
      SUBROUTINE MATIN(A, NVAR, B, NB, DET)
      DIMENSION A(NVAR, 1), B(NVAR, 1)
       PIVOTM = A(1,1)
       DET = 1.0
      DO 550 ICOL = 1, NVAR
       PIVOT = A(ICOL, ICOL)
      PIVOTM = AMIN1(PIVOT, PIVOTM)
       DET = PIVOT * DET
C
C     DIVIDE PIVOT ROW BY PIVOT ELEMENT
C
       A(ICOL, ICOL) = 1.0

      PIVOT = AMAX1(PIVOT, 1.E-20)
       PIVOT = A(ICOL, ICOL)/PIVOT
      DO 350 L=1,NVAR
  350  A(ICOL, L) = A(ICOL, L)*PIVOT
      IF(NB .EQ. 0) GO TO 371
      DO 370 L=1,NB
  370  B(ICOL, L) = B(ICOL, L)*PIVOT
C
C     REDUCE NON-PIVOT ROWS
C
  371 DO 550 L1=1,NVAR
       IF(L1 .EQ. ICOL) GO TO 550
       T = A(L1, ICOL)
       A(L1, ICOL) = 0.
      DO 450 L=1,NVAR
  450  A(L1, L) = A(L1, L) - A(ICOL, L )*T
      IF(NB .EQ. 0) GO TO 550
      DO 500 L=1,NB
  500  B(L1, L) = B(L1, L)-B(ICOL,L)*T
  550 CONTINUE
      RETURN
      END
```

```
       SUBROUTINE GASSO(ITYPE, NQ, A, B, C,LL)
      DIMENSION A(NQ),B(NQ),C(NQ,NQ)
       NP = NQ
       NR = NP/10
       LOW = 1
       LUP = 10
10    IF( NR )15,20,30
15    RETURN
20    LUP=NP
      IF(LOW .GT. LUP) RETURN
30    WRITE(LL,500) (J,J=LOW,LUP)
      GO TO (40,60,80,80),ITYPE
40    WRITE(LL,600)(A(J),J=LOW,LUP)
      GO TO 100
60    WRITE(LL,600) (B(J),J=LOW,LUP)
      GO TO 40
80    DO 90 I=LOW,LUP
90    WRITE(LL,720)I,(C(J,I),J=LOW,I)
      LOW2=LUP+1
      IF(LOW2 .GT. NP) GO TO 100
      DO 95 I=LOW2,NP
95    WRITE(LL,720)I,(C(J,I),J=LOW,LUP)
100    LOW = LOW + 10
       LUP = LUP + 10
       NR = NR - 1
       GO TO 10
500   FORMAT(/5X,I7,9(5X,I7))
600   FORMAT(5E12.4)
720   FORMAT(1H0,I3,9(1X,F12.4))
      END
```

APPENDIX H.5

Three-Parameter Estimation Model (FCN, k_v, k_l) with the Fixed MCN/TCN Ratio

- Example Program.
- Tables of Estimated Results.
- Plots of RSS vs MCN/TCN Ratios.

```
      PROGRAM TSRATIO(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,TAPE11)
      DIMENSION Y(25),TH(3),DIFF(3),SIGNS(3),SCRAT(6000)
      COMMON /B/ X(25),YP(7,61),DELT,NTSTEP,TT(61),NT1
      EXTERNAL MODEL
C
C*****************************************************************
C
C      THIS PROGRAM HAS PRESET MCN/TCN RATIO
C      IT IS ESTIMATING,FREE CN,VOL.COEFF. AND METAL DECAY COEFF.
C
C*****************************************************************
C
      DATA NP,MIT/3,15/
      DATA NOB/14/
      DATA NPROB/1/
      DATA EPS1,EPS2,FLAM,FNU/1.E-6,1.E-6,0.01,10./
      READ(5,*) (TH(I),I=1,NP)
      WRITE(6,206) (TH(I),I=1,NP)
  206 FORMAT(3F12.7)
      READ(5,*) (X(I),Y(I),I=1,NOB)
      WRITE(6,*) (X(I),Y(I),I=1,NOB)
      YAV=0.
      DO 113 I=1,NOB
  113 YAV=YAV+Y(I)
      YAV=YAV/FLOAT(NOB)
      TSS=0.
      DO 114 I=1,NOB
  114 TSS=TSS+(Y(I)-YAV)**2
      TSOS=TSS/(26000.**2)
      WRITE(6,115)TSOS
  115 FORMAT(1X,≠TOTAL SUM OF SQUARES IS≠E14.7)
      DO 12 J=1,NOB
      Y1=Y(J)/26000.
      Y(J)=Y1
      CALL PLOTPT(X(J),Y1,5)
   12 CONTINUE
      DELT=2.
      NTSTEP=X(NOB)/DELT
      DO 16 I=1,NP
      DIFF(I)=0.01
   16 SIGNS(I)=1.0
      CALL UWHAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT,
     +FLAM,FNU,SCRAT,5)
C     CALL MODEL (NPROB,TH,F,NOB,NP)
      DO 13 J=1,NT1
      T=TT(J)
      CALL PLOTPT (T,YP(1,J),4)
      CALL PLOTPT (T,YP(2,J),2)
      CALL PLOTPT (T,YP(3,J),20)
   13 CONTINUE
      CALL OUTPLT
      STOP
      END
```

```
      SUBROUTINE MODEL(NPROB,TH,F,NOB,NP)
      DIMENSION TH(3),F(25)
      COMMON /B/ X(25),YP(7,61),DELT,NTSTEP,TT(61),NT1
      REAL    YY(3),C(24),W(3,9),XX,TOL,XEND
      COMMON /A/ RKC,VK,UVKN
      EXTERNAL FCN1
      NW=3
      N=3
      XX=0.0
      ITMAX=1
      IF(NTSTEP.GT.60)ITMAX=(NTSTEP/60.)+1
      YY(1)=TH(1)
      YY(2)=0.205*TH(1)
      YY(3)=YY(1)+YY(2)
      F(1)=YY(1)+YY(2)
C     CONSTANT DELT MUST BE LESS THAN OR EQUAL TO MINIMUM
C     TIME BETWEEN OBSERVATIONS
      T=0.
      JOBS=2
      VK=TH(2)
      RKC=TH(3)
      TT(1)=T
      YP(1,1)=YY(1)
      YP(2,1)=YY(2)
      YP(3,1)=YY(3)
      TOL=0.0001
      IND=1
      DO 10 K=1,NTSTEP
        XEND=FLOAT(K)*DELT
        CALL DVERK (N,FCN1,XX,YY,XEND,TOL,IND,C,NW,W,IER)
        IF (IND.LT.0.OR.IER.GT.0)  GOTO 20
      T=T+DELT
      JPRED=(X(JOBS)/DELT)
      IF(JPRED.EQ.K)F(JOBS)=YY(3)
      IF(JPRED.EQ.K)JOBS=JOBS+1
      IF(((K/ITMAX)*ITMAX).EQ.K)GO TO 21
      GO TO 10
21    KK=(K/ITMAX)
      TT(KK+1)=T
      YP(1,KK+1)=YY(1)
      YP(2,KK+1)=YY(2)
      YP(3,KK+1)=YY(3)
 10   CONTINUE
20    CONTINUE
      NT1=KK+1
      RETURN
      END
```

```
      SUBROUTINE FCN1(N,XX,YY,YPRIME)
      COMMON /A/  RKC,VK,UVKN
      REAL       YY(N),YPRIME(N),XX
      YPRIME(1)=(RKC*YY(2))-(VK*YY(1))
      YPRIME(2)=YY(2)*(-RKC)
      YPRIME(3)=-VK*YY(1)
      RETURN
      END

      SUBROUTINE UNHAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,
     1  MIT, FLAM, FNU, SCRAT,LL)
      DIMENSION SCRAT(1)
      IA=1
      IB=IA+NP
      IC=IB+NP
      ID=IC+NP
      IE=ID+NP
      IF=IE+NP
      IG=IF+NOB
      IH=IG+NOB
      II = IH + NP * NOB
      IJ = IH
           CALL   HAUS9(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT
     1  ,FLAM,FNU,SCRAT(IA), SCRAT(IB), SCRAT(IC), SCRAT(ID),
     2  SCRAT(IE), SCRAT(IF), SCRAT(IG), SCRAT(IH), SCRAT(II),
     3  SCRAT(IJ),LL)
      RETURN
      END
```

```
      SUBROUTINE HAUS9(NPRBO, MODEL, NBO, Y,NQ,TH,DIFZ,SIGNS,EP1S,EP2S,
     1MIT,FLAM,FNU,    Q,P,E,PHI,TB,F,R,A,D,DELZ,LL)
C$    STORES(GA,Q,TEMP,A,P,SDEV,FNU,D,R,EPS,DELZ)
C
C     DIMENSION TH(NQ), DIFZ(NQ), SIGNS(NQ), Y(NBO)
C     DIMENSION Q(NQ), P(NQ), E(NQ), PHI(NQ), TB(NQ)
C     DIMENSION F(NBO), R(NBO)
C     DIMENSION A(NQ,NC), D(NQ,NQ), DELZ(NBO,NQ)
C
      DIMENSION TH(1), DIFZ(1), SIGNS(1), Y(1), Q(1), P(1), E(1),
     1   PHI(1), TB(1), F(1), R(1), A(1), D(1), DELZ(1)
      ACOS(X) = ATAN(SQRT(1.0/X**2 - 1.0))
      NP = NQ
      NPROB = NPRBO
      NOB = NBO
      EPS1 = EP1S
      EPS2 = EP2S
      NPSQ = NP * NP
       NSCRAC = 5*NP+NPSQ +2*NOB+NP*NOB
       WRITE(LL,1000) NPROB, NOB, NP, NSCRAC
      WRITE(LL,1001)
       CALL GASSO(1, NP, TH, TEMP, THEF,LL)
      WRITE(LL,1002)
       CALL GASSO(1, NP, DIFZ, TEMP, TEMP,LL)
      IF(MIN0(NP-1,50-NP,NOB-NP,MIT-1,999-MIT))99,15,15
 15   IF(FNU-1.0)99, 99, 16
 16   CONTINUE
      DO 19 I=1,NP
      TEMP = ABS(DIFZ(I))
      IF(AMIN1(1.0-TEMP, ABS(TH(I))))99, 99, 19
 19   CONTINUE
      GA = FLAM
      NIT = 1
      LAOS = 0
      IF(EPS1) 5,70,70
 5    EPS1 = 0
   70 SSQ = 0
      CALL MODEL(NPROB, TH, F, NOB, NP)
      DO 90 I = 1, NOB
      R(I) = Y(I) - F(I)
   90 SSQ=SSQ+R(I)*R(I)
      WRITE(LL,1003)SSQ
C
C                                       BEGIN ITERATION
C
 100  GA = GA / FNU
      INICNT = 0
      WRITE(LL,1004)NIT
 101  JS = 1 - NOB
      DO 130 J=1,NP
      TEMP = TH(J)
      P(J)=DIFZ(J)*TH(J)
      TH(J)= TH(J)+P(J)
      Q(J)=0
      JS = JS + NOB
```

```
C      WRITE(6,10)J
  10   FORMAT(1H ,*$$$*,I5)
C***
       CALL MODEL(NPROB, TH, DELZ(JS), NOB, NP)
       IJ = JS-1
       DO 120 I = 1, NOB
       IJ = IJ + 1
       DELZ(IJ) = DELZ(IJ) - F(I)
 120   Q(J) = Q(J) + DELZ(IJ) * R(I)
       Q(J)= Q(J)/P(J)
C                                                Q=XT*R (STEEPEST DESCENT)
  130  TH(J) = TEMP
       IF(LAOS) 131,131,414
 131   DO 150 I = 1, NP
       DO 151 J=1,I
       SUM = 0
       KJ = NOB*(J-1)
       KI = NOB*(I-1)
       DO 160 K = 1, NOB
       KI = KI + 1
       KJ = KJ + 1
 160   SUM = SUM + DELZ(KI) * DELZ(KJ)
       TEMP= SUM/(P(I)*P(J))
       JI = J + NP*(I-1)
       D(JI) = TEMP
       IJ = I + NP*(J-1)
 151   D(IJ) = TEMP
 150   E(I) = SQRT(D(JI))
 666   CONTINUE
       DO 153  I = 1, NP
       IJ = I-NP
       DO 153 J=1,I
       IJ = IJ + NP
       A(IJ) = D(IJ) / (E(I)*E(J))
       JI = J + NP*(I-1)
C153   A(JI) = A(IJ)
                                                 A= SCALED MOMENT MATRIX
       II = - NP
       DO 155 I=1,NP
       P(I)=Q(I)/E(I)
       PHI(I)=P(I)
       II = NP + 1 + II
C155   A(II) = A(II) + GA

       I=1
        CALL MATIN(A, NP, P, I, DET)
C                                                P/E = CORRECTION VECTOR
        STEP=1.0
       SUM1=0.
       SUM2=0.
       SUM3=0.
       DO 231 I=1,NP
       SUM1=P(I)*PHI(I)+SUM1
       SUM2=P(I)*P(I)+SUM2
       SUM3= PHI(I) * PHI(I) + SUM3
 231   PHI(I) = P(I)
        TEMP = SUM1/SQRT(SUM2*SUM3)
```

```
      TEMP = AMIN1(TEMP, 1.0)
      TEMP = 57.295*ACOS(TEMP)
      WRITE(LL,1041) DET, TEMP
 170  DO 220 I = 1, NP
      P(I) = PHI(I) *STEP / E(I)
      TB(I) = TH(I) + P(I)
 220  CONTINUE
      WRITE(LL,7000)
 7000 FORMAT(30H0TEST POINT PARAMETER VALUES      )
      WRITE(LL,2006) (TB(I), I = 1, NP)
      DO 221 I = 1, NP
      IF(SIGNS(I)) 221, 221, 222
 222  IF(SIGN(1.0,TH(I))*SIGN(1.0,TB(I))) 663, 221, 221
 221  CONTINUE
      SUMB=0
      CALL MODEL(NPROB, TB, F, NOB, NP)
      DO 230 I=1,NOB
      R(I)=Y(I)-F(I)
230   SUMB=SUMB+R(I)*R(I)
      WRITE(LL,1043)SUMB
      IF(SUMB - (1.0+EPS1)*SSQ) 662, 662, 663
 663  IF( AMIN1(TEMP-30.0, GA)) 665, 665, 664
665   STEP=STEP/2.0
      INTCNT = INTCNT + 1
      IF(INTCNT - 36) 170, 2700, 2700
  664 GA=GA*FNU
      INTCNT = INTCNT + 1
      IF(INTCNT - 36) 666, 2700, 2700
 662  WRITE(LL,1007)
      DO 669 I=1,NP
669   TH(I)=TB(I)
       CALL GASSO(1, NP, TH, TEMP, TEMP,LL)
      WRITE(LL,1040) GA, SUMB
      IF(EPS2) 229,229,225
  229 IF(EPS1) 270,270,265
 225  DO 240 I = 1, NP
      IF(ABS(P(I))/(1.E-20+ABS(TH(I)))-EPS2) 240, 240, 241
  241 IF(EPS1) 270,270,265
  240 CONTINUE
      WRITE(LL,1009)EPS2
      GO TO 280
 265  IF(ABS(SUMB - SSQ) - EPS1*SSQ) 266, 266, 270
 266  WRITE(LL,1010) EPS1
      GO TO 280
270   SSQ=SUMB
      NIT=NIT+1
      IF(NIT - MIT) 100, 100, 280
 2700 WRITE(LL,2710)
 2710 FORMAT(//115H0**** THE SUM OF SQUARES CANNOT BE REDUCED TO THE SUM
     1OF SQUARES AT THE END OF THE LAST ITERATION - ITERATING STOPS   /)
C
C                                                 END ITERATION
C
 280  WRITE(LL,1011)
      WRITE(LL,2001) (F(I), I = 1, NOB)
      WRITE(LL,1012)
      WRITE(LL,2001) (R(I), I = 1, NOB)
```

```
      WRITE(LL,1017)
 1017 FORMAT(////,* X PRIME-X MATRIX*)
      CALL GASSO(4,NP,TEMP,TEMP,D,LL)
      SSQ=SUMB
      IDF=NOB-NP
      WRITE(LL,1015)
      I=0
       CALL MATIN(D, NP, P, I, DET)
      DO 7692 I=1,NP
      II = I + NP*(I-1)
 7692 E(I) = SQRT(D(II))
      DO 340 I=1,NP
      JI = I + NP*(I-1) - 1
      IJ = I + NP*(I-2)
      DO 340 J = I, NP
      JI = JI + 1
      A(JI) = D(JI) / (E(I)*E(J))
      IJ = IJ + NP
  340  A(IJ) = A(JI)
       CALL GASSO(3, NP, TEMP, TEMP, A,LL)
      WRITE(LL,1016)
       CALL GASSO(1, NP, E, TEMP, TEMP,LL)
      IF(IDF) 341, 410, 341
  341 SDEV = SSQ / IDF
      WRITE(LL,1014) SDEV, IDF
       SDEV = SQRT(SDEV)
      DO 391 I=1,NP
      P(I)=TH(I)+2.0*E(I)*SDEV
391   TH(I)=TH(I)-2.0*E(I)*SDEV
      WRITE(LL,1039)
       CALL GASSO(2, NP, TB, P, TEMP,LL)
      LAOS = 1
      GO TO 101
  414 DO 415 K = 1, NOB
      TEMP = 0
      DO 420 I=1,NP
      DO 420 J=1,NP
      ISUB = K+NOB*(I-1)
      DEBUG1 = DELZ(ISUB)
C     DEBUG1 = DELZ(K + NOB*(I-1))
      ISUB = K+NOB*(J-1)
      DEBUG2 = DELZ(ISUB)
C     DEBUG2 = DELZ(K + NOB*(J-1))
      IJ = I + NP*(J-1)
      DEBUG3 = D(IJ)/(DIFZ(I)*TH(I)*DIFZ(J)*TH(J))
  420 TEMP = TEMP + DEBUG1 * DEBUG2 * DEBUG3
       TEMP = 2.0*SQRT(TEMP)*SDEV
      P(K)=F(K)+TEMP
  415 F(K)=F(K)-TEMP
      WRITE(LL,1008)
      IE=0
      DO 425 I=1,NOB,5
      IE=I+4
      IF(NOB-IE) 430,435,435
  430 IE=NOB
  435 WRITE(LL,2001) (P(J), J = I, IE)
  425 WRITE(LL,2006) (F(J), J = I, IE)
  410 WRITE(LL,1033) NPROB
```

```
      RETURN
99    WRITE(LL,1034)
      GO TO 410
1000 FORMAT(38H1NON-LINEAR ESTIMATION, PROBLEM NUMBER   I3,// I5,
    1  14H OBSERVATIONS, I5, 11H PARAMETERS  I7, 17H SCRATCH REQUIRED)
1001 FORMAT(/25H0INITIAL PARAMETER VALUES   )
1002 FORMAT(/54H0PROPORTIONS USED IN CALCULATING DIFFERENCE QUOTIENTS )
1003 FORMAT(/25H0INITIAL SUM OF SQUARES =   E12.4)
1004 FORMAT(/////45X,13HITERATION NO.  I4)
1007 FORMAT(/32H0PARAMETER VALUES VIA REGRESSION  )
1008 FORMAT(////54H0APPROXIMATE CONFIDENCE LIMITS FOR EACH FUNCTION VAL
    1UE     )
1009 FORMAT(/52H0ITERATION STOPS - RELATIVE CHANGE IN EACH PARAMETER LE
    1SS THAN    E12.4)
1010 FORMAT(/52H0ITERATION STOPS - RELATIVE CHANGE IN SUM OF SQUARES LE
    1SS THAN    E12.4)
1011 FORMAT(22H1FINAL FUNCTION VALUES  )
1012 FORMAT(////10H0RESIDUALS  )
1014 FORMAT(//24H0VARIANCE OF RESIDUALS =     ,E12.4,1H,I4,
    120H DEGREES OF FREEDOM    )
1015 FORMAT(////19H0CORRELATION MATRIX    )
1016 FORMAT(////21H0NORMALIZING ELEMENTS    )
1033 FORMAT(//19H0END OF PROBLEM NO.  I3)
1034 FORMAT(/16H0PARAMETER ERROR  )
1039 FORMAT(/71H0INDIVIDUAL CONFIDENCE LIMITS FOR EACH PARAMETER (ON LI
    1NEAR HYPOTHESIS)    )
1040 FORMAT(/9H0LAMBDA =E10.3, 4X,33HSUM OF SQUARES AFTER REGRESSION =
    1E15.7)
1041 FORMAT(14H DETERMINANT =  F12.4, 6X, 25H ANGLE IN SCALED COORD. =
    1  F5.2, 8HDEGREES    )
1043 FORMAT(28H0TEST POINT SUM OF SQUARES =    E12.4)
2001 FORMAT(/5E12.4)
2006 FORMAT(5E12.4)
      END
```

```
      SUBROUTINE MATIN(A, NVAR, B, NB, DET)
      DIMENSION A(NVAR, 1), B(NVAR, 1)
       PIVOTM = A(1,1)
       DET = 1.0
      DO 550 ICOL = 1, NVAR
       PIVOT = A(ICOL, ICOL)
      PIVOTM = AMIN1(PIVOT, PIVOTM)
       DET = PIVOT * DET
C
C     DIVIDE PIVOT ROW BY PIVOT ELEMENT
C
       A(ICOL, ICOL) = 1.0

      PIVOT = AMAX1(PIVOT, 1.E-20)
       PIVOT = A(ICOL, ICOL)/PIVOT
      DO 350 L=1,NVAR
  350  A(ICOL, L) = A(ICOL, L)*PIVOT
      IF(NB .EQ. 0) GO TO 371
      DO 370 L=1,NB
  370  B(ICOL, L) = B(ICOL, L)*PIVOT
C
C     REDUCE NON-PIVOT ROWS
C
  371 DO 550 L1=1,NVAR
       IF(L1 .EQ. ICOL) GO TO 550
       T = A(L1, ICOL)
       A(L1, ICOL) = 0.
      DO 450 L=1,NVAR
  450  A(L1, L) = A(L1, L) - A(ICOL, L)*T
      IF(NB .EQ. 0) GO TO 550
      DO 500 L=1,NB
  500  B(L1, L) = B(L1, L)-B(ICOL,L)*T
  550 CONTINUE
      RETURN
      END
```

```
       SUBROUTINE GASSO(ITYPE, NQ, A, B, C,LL)
      DIMENSION A(NQ),B(NQ),C(NQ,NQ)
       NP = NQ
       NR = NP/10
       LOW = 1
       LUP = 10
10    IF( NR )15,20,30
15    RETURN
20    LUP=NP
      IF(LOW .GT. LUP) RETURN
30    WRITE(LL,500) (J,J=LOW,LUP)
      GO TO (40,60,80,80),ITYPE
40    WRITE(LL,600)(A(J),J=LOW,LUP)
      GO TO 100
60    WRITE(LL,600) (B(J),J=LOW,LUP)
      GO TO 40
80    DO 90 I=LOW,LUP
90    WRITE(LL,720)I,(C(J,I),J=LOW,I)
      LOW2=LUP+1
      IF(LOW2 .GT. NP) GO TO 100
      DO 95 I=LOW2,NP
95    WRITE(LL,720)I,(C(J,I),J=LOW,LUP)
100    LOW = LOW + 10
       LUP = LUP + 10
       NR = NR - 1
       GO TO 10
500   FORMAT(/5X,I7,9(5X,I7))
600   FORMAT(5E12.4)
720   FORMAT(1H0,I3,9(1X,F12.4))
      END
```

TABLE H.5.1. ESTIMATED PARAMETER VALUES FOR COPPER-CYANIDE COMPLEX AT FIVE FIXED MCN/TCN RATIOS

			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Cu-CN	GIVEN	FCN_o	6.3×10^{-3}	6.7×10^{-3}	6.5×10^{-3}	6.3×10^{-3}	6.5×10^{-3}	6.3×10^{-3}	6.2×10^{-3}	6.6×10^{-3}
		k_v	3.9×10^{-2}	2.4×10^{-2}	7.4×10^{-3}	5.0×10^{-3}	3.4×10^{-2}	2.5×10^{-2}	2.3×10^{-2}	1.4×10^{-2}
		k_1	2.1×10^{-2}	7.1×10^{-3}	3.8×10^{-3}	3.3×10^{-3}	1.5×10^{-2}	2.4×10^{-3}	3.6×10^{-3}	3.1×10^{-3}
$\frac{MCN}{TCN}$	$= 0.0425$	FCN_o	6.8×10^{-3}	8.0×10^{-3}	6.6×10^{-3}	6.3×10^{-3}	6.6×10^{-3}	6.6×10^{-3}	6.4×10^{-3}	6.5×10^{-3}
		k_v	4.6×10^{-2}	1.4×10^{-2}	1.8×10^{-2}	1.6×10^{-2}	5.3×10^{-2}	2.2×10^{-2}	2.1×10^{-2}	1.4×10^{-2}
		k_1	5.2×10^{-10}	6.6×10^{-2}	9.9×10^{-10}	1.8×10^{-9}	1.1×10^{-10}	4.7×10^{-10}	1.2×10^{-10}	1.9×10^{-9}
$\frac{MCN}{TCN}$	$= 0.085$	FCN_o	7.0×10^{-3}	7.6×10^{-3}	6.7×10^{-3}	6.3×10^{-3}	7.2×10^{-3}	7.4×10^{-3}	6.9×10^{-3}	6.4×10^{-3}
		k_v	5.9×10^{-2}	1.5×10^{-2}	1.7×10^{-2}	1.5×10^{-2}	8.2×10^{-2}	1.7×10^{-2}	1.7×10^{-2}	1.4×10^{-2}
		k_1	4.6×10^{-3}	6.9×10^{-2}	2.9×10^{-10}	1.8×10^{-10}	2.8×10^{-3}	6.5×10^{-4}	1.9×10^{-10}	1.5×10^{-9}
$\frac{MCN}{TCN}$	$= 0.17$	FCN_o	6.3×10^{-3}	6.9×10^{-3}	6.5×10^{-3}	6.2×10^{-3}	6.5×10^{-3}	6.7×10^{-3}	6.5×10^{-3}	5.9×10^{-3}
		k_v	7.1×10^{-2}	1.5×10^{-2}	1.5×10^{-2}	1.5×10^{-2}	1.0×10^{-2}	2.0×10^{-2}	1.8×10^{-2}	1.7×10^{-2}
		k_1	1.2×10^{-2}	7.4×10^{-2}	4.9×10^{-10}	4.7×10^{-10}	6.6×10^{-3}	4.3×10^{-3}	2.9×10^{-3}	2.8×10^{-10}
$\frac{MCN}{TCN}$	$= 0.34$	FCN_o	5.0×10^{-3}	5.4×10^{-3}	5.2×10^{-3}	4.5×10^{-3}	5.0×10^{-3}	5.3×10^{-3}	5.2×10^{-3}	4.8×10^{-3}
		k_v	9.8×10^{-2}	1.5×10^{-2}	2.0×10^{-2}	1.1×10^{-2}	1.6×10^{-1}	2.5×10^{-2}	2.4×10^{-2}	3.7×10^{-2}
		k_1	2.3×10^{-2}	8.9×10^{-2}	3.1×10^{-3}	4.0×10^{-4}	1.2×10^{-2}	8.2×10^{-3}	6.7×10^{-3}	2.7×10^{-3}
$\frac{MCN}{TCN}$	$= 0.68$	FCN_o	2.5×10^{-3}	2.6×10^{-3}	2.5×10^{-3}	2.4×10^{-3}	2.5×10^{-3}	2.5×10^{-3}	2.5×10^{-3}	2.4×10^{-3}
		k_v	$5.2\times10^{+1}$	3.6×10^{-2}	5.2×10^{-2}	7.9×10^{-2}	$5.6\times10^{+1}$	4.6×10^{-2}	4.7×10^{-2}	3.9×10^{-1}
		k_1	3.4×10^{-2}	1.7×10^{-2}	6.2×10^{-3}	3.1×10^{-3}	4.1×10^{-2}	1.2×10^{-2}	1.1×10^{-2}	6.1×10^{-3}

TABLE H.5.2. ESTIMATED PARAMETER VALUES FOR ZINC-CYANIDE COMPLEX AT FIVE FIXED MCN/TCN RATIOS

			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Zn-CN	GIVEN	FCN_o	5.8×10^{-3}	5.2×10^{-3}	6.2×10^{-3}	5.0×10^{-3}	6.2×10^{-3}	6.4×10^{-3}	6.3×10^{-3}	6.0×10^{-3}
		k_v	3.9×10^{-2}	2.4×10^{-2}	7.4×10^{-3}	5.0×10^{-3}	3.4×10^{-2}	2.5×10^{-2}	2.3×10^{-2}	1.4×10^{-2}
		k_1	6.2×10^{-3}	1.9×10^{-2}	6.8×10^{-3}	4.5×10^{-3}	4.5×10^{-3}	1.8×10^{-2}	1.4×10^{-2}	9.6×10^{-3}
$\frac{MCN}{TCN}$	$= 0.0425$	FCN_o	6.3×10^{-3}	6.2×10^{-3}	6.4×10^{-3}	5.1×10^{-3}	7.2×10^{-3}	7.8×10^{-3}	7.8×10^{-3}	6.1×10^{-3}
		k_v	7.6×10^{-2}	1.8×10^{-2}	1.8×10^{-2}	1.5×10^{-2}	5.9×10^{-2}	2.1×10^{-2}	2.0×10^{-2}	1.5×10^{-2}
		k_1	1.5×10^{-2}	6.1×10^{-2}	1.6×10^{-9}	5.3×10^{-10}	21.7×10^{0}	6.1×10^{-2}	9.0×10^{-2}	1.3×10^{-10}
$\frac{MCN}{TCN}$	$= 0.085$	FCN_o	6.1×10^{-3}	5.9×10^{-3}	6.8×10^{-3}	5.1×10^{-3}	6.9×10^{-3}	7.4×10^{-3}	7.4×10^{-3}	6.3×10^{-3}
		k_v	8.4×10^{-2}	1.9×10^{-2}	1.6×10^{-2}	1.4×10^{-2}	7.1×10^{-2}	2.1×10^{-2}	2.0×10^{-2}	2.1×10^{-2}
		k_1	2.1×10^{-2}	6.2×10^{-2}	7.6×10^{-10}	1.1×10^{-9}	1.4×10^{-2}	6.1×10^{-2}	6.3×10^{-2}	1.4×10^{-3}
$\frac{MCN}{TCN}$	$= 0.17$	FCN_o	5.6×10^{-3}	5.3×10^{-3}	6.2×10^{-3}	5.3×10^{-3}	6.3×10^{-3}	6.7×10^{-3}	6.7×10^{-3}	5.8×10^{-3}
		k_v	1.1×10^{-1}	1.9×10^{-2}	1.8×10^{-2}	6.9×10^{-3}	8.4×10^{-2}	2.2×10^{-2}	2.1×10^{-2}	2.4×10^{-2}
		k_1	2.8×10^{-2}	6.7×10^{-2}	3.2×10^{-3}	1.4×10^{-3}	2.2×10^{-2}	6.3×10^{-2}	6.2×10^{-2}	4.5×10^{-3}
$\frac{MCN}{TCN}$	$= 0.34$	FCN_o	4.6×10^{-3}	4.2×10^{-3}	4.9×10^{-3}	4.2×10^{-3}	4.9×10^{-3}	5.3×10^{-3}	5.3×10^{-3}	4.6×10^{-3}
		k_v	1.7×10^{-1}	2.6×10^{-2}	2.5×10^{-2}	9.1×10^{-3}	1.1×10^{-1}	2.4×10^{-2}	2.2×10^{-2}	3.4×10^{-2}
		k_1	3.8×10^{-2}	2.3×10^{-2}	6.4×10^{-3}	3.0×10^{-3}	3.5×10^{-2}	6.6×10^{-2}	6.1×10^{-2}	7.7×10^{-3}
$\frac{MCN}{TCN}$	$= 0.68$	FCN_o	2.3×10^{-3}	2.0×10^{-3}	2.4×10^{-3}	2.1×10^{-3}	2.4×10^{-3}	2.5×10^{-3}	2.5×10^{-3}	2.3×10^{-3}
		k_v	5.6×10^{-1}	4.9×10^{-2}	6.6×10^{-2}	2.2×10^{-2}	8.2×10^{0}	2.6×10^{-2}	2.6×10^{-2}	1.3×10^{-1}
		k_1	5.4×10^{-2}	1.9×10^{-2}	9.2×10^{-3}	4.3×10^{-3}	4.3×10^{-2}	8.3×10^{-2}	5.7×10^{-2}	1.1×10^{-2}

TABLE H.5.3. ESTIMATED PARAMETER VALUES FOR NICKEL-CYANIDE COMPLEX AT FIVE FIXED MCN/TCN RATIOS

		20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Ni-CN GIVEN	FCN_0	$7.5x10^{-3}$	$6.3x10^{-3}$	$6.7x10^{-3}$	$5.2x10^{-3}$	$6.3x10^{-3}$	$6.3x10^{-3}$	$6.4x10^{-3}$	$5.5x10^{-3}$
	k_v	$3.9x10^{-2}$	$2.4x10^{-2}$	$7.4x10^{-3}$	$5.0x10^{-3}$	$3.4x10^{-2}$	$2.5x10^{-2}$	$2.3x10^{-2}$	$1.4x10^{-2}$
	k_1	$2.7x10^{-3}$	$8.1x10^{-4}$	$3.0x10^{-3}$	$2.7x10^{-3}$	$8.3x10^{-4}$	$1.5x10^{-3}$	$4.2x10^{-3}$	$4.1x10^{-3}$
$\frac{MCN}{TCN} = 0.0425$	FCN_0	$7.5x10^{-3}$	$6.3x10^{-3}$	$6.7x10^{-3}$	$5.3x10^{-3}$	$6.4x10^{-3}$	$6.4x10^{-3}$	$6.6x10^{-3}$	$5.5x10^{-3}$
	k_v	$3.5x10^{-2}$	$2.4x10^{-2}$	$1.8x10^{-2}$	$1.6x10^{-2}$	$3.5x10^{-2}$	$2.4x10^{-2}$	$2.1x10^{-2}$	$1.4x10^{-2}$
	k_1	$7.0x10^{-9}$	$2.7x10^{-9}$	$6.1x10^{-9}$	$3.3x10^{-9}$	$3.5x10^{-10}$	$3.5x10^{-9}$	$2.4x10^{-10}$	$2.2x10^{-9}$
$\frac{MCN}{TCN} = 0.085$	FCN_0	$7.5x10^{-3}$	$6.3x10^{-3}$	$6.7x10^{-3}$	$5.3x10^{-3}$	$6.4x10^{-3}$	$6.4x10^{-3}$	$6.8x10^{-3}$	$5.4x10^{-3}$
	k_v	$3.1x10^{-2}$	$2.5x10^{-2}$	$1.8x10^{-2}$	$1.6x10^{-2}$	$3.7x10^{-2}$	$2.3x10^{-2}$	$1.9x10^{-2}$	$1.5x10^{-2}$
	k_1	$2.1x10^{-10}$	$7.7x10^{-10}$	$4.2x10^{-10}$	$6.3x10^{-9}$	$4.0x10^{-10}$	$7.2x10^{-10}$	$1.0x10^{-9}$	$7.9x10^{-9}$
$\frac{MCN}{TCN} = 0.17$	FCN_0	$7.0x10^{-3}$	$6.3x10^{-3}$	$6.5x10^{-3}$	$5.3x10^{-3}$	$6.3x10^{-3}$	$6.4x10^{-3}$	$6.7x10^{-3}$	$4.9x10^{-3}$
	k_v	$1.8x10^{-2}$	$1.0x10^{-1}$	$1.9x10^{-2}$	$1.5x10^{-2}$	$8.8x10^{-2}$	$1.9x10^{-2}$	$1.7x10^{-2}$	$1.9x10^{-2}$
	k_1	$8.7x10^{-4}$	$1.7x10^{-3}$	$3.0x10^{-10}$	$6.3x10^{-11}$	$1.2x10^{-3}$	$5.9x10^{-5}$	$1.7x10^{-3}$	$1.2x10^{-10}$
$\frac{MCN}{TCN} = 0.34$	FCN_0	$5.6x10^{-3}$	$4.8x10^{-3}$	$5.2x10^{-3}$	$4.5x10^{-3}$	$4.9x10^{-3}$	$5.1x10^{-3}$	$5.3x10^{-3}$	$4.3x10^{-3}$
	k_v	$2.5x10^{-2}$	$1.4x10^{-1}$	$3.1x10^{-2}$	$1.9x10^{-2}$	$1.1x10^{+1}$	$2.8x10^{-2}$	$2.2x10^{-2}$	$5.0x10^{-2}$
	k_1	$4.5x10^{-3}$	$9.9x10^{-3}$	$1.4x10^{-3}$	$1.7x10^{-10}$	$5.6x10^{-3}$	$3.5x10^{-3}$	$5.2x10^{-3}$	$3.2x10^{-3}$
$\frac{MCN}{TCN} = 0.68$	FCN_0	$2.8x10^{-3}$	$2.4x10^{-3}$	$2.4x10^{-3}$	$2.0x10^{-3}$	$2.3x10^{-3}$	$2.4x10^{-3}$	$2.5x10^{-3}$	$2.0x10^{-3}$
	k_v	$7.9x10^{-2}$	$3.4x10^{-1}$	$3.3x10^{0}$	$4.5x10^{-2}$	$6.4x10^{+1}$	$6.9x10^{-2}$	$4.8x10^{-2}$	$2.2x10^{-1}$
	k_1	$8.1x10^{-3}$	$3.8x10^{-2}$	$4.4x10^{-3}$	$2.8x10^{-3}$	$2.3x10^{-2}$	$7.2x10^{-3}$	$8.9x10^{-3}$	$7.1x10^{-3}$

TABLE H.5.4. ESTIMATED PARAMETER VALUES FOR IRON-CYANIDE COMPLEX AT FIVE FIXED MCN/TCN RATIOS

			20°C AIR NO UV	20°C NO AIR NO UV	4°C AIR NO UV	4°C NO AIR NO UV	20°C AIR UV	20°C NO AIR UV	4°C AIR UV	4°C NO AIR UV
Fe-CN	GIVEN	FCN_0	$6.4x10^{-3}$	$6.2x10^{-3}$	$5.9x10^{-3}$	$4.1x10^{-3}$	$5.7x10^{-3}$	$5.7x10^{-3}$	$6.1x10^{-3}$	$5.7x10^{-3}$
		k_v	$3.9x10^{-2}$	$2.4x10^{-2}$	$7.4x10^{-3}$	$5.0x10^{-3}$	$3.4x10^{-2}$	$2.5x10^{-2}$	$2.3x10^{-2}$	$1.4x10^{-2}$
		k_1	$1.6x10^{-3}$	$2.6x10^{-3}$	$1.2x10^{-3}$	$7.4x10^{-4}$	$6.8x10^{-3}$	$2.2x10^{-2}$	$5.1x10^{-3}$	$4.0x10^{-3}$
$\frac{MCN}{TCN}$	$= 0.0425$	FCN_0	$6.5x10^{-3}$	$6.3x10^{-3}$	$5.9x10^{-3}$	$4.1x10^{-3}$	$6.0x10^{-3}$	$6.6x10^{-3}$	$6.2x10^{-3}$	$5.8x10^{-3}$
		k_v	$3.5x10^{-2}$	$2.3x10^{-2}$	$1.9x10^{-2}$	$1.6x10^{-2}$	$4.4x10^{-2}$	$2.3x10^{-2}$	$2.1x10^{-2}$	$1.3x10^{-2}$
		k_1	$3.2x10^{-9}$	$8.0x10^{-9}$	$7.3x10^{-9}$	$2.9x10^{-10}$	$1.4x10^{-10}$	$1.5x10^{-3}$	$3.9x10^{-9}$	$3.3x10^{-9}$
$\frac{MCN}{TCN}$	$= 0.085$	FCN_0	$6.5x10^{-3}$	$6.4x10^{-3}$	$6.0x10^{-3}$	$4.1x10^{-3}$	$6.5x10^{-3}$	$6.4x10^{-3}$	$6.2x10^{-3}$	$5.8x10^{-3}$
		k_v	$3.0x10^{-2}$	$2.2x10^{-2}$	$1.9x10^{-2}$	$1.7x10^{-2}$	$8.3x10^{-2}$	$2.5x10^{-2}$	$1.8x10^{-2}$	$1.1x10^{-2}$
		k_1	$2.8x10^{-10}$	$1.1x10^{-9}$	$2.2x10^{-10}$	$4.9x10^{-9}$	$1.7x10^{-3}$	$4.4x10^{-3}$	$5.3x10^{-11}$	$4.6x10^{-10}$
$\frac{MCN}{TCN}$	$= 0.17$	FCN_0	$6.6x10^{-3}$	$6.3x10^{-3}$	$6.1x10^{-3}$	$4.0x10^{-3}$	$5.8x10^{-3}$	$5.9x10^{-3}$	$6.1x10^{-3}$	$5.6x10^{-3}$
		k_v	$1.4x10^{-2}$	$1.9x10^{-2}$	$2.5x10^{-2}$	$1.8x10^{-2}$	$1.1x10^{-1}$	$2.9x10^{-2}$	$9.8x10^{-3}$	$6.9x10^{-3}$
		k_1	$1.3x10^{-3}$	$2.4x10^{-10}$	$2.1x10^{-4}$	$8.9x10^{-10}$	$5.2x10^{-3}$	$7.7x10^{-3}$	$2.7x10^{-3}$	$1.4x10^{-3}$
$\frac{MCN}{TCN}$	$= 0.34$	FCN_0	$5.2x10^{-3}$	$5.1x10^{-3}$	$4.8x10^{-3}$	$3.5x10^{-3}$	$4.5x10^{-3}$	$4.7x10^{-3}$	$4.9x10^{-3}$	$4.5x10^{-3}$
		k_v	$1.8x10^{-2}$	$2.5x10^{-2}$	$3.5x10^{-2}$	$5.9x10^{-2}$	$0.8x10^{+1}$	$4.1x10^{-2}$	$1.2x10^{-2}$	$8.8x10^{-3}$
		k_1	$4.9x10^{-3}$	$2.9x10^{-3}$	$4.0x10^{-3}$	$2.5x10^{-3}$	$9.7x10^{-3}$	$1.1x10^{-2}$	$4.9x10^{-3}$	$3.2x10^{-3}$
$\frac{MCN}{TCN}$	$= 0.68$	FCN_0	$2.5x10^{-3}$	$2.4x10^{-3}$	$2.2x10^{-3}$	$1.5x10^{-3}$	$2.2x10^{-3}$	$2.2x10^{-3}$	$2.3x10^{-3}$	$2.2x10^{-3}$
		k_v	$3.5x10^{-2}$	$6.3x10^{-2}$	$8.7x10^{-2}$	$1.5x10^{-1}$	$7.6x10^{+1}$	$1.0x10^{-1}$	$2.7x10^{-2}$	$1.9x10^{-2}$
		k_1	$8.2x10^{-3}$	$6.1x10^{-3}$	$8.4x10^{-3}$	$7.9x10^{-3}$	$4.2x10^{-2}$	$1.5x10^{-2}$	$6.5x10^{-3}$	$4.5x10^{-3}$

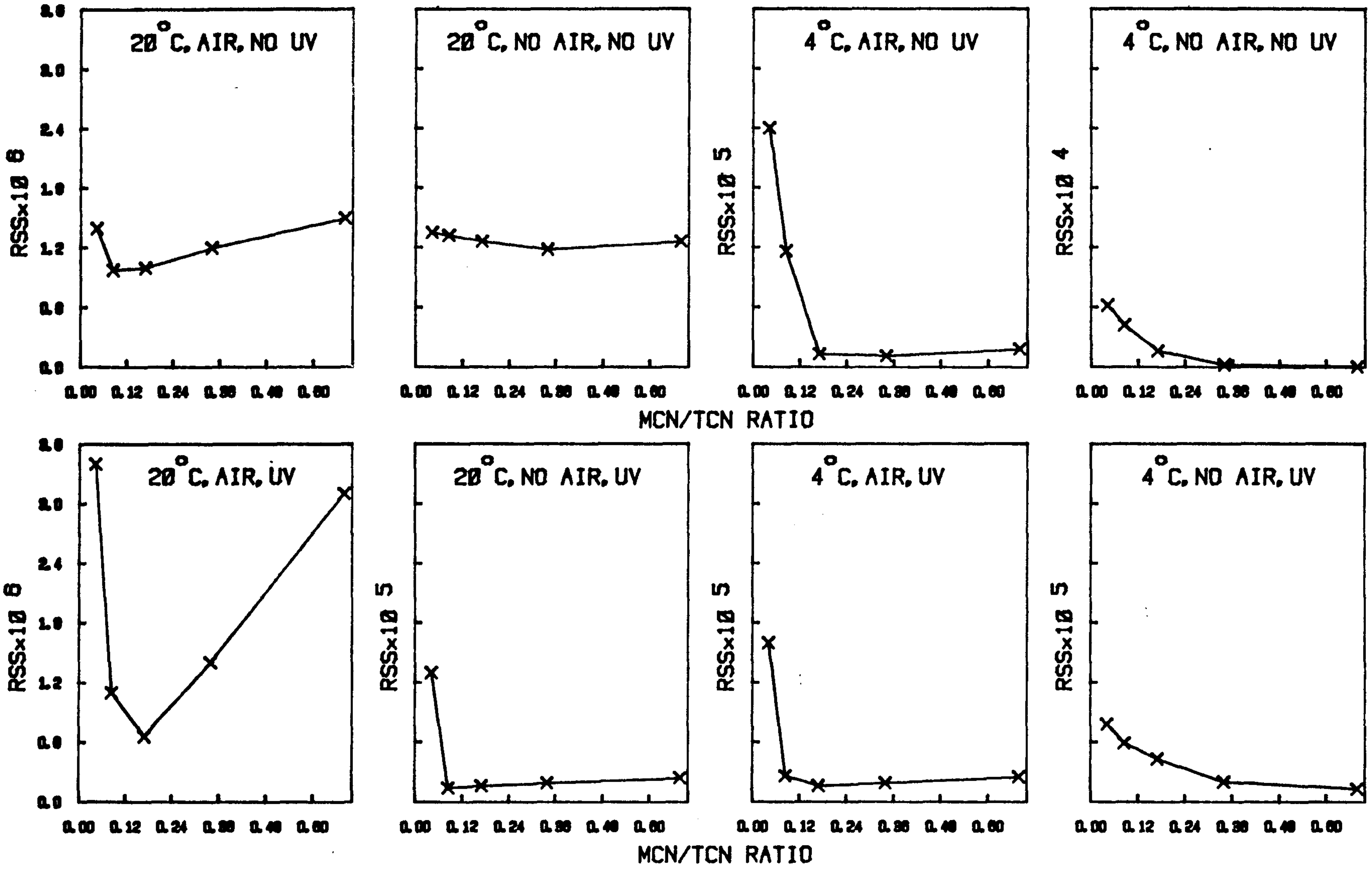


Figure H.5.1 Residual Sum of Squares versus MCN/TCN Ratios - Cu

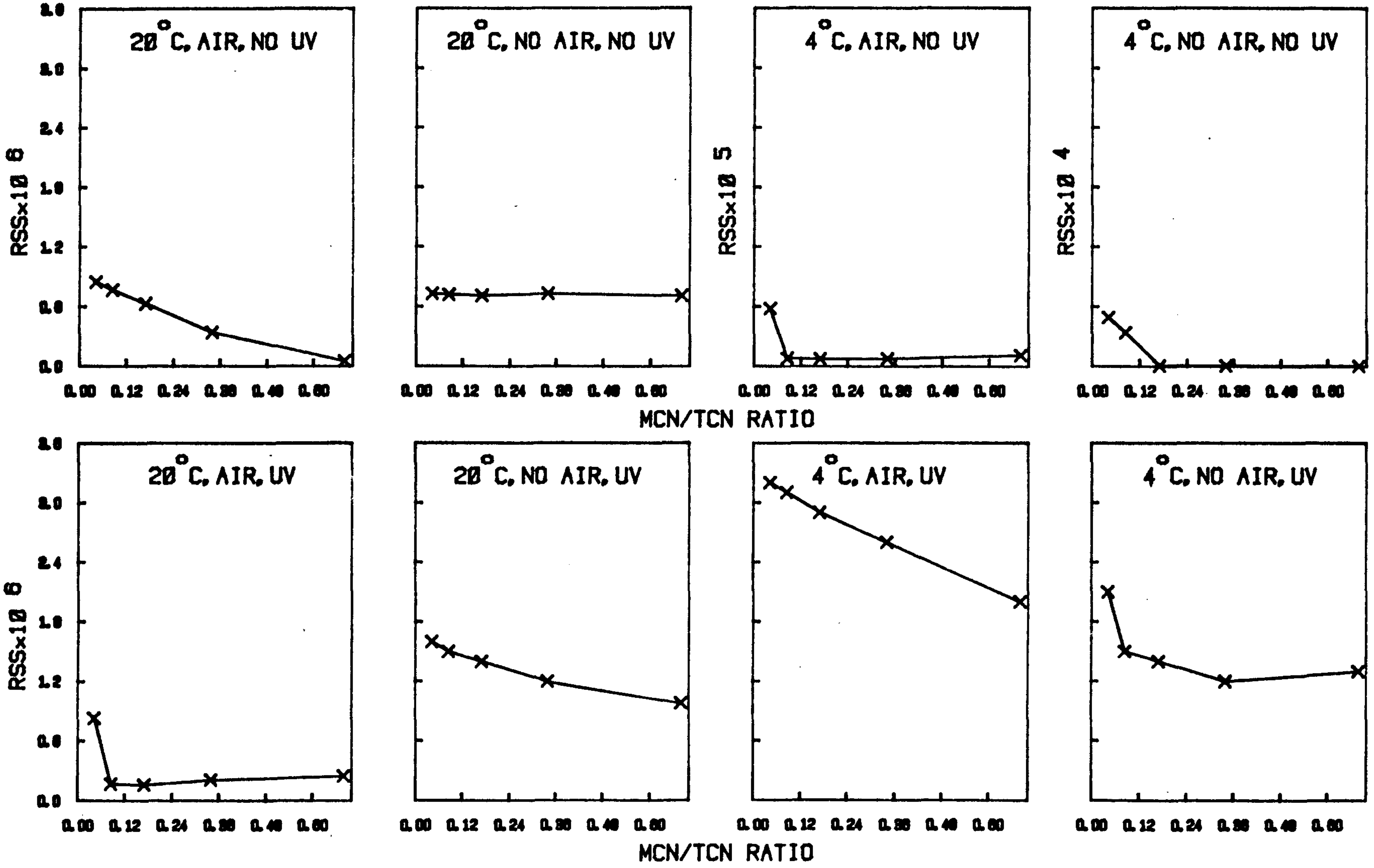


Figure H.5.2 Residual Sum of Squares versus MCN/TCN Ratios - Zn

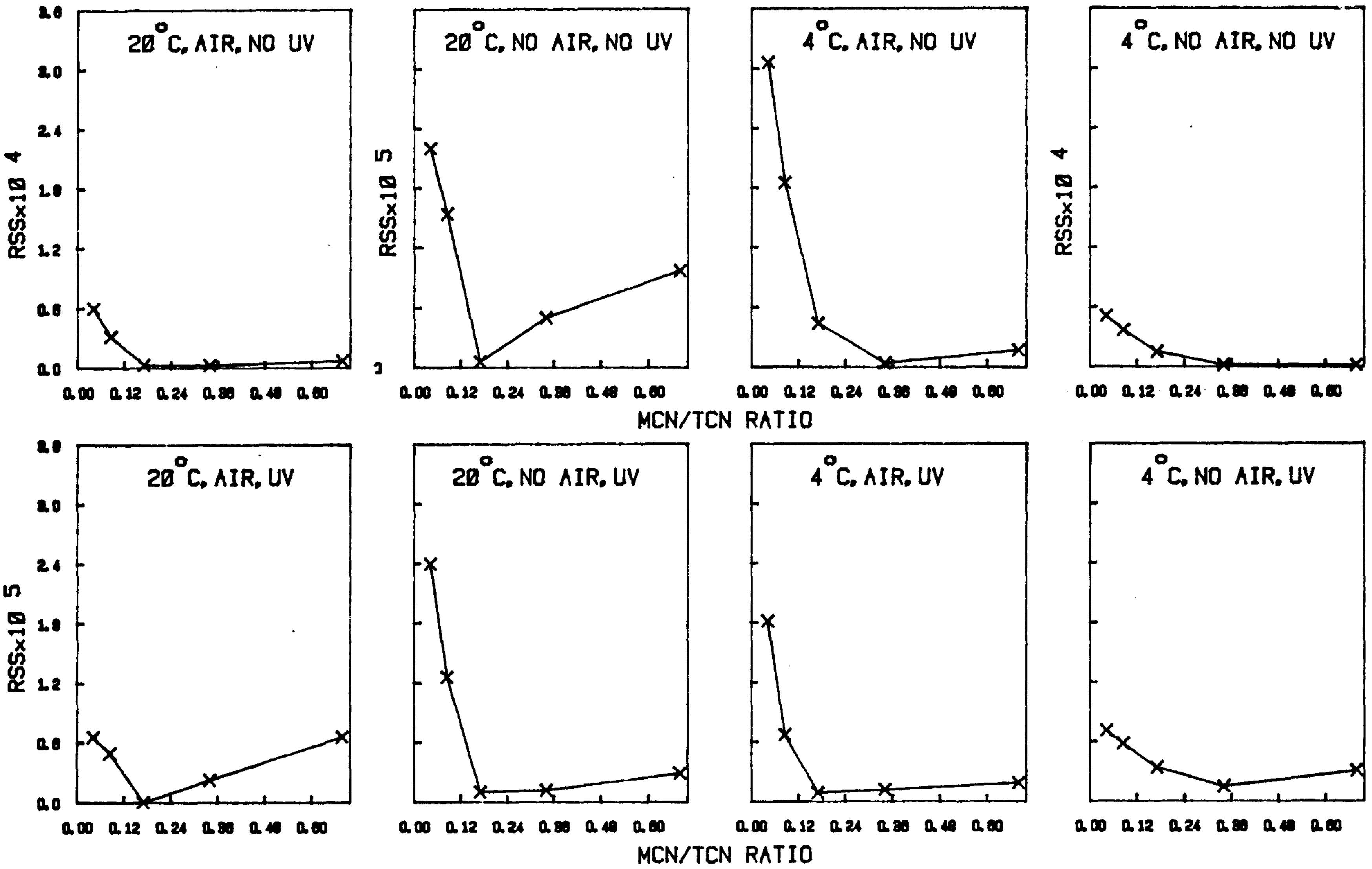


Figure H.5.3 Residual Sum of Squares versus MCN/TCN Ratios - Ni

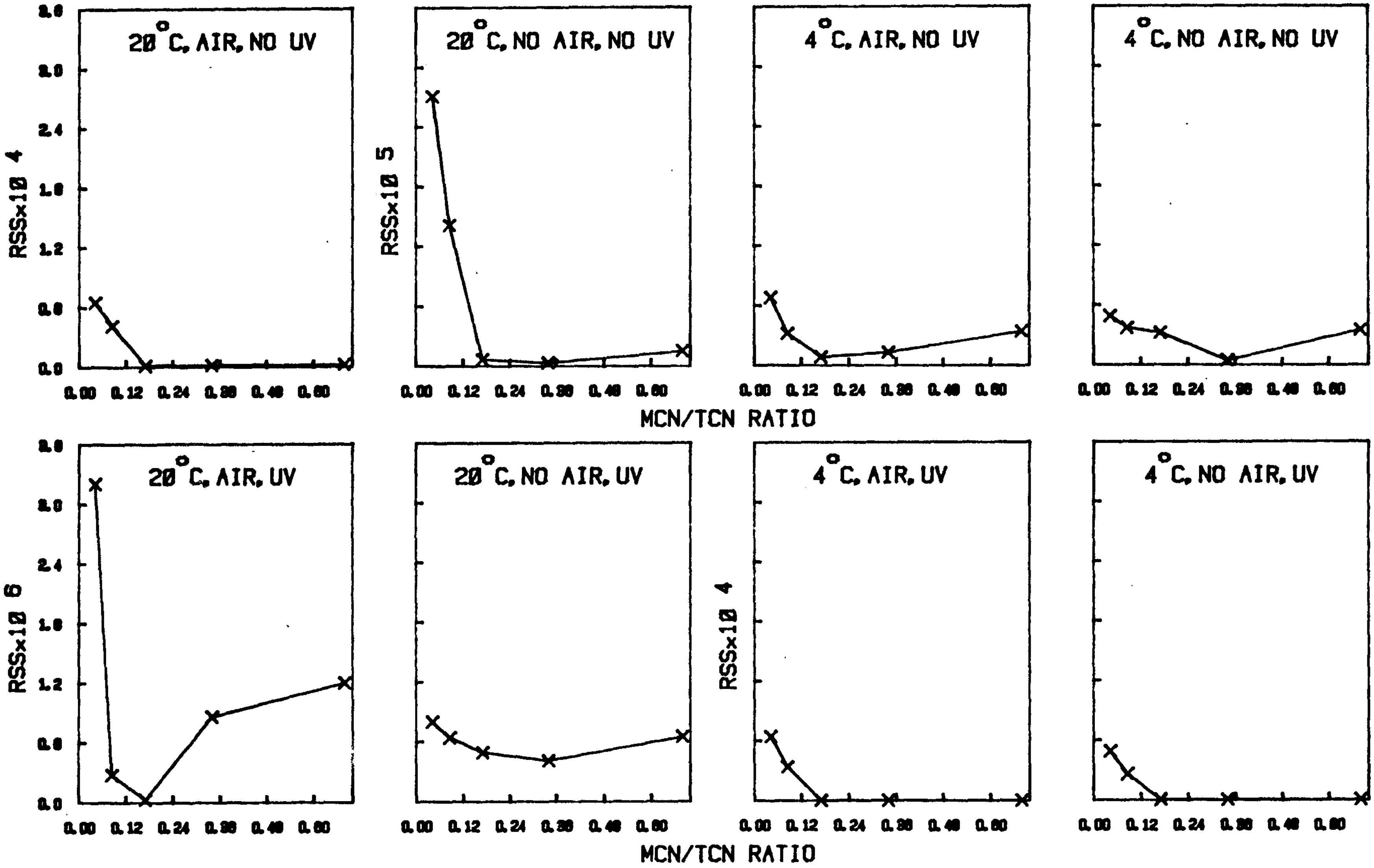


Figure H.5.4 Residual Sum of Squares versus MCN/TCN Ratios - Fe

APPENDIX H.6

Dot Diagrams

Estimated k_1 with Respect to Temperature

UV Light and Aeration at MCN/TCN = 0.17

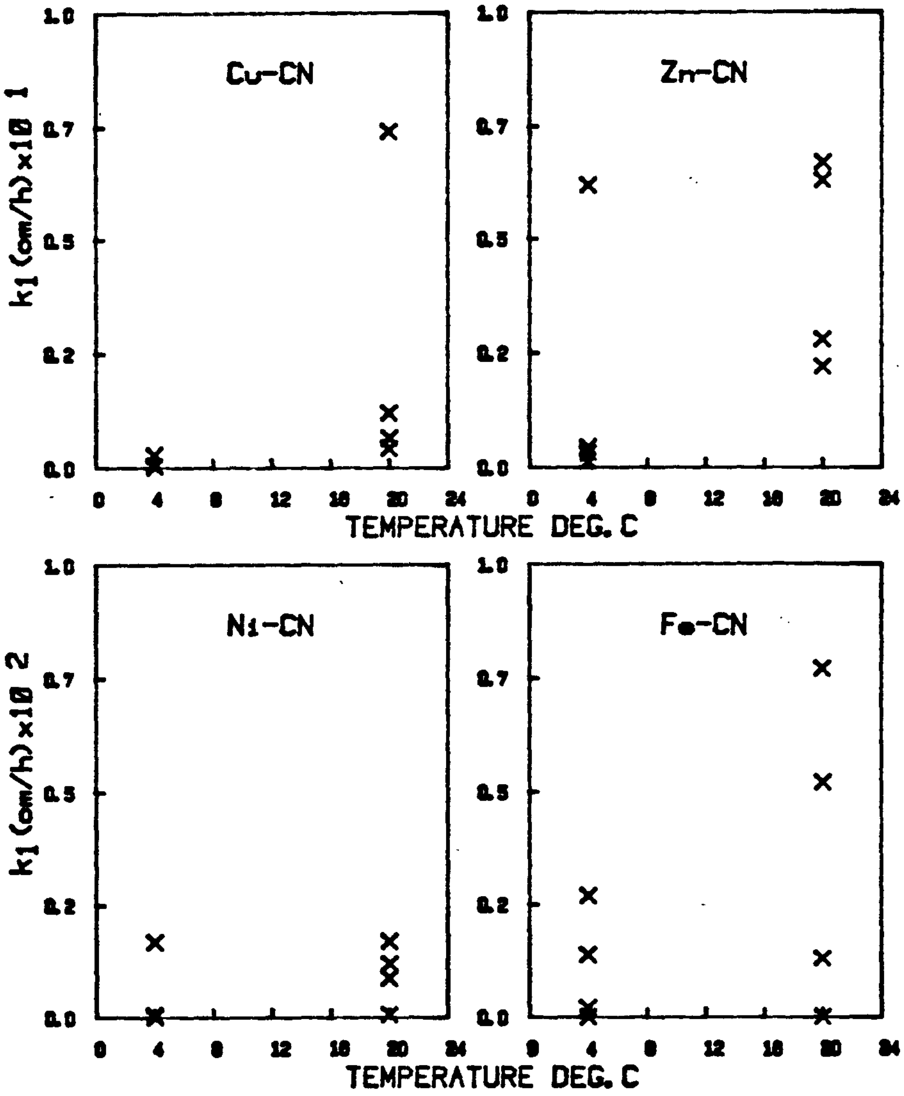


Figure H.6.1 Estimated k_1 at MCN/TCN = 0.17 versus Temperature

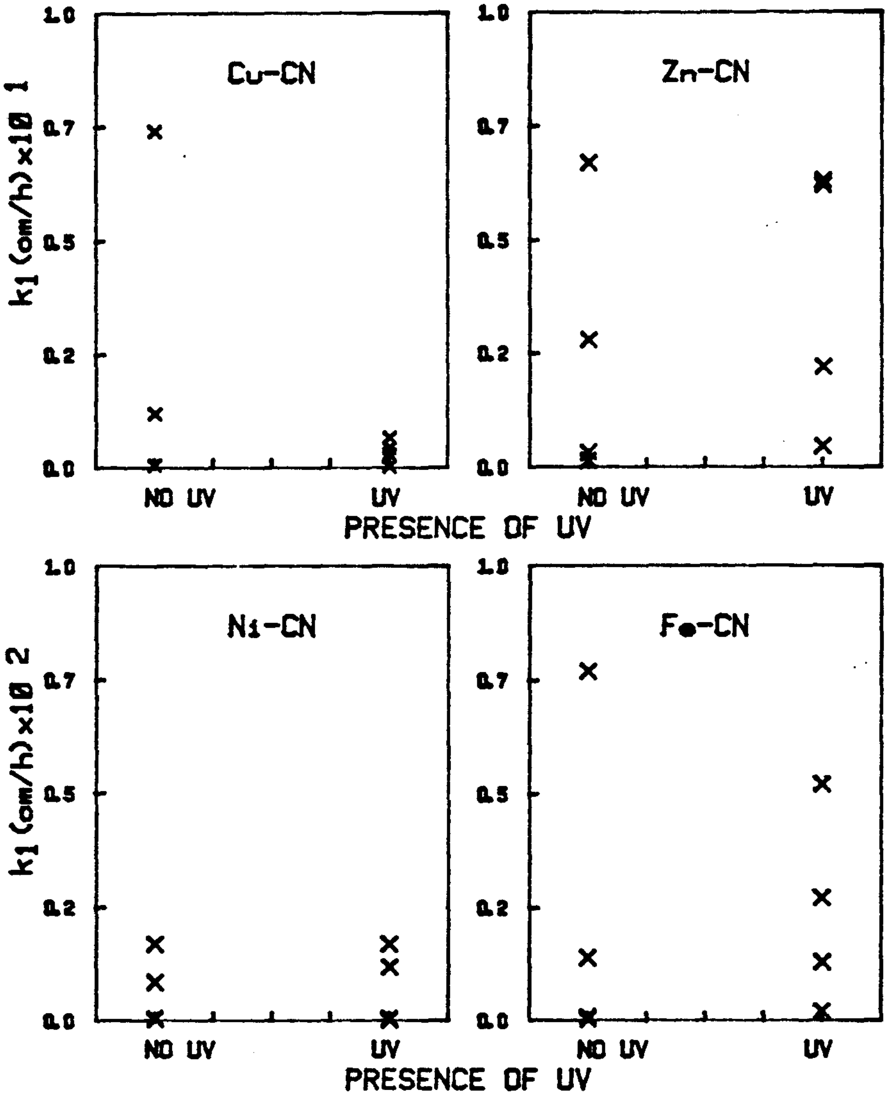


Figure H.6.2 Estimated k_1 at MCN/TCN = 0.17 versus UV Light

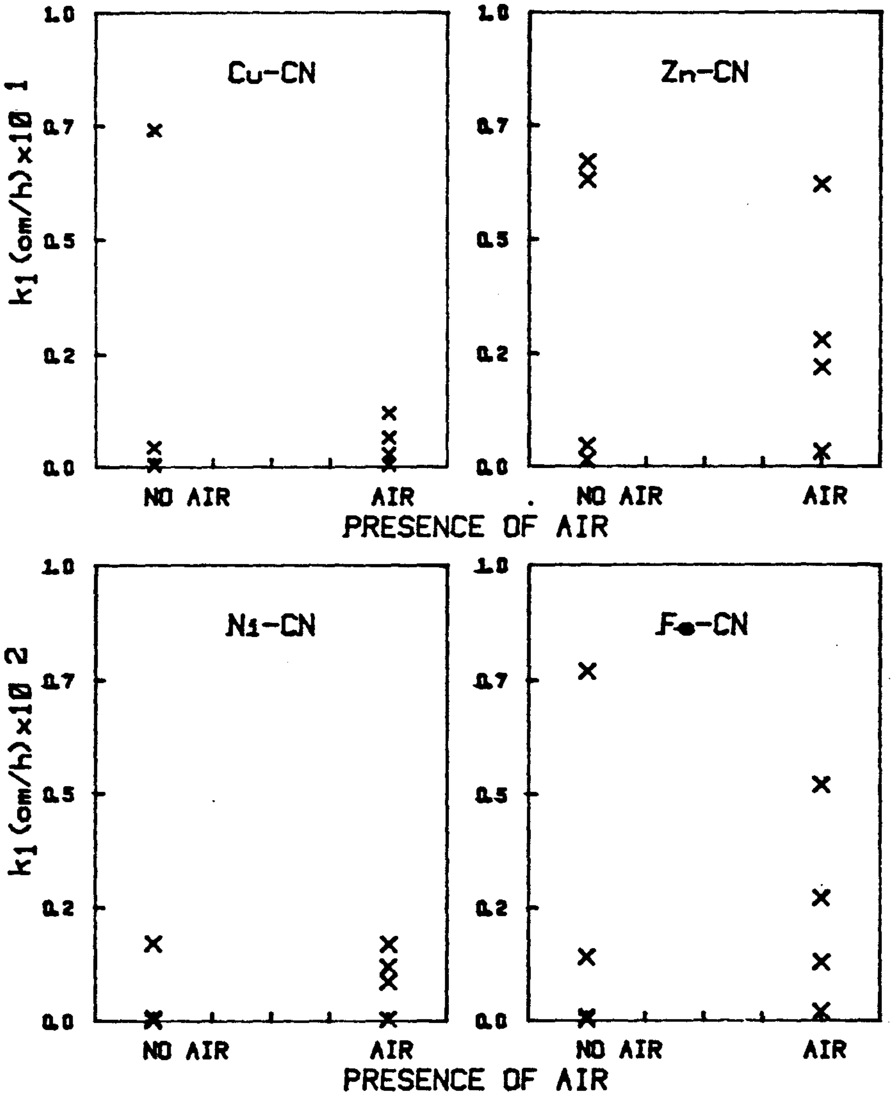


Figure H.6.3 Estimated k_1 at MCN/TCN = 0.17 versus Aeration

APPENDIX I

Low Mix Model Simulations

I.1 EXAMPLE CALCULATION FOR THE INITIAL VALUES OF METAL AND FREE CYANIDE IN THE LOW MIX

The single metallo-cyanide solutions and low-mix solutions theoretically have 17% of total cyanide tied up with the metal (17% of 200 mg/L). The difference is that in the low mix, the total concentration of four metals complexed 17% of the cyanide present. The four metals involved were Cu, Zn, Ni and Fe. This synthetic mix emulates the composition of one real gold mill effluent which contained about 7, 10, 2 and 2 mg/L of Cu, Zn, Ni and Fe respectively. Therefore, the low mix had the same concentrations of these metals. The value used for $[MCN]_o$ in the low mix was based upon the theoretical stoichiometry. It is calculated as follows:

Metals	Concentration (mg/L)	Theoretical Stoichiometry for the assumed complex	$[MCN]_o$ (mol/L)
Cu	7	$(CN)_3/Cu = 1.228$	0.00033
Zn	10	$(CN)_4/Zn = 1.592$	0.00062
Ni	2	$(CN)_4/Ni = 1.773$	0.00014
Fe	2	$(CN)_6/Fe = 2.795$	0.00022
			0.00131

Hence the total initial MCN (equal to 17% of TCN) is 0.00131 mol/L.

The total cyanide and metal concentrations are the only measurable initial concentrations. The total and free initial cyanide concentrations for the prepared low mix solutions are tabulated in Table I.1.1:

TABLE I.1.1. INITIAL VALUES FOR TOTAL AND FREE CYANIDE CONCENTRATIONS

Conditions		$[TCN]_o$ (mol/L)		$[FCN]_o$ (mol/L)	
Air	UV	4°C	20°C	4°C	20°C
+	+	0.00761	0.00722	0.00631	0.00592
+	-	0.00746	0.00769	0.00615	0.00638
-	+	0.00711	0.00765	0.00581	0.00635
-	-	0.00822	0.00761	0.00692	0.00631

The initial free cyanide concentration was calculated by subtracting calculated $[MCN]_o$ from measured $[TCN]_o$ concentrations.

e.g., 0.00746 - 0.00131 = 0.00615 mol/L of $[FCN]_o$.

I.2 THE EXAMPLE CALCULATION OF THE ULTRAVIOLET IRRADIATION RATE CONSTANT

The intensity of the light obtained from the UV lamp was calculated to be $I_o = 7.68 \times 10^{-4}$ einstein*/h.

Out of four single metallo-cyanide solutions only iron cyanide was affected by UV light (see conclusions from the experimental design). Therefore, the UV light rate constant (k_{uv}) was calculated using the results obtained on the iron cyanide solution.

If the metal decay constants k_1 were plotted against I_o=0 and I_o= 7.48×10^{-4} einstein/h, the slope (m) would be, for the conditions with and without UV light calculated as follows (assuming the full depth of the vessel is operative):

20, AIR, UV & NO UV m = $(0.0222 - 0.0026)/7.68 \times 10^{-4} = 25.5$

20, NO AIR, UV & NO UV m = $(0.0068 - 0.0016)/7.68 \times 10^{-4} = 6.9$

4, AIR, UV & NO UV m = $(0.00399 - 0.00074)/7.68 \times 10^{-4} = 4.3$

4, NO AIR, UV & NO UV m = $(0.0051 - 0.0012)/7.68 \times 10^{-4} = 5.2$

Since the first slope is an order of magnitude different from the other three it was rejected in taking an average. Therefore, the average m value for the other three conditions is $\bar{m} = 5.5$ (einstein^{-1}).

---

* Einstein - a unit of light energy used in photochemistry equal to Avogadro's number times the energy of one photon of light of the frequency in question.

The UV light rate constant is proportional to the average light intensity, i.e., $k_{uv} = mI_a$. According to Beer's law (Moore, 1963) the average light intensity is equal

$$I_a = I_o/\varepsilon z \ (1-e^{-\varepsilon z})$$

where ε is the absorption coefficient or extinction coefficient (ε assumed to be equal to 10 cm^2/mol) (Kolthoff et al., 1969) and Z is the depth of the medium that lights go through (determined from the absorbance spectra by UV spectrophotometry to be 33 cm).

If the term in parenthesis is assumed negligible the k_{uv} becomes

$$k_{uv} = m \frac{I_o}{\varepsilon z} = \frac{5.5 \left[\frac{1}{\text{einst.}}\right] \text{ x } 7.68 \text{ x } 10^{-4} \left[\frac{\text{einst.}}{\text{h}}\right]}{10 \left[\frac{\text{cm}^2}{\text{mol}}\right] \text{ x } 33 \text{ cm x } \frac{55.4 \text{ mol}}{1\text{L}} \text{ x } \frac{1\text{L}}{1000 \text{ cm}^3}} = 0.0023 \ (\text{h}^{-1})$$

APPENDIX I.3

The Results of the Low Mix Model Fit and the Example of The Computer Programs Used

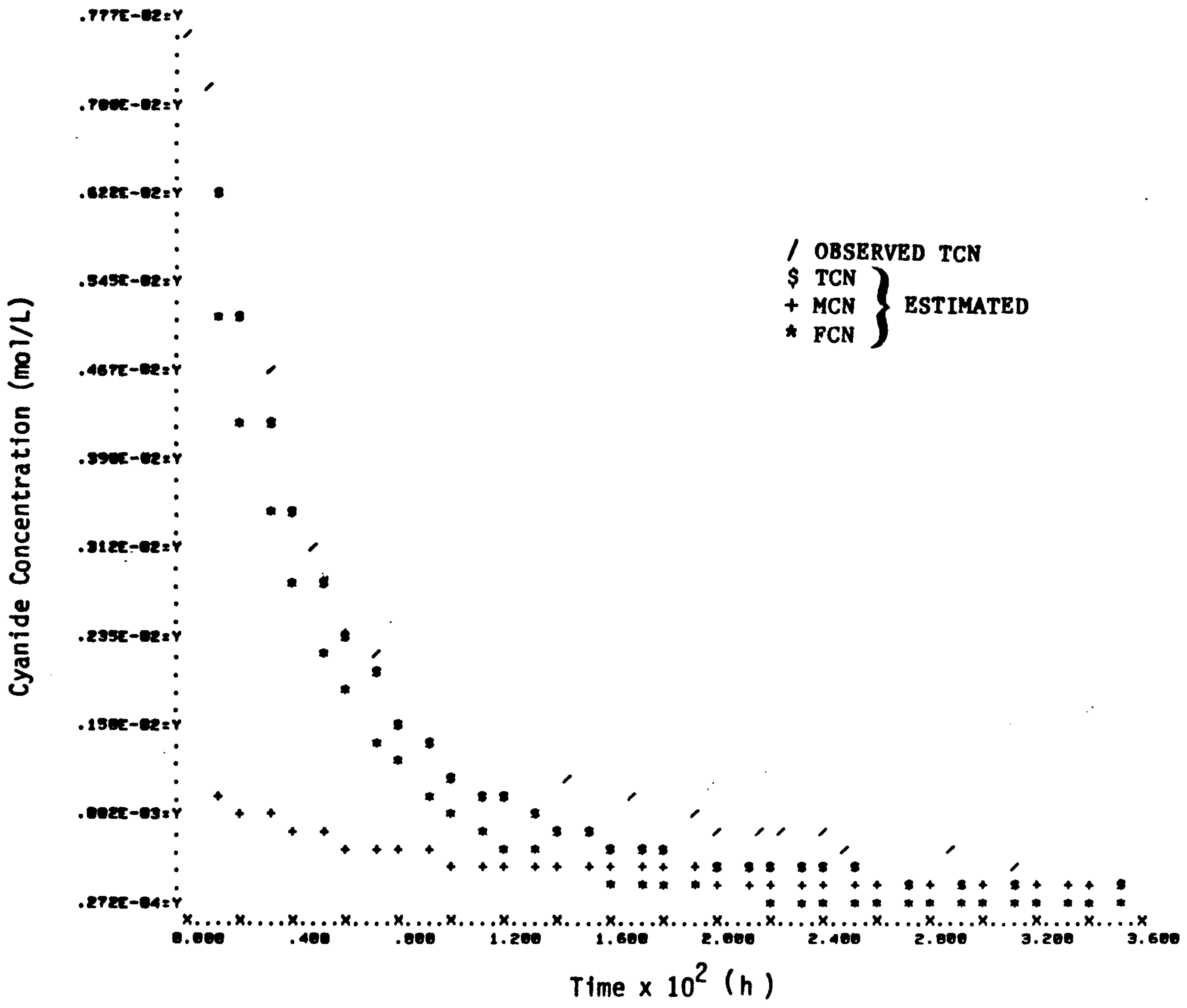


Figure I.3.1 Low Mix - 20°C, NO AIR, NO UV

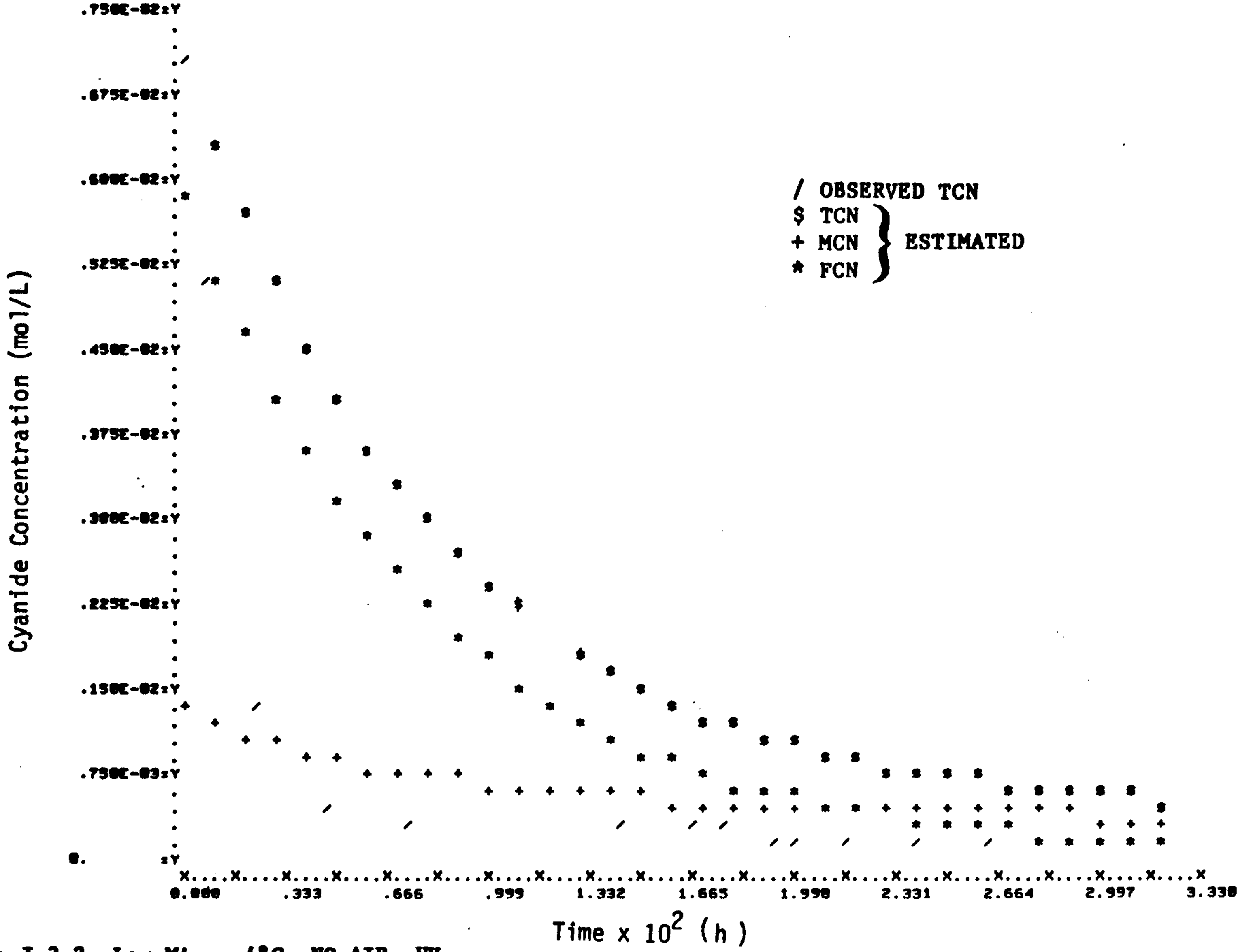


Figure I.3.2 Low Mix - 4°C, NO AIR, UV

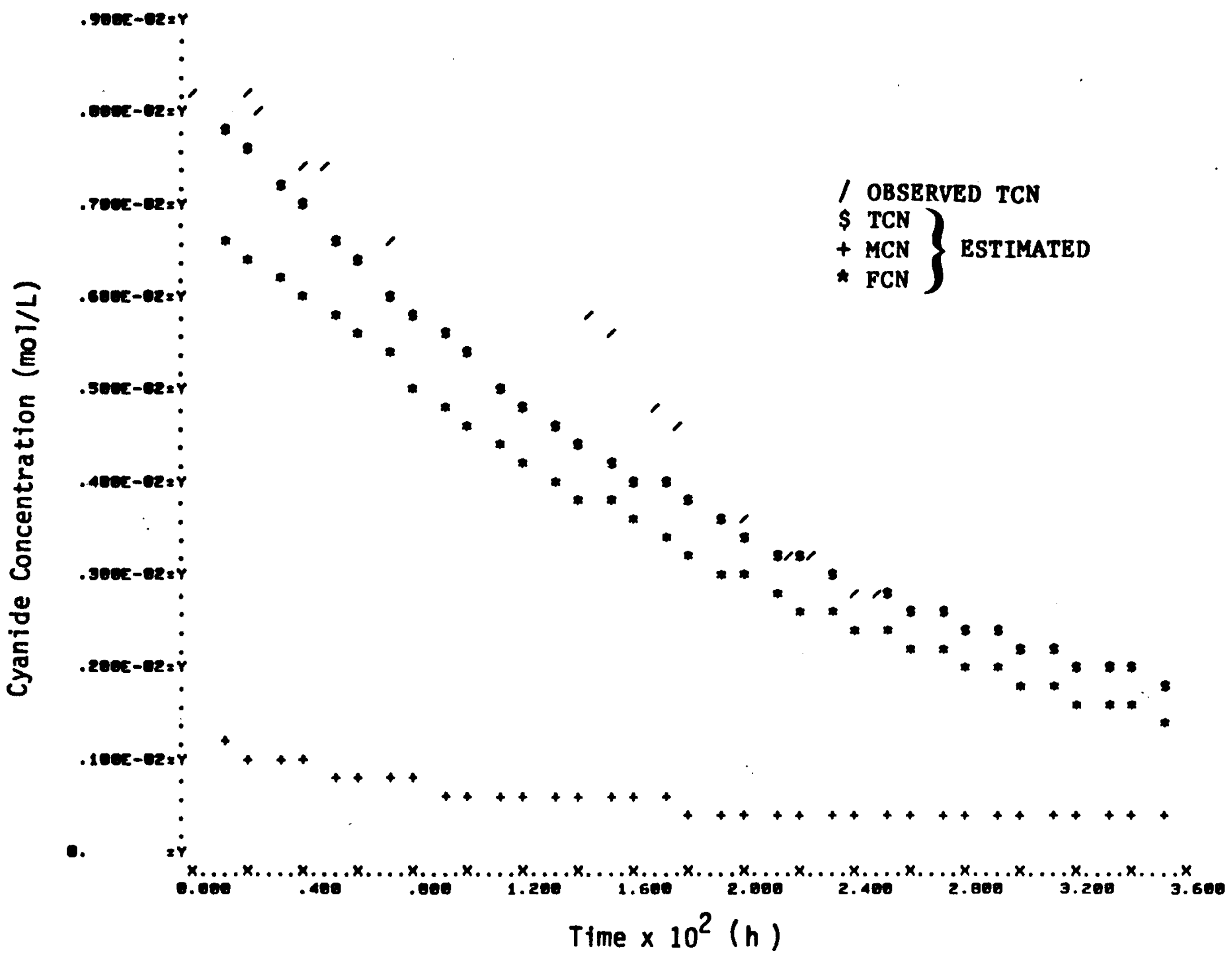


Figure I.3.3 Low Mix - 4°C, NO AIR, NO UV

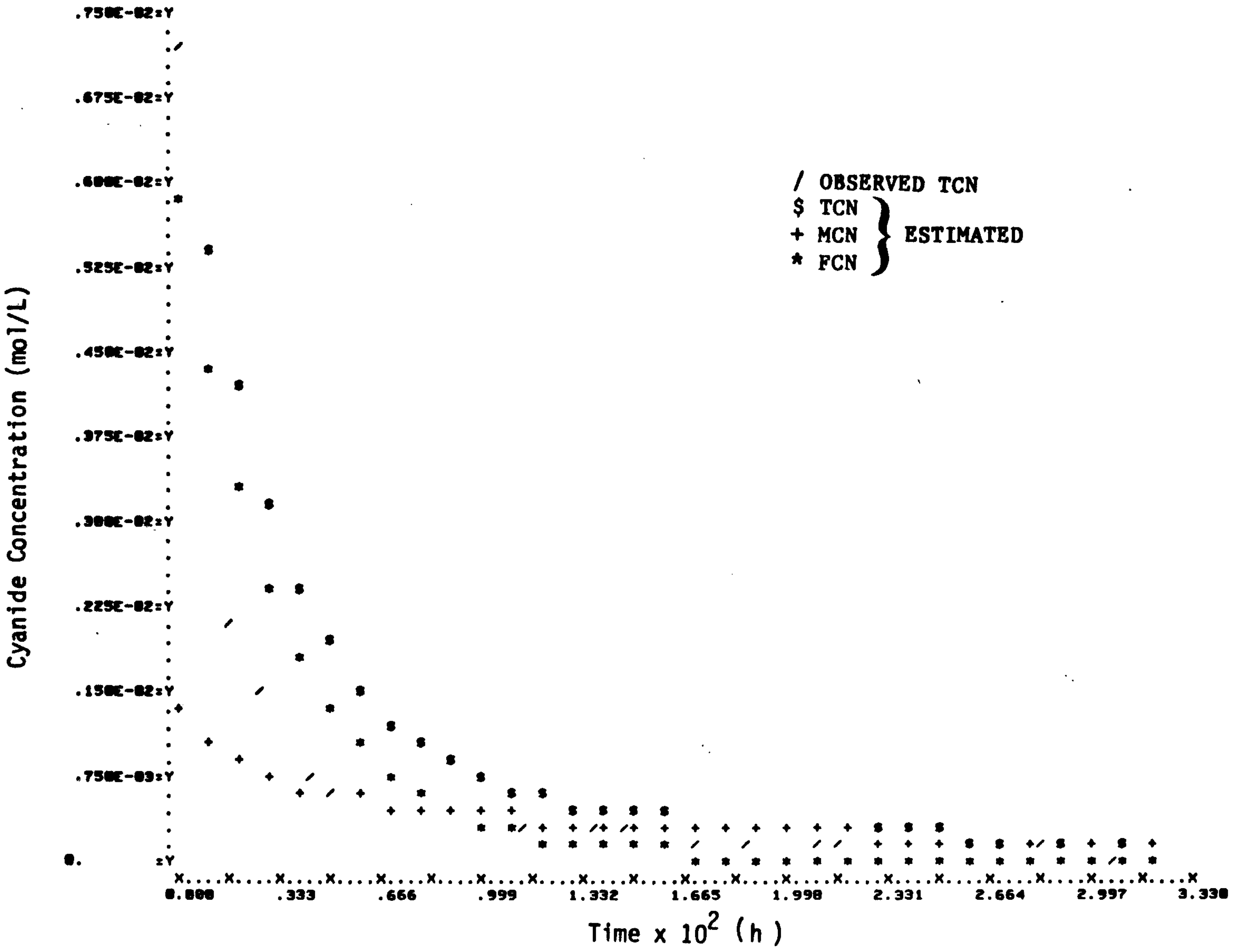


Figure I.3.4 Low Mix - 20°C, AIR, UV

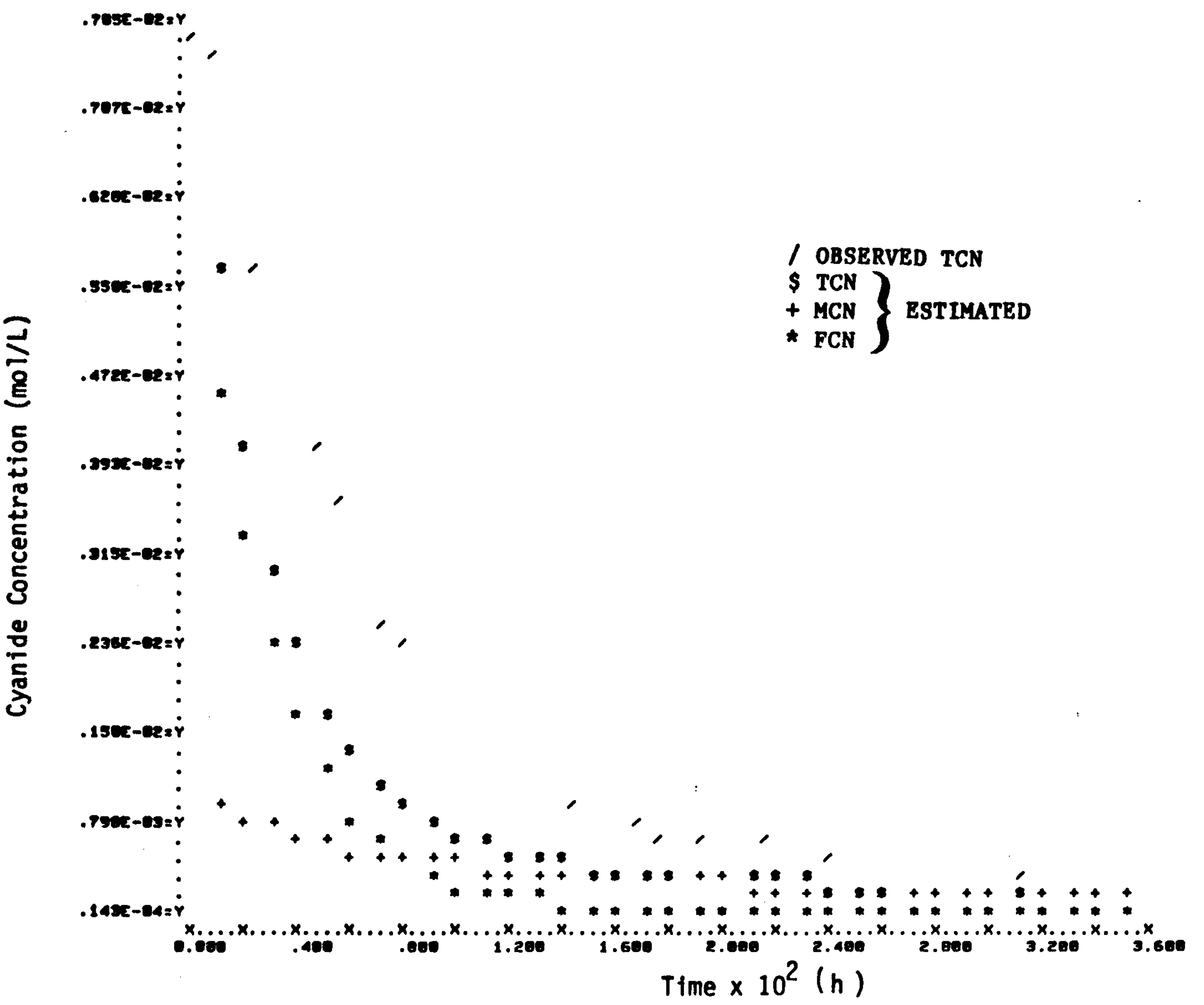


Figure I.3.5 Low Mix - 20°C, AIR, NO UV

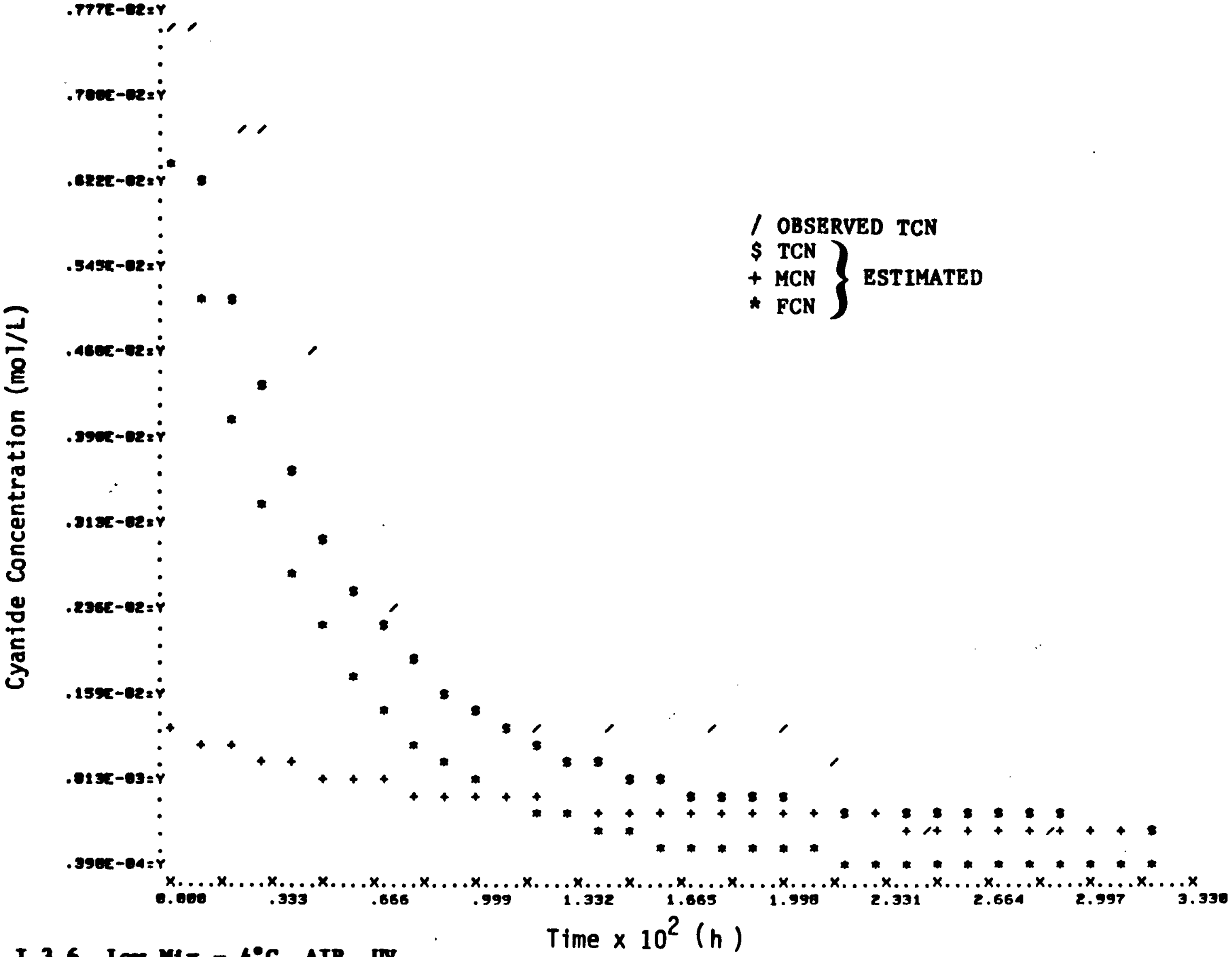


Figure I.3.6 Low Mix - 4°C, AIR, UV

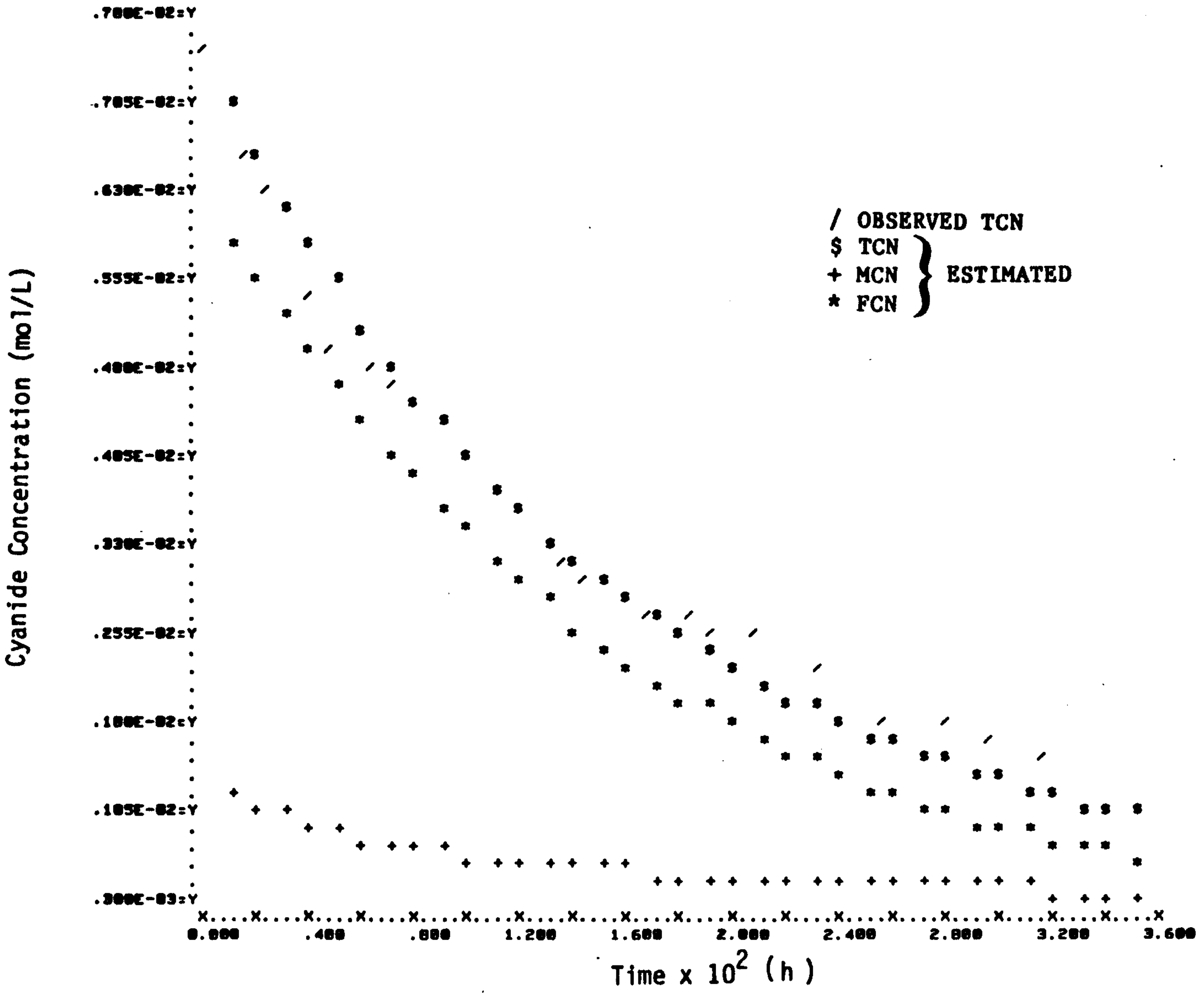


Figure I.3.7 Low Mix - 4°C, AIR, NO UV

```
      PROGRAM MIX  (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,TAPE11)
      DIMENSION TH(12)
      REAL      Y(7),C(24),W(7,9),X,TOL,XEND
      COMMON /A/ RKC,RKZ,RKN,RKF,RKV,VK,V,AS
      EXTERNAL FCN1
      READ(11,*) (TH(I),I=1,12)
      WRITE(6,*) (TH(I),I=1,12)
      NW=7
      N=7
      X=0.0
      Y(1)=TH(1)
      Y(2)=TH(2)
      Y(3)=Y(1)+Y(2)
      Y(4)=TH(4)
      Y(5)=TH(5)
      Y(6)=TH(6)
      Y(7)=TH(7)
      RKC=TH(8)
      RKZ=TH(9)
      RKN=TH(10)
      RKF=TH(11)
      RKV=TH(12)
      VK=TH(3)
      V=2000.
      AS=47.78
      TOL=0.0001
      IND=1
      CALL PLOTPT(X,Y(1),4)
      CALL PLOTPT(X,Y(2),2)
      CALL PLOTPT(X,Y(3),20)
      WRITE(6,1000)
1000  FORMAT(10X,"X",12X,"Y(1)",12X,"Y(2)",12X,"Y(3)")
      WRITE(6,2000) X,Y(1),Y(2),Y(3)
2000  FORMAT(6X,F6.2,6X,F10.7,6X,F10.7,6X,F10.7)
      DO 10 K=1,32
      XEND=FLOAT(K)*10.
      CALL DVERK (N,FCN1,X,Y,XEND,TOL,IND,C,NW,W,IER)
      IF (IND.LT.0.OR.IER.GT.0)  GOTO 20
      WRITE(6,3000) X,Y(1),Y(2),Y(3)
3000  FORMAT(6X,F6.2,6X,F10.7,6X,F10.7,6X,F10.7)
      CALL PLOTPT(X,Y(1),4)
      CALL PLOTPT(X,Y(2),2)
      CALL PLOTPT(X,Y(3),20)
10    CONTINUE
      READ(11,*)NOBS
      DO 15 J=1,NOBS
      READ(11,*)XO,YO
      Y1=YO/26000
      WRITE(6,*)XO,Y1
      CALL PLOTPT(XO,Y1,5)
15    CONTINUE
      CALL OUTPLT
      STOP
20    CONTINUE
      STOP
      END
      SUBROUTINE FCN1(N,X,Y,YPRIME)
      DIMENSION TH(12)
      COMMON /A/ RKC,RKZ,RKN,RKF,RKV,VK,V,AS
      REAL      Y(N),YPRIME(N),X
      YPRIME(4)=-RKC*Y(4)
      YPRIME(5)=-RKZ*Y(5)
      YPRIME(6)=-RKN*Y(6)
      YPRIME(7)=(-RKF*Y(7))-RKV*Y(7)
      YPRIME(2)=YPRIME(4)+YPRIME(5)+YPRIME(6)+YPRIME(7)
      YPRIME(1)=-YPRIME(2)-(VK*V/AS*Y(1))
      YPRIME(3)=-VK*V/AS*Y(1)
      RETURN
      END
```

```
        PROGRAM DATA3(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,TAPE11)
      DIMENSION TH(11)
      INTEGER  N,IND,NW,IER,K
      REAL     Y(7),C(24),W(7,9),X,TOL,XEND
      COMMON /A/ RKC,RKZ,RKN,RKF,VK
C
C***********************************************************************
C
C      THIS PROGRAM DOES MODELLING OF A MIX WITH NO UV EFFECT! IT REQUIRES
C     TH(11),NOBS AND DATA SET
C
C ***********************************************************************
C
      EXTERNAL FCN1
      READ(11,*) (TH(I),I=1,11)
      WRITE(6,*) (TH(I),I=1,11)
      NW=7
      N=7
      X=0.0
      Y(1)=TH(1)
      Y(2)=TH(2)
      Y(3)=Y(1)+Y(2)
      Y(4)=TH(4)
      Y(5)=TH(5)
      Y(6)=TH(6)
      Y(7)=TH(7)
      RKC=TH(8)
      RKZ=TH(9)
      RKN=TH(10)
      RKF=TH(11)
      VK=TH(3)
      TOL=0.0001
      IND=1
      WRITE(6,2000)
 2000 FORMAT(10X,"X",12X,"Y(1)",12X,"Y(2)",12X,"Y(3)")
      WRITE(6,7000) X,Y(1),Y(2),Y(3)
 7000 FORMAT(6X,F6.2,6X,F10.7,6X,F10.7,6X,F10.7)
      DO 10 K=1,35
        XEND=FLOAT(K)*10.
        CALL DVERK (N,FCN1,X,Y,XEND,TOL,IND,C,NW,W,IER)
        IF (IND.LT.0.OR.IER.GT.0)  GOTO 20
        WRITE(6,3000) X,Y(1),Y(2),Y(3)
```

```
 3000 FORMAT(6X,F6.2,6X,F10.7,6X,F10.7,6X,F10.7)
      CALL PLOTPT(X,Y(1),4)
      CALL PLOTPT(X,Y(2),2)
      CALL PLOTPT(X,Y(3),20)
   10 CONTINUE
      READ(11,*)NOBS
      DO 12 J=1,NOBS
      READ(11,*)XO,YO
      Y1=YO/26000
      WRITE(6,*)XO,Y1
      CALL PLOTPT(XO,Y1,5)
   12 CONTINUE
      CALL OUTPLT
      STOP
   20 CONTINUE
      STOP
      END

      SUBROUTINE FCN1(N,X,Y,YPRIME)
      DIMENSION TH(11)
      COMMON /A/ RKC,RKZ,RKN,RKF,VK
      INTEGER  N
      REAL     Y(N),YPRIME(N),X
      YPRIME(1)=(RKC*Y(4))+(RKZ*Y(5))+(RKN*Y(6))+(RKF*Y(7))-
     +(VK*Y(1))
      YPRIME(2)=-(RKC*Y(4))-(RKZ*Y(5))-(RKN*Y(6))-(RKF*Y(7))
      YPRIME(3)=-VK*Y(1)
      YPRIME(4)=-RKC*Y(4)
      YPRIME(5)=-RKZ*Y(5)
      YPRIME(6)=-RKN*Y(6)
      YPRIME(7)=-RKF*Y(7)
      RETURN
      END
$
--EOR--
 .0069231 .00129 .005026 .0003342 .000618 .0001377 .000217 .00295 .01703 .0004373 .001445
          X             Y(1)              Y(2)              Y(3)
        0.00          .0069231          .0012900          .0082131
       10.00          .0066952          .0011756          .0078708
       20.00          .0064621          .0010781          .0075402
       30.00          .0062266          .0009947          .0072213
       40.00          .0059912          .0009231          .0069143
       50.00          .0057576          .0008615          .0066190
```

```
 60.00          .0055273          .0008082          .0063355
 70.00          .0053014          .0007620          .0060634
 80.00          .0050807          .0007217          .0058025
 90.00          .0048661          .0006865          .0055526
100.00          .0046570          .0006554          .0053133
110.00          .0044563          .0006280          .0050842
120.00          .0042617          .0006035          .0048652
130.00          .0040741          .0005816          .0046557
140.00          .0038936          .0005619          .0044555
150.00          .0037202          .0005441          .0042642
160.00          .0035537          .0005278          .0040815
170.00          .0033940          .0005129          .0039069
180.00          .0032410          .0004991          .0037402
190.00          .0030946          .0004864          .0035810
200.00          .0029545          .0004745          .0034290
210.00          .0028205          .0004634          .0032839
220.00          .0026925          .0004529          .0031454
230.00          .0025701          .0004431          .0030132
240.00          .0024533          .0004337          .0028870
250.00          .0023417          .0004248          .0027665
260.00          .0022353          .0004162          .0026515
270.00          .0021336          .0004081          .0025417
280.00          .0020367          .0004002          .0024369
290.00          .0019442          .0003927          .0023369
300.00          .0018560          .0003854          .0022414
310.00          .0017719          .0003784          .0021503

0. .008230769230769
19. .008115384615385
24. .007961538461538
41. .0075
48. .007423076923077
72. .006615384615385
144. .005846153846154
151. .005538461538462
168. .004884615384615
175. .004538461538462
199. .003580461538462
216. .003253846153846
223. .003219230769231
241. .002815384615385
247. .002792307692308
312. .002119230769231
```

APPENDIX J

Example Calculations for:

- High Mix Model Simulations.
- Barren Solution Model Simulations.
- Effect of pH.

J.1 EXAMPLE CALCULATION FOR THE INITIAL VALUES OF METAL AND FREE CYANIDE IN THE HIGH MIX

The high mix cyanide solution was designed to have metals complexing with 117% of total cyanide (200 mg/L). Hence, when complexes with the metals Cu, Zn, Ni and Fe are formed, there is an excess of free metal. The characteristics of the real gold mill effluent was emulated as with the low mix, but there was proportional increase in the metal concentration. Therefore, the values were:

Metals (mg/L)	Theoretical Stoichiometry	$[MCN]_o$ (mg/L)	$[MCN]_o$ (mol/L)
Cu = 48.7	$(CN)_3/Cu$ = 1.228	59.79	0.002298
Zn = 69.5	$(CN)_4/Zn$ = 1.592	110.68	0.004254
Ni = 13.9	$(CN)_4/Ni$ = 1.773	24.66	0.000948
Fe = 13.9	$(CN)_6/Fe$ = 2.795	38.87	0.001494
			0.008994

Total initial metal cyanide concentration 234.00 mg/L = 0.008994 (mol/L).

The total cyanide concentrations recorded for the prepared high mix solutions were as tabulated:

Conditions		$[TCN]_o$(mol/L)	
AIR	UV	4°C	20°C
+	+	0.00692	0.00742
+	-	0.00761	0.00765
-	+	0.00738	0.00734
-	-	0.00761	0.00753

In order to determine metal cyanide concentrations and avoid having negative initial values for free cyanide (because our metal cyanide is higher than the total cyanide concentration) the calculations were carried out in two ways:

i) For the first simulation assuming that we were dealing with $MCN_o = TCN_o$, 15 to 23.1% of each [MCN] was calculated and subtracted from the metal cyanide concentration, in which case the sum of individual concentrations became equal TCN_o. For example, for the lowest TCN = 0.00692 mol/L, 23.1% of each MCN was substracted in order to obtain $MCN_o = TCN_o$.

Cu - CN = 0.001767 mol/L
Zn - CN = 0.003271
Ni - CN = 0.000729
Fe - CN = 0.001149

Adjusted $[MCN]_o$ = 0.00692 mol/L

Other conditions are as tabulated:

Conditions		% MCN Substracted	
AIR	UV	4°C	20°C
+	+	23.1	12.4
+	-	16.0	15.0
-	+	18.0	18.3
-	-	16.0	16.2

ii) When high mix cyanide solution was made the Cu, Zn and Ni salts were added to the cyanide solution first and $Fe(CN)_6^{3-}$ the last. The assumption for the second simulation was that during this process the complexes of Cu-CN and Zn-CN break up easily releasing CN^-. Excess Ni and Fe maybe present to react with freed CN^- before it can be lost by volatilization. Hence, net effect, kinetically, is that Fe and Ni have their full equivalent of CN^- and the remainder is assigned to Cu and Zn. Therefore, 56 to 66.5% of total Cu and 75 to 86.5% of total Zn concentration form a complex with present cyanide, as tabulated:

Conditions		% Cu - CN		% Zn - CN	
AIR	UV	4°C	20°C	4°C	20°C
+	+	56.0	63.0	75.0	83.0
+	-	65.0	66.5	86.5	86.0
-	+	63.0	62.0	82.0	82.5
-	-	65.0	64.0	86.5	85.0

In the case of the lowest measured total cyanide, for example the individual metal cyanide concentrations became:

Cu - CN (56%) = 0.001287 mol/L
Zn - CN (75%) = 0.003190
Ni - CN (100%) = 0.000948
Fe - CN (100%) = 0.001494

Adjusted $[MCN]_o$ = 0.00692 mol/L

J.2 EXAMPLE CALCULATION OF THE INITIAL CYANIDE CONCENTRATIONS FOR THE MODEL APPLICATION ON BARREN SOLUTIONS

When the experiments commenced the main characteristics for the examined barren solutions were:

Barren Solution	TCN (mol/L)	Cu_T (mg/L)	Zn_T (mg/L)	Ni_T (mg/L)	Fe_T (mg/L)	pH
#1	0.00558	7.8	31.0	1.5	0.1	11.5
#2	0.01134	15.0	127.0	0.7	5.7	12.0
#3	0.00490	7.7	1.1	0.5	10.0	11.6

The possible presence of any other metal or ligand in these barren solutions was at this point omitted from consideration.

Assuming only the presence of the same complexes as in synthetic solutions and taking into consideration their theoretical stoichiometry, the initial metal and free cyanide concentrations were calculated as in the following example (#1 barren solution):

Metal	Theoretical Stoichiometry	$[MCN]_o$ (mol/L)
Cu = 7.8 mg/L	$(CN)_3/Cu = 1.228$	0.000368
Zn = 31.0	$(CN)_4/Zn = 1.592$	0.001898
Ni = 1.5	$(CN)_4/Ni = 1.773$	0.000102
Fe = 0.1	$(CN)_6/Fe = 2.795$	0.000011
		0.002379

Total theoretical $[MCN]_o$ concentration = 0.002379 (mol/L)

The total cyanide determined analytically in this barren solution was $[TCN]_o = 0.0055769$ (mol/L). The initial free cyanide concentration was obtained by subtracting calculated $[MCN]_o$ from the measured $[TCN]_o$.

The same stoichiometry was applied for the other two barren solutions according to their metal and total cyanide content.

J.3 MODELLING EFFECTS OF pH UPON VOLATILIZATION OF HCN

The model equations used for the synthetic mixes were all made with the fixed pH of 7.0 in mind. When the model was to be used on the barren solutions certain adjustments had to be made on the equations to compensate for the change in pH during the degradation process.

It has been assumed (Chapter 7), that HCN and CN^- are in equilibrium according to the reaction:

$$[HCN] \rightleftarrows [H^+] + [CN^-]$$

The dissociation constant for this reaction is

$$K_a = \frac{[H^+]\ [CN^-]}{[HCN]} = 4.93 \times 10^{-10} \quad (pKa = 9.3)$$

Therefore

$$K_a\ [HCN] = [H^+]\ [CN^-]$$

and the $[CN^-]$ is defined as

$$[CN^-] = \frac{Ka\ [HCN]}{[H^+]} \qquad (1)$$

The term "free cyanide" is defined as the sum of the molecular HCN and cyanide ion CN^-; i.e.,

$$[FCN] = [HCN] + [CN^-]$$

If we replace the $[CN^-]$ with the value from Eq. (1) total free cyanide will be equal

$$[FCN] = [HCN] + \frac{Ka[HCN]}{[H^+]} = [HCN] \quad (1 + \frac{Ka}{[H^+]})$$

From here the concentration of molecular HCN is equal to

$$[HCN] = \frac{[FCN]}{1 + \frac{Ka}{[H^+]}} \tag{2}$$

From the definitions for pH and pKa values

$$[H^+] = 10^{-pH} \quad \text{and} \quad K_a = 10^{-pK}$$

When replaced in the Eq. (2) the HCN concentration becomes equal

$$[HCN] = \frac{[FCN]}{1 + \frac{10^{-pK}}{10^{-pH}}} \tag{3}$$

At pH of 7 [HCN] = 0.995 [FCN], justifying the approximation used in modelling the synthetic solutions that [HCN] equals FCN. Therefore, the value for molecular HCN in the model was replaced by the equation (3).

The computer program used for the model simulation on barren solutions called BARRMIX is attached.

- **Example Computer Program Used for Modelling on Barren Solutions**

```
      PROGRAM BARRMIX(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,TAPE11)
      DIMENSION TH(12),PH(40),TOBS(40)
      REAL      Y(7),C(24),W(7,9),X,TOL,XEND
      COMMON /A/ RKC,RKZ,RKN,RKF,UVK,VK,PH1
      EXTERNAL FCN1
      READ(11,*) (TH(I),I=1,12)
      WRITE(6,*) (TH(I),I=1,12)
      READ(11,*)NOBS
      DO 15 J=1,NOBS
      READ(11,*)XO,YO,PH1
      Y1=YO/26000
      PH(J)=PH1
      TOBS(J)=XO
      WRITE(6,*)XO,Y1,PH1
      CALL PLOTPT(XO,Y1,5)
15    CONTINUE
      PH(NOBS+1)=PH(NOBS)
      TOBS(NOBS+1)=TOBS(NOBS)+50.
      NW=7
      N=7
      X=0.0
      Y(1)=TH(1)
      Y(2)=TH(2)
      Y(3)=Y(1)+Y(2)
      Y(4)=TH(4)
      Y(5)=TH(5)
      Y(6)=TH(6)
      Y(7)=TH(7)
      RKC=TH(8)
      RKZ=TH(9)
      RKN=TH(10)
      RKF=TH(11)
      UVK=TH(12)
      VK=TH(3)
      TOL=0.0001
      IND=1
C     CALL PLOTPT(X,Y(1),4)
      CALL PLOTPT(X,Y(2),2)
      CALL PLOTPT(X,Y(3),20)
      WRITE(6,1000)
```

```
 1000 FORMAT(10X,"X",12X,"Y(1)",12X,"Y(2)",12X,"Y(3)")
      WRITE(6,2000) X,Y(1),Y(2),Y(3)
 2000 FORMAT(3X,F10.5,6X,F10.7,6X,F10.7,6X,F10.7)
      DO 10 K=1,132
      XEND=FLOAT(K)*10.
      I2=XEND
      DO 30 I=1,NOBS
      I1=TOBS(I)
      I3=TOBS(I+1)
      IF(I1.LE.I2.AND.I2.LE.I3)GO TO 31
30    CONTINUE
31    PH1=PH(I)
      WRITE(6,*)PH1
      CALL DVERK (N,FCN1,X,Y,XEND,TOL,IND,C,NW,W,IER)
      IF (IND.LT.0.OR.IER.GT.0)  GOTO 20
      WRITE(6,3000) X,Y(1),Y(2),Y(3)
 3000 FORMAT(3X,F10.5,6X,F10.7,6X,F10.7,6X,F10.7)
C     CALL PLOTPT(X,Y(1),4)
      CALL PLOTPT(X,Y(2),2)
      CALL PLOTPT(X,Y(3),20)
 10   CONTINUE
      CALL OUTPLT
      STOP
 20   CONTINUE
      STOP
      END
      SUBROUTINE FCN1(N,X,Y,YPRIME)
      DIMENSION TH(12),PH(40),TOBS(40)
      COMMON /A/ RKC,RKZ,RKN,RKF,UVK,VK,PH1
      REAL     Y(N),YPRIME(N),X
      PK1=9.0
      YPRIME(4)=-RKC*Y(4)
      YPRIME(5)=-RKZ*Y(5)
      YPRIME(6)=-(RKN*Y(6))
      YPRIME(7)=(-RKF*Y(7))-UVK*Y(7)
      YPRIME(2)=YPRIME(4)+YPRIME(5)+YPRIME(6)+YPRIME(7)
      YPRIME(1)=-YPRIME(2)-(VK*Y(1)/(1+10**(-PK1)/10**(-PH1)))
      YPRIME(3)=-VK*Y(1)/(1+10**(-PK1)/10**(-PH1))
      RETURN
      END
```