FLOCCULATION OF METAL HYDROXIDES WITH POLYMERS

FLOCCULATION OF METAL HYDROXIDES WITH POLYMERS-
OPTIMIZATION AND KINETIC MODELLING

By

PETER MELVIN HUCK, B.A.Sc., M.A.Sc.

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AUTHOR : Peter Melvin Huck, B.A.Sc., M.A.Sc.
(University of Waterloo)

SUPERVISOR: Professor K.L. Murphy

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ABSTRACT

This study determined optimum conditions for the use of polymers in flocculation of metal hydroxides present in neutralized mine drainage. Using the criterion of supernatant particulate metal concentration following flocculation and settling, optimum polymer properties and mixing conditions were obtained for both strong and weak simulated minewaters containing iron. It was shown that these conditions also provided minimum metal residuals (less than 0.3 mg/l) for simulated minewaters containing copper or zinc. For two-metal systems, the residual particulate metal concentrations achieved were lower than for the corresponding single-metal systems.

Near the optimum, mixing conditions were more important than polymer properties. Optimum mixing times decreased greatly as minewater strength increased, as would be expected from kinetic considerations. Optimum mixing speeds increased moderately with increasing initial metal concentration, probably because of a corresponding increase in floc strength. Polymer molecular weight had no effect over the range investigated. The polymer degree of hydrolysis was unimportant in the range from 2 to 35 percent for the three metals at various initial concentrations. The optimum polymer dosage was not narrowly defined, but could be related to the minewater strength as 1.7×10^{-3} the initial metal concentration.

Experiments performed to determine the best kinetic model for the process demonstrated that it could not be represented by a simple aggregation model and that none of the available models incorporating floc breakup were adequate. A new model was proposed which incorporated for the first time the decrease in the aggregation rate with time because of the shortening of the adsorbed polymer loops, and the existence of a critical mixing intensity for floc breakup. This model, which is second order in particle concentration, was found to predict satisfactorily the results obtained with the simulated iron, copper and zinc minewaters. Although the aggregation rate was greater for zinc than for iron or copper, the achievable supernatant particulate concentration was independent of metal type. The critical mixing intensity for floc breakup was found to increase with increasing initial metal concentration.

The model was tested on three actual minewaters and was found to give satisfactory predictions.

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1 . INTRODUCTION

Increasing industrial waste discharges and increasing demand on water resources have focused attention on heavy metals as pollutants. Large volumes of effluent having high dissolved metal concentrations are produced in base metal mining. The conventional treatment of these acidic effluents involves the addition of lime to precipitate the metals as hydroxides (Huck _et al._,1975). Although other methods such as reverse osmosis are being developed (EPA, 1972) lime precipitation will remain an important process where large volumes are to be treated, because of its low cost.

One of the disadvantages of the treatment of metal-bearing wastes by this method is the low natural sedimentation rate of metal hydroxide precipitates, necessitating low overflow rates for clarifiers. In addition, if proposed national effluent standards (Canada. Dept. of the Environment, 1975) are to be met, virtually complete solid-liquid separation must be achieved in these units. The addition of a synthetic polymer has been found to aid particle aggregation, thereby increasing the sedimentation rate and decreasing the suspended solids concentration of the supernatant (Huck _et al._, 1975).

The selection of an optimum polymeric flocculant for a given situation has been difficult because of the lack of information both of the properties of commercial flocculants and of the effect of those properties on the flocculation of metal hydroxides. The determination of optimum operational conditions has been hampered by the absence of information on the mixing requirements of the process. The usual testing programmes with commercially available polymers are essentially empirical and do not allow generalization of the results beyond the wastewater being tested, nor an identification of the polymer characteristics which produced optimum behaviour. The need was therefore for information on the optimum polymer properties and operational conditions for given types and strengths of minewaters and for a rational means for assessing polymers.

The objective of this research was to investigate at bench scale the flocculation of heavy metal hydroxides by synthetic organic polymers, specifically:

1. to determine, for the practical range ~~of~~ interest of the major variables, the flocculation response as measured by supernatant particulate metal concentrations,
2. to determine, for minewaters of specified strengths containing single metals, the levels of the polymer and mixing variables required to produce optimum flocculation,

3. to predict from the single-metal systems, optimum conditions for two-metal systems and to evaluate these experimentally, and

4. to develop a modelling technique for specifying the mixing requirements and polymer properties for optimum flocculation in a given precipitation/flocculation/clarification situation.

2 BACKGROUND

2.1 Mine Drainage

2.1.1 Formation and Characteristics

Mine drainage is water which enters a mine either naturally or intentionally and must be pumped out so that mine operations can continue. The chemical composition of the minewater is determined by the nature of the ore body or coal seam being mined. When sulphides are present, as for coal and most base metal mines, their exposure to the air by the mining operations results in oxidation, the products of which dissolve in the minewater. The overall reaction for the oxidation of pyrite (EPA, 1971b) is:

$$FeS_2 + 3\ 3/4\ O_2 + 3\tfrac{1}{2}\ H_2O \rightarrow 2\ H_2SO_4 + Fe(OH)_3 \qquad (2\text{-}1)$$

Since similar reactions occur in the oxidation of other metal sulphides, the minewater from sulphide ore bodies is acidic and contains heavy metals. The concentrations of the major ions in an acid mine drainage from the Province of New Brunswick are given in Table 2-1.

2.1.2 Conventional Treatment

There are two objectives in the treatment of acid mine drainage:

1. raising the pH to a near neutral value, and
2. reducing the concentration of heavy metals.

TABLE 2-1

COMPOSITION OF SAMPLE OF REAL MINEWATER[*]

CONSTITUENT	CONCENTRATION (mg/l)
SO_4	1195
Fe^{+3}	131
Fe^{+2}	0.2
Zn	138
Cu	26
Mn	30
Pb	0.8
Ca	77
Mg	32
Fe + Zn + Cu + Mn + Pb	= 326 mg/l
$(Fe + Zn + Cu + Mn + Pb)/SO_4$	= 0.27

---

[*] Obtained from Heath Steele Mines, Newcastle, New Brunswick

Conventional treatment accomplishes both these objectives by the addition of lime to raise the pH to at least 7. This neutralizes the acidity and precipitates the metals as hydroxides. Such treatment has typically been carried out in tailings ponds. However, the need for greater process control to meet proposed effluent standards (Canada. Dept. of the Environment, 1975) has initiated a trend towards the installation of mechanical treatment plants. A flowsheet for a pilot plant which includes effluent polishing by sand filtration is shown in Figure 2-1. This plant employs sludge recycle to increase sludge density and uses two stage neutralization with oxidation of ferrous iron in the first stage. In pilot studies of the minewater with characteristics listed in Table 2-1, flocculation with a polymer prior to clarification was found to increase the settling rate of the slurry and reduce its suspended solids concentration (Table 2-2).

2.2 Flocculation

2.2.1 Definition

Flocculation according to La Mer and Healy (1963) is the formation of a floc or loosely fibrous structure like a tuft of wool. It is a special case of coagulation and is usually brought about by macromolecules (polyelectrolytes).

2.2.2 Use of Polymers

Polymers effective as flocculants may be positively charged (cationic), negatively charged (anionic),

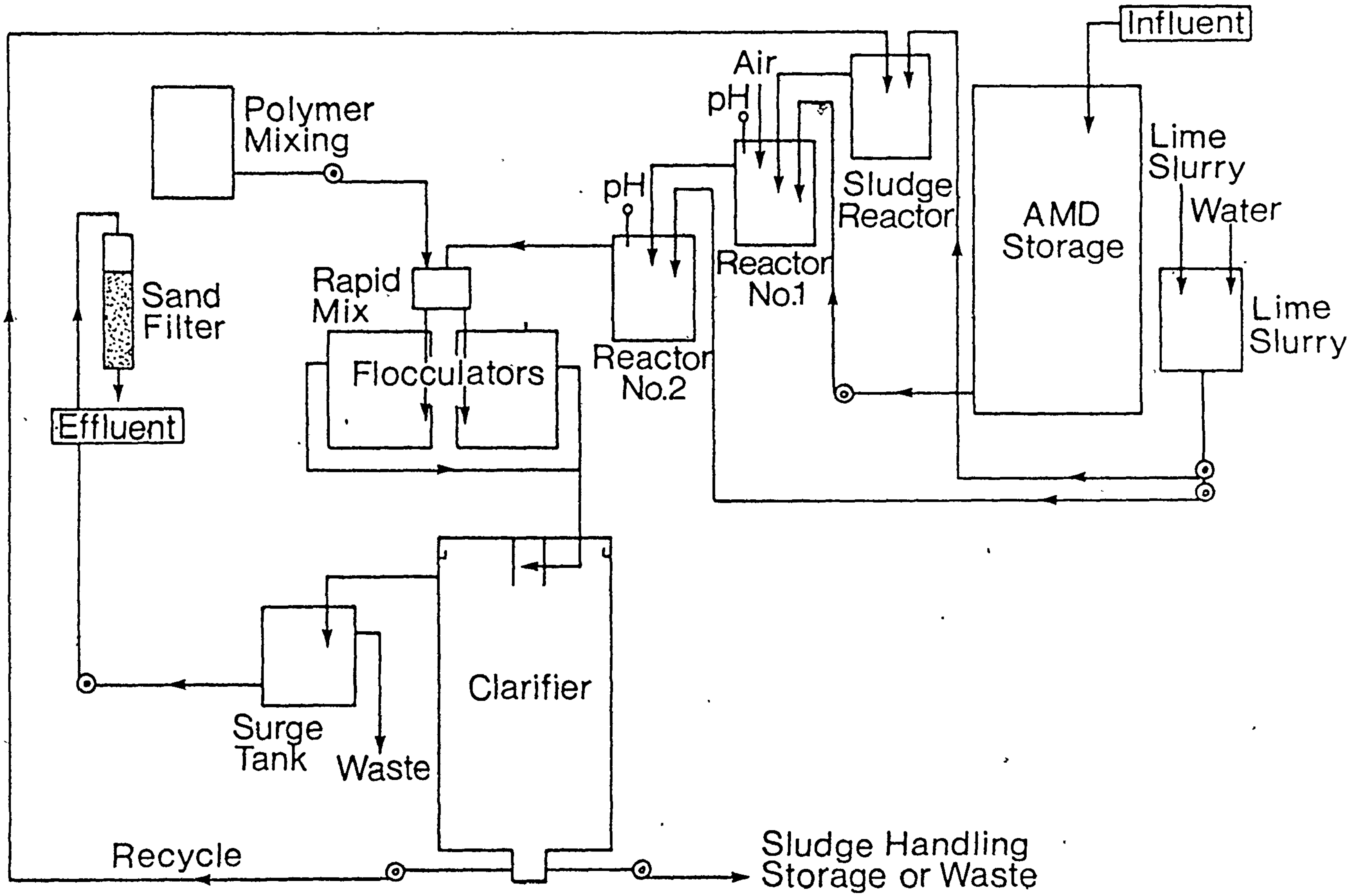

FIGURE 2-1: FLOWSHEET FOR MINEWATER TREATMENT PILOT PLANT[1]

---

[1] AFTER HUCK AND LE CLAIR (1976)

TABLE 2-2

EFFECT OF POLYMER ADDITION ON CLARIFIER EFFLUENT METAL CONCENTRATIONS AND SLURRY SETTLING RATE (PILOT PLANT DATA)

CONDITION	METAL[1]			SETTLING RATE[2]
	Fe	Zn	Cu	
No Polymer	2.24	3.22	0.58	1.78
Polymer	0.20	0.11	0.06	7.31

---

[1] Particulate metal concentration, mg/l

[2] Meters/hour

or electrically neutral (nonionic). Anionic flocculants have molecular weights in excess of one million (Pulaski, 1968), and are conventionally polyacrylamide. Their charge is expressed as the degree of hydrolysis or fraction of amide groups converted to carboxyl groups. The charge may affect adsorption but principally influences configuration in solution.

Flocculation by polymers is brought about by bridging (Ruehrwein and Ward, 1952; Michaels and Morelos, 1955; LaMer and Smellie, 1956). The bridging theory postulates that a polymer molecule becomes adsorbed on two or more particles, binding them together. The adsorption of the polymer is generally thought to involve chemical bonding rather than physical forces (AWWA, 1971). This is especially true in the flocculation of negatively charged particles by an anionic polymer. The size of the aggregates is limited only by the shear gradient in the system and by the amount of polymer initially adsorbed. Restabilization (non-flocculation) has been observed to be caused by the adsorption of an excessive amount of polymer, filling up sites for bridging.

Data for the adsorption of polymer in various systems have been found to fit the Langmuir adsorption isotherm (AWWA, 1971):

$$\frac{\theta}{(1-\theta)} = bP \qquad (2-2)$$

where θ is the fraction of adsorbent surface covered by adsorbed segments,

b is the equilibrium constant for the adsorption-desorption reaction, and

P is the activity of the polymer in solution.

Although the mathematical theory developed by LaMer and coworkers predicts maximum flocculation when the particle surface is half covered by polymer molecules ($\theta=\frac{1}{2}$), other factors such as particle concentration, interparticle repulsive forces, solution ionic strength, polymer configuration in the adsorbed state, and intensity and duration of agitation are probably more important than the parameter θ in determining the extent of destabilization (AWWA, 1971).

The overall flocculation reaction involves several steps in series:

1. transport of the polymer molecule to the particle surface,
2. adsorption of one or more segments of the polymer molecule to the surface of the particle, and
3. iteration of these two steps with the combined particle-polymer units (floc growth) until the limiting floc size for the system is reached.

The polymer adsorption step is essentially irreversible (Birkner and Edzwald, 1969). The overall reaction is quite rapid, and has been made to go to completion in as short a time as 2 seconds at very high shear rates (Huck and LeClair, 1974). This would suggest that the reaction is transport limited, as has been shown by Black et al. (1965) and Birkner and Morgan (1968) for adsorption of cationic polymers onto the surface of negatively-charged particles.

2.2.3 Physical Parameters

The physical parameters directly affecting the performance of a flocculation reactor are the residence time, its distribution, the total power input, and the properties of the turbulence field (Argaman and Kaufman, 1970).

With respect to residence time distribution, Argaman and Kaufman (1970) have shown that compartmentalization of a continuous-flow system improves flocculation performance for a given residence time, and therefore plug flow conditions are optimal. These authors also indicated that the properties of the turbulence field were dependent upon the stirring or mixing mechanism.

The effect of residence time and total power input may be predicted from the kinetic equation for flocculation. Although the basic kinetic expressions were derived by von Smoluchowski (1916, 1927), the application to water treatment was made by Camp and Stein (1943). They obtained for spherical particles:

$$\frac{dN}{dt} = -\frac{2}{3}\eta d^3 N_o N G \qquad (2-3)$$

or

$$N = N_o e^{-\frac{2}{3}\eta d^3 N_o G t} \qquad (2-4)$$

where N is the number of primary particles present at time t,

N_o is the number of primary particles present initially,

η is the collision efficiency or fraction of collisions resulting in aggregation, d is the particle diameter, and

G is the root mean square (rms) velocity gradient.

Camp and Stein defined G as:

$$G = \sqrt{\frac{\varepsilon}{\nu}} \qquad (2\text{-}5)$$

where ε is the total power dissipated per unit mass of fluid, and

ν is the kinematic viscosity.

Equation 2-4 indicates that the performance or number of particles removed increases with an increase in either residence time or total power input (velocity gradient). Equation 2-3 indicates that the aggregation rate increases with increased initial particle concentration.

Although Equation 2-4 suggests that unlimited increases in velocity gradient will improve performance, Argaman and Kaufman (1970) have developed a more sophisticated model which demonstrates that for a given residence time, the performance increases almost linearly with the velocity gradient until a maximum value is reached beyond which any further increase causes a decrease in performance. They attribute this decrease to floc breakup, or the erosion of previously-flocculated particles from floc surfaces. Andreu-Villegas and Letterman (1976) have also identified an optimum velocity gradient value, G^*, the existence of which they attribute to floc breakup. They found that G^* decreased with increased residence time, t, and that the relationship could be described mathematically as

$$(G^*)^{2.8}t = K \qquad (2\text{-}6)$$

where K is constant.

Birkner and Morgan (1968) in studying the kinetics of the flocculation of dilute colloidal suspensions with polymers, found that at the optimum polymer dose, the apparent rate of decrease in total particle concentration could be represented by a first-order reaction equation in the initial phase of flocculation. At longer reaction times, floc breakup caused a departure from this relationship.

Akers (1972) notes that adsorbed polymer loops are initially long and become shorter as more segments are adsorbed. Since these shorter loops are less efficient, the collision efficiency (Equation 2-3) and therefore flocculation rate decrease with time.

Successful flocculation is dependent on the method of initial mixing of the flocculant and the slurry. Rapid mixing is usually employed since studies with coagulants such as alum have indicated that speedy, thorough dispersion is important (Hudson and Wolfner, 1967). A design in which rapid mixing is continued until floc particles reach nearly equilibrium sizes, followed by a tapered flocculation velocity gradient path, is suggested for optimum sedimentation (TeKippe and Ham, 1971). Vrale and Jorden (1971) found that the rms velocity gradient by itself was inadequate for characterizing rapid mix unit efficiency since performance was dependent on the residence time distribution. For adsorptive destabilization with alum, a plug flow tubular reactor appeared to be most efficient. Benedek and Bancsi (1976), in a study on the flocculation of sewage using alum followed by polymer, found that only 30 seconds rapid mix were required after polymer addition. In the flocculation of surface waters with cationic polymers, Morrow and Rausch (1974) found that rapid mix velocity gradients greater than 400 sec^{-1} were necessary if the polymers were to be used as primary coagulants. Optimum coagulation occurred in less than two minutes and a separate flocculation step was not required. An increase in the velocity gradient decreased the retention time and polymer dosage necessary to effect colloid destabilization.

As indicated above, the mixing arrangement in flocculation influences the turbulence field. It also determines the degree of suspension achieved when flocculating dense or concentrated slurries which may be encountered in minewater treatment practice. Optimization of mixing requires specification of the time, and of the speed, size and type of impeller. The last of these can be established from theoretical considerations. Maximization of speed within the constraints of floc breakup minimizes the required reaction time (Equation 2-3) and therefore reduces capital cost. Since it is high shear which is harmful to flocs, speed can be maximized by the use of an axial flow type of impeller (i.e. a propeller) to minimize particle contact with the highest shear region, the impeller tip. In coagulation of clays, Hahn and Klute (1975) found a propeller superior to a turbine at high rotational speeds. Such speeds are likely to be used in flocculation with polymers.

The question of whether to use a large or small impeller can also be answered on the basis of theoretical considerations. The same power input can give greatly different flow conditions, as shown by the relationship for impeller discharge (Uhl and Gray, 1966). For fluid friction losses assumed equal to zero:

$$P = QH\rho \tag{2-7}$$

where P is power

Q is flow or discharge

H is theoretical impeller head, and

ρ is fluid density.

The theoretical head, H, appears as kinetic and static heads if there are no friction losses in the impeller. It is given by:

$$H \propto \omega^2 r^2 \tag{2-8}$$

where ω is angular velocity, and

r is the radial distance from the centre of rotation.

Discharge, Q is given by

$$Q \propto nD^3 \tag{2-9}$$

where n is rotational speed, and

D is the impeller diameter.

For a given power input, QH and therefore n^3D^5 is constant, since ω is linearly related to n and r is linearly related to D. Such a result can also be obtained from the Power Number,

$$Np = \frac{Pg_c}{D^5 n^3 \rho} \qquad (2\text{-}10)$$

where g_c is the gravitational constant.

For a given power investment, an increase in impeller size gives an increase in circulation and a decrease in head. Since this should aid flocculation, and assist suspension of heavy slurries, the largest feasible impeller should be used. As indicated above, the propeller is the preferred impeller type.

2.2.4 Heavy Metal Hydroxides

Base metal mine drainage normally contains significant concentrations of iron, zinc and copper. However, only the aqueous chemistry of iron has been extensively studied, and most of these physical chemistry studies were performed at iron and total ionic concentrations much below those of metal-bearing wastewaters. Even investigations of iron as a hydrolyzing metal coagulant in water treatment (Singley and Black, 1967; Stumm and Morgan, 1962; Stumm and O'Melia, 1968) are of limited use since in the present research, iron is the coagulated rather than the coagulating species, and is present as a precipitate prior to flocculation. The only relevant conclusions from the work of Stumm and Morgan (1962) are that coagulant metal ions such as iron are hydrolyzed in aqueous solution, that considerable evidence exists to support the view that iron hydroxide precipitates are polynuclear complexes, and that complex formation occurs between coagulant metal ions such as iron and functional groups such as carboxylic groups which occur in polymers.

2.3 Previous Studies

The few reported studies on polymer flocculation of metal hydroxides are cursory. Schwoyer and Luttinger (1972), in discussing polymer conditioning for the dewatering of metal hydroxide sludges, mention only the need for high molecular weight and (usually) for a polymer with charge opposite to that of the sludge particles. EPA (1970) investigated the addition of various substances including anionic polymers to achieve the isoelectric point for ferrous and ferric hydroxide sludges. Dosages were obtained for various polymers and brief tests were carried out on the improvement in settling rate caused by their addition. Another EPA study (1971a) examined the flocculation of quartz suspensions using calcium chloride and either starch or synthetic polymers and provided some discussion of the mechanism of action. Mixing was not a study parameter.

2.4 Identification of Flocculation Variables

The variables which can affect flocculation in minewater are:

Minewater

1. Heavy metal species
2. Heavy metal concentration
3. Strength (e.g. sulphate concentration)

Polymer

1. Molecular weight
2. Degree of hydrolysis
3. Concentration
4. Type
5. Details of manufacture

Process

1. Dispersion (rapid mix) horsepower
2. Dispersion (rapid mix) time
3. Flocculation horsepower
4. Flocculation time
5. Residence time distributions (dispersion and flocculation)
6. Flocculation pH
7. Method of base addition
8. Choice of neutralizing agent
9. Method of polymer addition
10. Type and size of impeller

Since it was not possible to investigate all of these, the major ones were identified based on the information presented in preceding sections. They were the ones examined in this research, while the others were held constant. Their settings are discussed in Section 2.4.2.

2.4.1 Major Variables

The major variables were:

Minewater

1. Heavy metal species
2. Strength (e.g. sulphate concentration)

Polymer

1. Molecular weight
2. Degree of hydrolysis
3. Concentration

Process

1. Dispersion (rapid mix) horsepower
2. Dispersion (rapid mix) time
3. Flocculation horsepower
4. Flocculation time

Except for final verification experiments with real minewater, simulated minewater was used throughout the study. The heavy metal ions included in the formulation were those found in significant quantities in New Brunswick base metal mine drainages: iron, zinc and copper.

Generally speaking, flocculation success should be proportional to polymer molecular weight, or chain length. Although increased chain length gives longer extended polymer segments thereby facilitating bridging, an increase in molecular weight above a certain level should have little additional benefit because the extended segments are already long enough to overcome the electrical repulsion between particles. Similarly, changes in molecular weight below the minimum required for flocculation will have no effect on the system.

Polymer degree of hydrolysis determines both the configuration of the polymer in solution and, for a system containing anionic polymers and negatively-charged particles, the magnitude of the repulsive forces resisting bonding. An increase in polymer charge increases the extension of the molecules in solution, thereby increasing the probability of contact between the molecule and a particle (Ishige et al., 1974). However, too high a negative charge interferes with particle-polymer bonding (AWWA, 1971). Thus it is to be expected that there is an optimum degree of hydrolysis for a given system.

As indicated by the Langmuir isotherm (Section 2.2.2), polymer concentration or activity determines the equilibrium surface coverage (θ) and hence the success of flocculation. At low activities, θ increases directly with activity, but at higher activities θ approaches a limiting value of 1. It was therefore expected that flocculation would improve with increased polymer dosage up to an optimum value. Above this dosage many adsorption sites are filled and bridging is hindered (AWWA, 1971). Although high dosages may lead to restabilization in some systems, this does not seem to occur in minewater systems (Huck and LeClair, 1974). The dosage required for effective flocculation may be expected to decrease with increasing molecular weight, and be at a minumum at the optimum degree of hydrolysis.

All four mixing variables (dispersion horsepower, dispersion time, flocculation horsepower and flocculation time) are interrelated. In general, as the horsepower increases the time may be expected to decrease (Section 2.2.3). Since flocculation begins as soon as some dispersion has occurred, an increase in dispersion time may be expected to decrease the required flocculation time. A high dispersion horsepower applied for a short time should aid uniform distribution of the polymer prior to the occurrence of appreciable flocculation, thus giving more uniform flocculation. However, too high a horsepower may damage flocs which have begun to form.

2.4.2 Minor Variables

The minewater parameter which was not varied independently was heavy metal concentration. In real systems, it is correlated with sulphate, in accordance with the mechanism for the formation of acid mine drainage. As an example, for pyrite (EPA, 1971b):

$$FeS_2 + 3\ 3/4\ O_2 + 3\tfrac{1}{2}\ H_2O \rightarrow 2\ H_2SO_4 + Fe(OH)_3 \qquad (2\text{-}10)$$

Although the exact ratio of metal to sulphate depends on the ore(s) at a given site, a representative value based on reported compositions of New Brunswick ores (Montreal Engineering Co., 1972) was calculated to be 0.3. This value was used for this research.

The polymer parameters which were held constant were type and details of manufacture.

Previous work (Huck and LeClair, 1974) had shown that anionic polymers were best for minewater flocculation. Since anionic flocculants are invariably polyacrylamide, it was used in this study.

The details of the polymer manufacture include the use of additives such as surfactants as well as the molecular weight distribution. This factor was standardized by use of one stock polymer containing no additives, for which the molecular weight distribution was measured. A large enough quantity of polymer was obtained initially to permit all experiments to be performed from that batch.

The process parameters which were not varied in this research were residence time distributions, flocculation pH, method of base addition, choice of neutralizing agent, method of polymer addition, and type and size of impeller.

Since only batch experiments were performed, the residence time distribution was that of a plug flow tubular reactor (PFTR).

The pH of flocculation is governed by hydroxide solubility considerations for maximum dissolved metal removal. Therefore, flocculation must be optimized for whatever pH is optimum for precipitation. On the basis of previous studies with base metal mine drainage (Huck et al., 1975) a precipitation pH of 9.5 was employed for this study.

The concentration and rate of addition of base influence the relative rates of nucleation and particle growth and therefore determine the size and number of particles which are formed from a given initial concentration of metal. A standard precipitation procedure employing a controlled rate of addition of base was employed.

The choice of sodium or calcium hydroxide as the neutralizing agent may affect flocculation, because of the difference in valence of the two cations. Also, with calcium hydroxide, unreacted lime particles may be present, and calcium sulphate will be precipitated at high sulphate concentrations. Because of the practical orientation of this research, calcium hydroxide was employed as the precipitating agent.

A standard polymer solution concentration was added for all strength minewaters. The polymer was always added at the start of rapid mixing.

As discussed in Section 2.2.3, the optimum type of impeller for this application is the largest feasible propeller. Accordingly, a propeller was used, with size chosen towards the upper end of recommended impeller to tank diameter ratios (approximately 0.5). The use of only one type of impeller fixed the properties of the turbulence field.

2.5 Process Criterion

A number of criteria have been used to measure flocculation success. These include supernatant particle concentrations, slurry settling rate, floc size and density, and settled sludge volume.

The criterion chosen for this study was supernatant particulate metal concentration following settling. Previous pilot plant studies (Huck <u>et al.</u>, 1975) had shown that while polymer increased slurry settling rate and reduced supernatant metal concentrations, the latter was more difficult to optimize, because achievement of rapid settling did not guarantee maximum particulate metal removal. Residual particulate metal concentrations on the order of 0.2 mg/l will be necessary in environmentally sensitive areas.

3 MODELLING THE FLOCCULATION PROCESS

Two types of modelling are possible: empirical and mechanistic. The former is suitable when it is not necessary or feasible to understand a phenomenon. This may occur in optimization of an operating process. The latter is required when understanding is necessary and is the only valid model when extension to substantially different conditions is required.

3.1 Empirical Modelling

Empirical modelling was used in addressing the first three research objectives, i.e. in the determination, for various types of minewaters, of the optimum settings of the variables identified in Section 2.4.1. The Response Surface method developed by Box (Davies, 1956) was employed. This envisages the measured experimental result or response as a surface in *m* dimensions where *m* is the number of independent variables. It is assumed that the surface can be represented by a general second order equation in these *m* variables. Although this is usually possible, transformation of some of the independent variables may be required. A response governed by 3 variables would be represented as:

$$\hat{y} = b_o + b_1x_1 + b_2x_2 + b_3x_3 + b_{11}x_1^2 + b_{22}x_2^2 + b_{33}x_3^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 \qquad (3\text{-}1)$$

where $\hat{y}$ is the predicted response,

x_1, x_2, x_3 are the settings of the independent variables (usually in coded form), and

b_i, b_{ii} and b_{ij} are the model coefficients to be estimated.

The estimation of all coefficients requires a three-level factorial experiment, i.e. one in which three settings of each independent variable are used. These coefficients are also known as effects.

In optimization, the whole response surface is not of interest. Rather, the objective is to "climb" to the highest point on the surface in as few experiments as possible, i.e. by following the Path of Steepest Ascent (Davies, 1956). This procedure assumes that, except in the region of the optimum, only the linear terms in Equation 3-1 are important. Their estimation, requiring only a two-level factorial experiment, permits calculation of the surface slope. Since initial conditions are normally remote from the optimum, the procedure is started by performing a two-level design to determine the magnitude and direction of the slope. The slope values show the relative amounts each factor should be varied to give a maximum response increase, i.e. they give the Path of Steepest Ascent. Trials are performed along this path until no increase in response is observed. Another factorial experiment is conducted to determine a new direction, and the process is repeated. When no further increases in response can be obtained, i.e. a stationary point has been reached, a three-level experiment is performed to define the surface in the local area. This indicates whether a global optimum or merely a local optimum has been reached. If it is the latter, the new direction for experimentation is indicated. If it is the former, the exact location of the optimum and the corresponding response can be determined.

Interpretation of the second order model for two or more independent variables is assisted by canonical analysis (Davies, 1956). This transformation expresses the equation in standard form, revealing whether it describes an ellipse, hyperbola, etc. It translates the origin to the current optimum conditions (local or global) and rotates the axes to eliminate cross-product terms. For example, Equation 3-1 would be expressed as:

$$\hat{Y} - Y_s = B_{11}X_1^2 + B_{22}X_2^2 + B_{33}X_3^2 . \qquad (3\text{-}2)$$

where Y_s is the predicted response at the current optimum,

B_{ii} are coefficients, and

X_i are transformed variables.

The B_{ii} are eigenvalues and the X_i's are expressed in terms of the x_i's through eigenvectors.

The two-level designs used were the standard factorial and fractional factorial designs. The three-level designs employed were of the type devised by Box and Behnken (1960). They are incomplete three-level factorials constructed by combining two-level factorial designs with incomplete block designs. For only two factors, standard 3^2 designs are used.

The results of the two-level factorial designs were usually assessed using half-normal plots (Daniel, 1959). The abscissa of this plot is the absolute value of the effect and the ordinate is the probability, Pr_i, given by:

$$Pr_i = (i - 1/2)/n, \quad i = 1,2,\ldots, n \qquad (3\text{-}3)$$

where n is the number of effects.

If no effects are real, all will lie on a straight line passing through the origin, whereas if some are real, they will lie to the right of this line. Although quantitative analysis is possible using this technique, it was not required in this study. The technique was also used to give a qualitative indication of significant effects in the first three-level design performed.

3.2 Mechanistic Modelling

3.2.1 Definition

A mechanistic model is one which is based on the underlying phenomena governing a process, i.e. chemical kinetics or fluid mechanics. To fulfill research objective #4, a mechanistic model was obtained for the flocculation of metal hydroxides with polymers.

3.2.2 Procedure

In general, the steps involved in obtaining the best model for a given process are:

1. identification of available models, possible modification of these to suit the existing situation, and possible development of new ones,
2. determination of the best of these models,
3. determination of precise parameter estimates for the best model, and
4. assessment of the adequacy of the model obtained.

If the resulting model is adequate, the process stops. If not, the procedure must be repeated with more sophisticated models.

Successful completion of steps 2 and 3 requires appropriate experimental designs. The best experimental conditions for discrimination among available models (step 2) are those for which the models' predictions differ the greatest, relative to their limits of error. Box and Hill (1967) have developed a criterion for identification of these conditions. Their procedure, summarized in Appendix A, is based on information theory, and uses a measure of information or entropy. The entropy, S, of a number of states or models, M_i, each with probability $Pr(M_i)$, is

$$S = -\sum_{i=1}^{m} Pr(M_i) \ln Pr(M_i) \tag{3-4}$$

Large values of S indicate high uncertainty or disorder. The minimum entropy, zero, corresponding to certainty, is achieved when the probability of one model is unity and that of all other models is zero. Their criterion therefore selects experimental conditions which maximize the expected decrease in entropy.

The procedure is iterative. It is begun by obtaining initial parameter estimates for each model, either from available data or from preliminary experimentation. Initial (usually equal) probabilities are assigned to each model and an operability region, limiting the conditions over which experiments are to be conducted, is defined. Based on this initial information, the criterion, D, is calculated for a number of experimental conditions within the operability region. It incorporates the predictions of different models and their variance. An experiment is then performed where D is maximum. This experimental result is used to update both the parameter estimates for each model and the model probabilities. The value of D is again calculated over the operability region, and an experiment performed where D is maximum. This procedure is repeated until the probability of one model exceeds a predetermined level, typically 0.99, at which point that model is accepted as being "true".

Since in general the conditions best for discrimination are not optimal for obtaining precise parameter estimates (step 3), several further experiments are usually required for this purpose. These serve to narrow the confidence interval on values predicted using the model. Although the conditions for these experiments can be selected using various criteria, MacGregor (1976) suggests maximization of the determinant of $\underline{X}'\underline{X}$, the matrix of experimental conditions. This provides a single overall criterion of parameter precision which is independent of the scale of measurement. This criterion was used for this research and is defined in Appendix A. Parameter estimates were obtained by least squares, also described in Appendix A.

Modelling assessment (step 4) can be performed using various standard techniques including examination of residuals and lack of fit tests (Himmelblau, 1970). If the best model is found to be inadequate, a further iteration of the discrimination procedure with more refined models is required. The existing data can be utilized and further experiments may be performed if necessary. The previous "best" model should be included to ensure that the more complicated models are indeed superior.

3.2.3 Model Formulation

This section summarizes the detailed model development presented in Appendix B. All models are developed for batch or plug flow tubular reactor (PFTR) systems. Four models are considered: the von Smoluchowski model, the Argaman-Kaufman model, the LaMer-Healy model and a modified LaMer-Healy model. Only the LaMer-Healy model was originally derived with reference to flocculation with polymers.

3.2.3.1 Simple Aggregation Models

Although the Argaman-Kaufman and LaMer-Healy models include floc breakup terms, only the particle aggregation terms for these models are considered in this section.

Von Smoluchowski Model

Von Smoluchowski (1916, 1917) derived the basic kinetic expressions for the collision frequencies of suspended particles under Brownian motion and laminar flow regimes. Camp and Stein (1943) generalized von Smoluchowski's equation to include turbulent flow conditions by defining a root mean square (rms) velocity gradient, G, which they substituted for the velocity gradient in laminar flow. For spherical particles, the rate of disappearance is:

$$\frac{dN}{dt} = -\frac{2}{3}\eta d^3 N_o N G \qquad (3\text{-}5)$$

where N is the number of primary particles present at time t,

N_o is the number of primary particles present initially,

η is the fraction of collisions resulting in aggregation,

d is the particle diameter, and

G is the rms velocity gradient.

Camp and Stein defined G as

$$G = \sqrt{\frac{\varepsilon}{\nu}} \qquad (3\text{-}6)$$

where ε is the total power dissipated per unit mass of fluid, and

ν is the kinematic viscosity.

Integration of Equation 3-5 for the appropriate boundary conditions gives the relationship:

$$N = N_o\, e^{-K' N_o G t} \qquad (3\text{-}7)$$

where K' is equal to $\frac{2}{3}\eta d^3$.

Argaman - Kaufman Model

Argaman and Kaufman (1970) noted that the application of von Smoluchowski's theories to turbulent flocculation required that the particles be much smaller than the smallest scale of turbulence, an assumption which was not justified in the flocculation systems encountered in water treatment practice. To account for the length and time scale over which turbulent velocity fluctuations occur, they developed a diffusion coefficient for particles and flocs based on the turbulence energy spectrum. They postulated that in a continuous flow flocculation reactor, primary particles were removed from suspension principally by collision with previously formed flocs. This was considered applicable to a batch or PFTR system, except for the first small fraction of time. Their rate equation for the aggregation of primary particles is:

$$\frac{dN}{dt} = -4\pi\eta K_S R_F{}^3 N_F N\ \overline{u^2} \tag{3-8}$$

where η, N and t are as in Equation 3-5,

K_S is a proportionality coefficient expressing the effect of the turbulence energy spectrum on the particle diffusion coefficient (For a particular turbulence field and particle size, K_S is constant.),

R_F is floc radius,

N_F is number of flocs, and

$\overline{u^2}$ is the mean square velocity fluctuation.

This equation is similar to Equation 3-5 except that $\overline{u^2}$ replaces G. However, $\overline{u^2}$ can be replaced by $K_P G$, where K_P is a performance parameter characterizing the stirring arrangement. If polymer concentration is expressed as a function of initial particle concentration, N_O, and floc radius is expressed as a function of the number of particles remaining in suspension, Equation 3-8 then becomes:

$$\frac{dN}{dt} = -\frac{1}{K_3} N(N_o - N)G \tag{3-9}$$

where K_3 is equal to $1/(4\pi\eta K_S K_P R^3)$, and

R is the radius of primary particles.

Integration of this equation, after separation of variables to render it exact, gives:

$$N = \frac{N_o(N_o-1)e^{-K_3 N_o G t}}{1+(N_o-1)e^{-K_3 N_o G t}} \tag{3-10}$$

LaMer-Healy Model

LaMer and Healy (1963) developed a kinetic model as part of their quantitative treatment of flocculation with polymers. Since they considered only a fixed intensity of agitation, the rms velocity gradient, G, was used here to represent the intensity of agitation.

LaMer and Healy postulated that the probability of building flocs was proportional to the fraction of the particle surface covered by polymer, θ, and to the fraction uncovered $(1-\theta)$. They considered an essentially bimolecular process where the number of floc nuclei and the number of particles per unit volume available to add to the floc nuclei were both proportional to N, i.e. the process was second order in N. They therefore obtained:

$$\frac{dN}{dt} = -K_1' N^2 \theta(1-\theta)G \tag{3-11}$$

where K_1' is constant.

Considering θ constant with time, Equation 3-11 can be integrated to give:

$$N = \frac{N_o}{K_1'\theta(1-\theta)N_oGt+1} \quad . \qquad (3\text{-}12)$$

In Appendix B, consideration is given to what form of relationship, if any, exists between θ and N_o, so that the model can be used with different initial particle concentrations. For polymer dosages used in practice, the approximate relationship obtained was

$$\theta(1-\theta) = K_x N_o^{-\frac{1}{2}} \qquad (3\text{-}13)$$

where K_x is constant.

Equation 3-12 then becomes

$$N = \frac{N_o}{K_4 N_o^{\frac{1}{2}} Gt+1} \qquad (3\text{-}14)$$

where K_4 is equal to $K_1'K_x$.

Modified LaMer-Healy Model

The second order form of the LaMer-Healy model occurs because of the assumption that the number of floc nuclei is proportional to N, the number of unflocculated particles. Since N decreases with time, the number of nuclei also decreases with time. For the other models, it was assumed in this development that the number of nuclei was proportional to the initial number of particles. Therefore, a modified

LaMer-Healy model was developed, incorporating this latter assumption. The differential equation was:

$$\frac{dN}{dt} = -K_1'K_1N_oN\theta(1-\theta)G \qquad (3\text{-}15)$$

where K_1N_o is the number of floc nuclei.

Substituting for $\theta(1-\theta)$ and integrating, there is obtained:

$$N = N_oe^{-K_5N_o^{1/2}Gt} \qquad (3\text{-}16)$$

where K_5 is equal to $K_1'K_1K_x$.

Comparison

The four simple aggregation models are listed in Table 3-1. All but the unmodified LaMer-Healy model are exponential decay models. For large values of the exponent, the Argaman-Kaufman model approaches the von Smoluchowski model except that the pre-exponential term is N_o^2 rather than N_o. The modified LaMer-Healy model is similar to the von Smoluchowski model except for the $N_o^{1/2}$ term in the exponent.

3.2.3.2 Models with Floc Breakup Terms

A major refinement which can be made to the models developed in Section 3.2.3.1 is the inclusion of the floc breakup term for the Argaman-Kaufman and LaMer-Healy models.

TABLE 3-1

SIMPLE AGGREGATION MODELS

1. Von Smoluchowski	$N = N_o e^{-K' N_o G t}$
2. Argaman-Kaufman	$N = \dfrac{N_o(N_o-1)e^{-K_3 N_o G t}}{1+(N_o-1)e^{-K_3 N_o G t}}$
3. LaMer-Healy	$N = \dfrac{N_o}{K_4 N_o^{\frac{1}{2}} G t+1}$
4. LaMer-Healy (Modified)	$N = N_o e^{-K_5 N_o^{\frac{1}{2}} G t}$

Argaman-Kaufman Model

Argaman and Kaufman (1970) consider one of the more credible breakup mechanisms to be the stripping of individual primary particles from the floc surfaces. By this model, the rate at which primary particles are released depends on the surface shear, the floc size, and the size of the primary particles. As the shearing stress depends on $\overline{u^2}$ or K_pG, a possible expression for the rate of formation of primary particles due to floc breakup is given by:

$$\left.\frac{dN}{dt}\right)_{\text{Breakup}} = B\ R_F^2\ \frac{N_F}{R^2}\ K_pG \qquad (3\text{-}17)$$

where B is the breakup constant.

This expression may be added to that of Equation 3-8 to give an overall expression for the change in the number of unflocculated particles with respect to time. Substituting for R_F and N_F, there is obtained:

$$\frac{dN}{dt} = -\frac{1}{K_3}\ N(N_o-N)G + K_6GN_o{}^{1/3}(N_o-N)^{2/3}G \qquad (3\text{-}18)$$

where K_3 is $1/(4\pi\eta K_SK_PR^3)$ as in Equation 3-9, and K_6 is equal to $B\ K_1{}^{1/3}K_P$.

An analytical solution could not be obtained for Equation 3-18. To obtain a potentially useful model, it was decided to simplify the expression rather than attempt a numerical solution. R_F was assumed constant with time, an assumption which is valid except at the beginning of flocculation, which is not of interest here (Appendix B). There was then obtained:

$$\frac{dN}{dt} = -K_7 N_o NG + K_8 N_o G \qquad (3\text{-}19)$$

where K_7 is $1/K_3$, and

K_8 is equal to B $K_P K_1^{1/3}$.

A similar equation form but without N_o and G was obtained by Parker et al. (1970) in an application of the work of Argaman and Kaufman to biological flocs.

Equation 3-19 can be readily integrated to give:

$$N = (N_o - K_9)e^{-K_7 N_o G t} + K_9 \qquad (3\text{-}20)$$

where K_9 is equal to K_8/K_7.

LaMer-Healy Model (Unmodified)

LaMer and Healy (1963) express the increase in number of particles with time (floc breakup) as:

$$\frac{dN}{dt} = K_2^{'} R_F \qquad (3\text{-}21)$$

where $K_2^{'}$ is constant to a first approximation. This applied for a given degree of agitation, a given and not too great total concentration of flocs and a constant floc shape. Under these conditions, the drag on a floc varies approximately with the characteristic linear dimension of the floc, which is R_F if the floc is approximately spherical.

The authors propose the relationship:

$$K_2' = K_2[\theta(1-\theta)]^{-1}. \tag{3-22}$$

The overall rate of generation of primary particles through breakup, incorporating the effect of intensity of agitation, is

$$\left.\frac{dN}{dt}\right)_{\text{Breakup}} = \frac{K_2 R_F K_1 N_o G}{\theta(1-\theta)} \tag{3-23}$$

where K_2 is constant.

Combining this with Equation 3-11 and substituting for $\theta(1-\theta)$ and R_F, there was obtained:

$$\frac{dN}{dt} = -\,K_1' K_X N_o^{-\frac{1}{2}} N^2 G + K_1^{2/3}\,\frac{K_2}{K_X}\;R\,N_o^{7/6}(N_o-N)^{1/3}G \tag{3-24}$$

where K_X is as in Equation 3-13.

This could not be solved analytically and it was decided, as for the Argaman-Kaufman model, to make the simplifying assumption that R_F was constant with time. With this assumption, Equation 3-24 becomes:

$$\frac{dN}{dt} = -\,K_1' K_X N_o^{-\frac{1}{2}} N^2 G + \frac{K_{10} N_o^{3/2} G}{K_X} \tag{3-25}$$

where K_{10} is equal to $K_1 K_2 R_F$.

The integrated form of Equation 3-25 is:

$$N = \frac{-N_o}{K_{12}} \cdot \frac{(1-K_{12}) - (1+K_{12})e^{K_{11}N_o^{\frac{1}{2}}Gt}}{(1-K_{12}) + (1+K_{12})e^{K_{11}N_o^{\frac{1}{2}}Gt}} \tag{3-26}$$

where K_{11} is equal to $2\sqrt{K_1' K_{10}}$, and

K_{12} is equal to $\sqrt{K_X\,K_1'/K_{10}}$.

LaMer-Healy Model (Modified)

The floc breakup term, including the effect of number of flocs, is Equation 3-23. Combining this with Equation 3-15 and substituting for $\theta(1-\theta)$ and R_F there is obtained:

$$\frac{dN}{dt} = - K_1^{'} K_1 K_X N_o^{1/2} N G + K_1^{2/3} \frac{K_2}{K_X} R N_o^{7/6} (N_o - N)^{1/3} G \qquad (3\text{-}27)$$

Again it was decided to make the simplifying assumption that R_F was constant with time. Equation 3-27 then becomes:

$$\frac{dN}{dt} = -K_5 N_o^{1/2} N G + K_{13} N_o^{3/2} G \qquad (3\text{-}28)$$

where K_5 is equal to $K_1^{'} K_1 K_X$ as in Equation 3-16, and K_{13} is equal to $K_1 K_2 R_F / K_X$.

This equation can be integrated readily to give:

$$N = N_o (1 - K_{14}) e^{-K_5 N_o^{1/2} G t} + K_{14} N_o \qquad (3\text{-}29)$$

where $K_{14} = K_{13}/K_5$ or $\dfrac{K_2 R_F}{K_1^{'} K_X^2}$.

Comparison

The three models are listed in Table 3-2. The unmodified LaMer-Healy model is complicated and is difficult to relate to the physical situation. The Argaman-Kaufman and modified LaMer-Healy models show similarities, but the latter seems more reasonable because of the presence of N_o in the linear term.

TABLE 3-2

MODELS WITH FLOC BREAKUP

1. Argaman-Kaufman	$N = (N_o - K_9)e^{-K_7 N_o G t} + K_9$
2. LaMer-Healy	$N = \frac{-N_o}{K_{12}} \cdot \frac{(1-K_{12})-(1+K_{12})e^{K_{11} N_o^{\frac{1}{2}} G t}}{(1-K_{12})+(1+K_{12})e^{K_{11} N_o^{\frac{1}{2}} G t}}$
3. LaMer-Healy (Modified)	$N = N_o(1-K_{14})e^{-K_5 N_o^{\frac{1}{2}} G t} + K_{14} N_o$

3.2.3.3 Further Refinements

If necessary, the models can be refined further by not assuming that only flocculated particles settle during the 20 minutes prior to sampling. Possible differences in floc resistance to breakup, as a function of ionic strength, could be included.

4 EQUIPMENT AND PROCEDURES

4.1 Experimental Apparatus

The necessary experimentation was conducted at bench scale in batch experiments, using prepared solutions containing sulphate plus the appropriate heavy metal ions. The various times in each experiment (mixing, polymer addition, sampling) were controlled by an electronic programmable sequencer, described in Appendix C.

The flocculation testing technique used had been developed previously (Huck and LeClair, 1974) and was a modification of the standard jar test procedure. An ELB agitator drive* with speed continuously variable from 0 to approximately 1,000 rpm was used. Speed was measured by a tachometer and energy input calculated from power data supplied by the manufacturer as described in Appendix C. A square pitch marine propeller 4 inches in diameter was used as the impeller. The experimental vessel was cylindrical, 21.6 cm (8.5 in) in diameter and 25.4 cm (10 in) high. A liquid depth of 12.7 cm (5.0 in) was used. Four baffles were provided, 90° apart. Solenoid valves were used to effect polymer addition and sample withdrawal: the former by means of a slight air pressure and the latter by gravity. The apparatus is shown in Figure 4-1.

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*A product of Chemineer, Inc., Dayton, Ohio

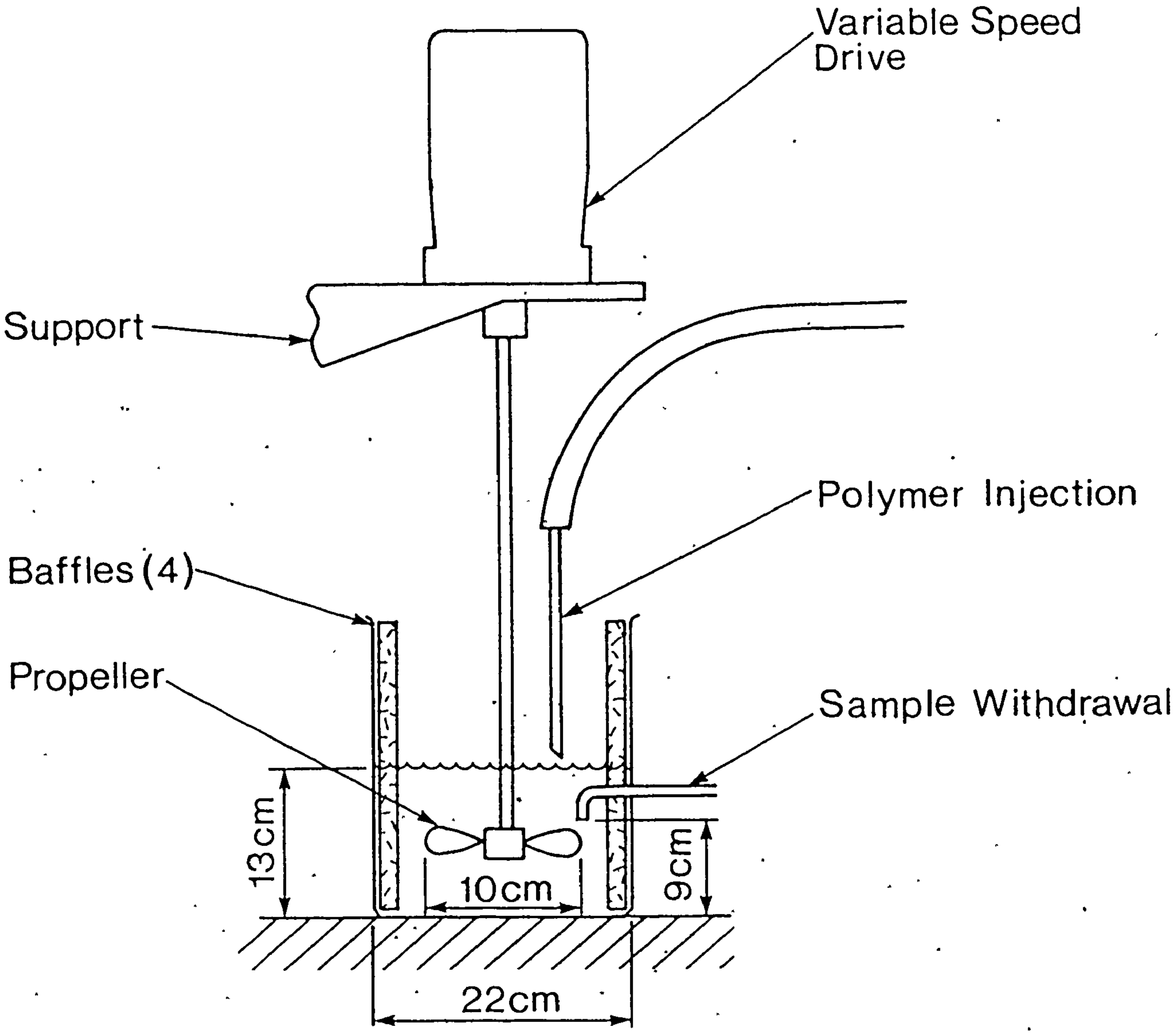

FIGURE 4-1: EXPERIMENTAL APPARATUS

Approximately 4.5 litres of slurry were flocculated in each test. This volume was sufficiently large to permit use of equipment of the size recommended for bench-scale mixing studies on suspensions (Uhl and Gray, 1967), yet not so great as to require excessive quantities of chemicals for the simulated minewater.

4.2 Preparation of Polymer

Percol 720*, a nonionic polyacrylamide, was used as the stock polymer. Its molecular weight distribution was determined by Gel Permeation Chromatography as described by Abel-Alim and Hamielec (1974). Different molecular weights were obtained for the first part of the study by mechanically degrading a solution of the original polymer. Various anionic polymers were produced by hydrolyzing Percol 720 to the required degree with sodium hydroxide using a procedure described by Benedek _et al._ (1976). Details of all of these procedures are given in Appendix D.

Polymer stock solutions were made up at 0.5 percent by weight and diluted to 0.1 percent just prior to use.

4.3 Preparation of Minewater

As stated in Section 2.4.2, all simulated minewater was prepared with a metal-to-sulphate ratio of 0.3 by weight, using the sulphate salt of the metal. The quantity of this

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*Obtained from Allied Colloids (Canada) Limited, Toronto, Ontario necessary to achieve the desired metal concentration was dissolved in distilled water and any additional sulphate required to achieve the 0.3 ratio was added in the form of sulphuric acid. Iron minewaters were prepared with the metal in the ferric form. In general, minewater was prepared one or two days prior to use.

4.4 Test Procedure

Minewater was neutralized in 15- or 20- litre batches, a quantity normally sufficient for one half day's testing. A 10 percent slurry of reagent grade lime was used. The estimated quantity of lime required to raise the pH to 9.5 was added normally in five equal aliquots at intervals of five minutes. Trimming to pH 9.5 was accomplished by adding either minewater or more lime. Fifteen minutes were normally required for the pH to stabilize at 9.50 ± 0.05. This period before the 4.5 l for the first test was withdrawn permitted quasi-equilibrium dissolved metal concentrations to be obtained. The pH was adjusted to 9.50 ± 0.05 immediately prior to withdrawing a sample for subsequent tests.

To begin a test, the baffled reaction vessel containing the slurry was positioned beneath the mixer, the effluent sampling line connected, the polymer solution drawn up into the discharge pipette, and the timer started. After mixing the slurry for 30 seconds to ensure full suspension, the polymer was added in less than 0.5 seconds and rapid mixing (polymer dispersion) was carried out for the time specified for that test. The mixer was then shut off automatically for five seconds and the speed adjusted manually to whatever lower value was being employed for the flocculation step. After flocculation for the specified length of time, the mixer was shut off automatically and the slurry allowed to settle. Supernatant samples were withdrawn automatically after 20 minutes settling. In single-stage mixing experiments no change of mixer speed was required. The complete timing sequence may be found in Appendix C.

For actual minewaters containing ferrous iron, a modified neutralization was used. The pH was raised to 7.5, aeration was provided to oxidize the ferrous iron to ferric iron, and then the neutralization was completed to pH 9.5.

4.5 pH Measurements

pH measurements were made with an Orion Research model 701 or Model 7060 digital pH meter having a readout to the nearest 0.01 unit. Scaling of the standard combination electrode probes during minewater neutralization required their replacement on a monthly basis. pH control was good at the beginning of the programme with daily checks of the meter against buffers and evolved later to buffer checks between individual flocculation tests.

4.6 Sample Preparation and Analysis

Supernatant samples were collected in 4-oz polypropylene or polyethylene bottles which had been acid washed with approximately 1.5 N hydrochloric acid. Following acidification with concentrated nitric acid, the samples were analyzed by the Wastewater Technology Centre's Analytical Services Section using direct aspiration atomic absorption spectrophotometry. The results were defined as total extractable metal. Near optimum conditions, where the soluble fraction became significant, both total and filterable determinations were made. Filtration was through a 0.45μm filter.

5 DISCUSSION OF RESULTS

5.1 Optimization Studies

Optimization of the process for the independent variables identified in Section 2.4 was conducted using the Path of Steepest Ascent and Response Surface techniques discussed in Section 3.1. All experimental designs and results are tabulated in Appendix E.

5.1.1 Studies with Minewaters Containing Iron

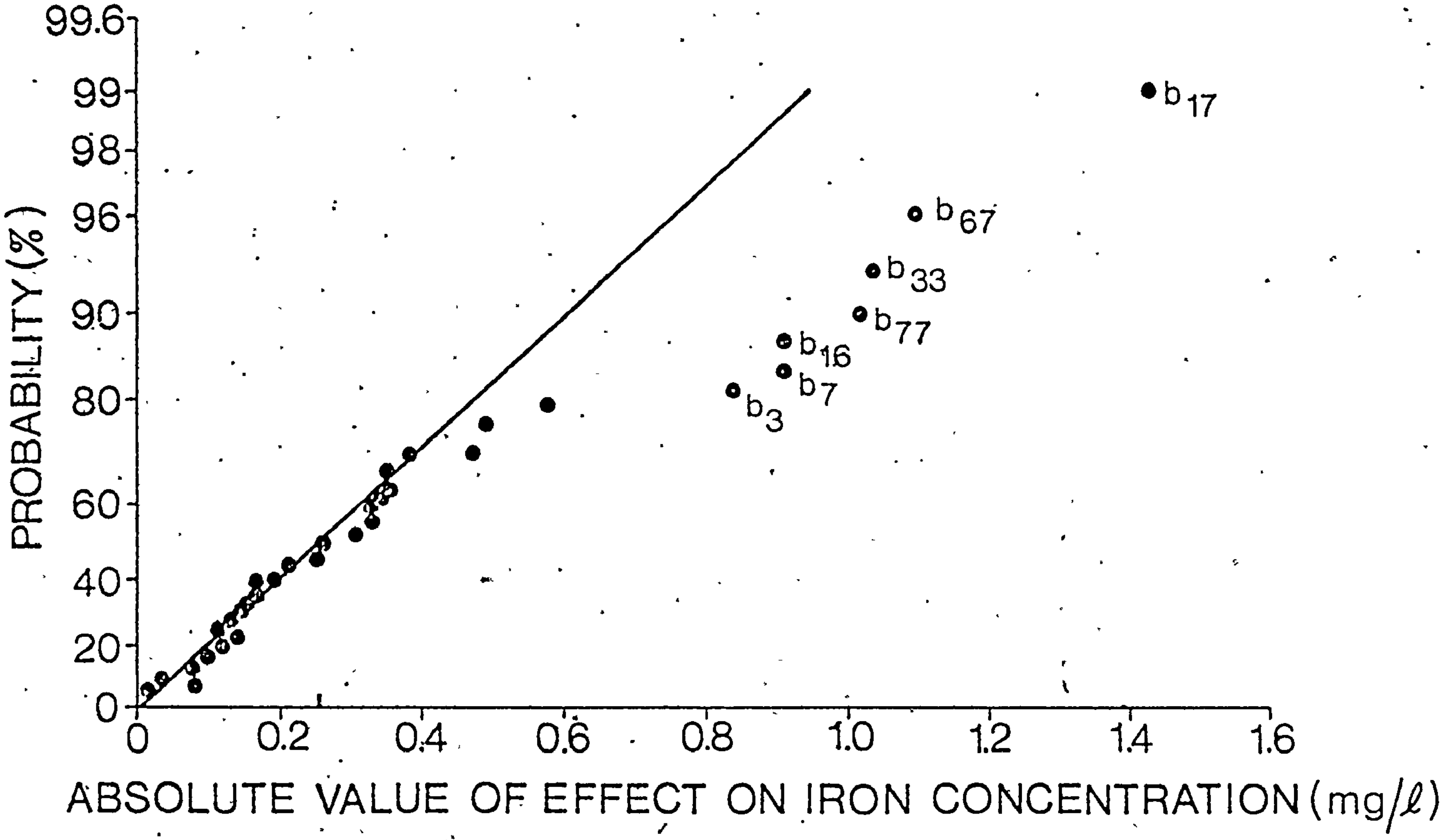
Minewaters containing iron were used for initial studies because iron is the most common constituent of many base metal mine drainages.

The practical range of each of the independent variables was estimated either from previous studies (Huck and LeClair, 1974) or from preliminary experimentation. This experimental region was examined using a 3-level factorial design of the type described by Box and Behnken (1960). Flocculation speed, which appeared to be least critical was held constant in this experiment to reduce the number of runs required.

Effects were calculated and a quadratic model fitted using a computer programme given in Appendix G. As described in Section 3.1, a half-normal plot was used to suggest which effects might be significant. These significant effects, labelled in Figure 5-1, are listed in Table 5-1 with their physical meanings. A negative effect indicates a lower iron concentration and therefore improved performance at higher levels of the variable.

Flocculation time and degree of hydrolysis each showed negative linear and positive quadratic effects, indicating the existence of optima in the region of the design. Two of the three significant interaction effects involved flocculation time. A deterioration of effluent quality was indicated when high flocculation times were used at high initial metal concentrations or combined with high rapid mix times. A high dispersion time was also harmful at the high initial metal concentrations.

To give the response for equal percentage changes in the independent variables, normalization using a range factor was necessary. In this experiment the range factor, defined as the +1 variable setting divided by the 0 setting was identical for the two variables whose linear terms were significant. (Appendix E). Flocculation time and degree of hydrolysis were the two most important variables, and initial metal concentration and polymer concentration appeared to have no effect over approximately an order of magnitude. This confirmed previous findings (Huck <u>et al.</u>, 1975) that the final metal concentration was essentially independent of the minewater strength. It also suggested that the optimum for



<u>FIGURE 5-1:</u> DISTRIBUTION OF EFFECTS OF DESIGN VARIABLES ON SUPERNATANT IRON CONCENTRATION (FIRST EXPERIMENT)

TABLE 5-1

SIGNIFICANT EFFECTS OF VARIABLES ON IRON CONCENTRATION (FIRST EXPERIMENT)

TYPE	VARIABLE(s)	EFFECT mg/l
Linear	b_7 Flocculation time	-0.91
	b_3 Hydrolysis	-0.84
Quadratic	b_{33} Hydrolysis	1.04
	b_{77} Flocculation time	1.02
Iteraction	b_{17} Initial metal conc'n x Flocc'n time	1.43
	b_{67} Dispersion time x Flocc'n time	1.10
	b_{16} Initial metal conc'n x Dispersion time	0.91

polymer concentration (dosage) would not be narrowly defined.

The data from this experiment were used to select starting conditions for optimization. Because minewater strength cannot normally be varied in practice and because initial metal concentration had shown significant interaction with mixing times, parallel investigations using the Path of Steepest Ascent (PSA) were conducted for high and low strength minewaters. Flocculation speed was introduced as a variable and molecular weight was eliminated because it had been shown to be unimportant over the range investigated.

Two-level factorial designs were used to approach the optimum by the Path of Steepest Ascent. Table 5-2 shows the information accumulated on the location of the optimum for each variable.

Initially, optimization was to be considered complete when variations in the independent variables of the magnitude shown in Table 5-3 produced no significant changes in iron concentrations. After several experiments, however, the improvements being obtained were of the same magnitude as the variability in the results. The reproducibility of a test performed on different days was found to be on the order of 0.1 mg/l (Table 5-4). This was attributed to different polymer and minewater batches, and to the impossibility of achieving exact reproducibility during neutralization with lime. A new criterion was established: that optimization would end when effects of less than 0.1 mg/l were obtained

TABLE 5-2

INFORMATION ACCUMULATED ON THE LOCATION OF THE OPTIMUM -IRON MINEWATERS

a. STRONG MINEWATER

VARIABLE	EXPERIMENT NUMBER			
	3.1.1	3.1.5	3.1.7	3.1.9
Hydrolysis (%)	< 10	< 8	4 to 8	2 to 8
Polymer conc'n (mg/g SO_4)	<1.0	$\leq$0.5	$\leq$0.3	$\leq$0.1
Dispersion speed (rpm)	>300	$\geq$550	no change	
Dispersion time (sec)	>5	5 to 12	no change	
Flocc'n speed (rpm)	$\geq$ 55	55 to 65	no change	
Flocc'n time (min)	>0.5	0.5 to 2.75	no change	

b. WEAK MINEWATER

VARIABLE	EXPERIMENT NUMBER		
	3.1.2	3.1.6	3.1.8
Hydrolysis (%)	< 20	$\leq$ 4	2 to 4
Polymer conc'n (mg/g SO_4)	$\leq$1.0	$\leq$0.5	0.1 to 0.5
Dispersion speed (rpm)	<600	$\leq$325	100 to 325
Dispersion time (sec)	> 30	30 to 45	no change
Flocc'n speed (rpm)	> 35	35 to 45	no change
Flocc'n time (min)	> 10	10 to 15	no change

TABLE 5-3

ORIGINAL CRITERIA FOR ACHIEVEMENT OF OPTIMIZATION

PARAMETER	HOW SPECIFIED
1. Molecular weight	required minimum molecular weight, to nearest million
2. Degree of hydrolysis	to within ½% if <5% to within 1% if ≥5%
3. Polymer dose	to within 10%
4. Dispersion horsepower	to within 10% (expressed as rpm)
5. Dispersion time	to within 0.5 sec. if <5 sec to within 1 sec. if <10 sec. to within 10% if ≥ 10 sec.
6. Flocculation horsepower	to within 5% (expressed as rpm)
7. Flocculation time	to within 1 sec. if <10 sec. to within 10% if ≥10 sec.

TABLE 5-4

EXAMPLE OF REPRODUCIBILITY OF IRON RESULTS

EXPERIMENT NUMBER	RESIDUAL IRON CONCENTRATION (mg/l)
3.1.7	0.13
3.1.9	0.23

CONDITIONS

Hydrolysis	4%
Polymer conc'n	0.3 mg/g SO_4
Dispersion Speed	550 rpm
Dispersion time	12 sec
Flocc'n speed	100 rpm
Flocc'n time	2.0 min

Strong minewater (SO_4 = 8,000 mg/l)

for all variables. It was assumed that this would indicate that the region of the optimum had been reached.

Three-level experiments were then conducted to model the response surface of the vicinity of the optimum. The polymer and mixing variables were examined in separate experiments to reduce the number of runs required, and to make the results easier to interpret. This separation was justified because there was no theoretical reason for interactions between the two groups of variables, and because previous experiments had not shown significant interactions between the two groups.

The variables in each experiment were set at their inferred optima, and at 0.5 and 1.5 times these values. It was anticipated that optima (minima) for all variables at both strengths could be obtained. However, given the expected flatness of the response surfaces, it was recognized that this might not be possible. The response surfaces obtained are plotted in Figure 5-2 (a to c) from equations given in Appendix E. The contours for the rapid mix variables are shown for the midpoint values of the flocculation variables, and vice versa. For low strength minewater, true minima were obtained for rapid mix conditions (Figure 5-2a), for flocculation conditions (Figure 5-2b) and for degree of hydrolysis (Figure 5-2c). Although Figure 5-2c did not show a minimum for polymer concentration or dosage, the low predicted metal concentrations indicated that further improvements could not be expected,

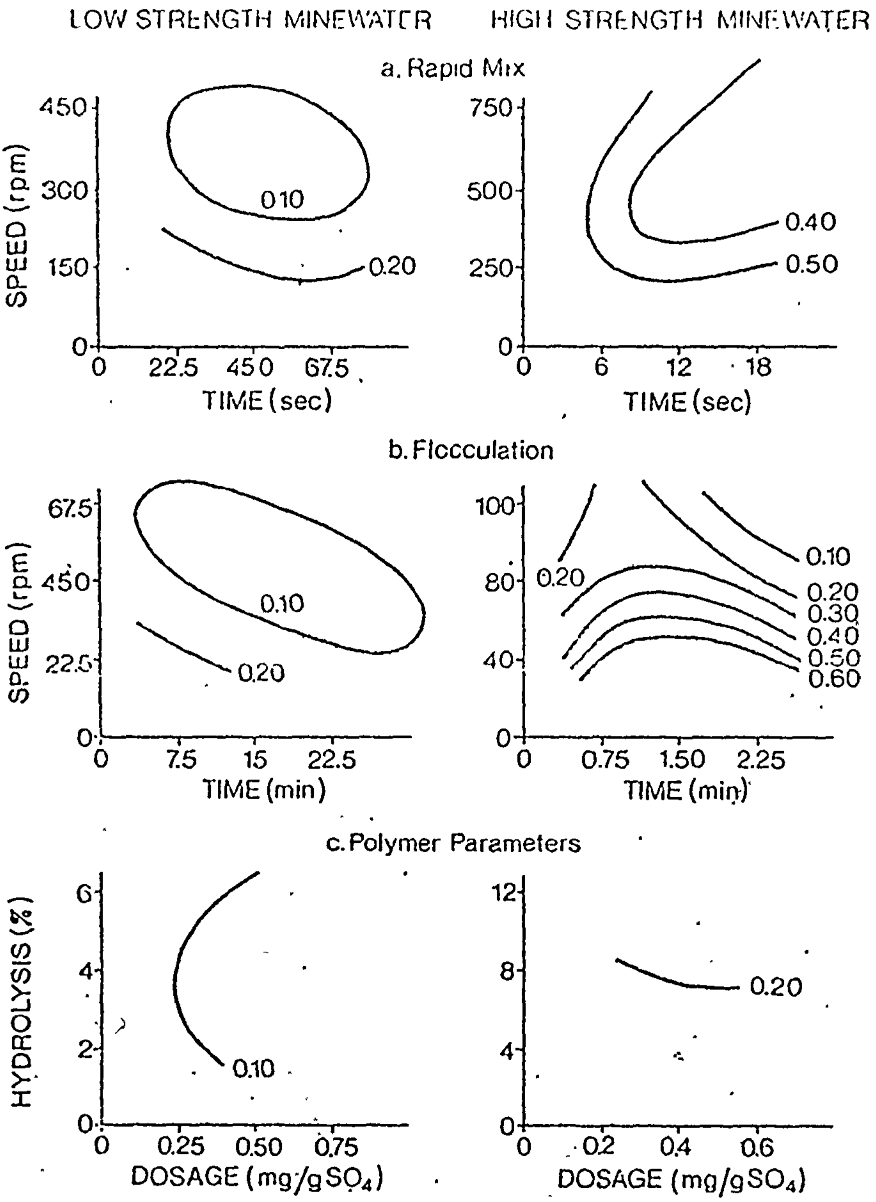


FIGURE 5-2: RESPONSE SURFACE CONTOURS OF SUPERNATANT IRON CONCENTRATION (MG/L) NEAR OPTIMUM

and an optimum dosage was assumed.

For high strength minewater, Figure 5-2a indicated the need for higher rapid mix speeds and times, and Figure 5-2b indicated a saddle point for flocculation speed and time. Since these results contradicted the previous data, the experiment was repeated. As a different saddle point was obtained and the reproducibility of many test results was poor, the optimum conditions were inferred from the previous two-level experiments. Flocculation speed and polymer concentration were set higher than the inferred upper limit after a review of the results. Dosage, hydrolysis and type of lime were then investigated, using these conditions. Type of lime was included since a change to a new supplier was being considered. A two-level experiment was performed to complement existing information and permit location of the optimum by inference. Since neither lime nor polymer properties (Figure 5-2c) had significant effects, optimum polymer dose and hydrolysis could be estimated. The iron levels obtained were in the 0.1 to 0.2 mg/l range, indicative of optimum conditions.

Table 5-5 shows the optimum conditions for the two minewater strengths. Optimum times decreased substantially with increased minewater strength, optimum speeds increased moderately and optimum polymer parameters remained unchanged. The decrease in mixing times would be expected from kinetic considerations. The increase in speeds suggests formation of

TABLE 5-5

LEVELS OF VARIABLES PRODUCING MINIMUM SUPERNATANT PARTICULATE IRON CONCENTRATIONS

VARIABLE	MINEWATER STRENGTH	
	HIGH	LOW
Hydrolysis (%)	4	4
Polymer conc'n (mg/g SO_4)	0.5	0.5
Dispersion speed (rpm)	500	372*
Dispersion time (sec)	12	49*
Flocculation speed (rpm)	100	45*
Flocculation time (min)	1.5	17.4*
Residual particulate iron concentration (mg/l)	0.1-0.2	0.05-0.1

---

*Predicted from three-level experiments. Other values estimated from two-level experiments.

denser and therefore tougher flocs at higher strengths. The lack of change in hydrolysis suggests that charge neutralization is not involved in flocculation of metal hydroxides.

The strong dependence of the mixing times on minewater strength suggests that they, rather than polymer properties, should be the prime objects of investigation in polymer flocculation studies.

The general flatness of the response surfaces, even for mixing, indicates that there is a range of operating conditions which will produce quite similar results. An opportunity therefore exists for cost minimization.

Because changes in the independent variables of 50 percent on either side of their optimum values did not produce substantial differences in residual iron concentration, it was decided to vary them over a much wider range in order to establish qualitative operating limits. To minimize the number of experiments, each of the six variables was investigated one at a time while the others were held at their optima. High strength minewater was used for all except the polymer dosage experiment which was done with low strength minewater to reduce polymer use. The results (Figure 5-3) show that there is a wide range of nearly equivalent operating conditions. They further show that all the variables are more steeply bounded on the lower side - i.e. the problem is mainly one of minimization of the variables and hence of the cost.

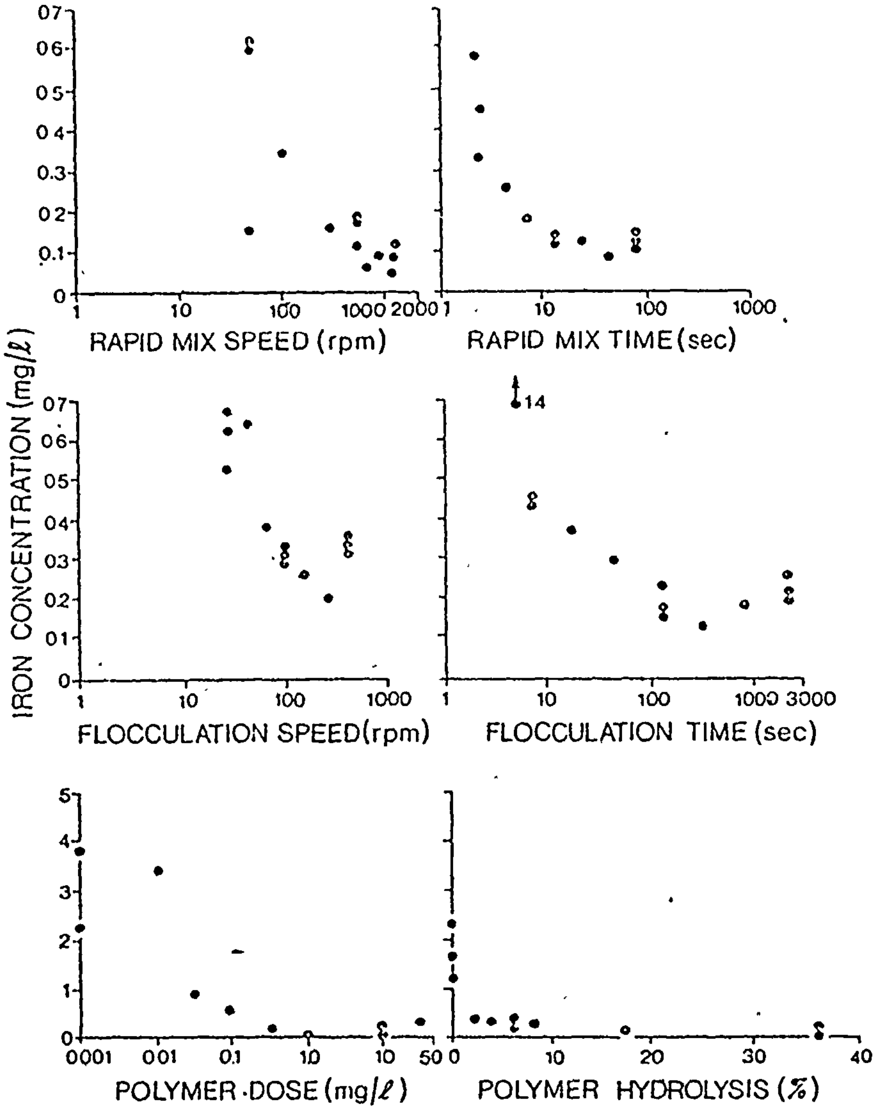


FIGURE 5-3: SUPERNATANT IRON CONCENTRATIONS AS A FUNCTION OF EACH VARIABLE OVER AN EXTENDED RANGE

In particular, the settings of the polymer variables were not very critical: neither variations in dosage of approximately an order of magnitude on either side of the optimum nor changes in degree of hydrolysis between 2 and 35 percent produced measurable effects. This is a further indication of the greater importance of the mixing conditions.

5.1.2 Studies with Minewaters Containing Zinc and Copper

It was hypothesized that the mixing conditions would be the same for all metals at a given minewater strength, but that the optimum polymer dosage or degree of hydrolysis might be different. Accordingly, for zinc and copper minewaters of both high and low strength, 3^2 experiments were conducted with polymer dosage and degree of hydrolysis as variables. The designs were centred on the optimum values found for the iron minewater of the same strength. As there is no theoretical reason for particulate residuals to be exactly the same for different metals, it was assumed that if the metal residuals for zinc and copper were approximately the same as those for iron, the first part of the hypothesis would be confirmed. If the response surface showed an optimum, the second part would be substantiated, although flatness of the response surface in the vicinity of the optimum might make it impossible to show a true minimum.

A typical response surface for low strength minewater containing copper is shown in Figure 5-4. This surface is described by the equation:

$$\hat{y} = 0.190 - 0.028\ X_1 - 0.018\ X_2 - 0.025\ X_1^2 + 0.035\ X_2^2 - 0.015\ X_1X_2 \qquad (5-1)$$

where $\hat{y}$ is predicted copper concentration, mg/l

X_1 is hydrolysis) coded in standard form: midpoint =0
) " -50%=-1
X_2 is dosage) " +50%=+1

Although the response surface is a saddle point and not a true minimum, it is very flat. An analysis of variance (Table 5-6) showed that, over the range investigated, neither hydrolysis nor polymer dosage had a significant effect on supernatant particulate copper concentrations. Thus there was no evidence that other experimental conditions would be better.

Comparisons between iron and the other metals were made using replicated midpoints of the 3^2 designs. Three trials were performed on each of two days for each metal and strength. Since neither the first nor the second trial was performed for all metals on the same day, a two-way analysis of variance (days and metals) could not be used and the data were analyzed using t-tests (Tables 5-7 and 5-8). Although these showed significant differences between metals, they also indicated significant differences for the same metal on different days. While it was not possible to show that there was a single population with respect to metal, the results

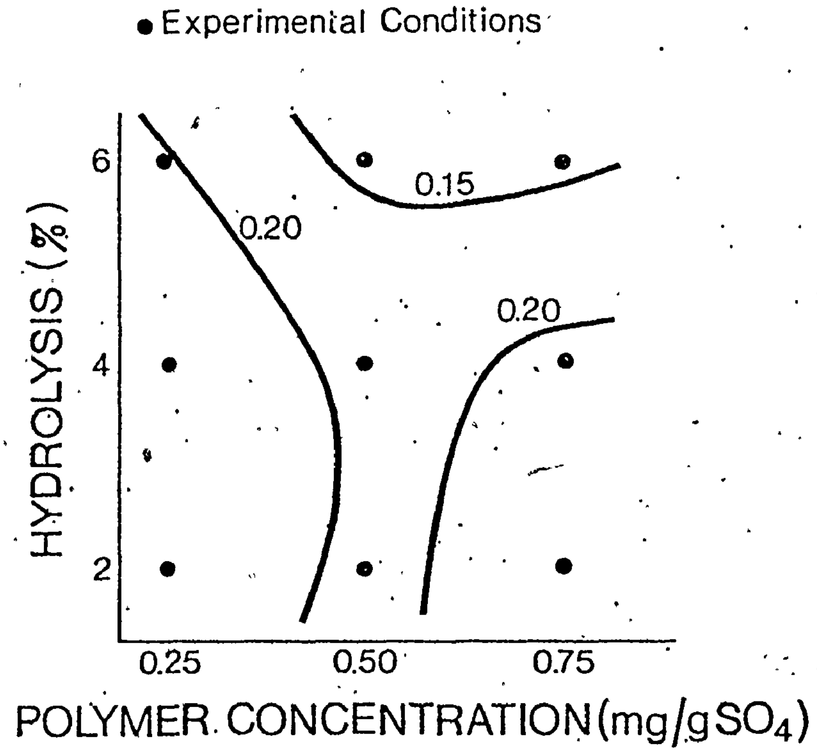


FIGURE 5-4: RESPONSE SURFACE CONTOURS OF SUPERNATANT COPPER CONCENTRATION (MG/L) FOR LOW STRENGTH MINEWATER

TABLE 5-6

ANALYSIS OF VARIANCE FOR SUPERNATANT PARTICULATE COPPER CONCENTRATIONS (LOW STRENGTH MINEWATER)

SOURCE	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE	$F_{CALC.}$	$F_{1,4(0.05)}$
A_L	1	0.00482	0.00482	3.82	7.71
A_Q	1	0.00125	0.00125	0.99	7.71
B_L	1	0.00202	0.00202	1.60	7.71
B_Q	1	0.00245	0.00245	1.94	7.71
AB	4	0.00506	0.00126	——	——
TOTAL	8	0.01560	————		

A - Hydrolysis
B - Polymer concentration
L - Linear
Q - Quadratic

NOTE: Use of the interaction mean square as a measure of the error mean square assumes no interaction between A and B.

TABLE 5-7

COMPARISON OF PARTICULATE METAL CONCENTRATIONS FOR IRON, ZINC AND COPPER (LOW STRENGTH MINEWATER)

a. RESULTS

TRIAL	n[1]	Metal[2]					
		Fe		Zn		Cu	
		$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
First	3	0.030	0.0100	0.110	0.0866	0.127	0.0058
Second	3	0.127	0.0252	0.220	0.1000	0.350	0.0264
Overall	6	0.078	0.0556	0.165	0.1030	0.238	0.1240

[1] Number of data points

[2] $\bar{x}$ and σ are in mg/l

b. t-TESTS

COMPARISON	d.f.	F_{calc}	F_{tab} (α=0.05)	t_{calc}	t_{tab} (α=0.05)	SIGNIFICANCE
Between Trials						
Fe	2,2	6.35	19.00	6.188	2.776	Yes
Zn	2,2	1.33	19.00	1.440	2.776	No
Cu	2,2	20.93	19.00	*	2.776	—
Between Metals						
Fe vs Zn	5,5	3.43	5.05	1.821	2.228	No
Fe vs Cu	5,5	4.97	5.05	2.884	2.228	Yes

* F_{tab} exceeded; t-test not possible

TABLE 5-8

COMPARISON OF PARTICULATE METAL CONCENTRATIONS FOR IRON, ZINC AND COPPER (HIGH STRENGTH MINEWATER)

a. RESULTS

TRIAL	n[1]	Metal[2]					
		Fe		Zn		Cu	
		$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
First	3	0.127	0.0115	0.237	0.0802	0.273	0.2830
Second	3	0.143	0.0551	0.257	0.0252	0.510	0.1220
Overall	6	0.135	0.0367	0.247	0.0543	0.392	0.2340

[1] Number of data points [2] $\bar{x}$ and σ are in mg/l

b. t-TESTS

COMPARISON	d.f.	F_{calc}	F_{tab} (α=0.05)	t_{calc}	t_{tab} (α=0.05)	SIGNIFICANCE
Between Trials						
Fe	2,2	22.75	19.00	*	2.776	——
Zn	2,2	10.16	19.00	0.412	2.776	No
Cu	2,2	5.41	19.00	1.334	2.776	No
Between Metals						
Fe vs Zn	5,5	2.18	5.05	4.185	2.228	Yes
Fe vs Cu	5,5	40.58	5.05	*	2.228	——

$^{*}F_{tab}$ exceeded; t-test not possible were all of similar magnitude. This, coupled with the flatness of the response surfaces, was interpreted to mean that the optima were the same for all metals tested.

Two-metal systems were investigated at both high and low minewater strengths. Using minewaters containing equal amounts by weight of copper and zinc and iron and zinc, trials were conducted at conditions corresponding to the midpoints of the 3^2 designs for single metals. The results were compared to the single-metal systems using t-tests (Tables 5-9 and 5-10). Although significance was demonstrated for only one comparison, the results in all but one case were substantially lower in the two-metal systems. This indicated that single-metal systems provided an upper bound on obtainable levels.

5.2 Mechanistic Modelling

5.2.1 Introduction

On the basis of the optimization studies, it was decided that the most useful model would be one which predicted residual metal concentrations as a function of minewater strength and mixing time, i.e. a kinetic model of the type presented in Section 3.2.3. The objective was to provide a useful model for design rather than a theoretical model. Therefore, the criterion of flocculation success was the supernatant particulate metal concentration following flocculation and settling, as in the optimization studies, rather

TABLE 5-9

COMPARISON OF PARTICULATE METAL RESULTS FOR TWO-METAL AND ONE-METAL SYSTEMS (LOW STRENGTH MINEWATER)

a. RESULTS

SYSTEM	n[1]	Metal[2]					
		Fe		Zn		Cu	
		$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
One-metal	6	0.078	0.0556	0.165	0.1030	0.238	0.1240
Fe/Zn	3	0.017	0.0058	0.103	0.1210	———	———
Cu/Zn	3	———	———	0.263	0.2000	0.013	0.0058

[1] Number of data points

[2] $\bar{x}$ and σ are in mg/l

b. t-TESTS

COMPARISON	d.f.	F_{calc}	F_{tab} (α=0.5)	t_{calc}	t_{tab}[3] (α=0.05)	SIGNIFICANCE
Fe vs Fe/Zn	5,2	91.90	19.30	*	———	—
Zn vs Fe/Zn	2,5	1.38	5.79	0.808	1.895	No
Zn vs Cu/Zn	2,5	3.77	5.79	1.005	2.365	No
Cu vs Cu/Zn	5,2	457.07	19.30	*	———	—

[3] One-sided tests were used whenever the mean for the two-metal system was lower than that for the one metal system

* F_{tab} exceeded; t-test not possible

TABLE 5-10

COMPARISON OF PARTICULATE METAL RESULTS FOR TWO-METAL AND ONE-METAL SYSTEMS (HIGH STRENGTH MINEWATER)

a. RESULTS

SYSTEM	n[1]	Metal[2]					
		Fe		Zn		Cu	
		$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
One-metal	6	0.135	0.0367	0.247	0.0543	0.392	0.2340
Fe/Zn	6	0.017	0.0121	0.078	0.0608	———	———
Cu/Zn	6	———	———	0.060	0.0533	0.225	0.0826

[1] Number of data points   [2] $\bar{x}$ and σ are in mg/l

b. t-TESTS

COMPARISON	d.f.	F_{calc}	F_{tab} (α=0.05)	t_{calc}	t_{tab}[3] (α=0.05)	SIGNIFICANCE
Fe vs Fe/Zn	5,5	9.20	5.05	*	———	—
Zn vs Fe/Zn	5,5	1.25	5.05	5.079	1.812	Yes
Zn vs Cu/Zn	5,5	2.32	5.05	0.545	1.812	No
Cu vs Cu/Zn	5,5	19.29	5.05	*	———	—

[3] One-sided test

* F_{tab} exceeded;   t-test not possible

than the number of primary particles remaining after flocculation alone. It was hypothesized that unflocculated particles would not settle in the time provided and that flocculation models could be used to represent the overall process. If this hypothesis were not tenable, a settling term would be required in the models. It was recognized that the predicted metal concentrations would be those obtainable with ideal clarifier operation.

It was decided to begin with simple aggregation models and to examine those involving floc breakup only if required. Although mixing speed was held constant initially, it was later varied to enhance the generality of the models.

The experimental conditions for model discrimination and parameter estimation were determined using the criteria described in Section 3.2.2 and the parameter estimates were obtained using nonlinear least squares. The data and parameter estimates are tabulated in Appendix F and sample runs of the computer programmes used for experimental design and parameter estimation are given in Appendix G.

5.2.2 Experimental Considerations

It was considered desirable to eliminate the separate rapid mix step used in the optimization studies, since noticeable flocculation took place during this step and its incorporation into the models would have increased their complexity greatly. Also, the practical impossibility of changing the mixing speed instantaneously between steps would give rise to a period of unknown mixing intensity.

Before deciding to model a single-stage process, however, it was necessary to establish whether single-stage mixing could provide adequate metal removals. Response surface experiments were conducted for strong and weak iron minewaters, to determine optimum conditions and levels attained for single-stage mixing. Although precise optima could not be defined because of the flatness of the response surface, optimum conditions were inferred. In Table 5-11, these are compared to the optimum conditions obtained for two-stage mixing. The single-stage mixing times are longer and the single-stage mixing speed is intermediate between rapid mix and flocculation conditions. Since the metal results were the same for both processes, it was considered acceptable to use single-stage mixing for modelling. Once a model incorporating speed had been obtained for single-stage mixing, it could be extended to a two-stage process.

To reduce the equipment fouling associated with iron minewaters, zinc minewaters were used for modelling as it had been previously shown in Section 5.1.2 that the iron and zinc optima were the same.

Particle weight rather than particle number was measured, since by definition unflocculated particles do not change in size during flocculation. The use of this measurement assumed that particle size and density were independent

TABLE 5-11

COMPARISON OF OPTIMUM CONDITIONS FOR SINGLE-STAGE AND TWO-STAGE MIXING[1]

MINEWATER	MIXING SPEED (rpm)			MIXING TIME (sec)			IRON CONC'N[2] (mg/l)	
	1-stage	2-stage		1-stage	2-stage		1-stage	2-stage
		RM	Floc		RM	Floc.		
Strong	200-300	500	100	100-600	12	90	0.1-0.2	0.1-0.2
Weak	50-100	372	45	1200-1500	49	1045	≤0.1	≤0.1

[1] Results for two-stage mixing are from Table 5-5

[2] Particulate iron concentration

of initial particle concentration, an assumption which was verified qualitatively by experiment.

The operability region, or range over which the independent variables were examined, included mixing times from 10 to 1,000 sec and initial metal concentrations from 100 to 10,000 mg/l. This range was considered to encompass the limits encountered in practice. Mixing speed was held constant initially at a value obtained from the single stage mixing studies.

Replicated trials were performed at several points in the operability region to determine whether the data exhibited constant variance. The results shown in Table 5-12 encompassed the range of supernatant concentrations anticipated and indicated that the variance was approximately constant over that range. Transformation of the data and models,as discussed in Appendix A,was therefore not required. The variance calculated from these experiments was used for the discrimination procedure. The insensitivity of the procedure to the actual value of the variance was demonstrated when increasing it by a factor of 20 left the results unchanged.

Most discrimination data points were the mean of two or three replicates, since it involved little additional work to run one or two additional trials at the same conditions.

TABLE 5-12

VARIANCE OF PARTICULATE ZINC CONCENTRATIONS AS A FUNCTION OF MIXING TIME AND OBSERVED CONCENTRATION

INITIAL ZINC CONC'N (N_o) (mg/l)	MIXING TIME (t) (sec)	NO. OF REPLICATES (n)	SUPERNATANT ZINC CONC. Mean (mg/l)	Variance $(mg/l)^2$
150	5	5	1.76	0.048
150	50	5	1.14	0.051
150	1000	5	0.48	0.039
Weighted average variance:				0.046

5.2.3 Theoretical Models

5.2.3.1 Simple Aggregation Models

The four models - the von Smoluchowski model, the Argaman-Kaufman model and the two LaMer-Healy models - are listed in Table 3-1. The initial probability of each model was set at 0.25 and initial parameter estimates were obtained from one of the single-stage mixing trials with iron.

The calculated probabilities of the four models at each stage are shown in Table 5-13. After nine trials, the probability of the von Smoluchowski model had increased to unity, while that of the other three models had decreased almost to zero. Although the von Smoluchowski model was the best of the four, it was judged to be inadequate because it predicted essentially zero supernatant metal concentrations for long mixing times at which finite values were observed (Table 5-14). Since these observed values were surmised to be the result of floc breakup, it appeared that inclusion of a floc breakup term in the models was required.

5.2.3.2 Models with Floc Breakup Terms

The von Smoluchowski model was compared to three models with floc breakup terms: the Argaman-Kaufman model and the two LaMer-Healy models (Table 3-2). The iron data point was eliminated and the eight zinc data points were used to obtain the parameter estimates and their variance. The initial model probabilities were set at 0.25 and the existing data were used to obtain the probability histories (Table 5-15). After seven trials, the Argaman-Kaufman model achieved a

TABLE 5-13

PREDICTION AND PROBABILITY HISTORIES FOR SIMPLE AGGREGATION MODELS

EXP'T NO.	OBSERVED CONC'N[1] (mg/l)	PREDICTED CONC.[2] (mg/l)				MODEL PROBABILITIES			
		N_1	N_2	N_3	N_4	Pr_1	Pr_2	Pr_3	Pr_4
1	1.71	—	—	—	—	0.25	0.25	0.25	0.25
2	0.26	10^{-160}	0.0	0.18	10^{-76}	0.20	0.20	0.39	0.20
3	0.35	10^{-38}	10^{-82}	0.09	10^{-37}	0.15	0.15	0.54	0.15
4	0.05	10^{-160}	0.0	0.87	10^{-36}	0.33	0.33	0.01	0.33
5	0.45	0.12	0.01	0.56	2.96	0.72	0.26	0.01	0.01
6	0.25	0.38	0.28	0.18	2.29	0.90	0.04	0.06	10^{-14}
7	0.39	0.21	0.02	0.34	0.17	0.24	10^{-4}	0.76	10^{-14}
8	0.80	0.87	0.42	0.07	0.006	0.97	10^{-4}	0.03	10^{-16}
9	1.52	1.47	1.52	0.23	0.41	1.00	10^{-7}	10^{-6}	10^{-15}

[1] Observed and predicted values are particulate zinc concentrations

[2] Subscript 1 refers to the von Smoluchowski model
2 refers to the Argaman-Kaufman Model
3 refers to the LaMer-Healy Model
4 refers to the Modified LaMer-Healy Model

TABLE 5-14

COMPARISON OF OBSERVED AND PREDICTED PARTICULATE ZINC CONCENTRATIONS FOR THE VON SMOLUCHOWSKI MODEL

EXP'T NO.	INITIAL ZINC CONC'N (N_o) (mg/l)	MIXING TIME (t) (mg/l)	OBSERVED CONC'N (mg/l)	PREDICTED CONC'N (mg/l)
2	631	1000	0.26	10^{-160}
3	158	1000	0.35	10^{-38}
4	2512	251	0.05	10^{-160}
5	1585	10	0.45	0.12
6	398	16	0.25	0.38
7	398	10	0.39	0.21
8	100	25	0.80	0.87
9	100	10	1.52	1.47

TABLE 5-15

PREDICTION AND PROBABILITY HISTORIES FOR MODELS INCORPORATING FLOC BREAKUP

EXP'T NO.	OBSERVED CONC'N[1] (mg/l)	PREDICTED CONC'N[2] (mg/l)				MODEL PROBABILITIES			
		N_1	N_2	N_3	N_4	Pr_1	Pr_2	Pr_3	Pr_4
1	0.26	0.0	0.36	0.03	0.09	0.18	0.32	0.22	0.28
2	0.35	10^{-287}	0.36	0.01	0.02	0.10	0.61	0.12	0.17
3	0.05	0.0	0.36	0.12	0.35	0.20	0.47	0.18	0.15
4	0.45	10^{-25}	0.36	0.83	0.22	0.04	0.71	0.09	0.15
5	0.25	10^{-9}	0.36	0.26	0.06	0.02	0.74	0.11	0.13
6	0.39	10^{-4}	0.36	0.42	0.15	0.01	0.79	0.12	0.08
7	0.80	10^{-3}	0.36	0.08	0.02	10^{-4}	0.995	0.004	0.001
8	1.52	1.47	1.52	0.21	1.55	10^{-4}	0.999	10^{-10}	0.001

[1] Observed and predicted values are particulate zinc concentrations

[2] Subscript 1 refers to the von Smoluchowski Model
2 refers to the Argaman-Kaufman Model with floc breakup term
3 refers to the LaMer-Healy Model with floc breakup term
4 refers to the Modified LaMer-Healy Model with floc breakup term

probability of essentially unity. Examination of Table 5-15 indicated, however, that this model predicted a concentration of 0.36 mg/l for all trials except the last one, because only in the last trial did the aggregation term contribute to the result. Since this model could not predict observed differences in response when aggregation did not dominate (the first seven trials), it was rejected.

5.2.4 LaMer-Healy Semi-Empirical Model

As the available theoretical models had been rejected, it was necessary to devise a new model.

The first attempt involved alteration of one of the floc breakup models. The modified LaMer-Healy model looked most promising as Table 5-15 indicated that it predicted satisfactorily when aggregation dominated (trial #8) and did not predict a constant value throughout the rest of the operability region. Prior to alteration of this model, six additional experiments were run to provide more data in the breakup region and to improve the precision of the parameter estimates. With the inclusion of this data, the model was

$$N=N_o(1-0.6568 \times 10^{-4})e^{-0.2116 \times 10^{-3}N_o^{1/2}Gt} + 0.6568 \times 10^{-4}N_o \qquad (5-2)$$

Predicted response contours were compared to observed values in Figure 5-5. At long mixing times where floc breakup predominated, the model predicted that floc breakup would increase with increasing initial metal concentration. However, the two data points at 1000 seconds in Figure 5-5a

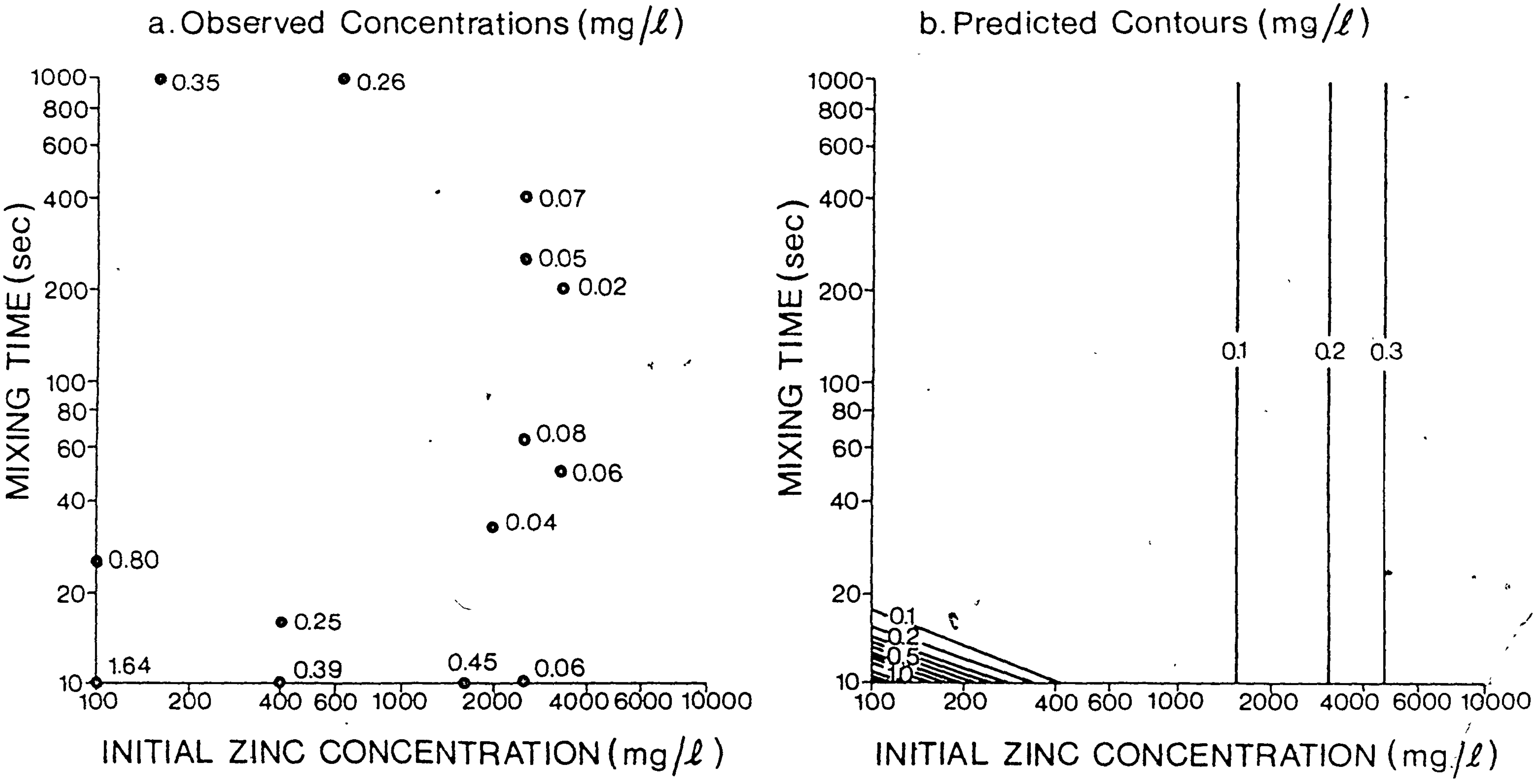


FIGURE 5-5: COMPARISON OF OBSERVED SUPERNATANT PARTICULATE ZINC CONCENTRATIONS WITH CONCENTRATIONS PREDICTED BY MODIFIED LA MER-HEALY MODEL INCORPORATING FLOC BREAKUP

(0.35 and 0.26 mg/l) were inconsistent with this model. It appeared therefore that floc breakup should be an inverse rather than a direct function of N_o. Since observation and available density data (Appendix F) suggested increased floc toughness at higher N_o values, it was hypothesized that incorporation of all the factors affecting floc breakup into the second term of Equation 3-28 would eliminate N_o giving

$$\frac{dN}{dt} = - K_5 N_o^{\frac{1}{2}} NG + K_{15} G \qquad (5\text{-}3)$$

where K_{15} is constant.

Integration of Equation 5-3 for the boundary conditions $N=N_o$ at t=0 and N=N at t=t gave

$$N = (N_o - \frac{K_{16}}{N_o^{\frac{1}{2}}}) e^{-K_5 N_o^{\frac{1}{2}} Gt} + \frac{K_{16}}{N_o^{\frac{1}{2}}} \qquad (5\text{-}4)$$

where K_{16} is equal to K_{15}/K_5.

Parameter estimation gave values for K_5 and K_{16} of 0.2364×10^{-3} and 6.334 respectively. Since the predictions of this model (Figure 5-6) were superior to those of the previous model and the residual sum of squares was lower (0.46 instead of 1.34), the new model was judged superior to the original modified LaMer-Healy model.

The parameter estimates obtained from the zinc data were used to predict results for two actual minewaters containing iron (Figure 5-7). Although the model predictions were acceptable for the weak (Quirke #2) minewater, they were

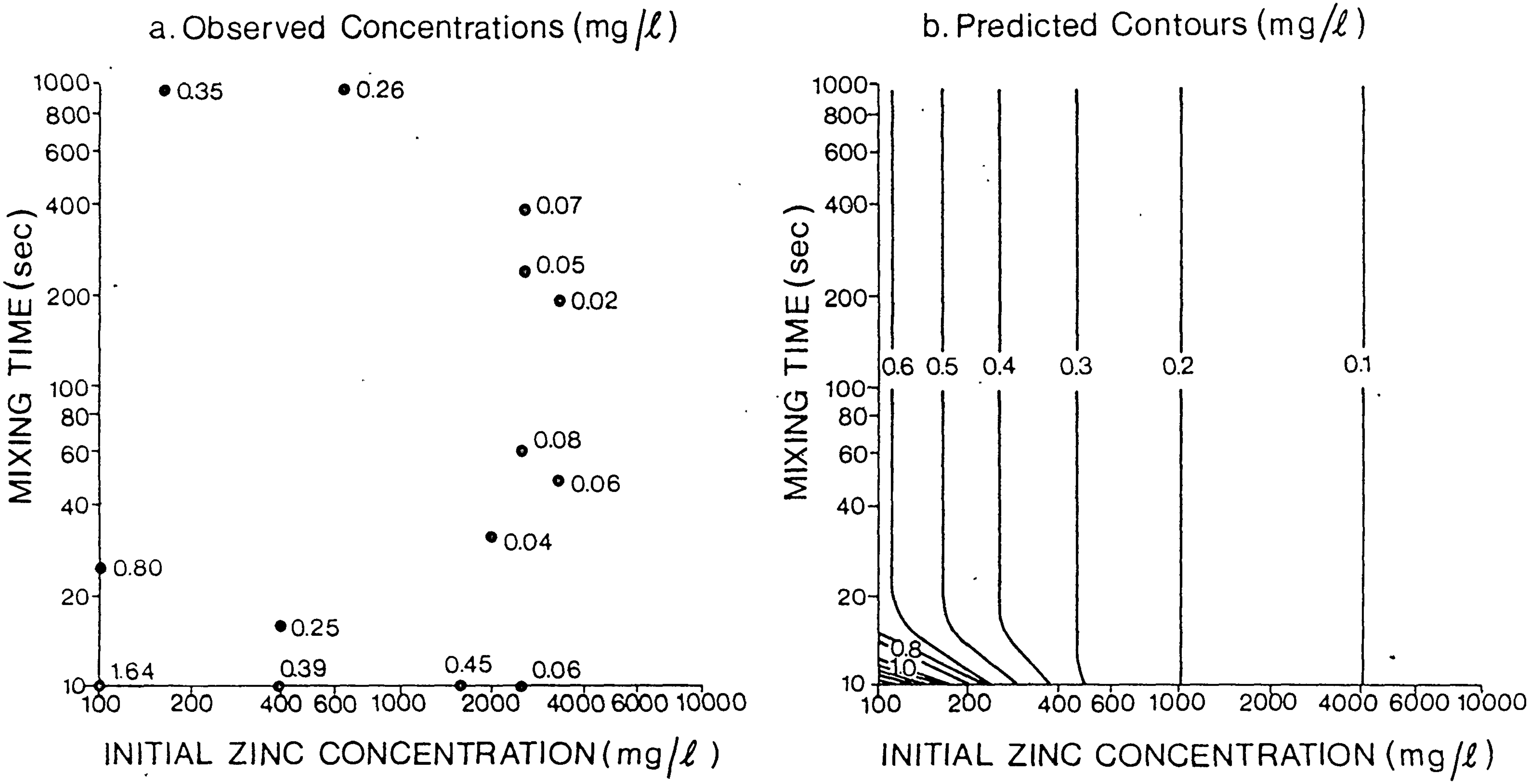


FIGURE 5-6: COMPARISON OF OBSERVED SUPERNATANT PARTICULATE ZINC CONCENTRATIONS WITH CONCENTRATIONS PREDICTED BY LA MER-HEALY MODEL (SECOND MODIFICATION)

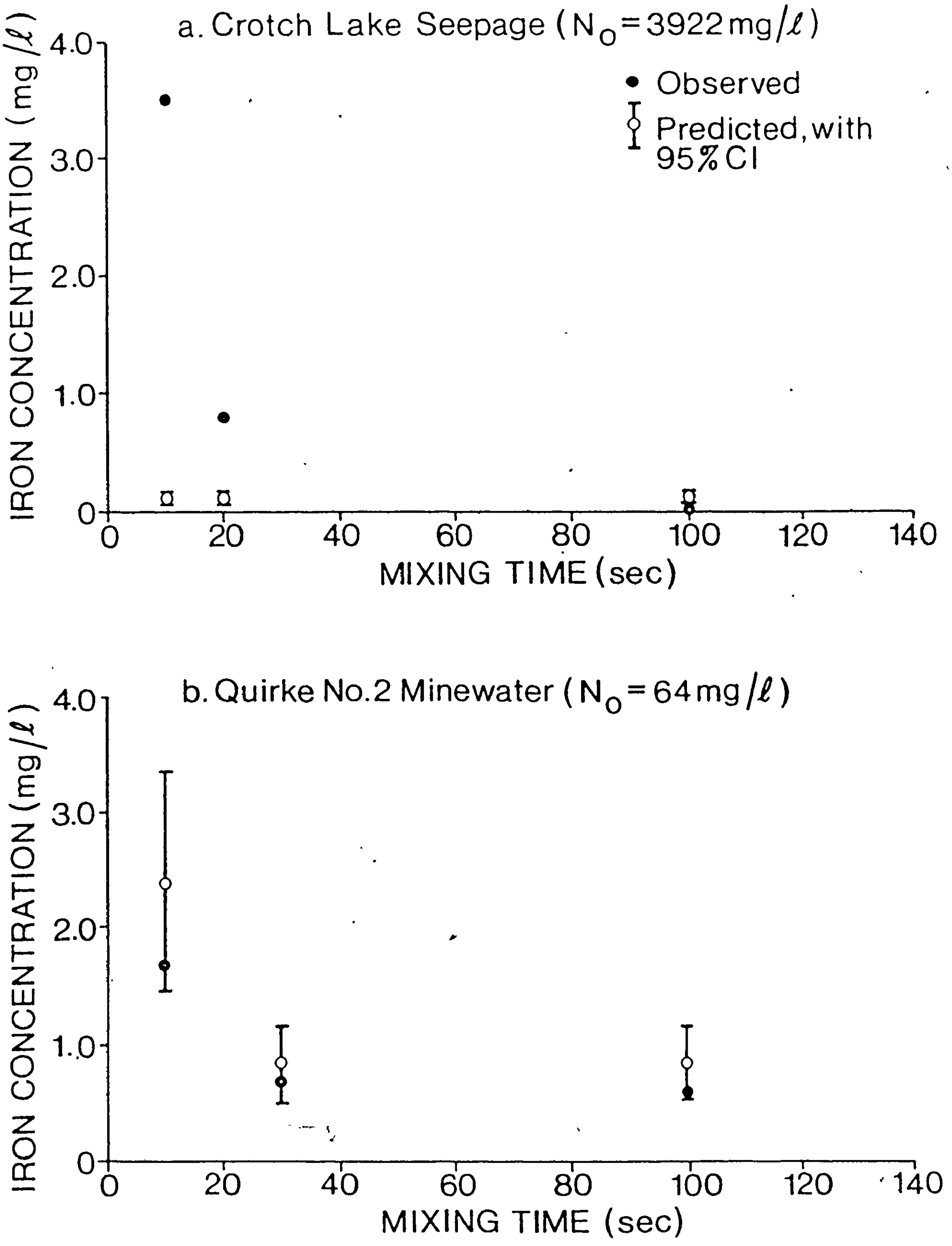


FIGURE 5-7: COMPARISON OF OBSERVED SUPERNATANT PARTICULATE METAL CONCENTRATIONS FOR TWO ACTUAL MINEWATERS WITH CONCENTRATIONS PREDICTED BY LA MER-HEALY MODEL (SECOND MODIFICATION)

too low for the strong (Crotch Lake) drainage. To establish whether this discrepancy at high strength occurred because of metal identity, experiments were performed with simulated Crotch Lake drainage. The results (Table 5-16) were lower than with the real minewater, but still higher than predicted. Attempts to estimate the model parameters for iron showed that the model form did not fit - the observed particle concentration was not as strong a function of time as the model predicted (Figure 5-8). Since Figure 5-7 and Table 5-16 had demonstrated that the particle concentration also was not as strong a function of N_o as predicted, the model was rejected for use with iron. It was thought that the rapid flocculation rate observed for zinc had masked this inadequacy.

5.2.5 Second Order Semi-Empirical Model

5.2.5.1 Development and Testing

Since it was desired to have one model form for all metal types, a new model was developed. The anomalies in the aggregation rate identified in the last section could be explained in two ways:

1. The rate of flocculation was actually decreasing with time, rather than being constant. As discussed in Section 2.2.3, this is explained by the adsorption of more polymer segments with time, leading to shorter and less efficient extended loops.
2. The rate of flocculation was proportional to N^2 rather than $N N_o$, i.e. the postulate of the original LaMer - Healy model was correct.

TABLE 5-16

COMPARISON OF OBSERVED AND PREDICTED[1] PARTICULATE METAL CONCENTRATIONS FOR STRONG[2] IRON MINEWATERS

	MIXING TIME (t) (sec)			
	10	20	50	100
Observed Concentrations (mg/l)				
Actual Minewater	3.50	0.80	—	0.01
Simulated Minewaters All ferric iron	1.10	0.62	0.42	0.36
Half ferrous iron[3]	0.73	0.34	0.12	0.04
Predicted Concentrations (mg/l)				
All Minewaters	0.10	0.10	0.10	0.10
95% CI (mg/l)				
All Minewaters	0.08-0.12	0.08-0.12	0.08-0.12	0.08-0.12

---

[1] Using the LaMer-Healy Model (second modification) as derived for zinc

[2] Initial iron concentration (M_o) = 3922 mg/l

[3] Oxidized to ferric iron just prior to flocculation

FIGURE 5-8

DEMONSTRATION OF INADEQUACY OF LA MER-HEALY MODEL FORM (SECOND MODIFICATION) FOR IRON DATA

$$N = \left(N_o - \cancelto{0}{\frac{K_{16}}{\sqrt{N_o}}}\right) e^{-K_5 \sqrt{N_o}\, t} + \frac{K_{16}}{\sqrt{N_o}}$$

$K_5 = 0.04587$

from zinc data

$K_{16} = 6.33$

Value of K_5 required if the model is to predict the iron concentration observed for the synthetic half-ferrous minewater at 10 sec (Table 5-15) is

$$K_5 = \frac{-1}{10\sqrt{3922}} \ln \left(\frac{0.73 - \frac{6.33}{\sqrt{3922}}}{3922} \right)$$

$$= 0.01395$$

The predicted value for 10 seconds is then

$$N = 3922e^{-0.01395\sqrt{3922} \times 10} + \frac{6.33}{\sqrt{3922}} \text{ mg/l}$$

$$= 0.63 \qquad +0.10 \text{ mg/l}$$

$$= 0.73 \text{ mg/l}$$

However, the predicted value for 20 seconds is then

$$N = 3922\, e^{-0.01395\sqrt{3922} \times 20} + 0.10 \text{ mg/l}$$

$$= 0.0001 \qquad + 0.10 \text{ mg/l}$$

$$\simeq 0.10 \text{ mg/l}$$

This value is too low by far.

Floc breakup was also reassessed after examination of iron data for a wide range of mixing speeds and times (Figure 5-9) indicated that substantial floc breakup did not occur below a certain level of mixing, represented by a critical Gt product. Above that level, which appeared to be approximately 80,000, supernatant metal concentration seemed to be directly proportional to Gt. The existence of a critical mixing level could provide an alternate explanation for the inconsistent data in Figure 5-5a which led to the rejection of the original modified LaMer-Healy model. Without these data, it is not possible to distinguish the first and second modifications. Neither model adequately described the supernatant concentrations obtained with the real minewaters (Figure 5-7) and consequently would be rejected.

The new information on aggregation and breakup suggested a model having a bimolecular, declining rate aggregation term and a breakup term for mixing levels above the critical value. The aggregation term was developed first as a model to be used for subcritical mixing conditions. The theoretically derived relationship between $\theta(1-\theta)$ and N_o (Equation 3-13), was replaced by

$$\theta(1-\theta) \propto N_o^a \qquad (5\text{-}5)$$

where a is an exponent to be estimated from the data.

The differential form of the aggregation term was then

$$\frac{dN}{dt} = -K'_{17} N^2 N_o^a Gt^b \qquad (5\text{-}6)$$

where K'_{17} is constant, and

b is an exponent to be estimated $(b<0)$.

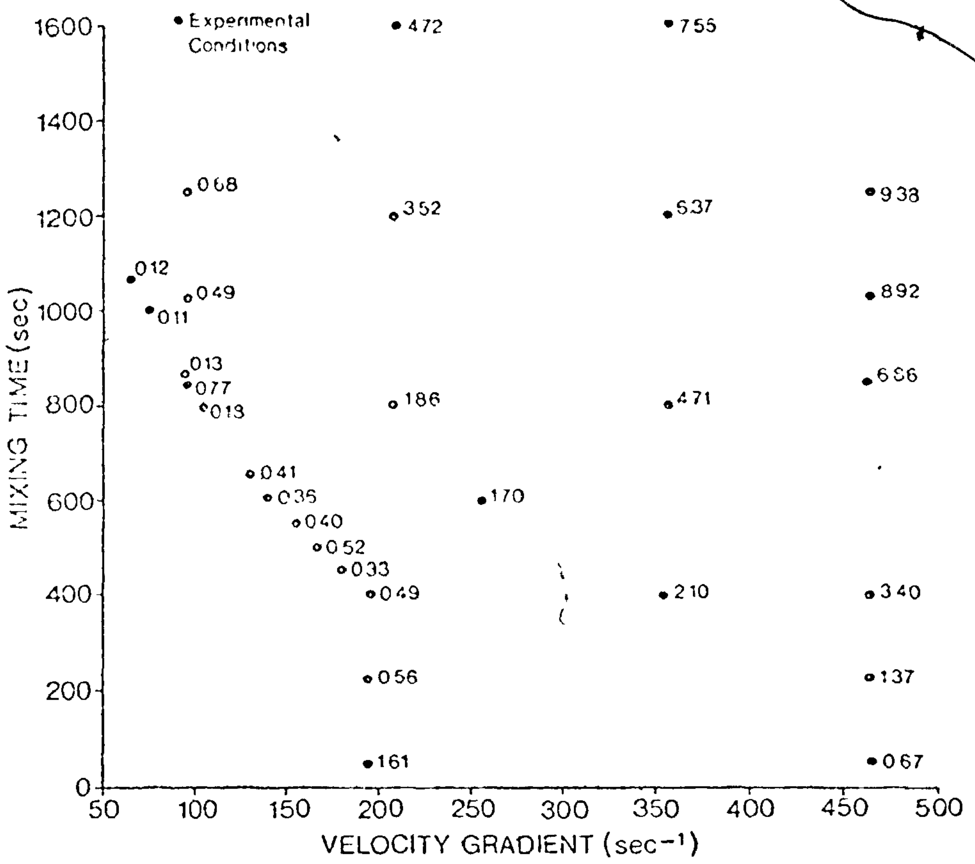


FIGURE 5-3: OBSERVED SUPERNATANT PARTICULATE IRON CONCENTRATIONS (MG/L) OVER A WIDE RANGE OF MIXING TIMES AND VELOCITY GRADIENTS

For the boundary conditions $N=N_o$ at $t=0$ and $N=N$ at $t=t$, Equation 5-6 can be integrated to give

$$N = \frac{N_o}{K_{17}N_o^{A}Gt^{B}+1} \tag{5-7}$$

where A is equal to a+1,

B is equal to b+1, and

K_{17} is equal to K'_{17}/B.

Equation 5-7 was fit to the zinc data after removal of two data points at t=1,000 sec which were above the critical limit identified in Figure 5-9. The model obtained was

$$N = \frac{N_o}{0.8922 \times 10^{-5}N_o^{1.87}Gt^{0.80}+1} \tag{5-8}$$

The fit (Figure 5-10) and residual sum of squares (0.40) were as good as with the LaMer-Healy model (second modification). For further verification, observed and predicted values were compared for eight additional data points (Table 5-17). The agreement was satisfactory and the model was accepted for zinc in the subcritical mixing region.

Fitting Equation 5-7 to iron data below the critical mixing level gave the following model:

$$N = \frac{N_o}{0.6320 \times 10^{-5}N_o^{1.77}Gt^{0.60}+1} \tag{5-9}$$

The predictions (Table 5-18) were satisfactory except at the highest initial iron concentration. Even so, the predictions for this concentration were better than those obtained at

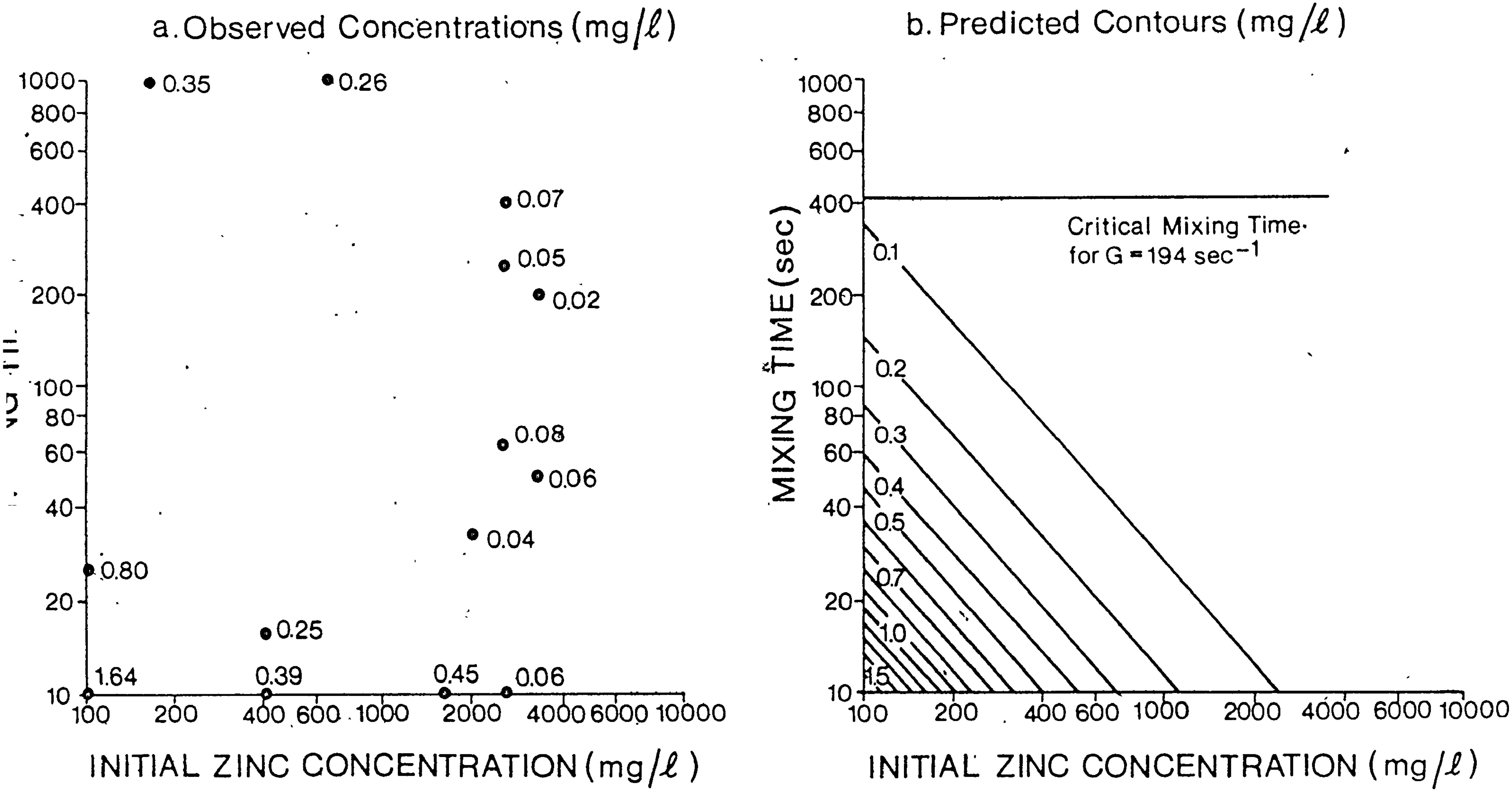


FIGURE 5-10: COMPARISON OF OBSERVED SUPERNATANT PARTICULATE ZINC CONCENTRATIONS WITH CONCENTRATIONS PREDICTED BY SECOND ORDER SEMI-EMPIRICAL MODEL

TABLE 5-17

COMPARISON OF OBSERVED AND PREDICTED PARTICULATE ZINC CONCENTRATIONS FOR ADDITIONAL TESTS (SECOND ORDER MODEL)

INITIAL ZINC CONC'N (mg/l)	VELOCITY GRADIENT (G) (sec^{-1})	MIXING TIME (t) (sec)	OBSERVED CONC'N (mg/l)	PREDICTED CONC'N (mg/l)	95% CI (mg/l)
200	194	25	0.37	0.44	0.40-0.48
		35	0.38	0.33	0.30-0.36
		50	0.46	0.25	0.23-0.27
		75	0.38	0.18	0.16-0.20
400	194	25	0.46	0.24	0.22-0.26
		35	0.38	0.18	0.16-0.20
		50	0.24	0.14	0.13-0.15
		75	0.20	0.10	0.09-0.11

TABLE 5-18

COMPARISON OF OBSERVED AND PREDICTED PARTICULATE IRON CONCENTRATIONS (SECOND ORDER MODEL)

INITIAL IRON CONC'N (N_o) (mg/l)	VELOCITY GRADIENT (G) (sec^{-1})	MIXING TIME (t) (sec)	OBSERVED CONC'N (mg/l)	PREDICTED CONC'N (mg/l)	95% CI (mg/l)
150	194	50	1.61	1.63	1.45-1.80
	194	224	0.56	0.67	0.59-0.74
	194	398	0.49	0.47	0.42-0.52
	180	450	0.33	0.47	0.42-0.52
600	66	10	4.25	4.34	3.87-4.81
	66	100	1.32	1.10	0.98-1.22
	66	150	0.89	0.86	0.76-0.95
	194	100	0.39	0.37	0.33-0.41
	338	10	1.52	0.85	0.76-0.94
	338	100	0.21	0.21	0.19-0.24
2400	66	10	1.13	1.50	1.34-1.67
	66	54	0.41	0.55	0.49-0.61
	66	98	0.28	0.38	0.34-0.42
	338	10	0.18	0.29	0.26-0.32
	338	54	0.07	0.11	0.10-0.12
	338	98	0.01	0.07	0.07-0.08
3922	194	10	1.10	0.35	0.31-0.39
	194	20	0.62	0.23	0.20-0.26
	194	50	0.42	0.13	0.12-0.15
	194	100	0.36	0.09	0.08-0.10

high concentrations with the LaMer-Healy model (second modification).

When Equation 5-7 was fit to copper data in the subcritical mixing region, the model obtained was

$$N = \frac{N_o}{0.1447 \times 10^{-3} N_o^{1.25} Gt^{0.34} + 1} \qquad (5\text{-}10)$$

Since the fit was satisfactory (Table 5-19), the model was accepted for copper. A model had therefore been obtained which satisfactorily described the aggregation behaviour of all three metals.

To extend the model to conditions above the critical breakup level, a breakup term was added to Equation 5-7. The complete model was then

$$N = \frac{N_o}{K_{17} N_o^A Gt^B + 1} + K_1^* \delta (G^C t^D - K_2^*) \qquad (5\text{-}11)$$

where K_1^* and K_2^* are constants to be estimated,
C and D are exponents to be estimated, and
δ is a parameter.

The parameter δ is defined as

$\delta=1$ for $G^C t^D > K_2^*$, and
$\delta=0$ for $G^C t^D \leq K_2^*$.

The exponents C and D were included in the model for generality.

TABLE 5-19

COMPARISON OF OBSERVED AND PREDICTED PARTICULATE COPPER CONCENTRATIONS (SECOND ORDER MODEL)

INITIAL COPPER CONC'N (N_o) (mg/l)	VELOCITY GRADIENT (G) (sec^{-1})	MIXING TIME (t) (sec)	OBSERVED CONC'N (mg/l)	PREDICTED CONC'N (mg/l)	95% CI (mg/l)
150	194	20	3.02	3.59	2.98-4.19
600		10	3.89	3.27	2.71-3.83
		20	3.04	2.59	2.14-3.03
		30	2.72	2.26	1.87-2.64
		60	2.26	1.78	1.48-2.09
		100	1.50	1.50	1.24-1.76
2400		20	0.96	1.84	1.52-2.15

Equation 5-11 was fit to the iron data in Figure 5-10 using the parameter estimates from Equation 5-9 for K_{17}, A and B. The model obtained was

$$N = \frac{N_o}{0.6320 \times 10^{-5} N_o^{1.77} Gt^{0.60} + 1} + 0.5244 \times 10^{-4} \delta (G^{1.13} t^{0.75} - 32670) \qquad (5\text{-}12)$$

The model was accepted after a comparison of the predicted values (Figure 5-11) and the observed values (Figure 5-10) indicated satisfactory agreement.

Experiments were performed at two other iron concentrations to determine whether the critical mixing level was a function of N_o. On the basis of limited data, the critical level appeared to be proportional to the square root of N_o.

5.2.5.2 Verification with Actual Minewaters

Fitting of Equation 5-7 to three real minewaters at mixing levels below the critical value gave the following model:

$$N = \frac{N_o}{0.3548 \times 10^{-3} N_o^{1.10} Gt^{0.75} + 1} \qquad (5\text{-}13)$$

Two of the minewaters contained iron, zinc and copper, and the values used for N and N_o were the sums of these three metals.

The satisfactory predictions (Table 5-20) indicated that the model was applicable to real minewaters.

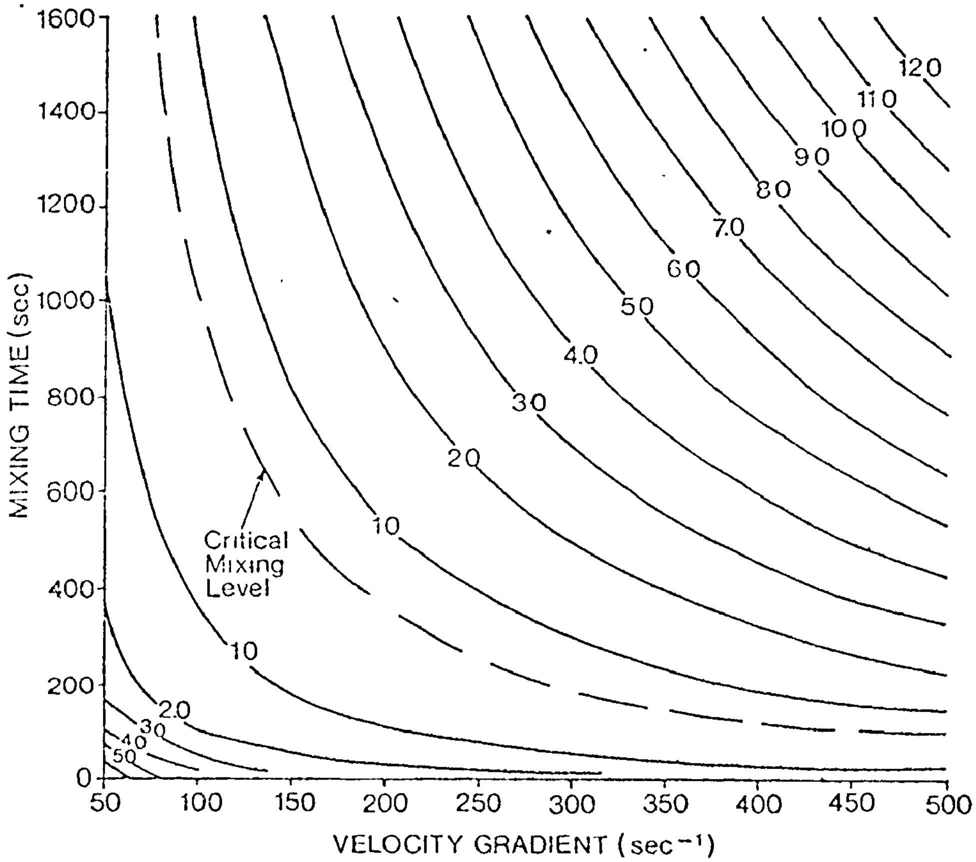


FIGURE 5-11: SUPERNATANT PARTICULATE IRON CONCENTRATIONS (MG/L) PREDICTED BY SECOND ORDER SEMI-EMPIRICAL MODEL WITH FLOC BREAKUP TERM

TABLE 5-20

COMPARISON OF OBSERVED AND PREDICTED PARTICULATE METAL CONCENTRATIONS FOR THREE REAL MINEWATERS (SECOND ORDER MODEL)

MINEWATER	INITIAL METAL CONC'N (N_O) (mg/l)	VELOCITY GRADIENT (G) (sec^{-1})	MIXING TIME (t) (sec)	OBSERVED CONC'N (mg/l)	PREDICTED CONC'N (mg/l)	95% CI (mg/l)
Quirke #2	64	194	10	1.69	1.66	1.49-1.83
			30	0.69	0.74	0.66-0.82
			100	0.58	0.30	0.27-0.33
GECo	367	194	10	1.22	1.43	1.28-1.58
			20	0.80	0.85	0.76-0.94
			70	0.37	0.33	0.30-0.37
			100	0.17	0.25	0.23-0.28
Brunswick #6	1257	194	10	1.46	1.26	1.13-1.40
			20	0.87	0.75	0.67-0.83
			50	0.26	0.38	0.33-0.42
			100	0.03	0.22	0.20-0.25

5.2.5.3 Interpretation

The general model describing the flocculation of metal hydroxides with polymers was found to be of the form:

$$N = \frac{N_o}{k_1 N_o^A G t^B + 1} + k_2 \delta (G^C t^D - k_3 N_o^E) \qquad (5\text{-}14)$$

The functional form of the model provides insights into the process. The fact that aggregation is second order with respect to particle concentration confirms the postulate of LaMer and Healy (1963) that flocculation takes place between species with adsorbed polymer and species with open surface. This means that the von Smoluchowski equation, which is conventionally used to describe water wastewater flocculation, and which is first order when constant total floc volume is assumed, is not applicable.

The evidence that flocculation rate decreases with time ($0<B<1$) even if particle concentration were constant confirms the information provided by Akers (1972) that extended polymer loops become shorter and therefore less efficient with time as more segments are adsorbed. Practically, this means that flocculation should be accomplished in as short a time and therefore at as high a speed as possible.

The exponent A in the aggregation term represents the relationship between the extent of polymer adsorption and N_o. In the present study, where the polymer dosage was $1.67 \times 10^{-3} N_o$, the value obtained for A indicated that the product $\theta(1-\theta)$ and hence the efficiency of flocculation increased with N_o. Since this result contradicted the theoretically derived relationship (Equation 3-13), a qualitative polymer adsorption isotherm was obtained. It confirmed the experimental result and indicated that the extent of polymer adsorption was not as high as had been assumed in deriving Equation 3-13. Even with the experimental relationship between $\theta(1-\theta)$ and N_o, the LaMer-Healy models would have been rejected because they did not incorporate the declining rate concept.

The particle aggregation rate for different metals is a function of the parameters k_1, A and B (Table 5-21). The differences in rate are attributed to different polymer-metal interaction energies. Although no explanation can be given for the differences in exponents, undue emphasis should not be attached to the values obtained because the exponents are correlated with the constant and none could be estimated precisely from the data.

The existence of a critical energy level for floc breakup suggests that the mechanism involves cleavage of the polymer chains. The dependence of the critical mixing level on N_o is undoubtedly related to the fraction of surface covered by polymer.

TABLE 5-21

COMPARISON OF THREE PARAMETERS OF THE SECOND ORDER MODEL FOR DIFFERENT MINEWATERS

Model: $N = \dfrac{N_o}{k_1 N_o^A G t^B + 1}$

MINEWATER	PARAMETER ESTIMATES[1]		
	k_1	A	B
Zinc	0.8922×10^{-5}	1.87	0.80
Iron	0.6320×10^{-5}	1.77	0.60
Copper	0.1447×10^{-3}	1.25	0.34
Actual	0.3548×10^{-3}	1.10	0.75

[1] The units of k_1 are $(mg/l)^{-A}(sec)^{(1-B)}$.

A and B are dimensionless.

5.3 Comparison of Modelling and Optimization Results

The kinetic modelling provided a mathematical representation of the dependence of mixing time on initial particle concentration identified in the optimization studies. The demonstration of increased floc toughness at higher N_o values explained why optimal mixing speeds increased with N_o. Although optimization indicated that mixing conditions were independent of metal type, modelling showed a faster aggregation rate for zinc than for iron or copper. Since the optimization was performed first for iron, and the same conditions tested for zinc and copper, the fact that shorter mixing times could have been used for zinc was not identified.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

1. The rate of flocculation of precipitated metal hydroxides with an anionic polymer was shown to be second order in metal concentration and to decrease with time as the adsorbed polymer loops became shorter. Floc breakup was exhibited above a definite energy level.

2. A new kinetic model was developed to describe the process after existing kinetic flocculation models were shown to be inadequate. The new model was:

$$N = \frac{N_o}{k_1 N_o^A G t^B + 1} + k_2\, \delta (G^C t^D - k_3 N_o^E)$$

where N is the supernatant particulate metal concentration following flocculation and settling,

N_o is the initial metal concentration,

G is the rms velocity gradient,

t is time,

k_1, k_2 and k_3 are constants,

A, B, C, D, and E are exponents, and

is a parameter equal to unity for $G^C t^D > k_3$ and equal to zero otherwise.

3. The model parameters were found to depend on metal identity, for simulated minewaters containing iron, zinc, or copper.

4. The particle aggregation rate, a function of k_1, A and B, was demonstrated to be more rapid for zinc than for iron or copper.

5. The values obtained for the exponent A demonstrated that increased surface coverage by polymer contributed to increased aggregation rates at higher initial metal concentrations.

6. On the basis of limited data, the exponent E was found to be approximately one-half.

7. The model was found to be applicable to real minewaters.

8. In the optimization phase of the study, it was shown that although no independent variables had sharply defined optima, the process was more sensitive to mixing conditions than to polymer properties and dosage. A suitable polymer dose was 1.7×10^{-3} N_o, and polymer degree of hydrolysis was unimportant over the range from 2 to 35 percent.

9. Particulate metal concentrations lower than 0.2 mg/l were achieved for all metals. Two-metal systems gave lower metal residuals than the corresponding single-metal systems.

6.2 Recommendations for Further Study

1. Studies should be undertaken to obtain precise estimates for the model parameters, particularly the exponents. If the values obtained are dependent on metal identity, theories to explain this dependency should be advanced and tested.

2. The models obtained should be restructured to accomodate two-stage mixing (i.e. to include rapid mixing) and verified experimentally.

3. Studies should be conducted to determine whether some floc breakup does occur below the critical energy input, by erosion of individual metal particles.

4. More data should be obtained to confirm the relationship obtained between N_o and the critical energy input for floc breakup. The critical level should be determined for different metals, and the actual means of breakup identified.

5. Investigations should be conducted to determine the lowest molecular weight polymer which can be used in flocculation of metal hydroxides, to minimize polymer cost.

6. Studies should be conducted with a number of minewaters to confirm the general applicability of the model.

7. Flocculation of tailings pond overflows and seepages should be studied to determine whether reagents added in ore processing affect flocculation. The flocculation of the metal hydroxides in the runoff from coal piles should be investigated.

8. Studies should be conducted to determine conditions which provide maximum slurry settling rate while maintaining an acceptable supernatant particulate metal concentration.

9. Measurements should be made of slurry viscosity at high N_o, to determine whether it is sufficiently greater than water that a correction should be applied to G values calculated for those conditions. Such a correction could influence the exponent on N_o in the aggregation term.

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APPENDIX A - COMPUTATIONAL ASPECTS OF MODELLING

A.1 Parameter Estimation

In general, a model can be represented as

$$y_u = \eta(X_{1u}, \ldots . X_{ku}; \ \beta_1, \ldots . \beta_p) + \varepsilon_u \tag{A-1}$$

where
y_u is the observed value at the u^{th} set of conditions,
$X_{1u}, \ldots . X_{ku}$ are the settings of the k independent variables at the u^{th} set of conditions,
$\beta_1, \ldots . \beta_p$ are the values of the p model parameters,
ε_u is the error associated with the u^{th} set of conditions, and
η is the functional relationship between the X's and β's.

The objective in fitting the model to the data is to obtain estimates of the model parameters, i.e. of $\underline{\beta}$. When the errors are normally distributed with mean zero and variance σ^2, least squares is the best estimator of $\underline{\beta}$. In other words, the best estimates of the β's are those which minimize $S(\underline{\beta})$, the sum of the squares of the differences between the observed values and those predicted by the model. $S(\underline{\beta})$ is given by:

$$S(\underline{\beta}) = \sum_{u=1}^{n} \epsilon_u^2 = \sum_{u=1}^{n} (y_u - \eta_u)^2 \qquad \text{(A-2)}$$

where n is the number of observations, and

η_u is the predicted value from the model at the u^{th} set of conditions.

Minimization is accomplished by differentiating Equation A-2 with respect to $\underline{\beta}$ and setting the derivative equal to zero. For the i^{th} parameter,

$$\frac{\partial S(\underline{\beta})}{\partial \beta_i} = -2\sum_{u=1}^{n} (y_u - \eta_u)\left[\frac{\partial \eta_u}{\partial \beta_i}\right]_{\hat{\underline{\beta}}} = 0, \qquad i=1,2,\ldots p. \qquad \text{(A-3)}$$

where $\hat{\underline{\beta}}$ is the least squares estimate of $\underline{\beta}$.

If the model is linear with respect to its parameters,

$$\frac{\partial \eta_u}{\partial \beta_i} \neq f(\underline{\beta}). \qquad \text{(A-4)}$$

The general linear model can be represented by:

$$\underline{Y} = \underline{X}\underline{\beta} + \underline{\varepsilon} \qquad \text{(A-5)}$$

and Equation A-3 becomes

$$-2\underline{X}'(\underline{Y}-\underline{X}\hat{\underline{\beta}}) = 0$$

$$\text{or} \quad \hat{\underline{\beta}} = (\underline{X}'\underline{X})^{-1}\underline{X}'\underline{Y} \tag{A-6}$$

provided $\underline{X}'\underline{X}$ is nonsingular. Thus for models linear with respect to their parameters (linear least squares) the parameter estimates can be obtained directly. If the model is not linear with respect to its parameters,

$$\frac{\partial \eta_u}{\partial \beta_i} = f(\underline{\beta}) \tag{A-7}$$

and $\hat{\underline{\beta}}$ cannot be obtained directly since, in effect, the answer must be known before the solution can be obtained. Since the solution of p simultaneous nonlinear algebraic equations is difficult, it is often easier to minimize $S(\underline{\beta})$ directly by a search technique in $\underline{\beta}$ space. Possible methods include minimization routines such as steepest descent and successive linearization of the model by expanding it in a Taylor series about some guessed parameter values $\underline{\beta_0}$. Steepest descent minimizes $S(\underline{\beta})$, by moving in the direction:

$$\left[\frac{-\partial S(\underline{\beta})}{\partial \beta_1}, \frac{-\partial S(\underline{\beta})}{\partial \beta_2}, \ldots, -\frac{\partial S(\underline{\beta})}{\partial \beta_p}\right].$$

It will always converge, but is very slow. Linearization minimizes the sum of squares based on the local linearization about $\underline{\beta}_0$. It provides a new guess, say $\underline{\beta}_1$, relinearizes the model, and repeats the process until convergence is obtained. Since steepest descent works best in the early stages of iteration and linearization is best near the end, Marquardt (1963) has developed an algorithm which gradually shifts from steepest descent to linearization as iteration progresses, combining the advantages of both. This algorithm is the basis of the nonlinear least squares programme, UWHAUS (Appendix G) used in this work. When using this programme, it is important to obtain reasonable starting guesses for the parameters.

For both linear and nonlinear models,

$$\text{Var}\ \hat{\underline{\beta}} = (\underline{X}'\underline{X})^{-1}\sigma^2 \tag{A-8}$$

and the individual 100(1-α)% confidence interval on β_i is given by:

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

where $t_{\nu}, \frac{\alpha}{2}$ is the t statistic for ν degrees of freedom, at significance level $\frac{\alpha}{2}$.

For two parameters, the joint confidence region for 100(1-α)% is given by:

$$S(\beta_0)\alpha = S(\hat{\underline{\beta}}) \left[1+\frac{p}{n-p} F_\alpha(p,n-p)\right] \tag{A-9}$$

where $F_\alpha(p,n-p)$ is the F value at the α significance level. (The probability level α will only be approximately correct for the nonlinear case).

For both the linear and nonlinear case, the variance of any predicted value $\hat{y}_k$ is:

$$\mathrm{Var}(\hat{y}_k) = \underline{x_k}(\underline{X}'\underline{X})^{-1}\underline{x_k}\,\sigma^2 \qquad \text{(A-10)}$$

and the 100(1-α)% confidence interval on η_k is given by:

$$\hat{y}_k \pm t_{\nu,\frac{\alpha}{2}} \sqrt{\mathrm{Var}(\hat{y}_k)} \quad .$$

Since the variance of both the parameter estimates and predicted values are proportional to $(\underline{X}'\underline{X})^{-1}$, experimental designs which minimize this quantity (i.e. maximize $\underline{X}'\underline{X}$) are to be preferred. Replication in itself will not produce precise estimates. For nonlinear situations, the best designs are sequential: an experiment is performed, parameter estimates updated, and a search made for experimental conditions which will maximize $\underline{X}'\underline{X}$. The next experiment is performed at these conditions and the procedure repeated until the desired precision is achieved.

Since least squares is only optimal when the errors are distributed as $N(0,\sigma^2)$, data must be transformed if necessary to provide constant variance. A common situation, that of the error being proportional to the magnitude (constant percentage error) requires a log transformation to achieve constant variance. Transformation of the data requires corresponding transformation of the model.

A.2 Model Discrimination

The model discrimination procedure developed by Box and Hill (1967) is given below. The $\underline{X}'\underline{X}$ matrix is an important quantity in this procedure.

1. Choose an operability region - the range over which each independent variable is to be varied.

2. Obtain initial parameter estimates for each model (from previous data or preliminary experimentation).

3. Assign initial probability to each model (usually equal).

4. Using a search routine to select values of $\underline{\xi_n}$, the experimental conditions, calculate $\hat{y}_n^{(i)}$ and σ_i^2 for each $\underline{\xi_n}$,

   where $\hat{y}_n^{(i)}$ is the concentration predicted by model i for the n^{th} experiment, and
   σ_i^2 is $\mathrm{Var}(\hat{y}_n^{(i)})$ or $\underline{X}_n^{(i)}[\underline{X}_i'\underline{X}_i]^{-1}\underline{X}_n^{(i)'}\sigma^2$.

5. Compute D, the criterion for each $\underline{\xi_n}$. D is defined as:

$$D = \sum_{i=1}^{m} \sum_{j=i+1}^{m} \Pr(M_i)\Pr(M_j)D_{ij} \qquad \text{(A-11)}$$

   where m is the number of models, and
   $\Pr(M_i)$ is the current probability of model i.

D_{ij} is defined as:

$$D_{ij}=\tfrac{1}{2}\left\{\frac{(\sigma_i^2-\sigma_j^2)^2}{(\sigma^2+\sigma_i^2)(\sigma^2+\sigma_j^2)}+[\hat{y}_n^{(i)}-\hat{y}_n^{(j)}]^2\left(\frac{1}{\sigma^2+\sigma_i^2}+\frac{1}{\sigma^2+\sigma_j^2}\right)\right\} \tag{A-12}$$

6. Run the experiment(s) at conditions which maximize D, and obtain y_n, the observed value.

7. Update the parameter estimates for each model.

8. Update the probability, Pr, of each model:

$$\Pr(M_i|\underline{y_n}) = \frac{\Pr(M_i|\underline{y_{n-1}})\,p(y_n|M_i)}{\sum_{i=1}^{m} \Pr(M_i|\underline{y_{n-1}})\,p(y_n|M_i)} \tag{A-13}$$

where $\Pr(M_i|\underline{y_n})$ is the probability of model i after n experiments,

$\Pr(M_i|\underline{y_n})$ is the probability of model i after (n-1) experiments, i.e. the previous probability, and

$p(y_n|M_i)$ is the probability of predicting the observed result with model i.

By definition, $p(y_n|M_i)$ =

$$\frac{1}{\sqrt{2\pi}\,\sqrt{\sigma^2+\sigma_i^2}}\exp-\left\{\frac{1}{2(\sigma^2+\sigma_i^2)}[y_n-\hat{y}_n^{(i)}]^2\right\} \tag{A-14}$$

9. Return to Step 4 to select conditions for next experiment.

   Once one P_i has exceeded the predetermined value, stop.

APPENDIX B - DEVELOPMENT OF MECHANISTIC MODELS

Four models are considered: the von Smoluchowski model, the Argaman-Kaufman model, the LaMer-Healy model and a modified LaMer-Healy model. Only the LaMer-Healy model was originally developed in the context of flocculation using polymers. All models are developed here for batch or plug flow tubular reactor (PFTR) systems.

B.1 Simple Aggregation Models

Although the Argaman-Kaufman and LaMer-Healy models include floc breakup terms, only the particle aggregation terms for these models are considered in this section.

B.1.1 Von Smoluchowski Model

Von Smoluchowski (1916,1917) derived the basic kinetic equations for the collision frequencies of suspended particles under Brownian motion and laminar flow regimes. Camp and Stein (1943), realizing that flocculation under turbulent conditions was of most importance in water treatment, generalized von Smoluchowski's equation to include turbulent flow conditions by defining a root mean square (rms) velocity gradient, G, which they substituted for the velocity gradient in laminar flow.

They expressed the collision frequency as:

$$H_{ij} = \frac{4}{3} N_i N_j R_{ij}^3 G \qquad \text{(B-1)}$$

where H_{ij} is the number of collisions per unit time per unit volume between particles of radii R_i and Rj,

N_i and N_j are the number concentrations of the colliding particles,

R_{ij} is the collision radius R_i+R_j, and

G is the rms velocity gradient.

Camp and Stein defined the rms velocity gradient as:

$$G = \sqrt{\frac{\varepsilon}{\upsilon}} \qquad \text{(B-2)}$$

where ε is the total power dissipated per unit mass of fluid, and

υ is the kinematic viscosity.

For a monodisperse suspension (i=j), the collision frequency is $\frac{1}{3} N^2 d^3 G$, where d is the particle diameter, since $N_i=N_j=N/2$, and $R_i=R_j=d/2$. The rate of disappearance of primary particles is then given as:

$$\frac{dN}{dt} = -\frac{2}{3} \eta N^2 d^3 G \qquad \text{(B-3)}$$

where η is the collision efficiency, or fraction of collisions that result in aggregation.

The rate of disappearance of particles is twice the frequency of successful collisions because two particles are removed by each successful collision. For spherical particles, the volume of colloidal particles per unit volume of suspension is:

$$\frac{\pi d^3}{6} N_o$$

where π is 3.14159...., and

N_o is the initial concentration of primary particles.

Equation B-3 then becomes:

$$\frac{dN}{dt} = -4 \frac{\eta}{\pi} G \left(\frac{\pi d^3}{6}\right) N_o N$$

$$= -\frac{2}{3} \eta d^3 G N_o N \qquad \text{(B-4)}$$

Integration of Equation B-4 for the boundary conditions $N=N_o$ at $t=0$ and $N=N$ at $t=t$, gives the relationship:

$$N=N_o e^{-K' N_o G t} \qquad \text{(B-5)}$$

where K' is equal to $\frac{2}{3} \eta d^3$.

Equation B-5 is referred to in this thesis as the von Smoluchowski model.

B.1.2 Argaman-Kaufman Model

Argaman and Kaufman (1970) noted that the application of von Smoluchowski's theories to turbulent flocculation required that the particles be much smaller than the smallest scale of turbulence, an assumption which was not justified in the flocculation systems encountered in water treatment practice. To account for the length and time scale over which turbulent velocity fluctuations occur, they developed a diffusion coefficient for particles and flocs based on the turbulence energy spectrum. They postulated that in a continuous flow flocculation reactor, primary particles were removed from suspension principally by collision with previously formed flocs. Since flocs are much larger than particles, their expression for H_{1F}, the rate of collision between primary particles and flocs, was:

$$H_{1F} = 4 \pi K_S R_F^3 N_F N \overline{u^2} \qquad \text{(B-6)}$$

where K_S is a proportionality coefficient expressing the effect of the turbulence energy spectrum on the diffusion coefficient (For a particular turbulence field and particle size, K_S is constant.),

R_F is floc radius,

N_F is number of flocs, and

$\overline{u^2}$ is the mean square velocity fluctuation.

This equation is similar to Equation B-1 except that $\overline{u^2}$ replaces G. Argaman and Kaufman did not attempt to prove their equation, but developed it to recognize the basic nature of the collision process in turbulent mixed reactors and to attempt a departure from the traditional assumption that von Smoluchowski's orthokinetic flocculation expression, as derived for laminar flow, was directly applicable under turbulent conditions.

The Argaman-Kaufman rate equation for the aggregation of primary particles is:

$$\frac{dN}{dt} = -4\pi\eta K_S R_F{}^3 N_F N \; K_p \; G \tag{B-7}$$

In this equation $\overline{u^2}$ has been replaced by K_pG, where K_p is a performance parameter characterizing the stirring arrangement.

Although the assumption that R_F is much greater than R, the unflocculated particle radius, is not true initially in a batch system, observation during the present research has indicated that floc growth is sufficiently rapid that this assumption is satisfied in all but the first small fraction of flocculation time.

For this research, it was assumed that K_S was constant. It was further assumed that N_F was constant, i.e. that "stinging" of iron particles with polymer to form floc nuclei occurred instanteneously, and that the number of nuclei did not change with time. Since in this study polymer concentration was made proportional to initial particle concentration, it was assumed that the number of nuclei was also proportional to initial particle concentration. This led to an expression for floc radius in terms of number of particles. The total floc volume was written as:

$$V = K_1 N_O \cdot \frac{4}{3}\pi R_F{}^3 \tag{B-8}$$

where V is the total floc volume, and

K_1 is constant $(0<K_1\leq 1)$.

The term K_1N_o is the number of flocs, and the term $\frac{4}{3}\pi R_F{}^3$ is the volume of a single floc. Since the total volume of floc is proportional to the number of particles removed from suspension,

$$V = \frac{4}{3}\pi R^3 (N_o - N). \qquad \text{(B-9)}$$

From equations B-8 and B-9:

$$R_F{}^3 = \frac{R^3}{K_1N_o}(N_o - N). \qquad \text{(B-10)}$$

Substituting this into Equation B-7 yields:

$$\frac{dN}{dt} = -4\,\pi\,\eta K_s K_P\, G\,\frac{R^3}{K_1N_o}(N_o - N)\, N_F\, N \qquad \text{(B-11)}$$

Assuming G to be constant with t and assuming R to be constant with t and $N_o{}^*$, and replacing N_F by K_1N_o, there is obtained:

$$\frac{dN}{dt} = -\frac{1}{K_3K_1N_o}(N_o - N)K_1N_oN\,G$$

or

$$\frac{dN}{dt} = -\frac{1}{K_3}\,N\,(N_o - N)G \qquad \text{(B-12)}$$

where K_3 is equal to $1/(4\,\pi\eta K_s K_P R^3)$.

The technique of separation of variables was used to render Equation B-12 exact, giving :

$$\frac{1}{K_3G}\,dt + \frac{dN}{N(N_o - N)} = 0\,. \qquad \text{(B-13)}$$

---

[*] The assumption that R was independent of N_o was verified qualitatively using a Coulter Counter. The mean diameter of ferric hydroxide particles was 3.0 μm at N_o=150 mg/l and 4.4μm at N_o=2400 mg/l. The respective standard deviations were 0.8 and 3.3μm.

This imposes the restriction $N \neq N_o$. Since, however, N_o will be large, the lower limit of integration can be set at (N_o-1) instead of N_o with negligible effect. The solution then becomes, for the boundary conditions $N=N_o-1$ at $t=0$ and $N-N$ at $t=t$,

$$N = \frac{N_o(N_o-1)e^{-K_3N_oGt}}{1+(N_o-1)e^{-K_3N_oGt}} \tag{B-14}$$

This is the Argaman-Kaufman model without floc breakup.

B.1.3 LaMer-Healy Model

LaMer and Healy (1963) developed a kinetic flocculation model as part of their quantitative treatment of flocculation with polymers. Since they considered only a fixed intensity of agitation, the rms velocity gradient, G,was used here to represent the intensity of agitation. They postulated that the probability of building flocs was proportional to the fraction of the particle surface covered by polymer,θ, and to the fraction uncovered (1-θ). They considered an essentially bimolecular process similar to the von Smoluchowski collision frequency equation (Equation B-1), where the number of floc nuclei and the number of particles per unit volume available to add to the floc nuclei were both proportional to N, i.e. the process was second order in N. They therefore obtained:

$$\frac{dN}{dt} = -K_1'N^2\theta(1-\theta)G \tag{B-15}$$

where K_1' is constant.

Considering θ constant with time, Equation B-15 then becomes:

$$\int_{N_o}^{N} -\frac{dN}{N^2} = K_1' \, \theta(1-\theta)G \int_{o}^{t} dt \qquad \text{(B-16)}$$

or

$$N = \frac{N_o}{K_1' \, \theta(1-\theta)N_oGt+1} \qquad \text{(B-17)}$$

For this research, the relationship between θ and N_o was determined so that the model could be used with different initial particle concentrations.

The relationship between θ and residual polymer concentration was first considered. If adsorption is assumed to follow the Langmuir model, then (Weber and Morris, 1964):

$$\theta = \frac{X}{X_m} = \frac{bC}{1+bC} \qquad \text{(B-18)}$$

or

$$C = \frac{X}{b(X_m-X)} \qquad \text{(B-19)}$$

where C is the residual polymer concentration or concentration remaining in solution at equilibrium,

X is the amount of polymer adsorbed per unit weight or solids, at concentration C,

X_m is the amount of polymer adsorbed per unit weight of solids to form a complete monolayer, and

b is a constant related to the energy of adsorption.

To obtain a relationship between C and N_o, consider a mass balance on a unit volume of slurry. Then:

$$P = C + P_{ads} \qquad \text{(B-20)}$$

where P is the total weight of polymer added, and

P_{ads} is the total weight of polymer adsorbed.

Since in this study P was made proportional to N_o, then:

$$\begin{aligned} C &= K\ N_o - X\ N_o \qquad \text{(B-21)} \\ &= N_o(K-X) \end{aligned}$$

where K is constant.

The right-hand sides of Equations B-19 and B-21 were equated to give:

$$X = N_o b(K-X)\ (X_m - X) \qquad \text{(B-22)}$$

The general solution for this quadratic equation is:

$$X = \frac{N_o bX_m + N_o bK + 1 \pm \sqrt{N_o^2 b^2 X_m^2 + N_o^2 K^2 - 2N_o^2 b^2 X_m K + 2N_o bX_m + 2N_o bK + 1}}{2N_o b} \qquad \text{(B-23)}$$

$$\text{or } \frac{X}{X_m} = \theta = 0.5 + 0.5\ \frac{K}{X_m} + \frac{1}{2N_o bX_m}$$

$$\pm\ \frac{1}{X_m}\ \frac{\sqrt{N_o^2 b^2 X_m + N_o^2 b^2 K^2 - 2N_o^2 b^2 X_m K + 2N_o bX_m + 2N_o bK + 1}}{4\ N_o^2 b^2} \qquad \text{(B-24)}$$

Since θ is a complicated function of N_o, it was necessary to make a simplifying assumption to obtain a result useful for modelling. It was assumed that K was equal to X_m, i.e.

the amount of polymer added would, if completely adsorbed, just give monolayer coverage. This value for K was considered representative of practical polymer dosages since LaMer and Healy (1963) showed theoretically that optimum flocculation was achieved at $\theta=0.5$. For $K=X_m$,

$$\theta = 1 + \frac{2}{N_o b X_m} - \sqrt{\frac{1}{N_o b X_m} + \frac{1}{4N_o^2 b^2 X_m^2}} , \qquad \text{(B-25)}$$

and the product of θ and $(1-\theta)$ is given by:

$$\theta(1-\theta) = \sqrt{\frac{1}{K_X' N_o} + \frac{1}{4K_X'^2 N_o^2}} - \frac{3}{2K_X' N_o} + \frac{1}{K_X' N_o}\sqrt{\frac{1}{K_X' N_o} + \frac{1}{4K_X'^2 N_o^2}} - \frac{1}{2K_X'^2 N_o^2} \qquad \text{(B-26)}$$

where K_X' is equal to bX_m.

A further approximation was necessary if this relationship was to be used. Since preliminary adsorption data indicated that the product $K_X' N_o$ was greater than unity, the largest contribution to the product $\theta(1-\theta)$ would be given by the quantity $\sqrt{\frac{1}{K_X' N_o}}$, and therefore as a first approximation,

$$\theta(1-\theta) = K_X N_o^{-\frac{1}{2}} \qquad \text{(B-27)}$$

where K_X is equal to $(K_X')^{-\frac{1}{2}}$

Using the result from Equation B-27, Equation B-17 (the LaMer-Healy model), becomes:

$$N = \frac{N_o}{K_4 N_o^{\frac{1}{2}} G t + 1} \qquad \text{(B-28)}$$

where K_4 is equal to $K_1'K_X$.

B.1.4 LaMer-Healy Model (Modified)

The second order form of the LaMer-Healy model occurs because of the assumption that the number of floc nuclei is proportional to N, the number of unflocculated particles. Since N decreases with time, the number of nuclei also decreases with time. For the other models, it was assumed in this development that the number of nuclei was proportional to the initial number of particles. Therefore, a modified LaMer-Healy model was developed, incorporating this latter assumption. The differential equation was:

$$\frac{dN}{dt} = -K_1'(K_1\ N_o)N\ \theta(1-\theta)G \qquad \text{(B-29)}$$

Substituting for $\theta(1-\theta)$, there is obtained:

$$\frac{dN}{dt} = -\ K_5 N_o^{1/2} NG \qquad \text{(B-30)}$$

where K_5 is equal to $K_1'K_1K_X$.

Equation B-30 can be readily integrated for the boundary conditions $N=N_o$ at $t=0$ and $N=N$ at $t=t$ to give:

$$N = N_o e^{-K_5 N_o^{1/2} Gt} \qquad \text{(B-31)}$$

B.2 Models with Floc Breakup Terms

A major refinement which can be made to the models developed in Section B.1 is the inclusion of the floc breakup term for the Argaman-Kaufman and LaMer-Healy models.

B.2.1 Argaman-Kaufman Model

Argaman and Kaufman (1970) consider one of the more credible breakup mechanisms to be the stripping of individual primary particles from the floc surfaces. By this model, the rate at which primary particles are released depends on the surface shear, the floc size, and the size of the primary particles. As the shearing stress depends on $\overline{u^2}$ or $K_P G$, a possible expression for the rate of formation of primary particles due to floc breakup is given by:

$$\left.\frac{dN}{dt}\right)_{\text{Breakup}} = B\, R_F^2 \frac{N_F}{R^2} K_P G \tag{B-32}$$

where B is the breakup constant.

This expression may be added to Equation B-7 to give an overall expression for the change in the number of unflocculated particles with respect to time:

$$\frac{dN}{dt} = -4\pi\eta K_S R_F{}^3 N_F N K_P G + B \frac{R_F{}^2}{R^2} N_F K_P G. \tag{B-33}$$

Before integrating this equation, it is necessary to substitute for R_F and N_F. Since

$$R_F{}^3 = \frac{R^3}{K_1 N_O} (N_O - N), \tag{B-10}$$

therefore:

$$R_F^2 = \frac{R^2}{K_1^{2/3} N_o^{2/3}} (N_o - N)^{2/3}. \qquad \text{(B-34)}$$

Since $N_F = K_1 N_o$, Equation B-34 may be written as:

$$\frac{dN}{dt} = -\frac{1}{K_3} N \ (N_o - N) G + K_6 N_o^{1/3} (N_o - N)^{2/3} G \qquad \text{(B-35)}$$

where K_3 is equal to $1/(4\pi\eta K_s K_p R^3)$ as in Equation B-12, and

K_6 is equal to $B\ K_1^{1/3} K_p$.

An analytical solution could not be obtained for Equation B-35. With the objective of obtaining a potentially useful model, it was decided to simplify the expression rather than attempt a numerical solution. The only simplification available was the assumption of constant floc size with respect to time. As Equation B-10 shows, this assumption is approximately satisfied except at the beginning of flocculation when N is of comparable magnitude to N_o. For $N << N_o$, $R_F^3 = R^3/K_1$, from Equation B-10. Equation B-33 then becomes:

$$\frac{dN}{dt} = -K_7 N_o N G + K_8 N_o G \qquad \text{(B-36)}$$

where K_7 is equal to $1/K_3$, and

K_8 is equal to $BK_p K_1^{1/3}$.

A similar equation form but without N_o and G was obtained by Parker *et al.* (1970) in an application of the work of

Argaman and Kaufman to biological flocs. Equation B-36 can be readily integrated for the boundary conditions $N=N_o$ at $t=0$ and $N=N$ at $t=t$ to give:

$$N = (N_o-K_9)e^{-K_7N_oGt}+K_9 \tag{B-37}$$

where K_9 is equal to K_8/K_7.

This is the Argaman-Kaufman model with floc breakup.

B.2.2 LaMer-Healy Model (Unmodified)

LaMer and Healy (1963) express the increase in number of particles with time (floc breakup) as:

$$\frac{dN}{dt} = K_2'R_F \tag{B-38}$$

where K_2' is constant to a first approximation.

This applies for a given degree of agitation, a given and not too great total concentration(of flocs-strictly, species containing flocculant and species with open surface)and a constant floc shape. Under these conditions, the drag on a floc varies approximately with the characteristic linear dimension of the floc, which is R_F if the floc is approximately spherical. The authors note the boundary conditions which must be satisfied and determine that K_2' must be a function of θ. They propose the relationship:

$$K_2' = K_2[\theta(1-\theta)]^{-1} \tag{B-39}$$

without attaching any significance to the terms making up the function. Therefore

$$\left.\frac{dN}{dt}\right)_{\text{Breakup}} = K_2 R_F / [\theta(1-\theta)] \qquad \text{(B-40)}$$

where K_2 is constant.

Since this result is for a unit number of flocs, the overall rate of generation of primary particles is proportional to the number of flocs, which has been assumed to be proportional to N_o. (Note that this implicitly assumes $R_F \neq f(N_o)$, a result also obtained from Equation B-10 for $N \ll N_o$.) The rate of generation is also proportional to G, the intensity of agitation. Thus:

$$\left.\frac{dN}{dt}\right)_{\text{Breakup}} = \frac{K_2 R_F K_1 N_o G}{\theta(1-\theta)} \qquad \text{(B-41)}$$

Combining this with Equation B-15 gives:

$$\frac{dN}{dt} = -K_1' N^2 \theta(1-\theta) G + \frac{K_1 K_2 R_F N_o G}{\theta(1-\theta)} \qquad \text{(B-42)}$$

Substituting for $\theta(1-\theta)$ and R_F from Equations B-27 and B-10 respectively, there is obtained:

$$\frac{dN}{dt} = -K_1' K_X N_o^{-\frac{1}{2}} N^2 G + K_1^{2/3} \frac{K_2}{K_X} \quad R N_o^{7/6} (N_o - N)^{1/3} G \qquad \text{(B-43)}$$

This could not be solved analytically and it was decided, as for the Argaman-Kaufman model, to make the simplifying assumption that R_F was constant with time. With this assumption, Equation B-42 becomes:

$$\frac{dN}{dt} = -K_1^{'}K_X\ N_o^{-\frac{1}{2}}N^2G + \frac{K_{10}}{K_X}\ N_o^{3/2}G \qquad \text{(B-44)}$$

where K_{10} is equal to $K_1K_2R_F$.

The integrated form of equation B-44 for the boundary conditions $N=N_o$ at $t=0$ and $N=N$ at $t=t$ is then:

$$t = \frac{1}{2\sqrt{K_1^{'}K_{10}}\ \sqrt{N_o}\,G}\ \ln\ \frac{N_o+K_X\sqrt{K_1^{'}/K_{10}}\ N}{N_o-K_X\sqrt{K_1^{'}/K_{10}}\ N}\ \cdot\ \frac{1-K_X\sqrt{K_1^{'}/K_{10}}}{1+K_X\sqrt{K_1^{'}/K_{10}}} \qquad \text{(B-45)}$$

Rearranging,

$$N = \frac{-N_o}{K_{12}}\ \cdot\ \frac{(1-K_{12})-(1-K_{12})e^{K_{11}N_o^{\frac{1}{2}}Gt}}{(1-K_{12})+(1+K_{12})e^{K_{11}N_o^{\frac{1}{2}}\ Gt}} \qquad \text{(B-46)}$$

where K_{11} is equal to $2\sqrt{K_1^{'}K_{10}}$, and

K_{12} is equal to $K_X\sqrt{K_1^{'}/K_{10}}$.

Equation B-46 is the LaMer-Healy model (unmodified) with floc breakup.

B.3.3 LaMer-Healy Model (Modified)

The floc breakup term, including the effect of number of flocs is Equation B-41. Combining this with Equation B-29 yields:

$$\frac{dN}{dt} = -K_1'K_1N_oN\theta(1-\theta)G + \frac{K_2R_FK_1N_oG}{\theta(1-\theta)} \qquad \text{(B-47)}$$

Substituting for $\theta(1-\theta)$ and R_F from Equations B-27 and B-10 respectively, there is obtained:

$$\frac{dN}{dt} = -K_1'K_1K_XN_o^{1/2}NG + K_1^{2/3}\frac{K_2}{K_X} R\ N_o^{7/6}(N_o-N)^{1/3}G \qquad \text{(B-48)}$$

Again it was necessary to make the simplifying assumption that R_F was constant with time. Equation B-47 then becomes:

$$\frac{dN}{dt} = -K_5N_o^{1/2}\ NG + K_{13}N_o^{3/2}G \qquad \text{(B-49)}$$

where K_5 is equal to $K_1'K_1K_X$ as in Equation B-30,

and

K_{13} is equal to $K_1K_2R_F/K_X$.

This equation can be integrated readily for the boundary conditions $N=N_o$ at $t=0$ and $N=N$ at $t=t$ to give:

$$N=N_o(1-K_{14})e^{-K_5N_o^{1/2}Gt} + K_{14}N_o \qquad \text{(B-50)}$$

where K_{14} is equal to K_{13}/K_5 or $\frac{K_2R_F}{K_1'K_X^2}$.

Equation B-50 is the modified LaMer-Healy model with floc breakup.

APPENDIX C - EQUIPMENT DETAILS

C.1 ELB Agitator Drive

The following information is provided:

Figure C-1: A calibration curve for the mixer (speed vs dial setting) obtained using a tachometer.

Figure C-2: (a and b) Water power data for the mixer, for square pitch propellers (from the mixer manual).

A sample calculation of G (rms velocity gradient)

Figure C-3: A graph showing G vs impeller speed for a 10.2 cm (4.0 in) diameter square pitch marine propeller.

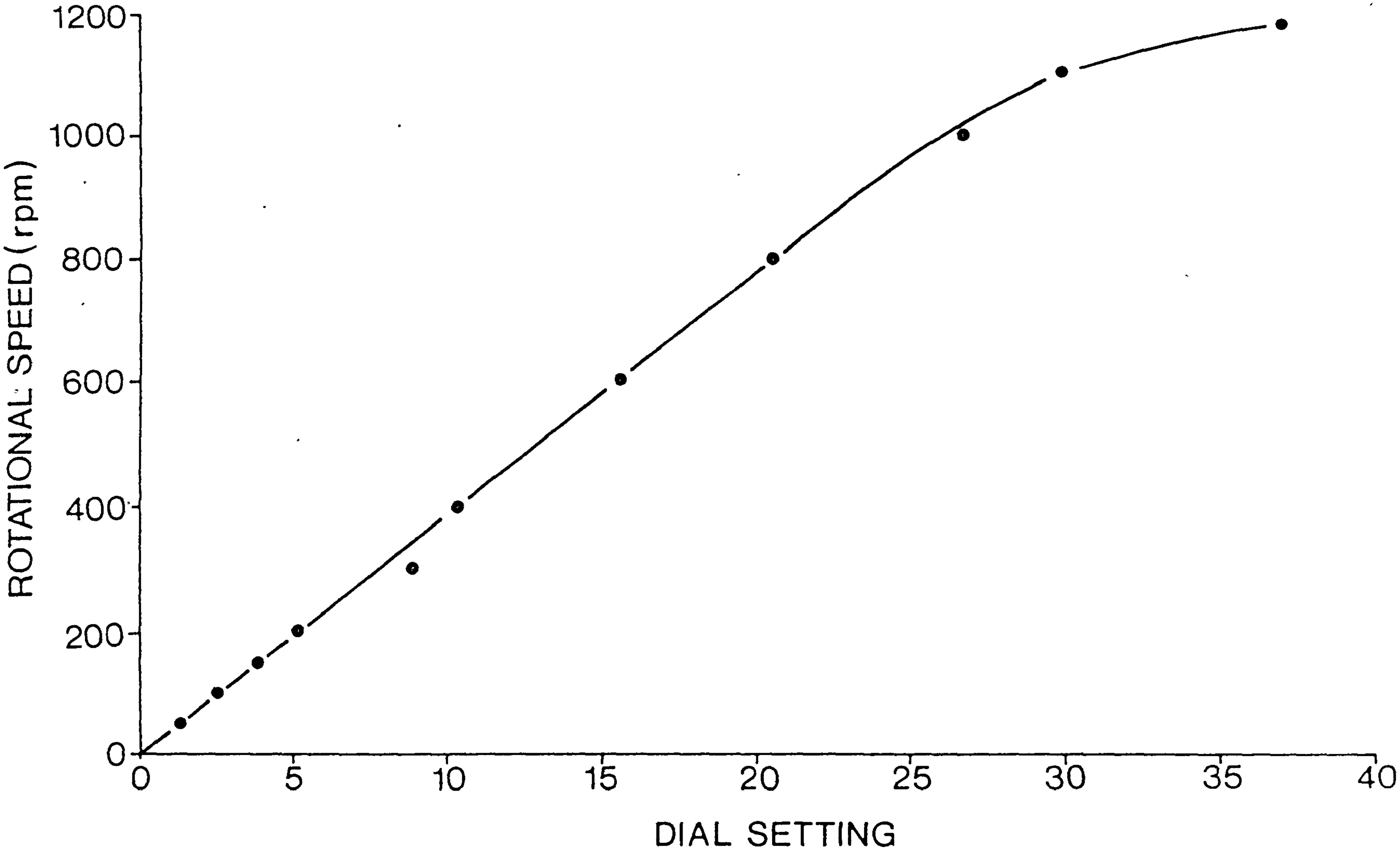


FIGURE C-1: ROTATIONAL SPEED AS A FUNCTION OF DIAL SETTING FOR ELB MIXER

FIGURE C-2a: WATER POWER DATA-SQUARE PITCH PROPELLERS - Basis: Power Number (N_p) = 0.40

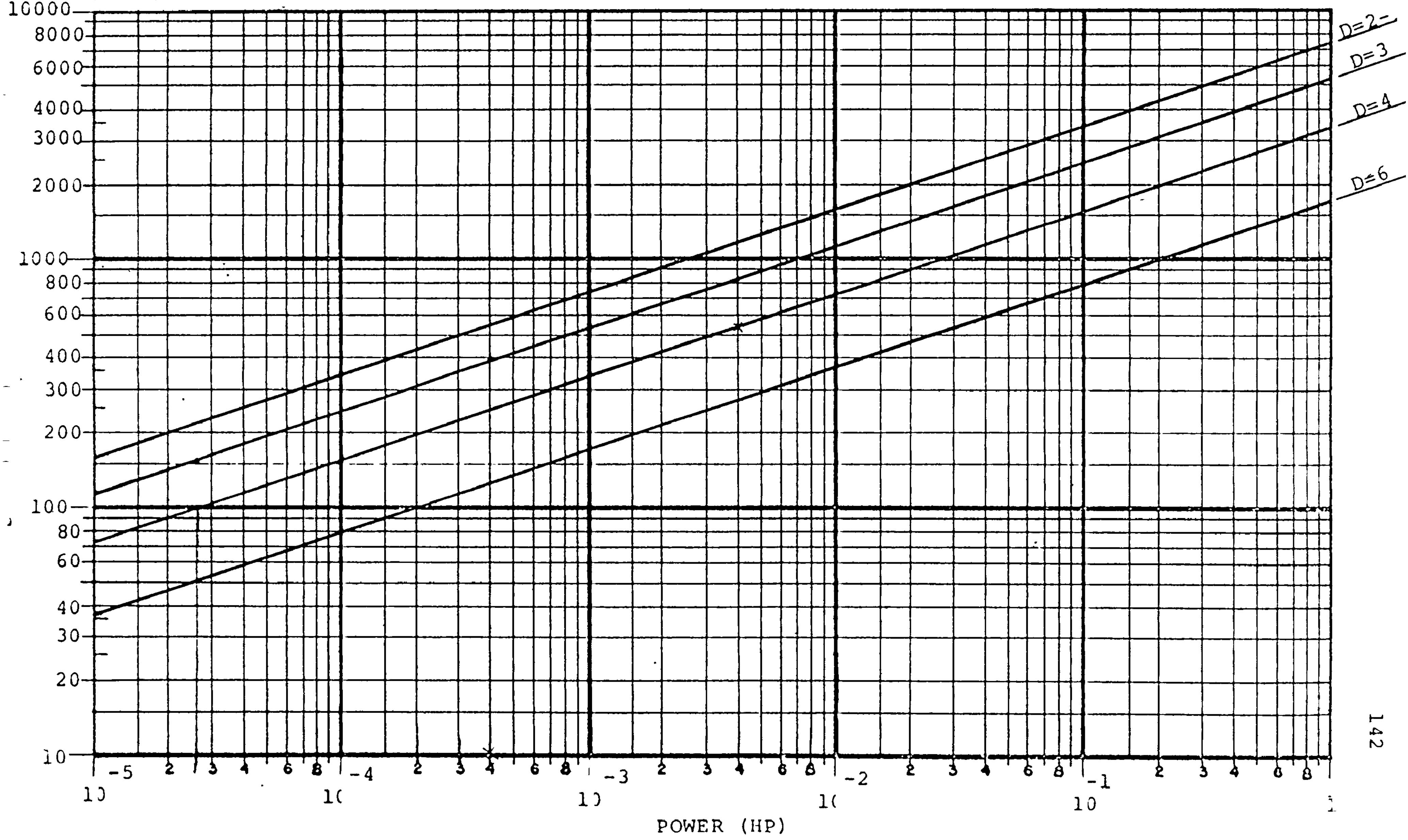
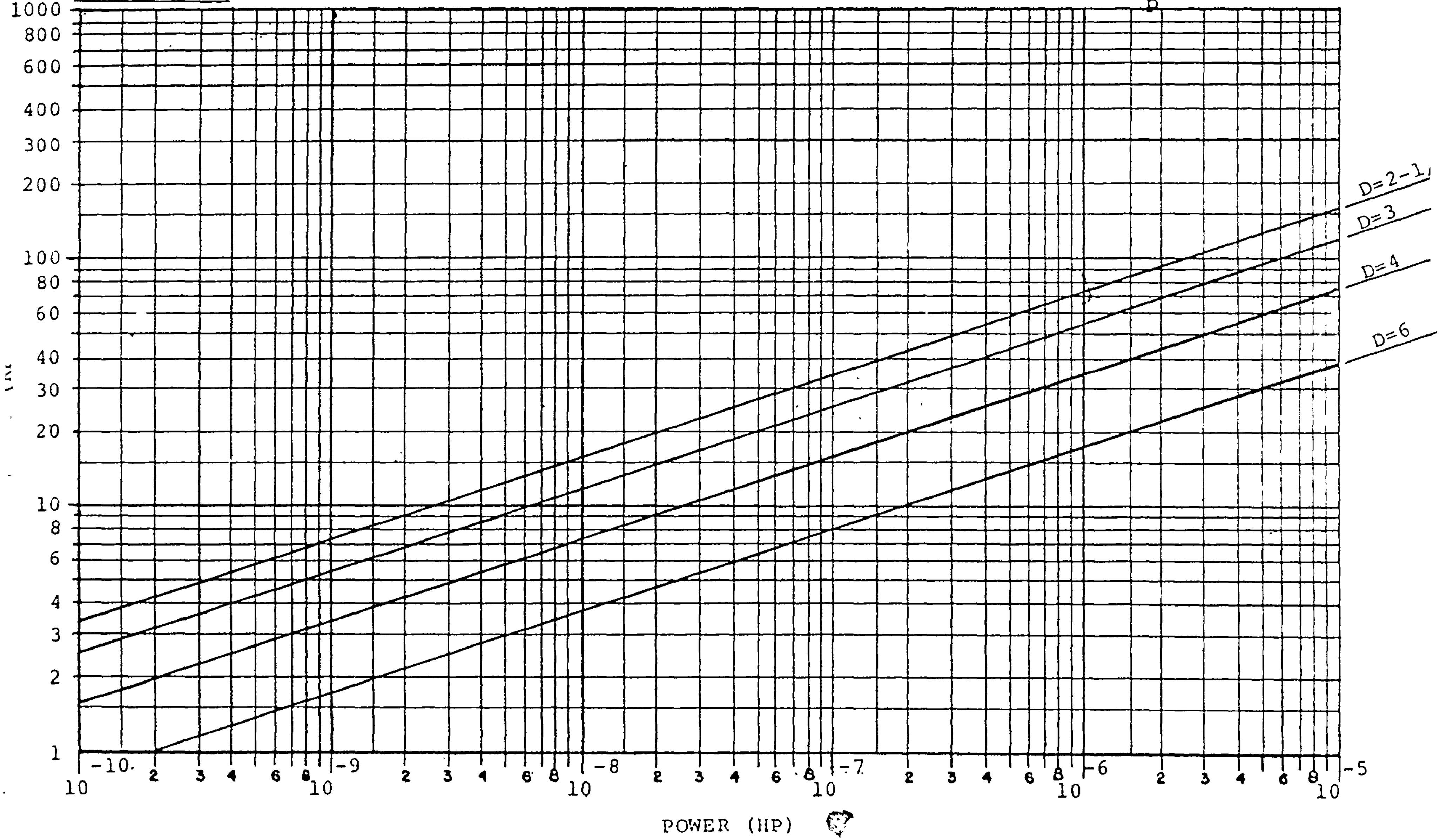


FIGURE C-2b: WATER POWER DATA-SQUARE PITCH PROPELLERS - Basis: Power Number (N_p) = 0.40



Sample Calculation of G (rms Velocity Gradient)

$$G = \sqrt{\frac{\varepsilon}{\nu}} \qquad (2\text{-}5)$$

Alternatively, G can be expressed as:

$$G = \left(\frac{P}{V\mu}\right)^{1/2} \qquad (C\text{-}1)$$

where P is the total power input to the fluid,

V is the volume of fluid, and

μ is the viscosity of the fluid.

For the apparatus used (8.5 in dia. vessel, 5.0 in liquid depth),

$$V = \pi r^2 h = \pi x \frac{(4.25)^2}{1728} x\ 5\ ft^3$$
$$= 0.164\ ft^3$$

Assuming the viscosity to be that of water,

$$\mu = 10^{-2}\ \text{poise}\ x\ \frac{2.089\ x\ 10^{-3} lb_f\ sec\ ft^{-2}}{\text{poise}} = 2.089\ x\ 10^{-5} lb_f sec\ ft^{-2}$$

Therefore:

$$G = \left[\frac{P}{0.164\ ft^3\ x\ 2.089\ x\ 10^{-5} lb_f\ sec\ ft^{-2}}\right]^{1/2} =$$

$$\left[\frac{P}{3.42\ x\ 10^{-6}\ lb_f\ sec\ ft}\right]^{1/2}$$

For 4-in propeller at 100 rpm in water (Figure C-2),

$$P = 2.7\ x\ 10^{-5}\ HP$$

Therefore:

$$G = \left[\frac{2.7\ x\ 10^{-5} HP\ x\ \frac{550\ lb_f\ ft\ sec^{-1}}{HP}}{3.42\ x\ 10^{-6}\ lb_f\ sec\ ft}\right]^{1/2} sec^{-1}$$

$$= 66\ sec^{-1}$$

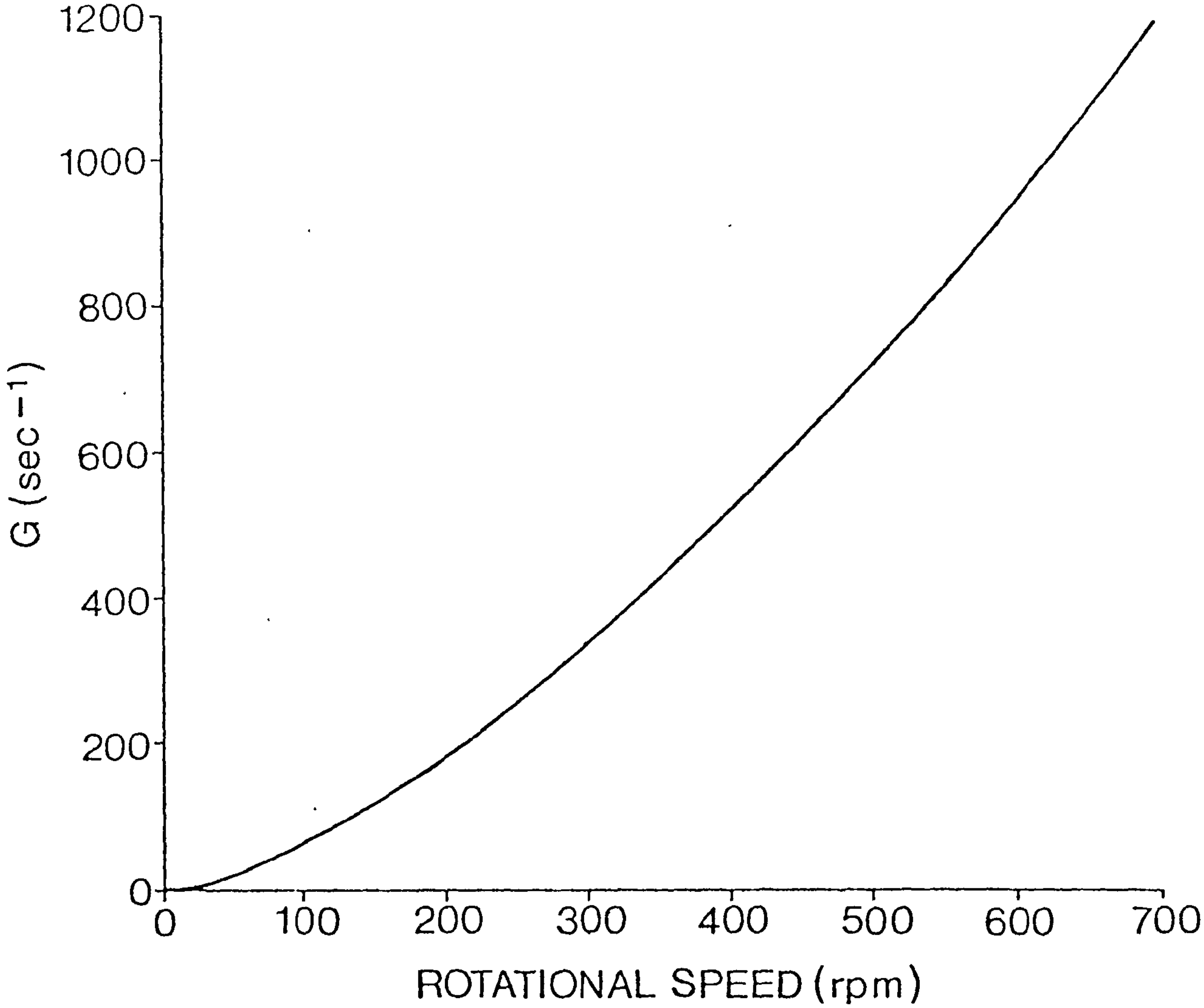


FIGURE C-3: VELOCITY GRADIENT AS A FUNCTION OF ROTATIONAL SPEED FOR THE APPARATUS USED IN THIS STUDY

C-2 Electronic Programmable Sequencer

The electronic programmable sequencer was designed and built by Messrs. J. Valdmanis, P.Eng., and M. Larocque of the Engineering Services Section, Canada Centre for Inland Waters. Included is Section One of their manual, giving general information on the unit, and a set of specifications. Figure C-4 shows the front panel and Figure C-5 gives the timing sequence used in these experiments.

PROGRAMMABLE SEQUENCER
OPERATING AND MAINTENANCE MANUAL

SECTION 1: GENERAL INFORMATION AND OPERATING INSTRUCTIONS

1.1 SCOPE OF MANUAL

This manual provides a description of electrical system design, performance specifications, and operating instructions along with photographs, drawings, parts lists, appendices and references. It shows the operation of a CCIW designed "Programmable Sequencer" for a typical field or laboratory application.

1.2 GENERAL DESCRIPTION

The overall function of the system can be defined as being a series of independent, timed (maximum 8 different), steps (maximum 31). Each step activates any selected number of relays (maximum 12) in the programmer.

The electrical control box is one standard 5-1/4" high, 19" chassis as seen in figure 1. This box is the source of all signals for the relays and contains all the manual controls and indicators. The outputs of this system are relay contact closures via multi-pin plugs on the back panel. Separate chassis hold the electromechanical solenoid valves and motors as necessary; these are not described in this manual. Figure 2 shows this programmable sequencer in a typical timing sequence.

1.3 CONTROL AND DISPLAY Figure 1, Front Panel

Display Channel: Channel or step in progress is indicated in binary by five LED lamps.

Manual Advance: Each time the switch is pressed the programmer advances one step. The switch is spring loaded.

Reset: Resets programmer to channel '0' when switch is pressed, and advances to channel '1' when switch is released. The switch is spring loaded.

Program Run/Halt: On the Run mode, the programmer is advanced manually or automatically.

On the Halt position, internal or manual advance signals have no control over the instrument; also in the Halt mode, the timing cycle for the selected step is halted and is complete only upon return to Run.

N.B. - If the instrument is reset manually during Halt mode, the programmer will reset to channel '0', with no automatic set to channel 1 after release of the switch.

Relay Enable/Inhibit: In the enable mode, the output relays are energized according to the program in progress.

In the inhibit mode, mainly used for testing purposes, no power is applied to the relays regardless of the program.

Time, Tumbwheel Switches: Units and tens (of seconds) of one presettable timing interval (column 1 PCB#2) is available on the front panel. Other timing selections are done on PCB#2 directly as described in Section 1.4.

Relay Output Lamps: LED lamps connected in parallel with the corresponding relay.

1.3 CONTROL AND DISPLAY Figure 1, Front Panel (Cont'd.)

Auto Reset to Channel 1: (Switch located on PCB#5, Program - Matrix Board).
ON the "ON" mode, system will automatically reset to channel '1' after the last channels timed interval.
ON the "OFF" mode, system will reset to channel '0' after the last channel and will remain there until manually advanced.

Power On/Off: Upon power turn on the control system resets to channel '0', 155 VAC and the 12 DC power supply output are fused separately.

Output Display: 12 LED lights correspond to the energization of the 12 output relays. When the Sequence Programmer is installed in a system it may be convenient to identify these lights with tape labels.

Output Relay Selection: This is not a front panel function. All outputs are energized according to the diode arrangement of the matrix cards. See Section 1.5. Relay contact selection can also be altered on the Relay Boards. See Section 2.1.9.

1.4 PROCEDURE FOR SETTING THE TIMING INTERVALS

Up to 8 different Timing Intervals are possible with this system. Among these, the first one, column 0, is usually used for initial delay after power turn on.

1.4.1 Determine the 8 lapses of time most likely to be used.

1.4.2 Remove PCB #2 (Timing Matrix Board) from the Programmable Sequencer. The eight Timing Intervals are numbered as column 0 to 7 and consist of 2 paths of DIP swithces each, coded as follows: (See Parts List 2).

	1	.1 sec.		
Switches	2	1 sec.	Clock Rate Selection	
(BLACK)	3	10 sec.		
	4	Spare		
	5	"1"		
(YELLOW)	6	"2"	Unit Bits	
	7	"4"		
	8	"8"		
	1	"1"		12 Bits Resolution
(RED)	2	"2"	Tens Bits	
	3	"4"		
	4	"8"		
	5	"1"		
(BLUE)	6	"2"	Hundred Bits	
	7	"4"		
	8	"8"		

1.4.3 To code, simply select the proper clock rate, and the proper countdown value.

Example for 731 sec.

A. Select the one second pulse in the clock rate selection (Black, Switch 2).

B. Select Bit Value "1" in the units (YELLOW) 1
Bit Value "1","2" in tens (RED) 30
Bit Value "1","2","4" in hundreds (BLUE) 700
TOTAL:- 731 Sec.

1.5 PROCEDURE FOR SETTING RELAY OUTPUTS AND SELECTING THE TIMING INTERVALS

Output "on" (off) states correspond directly to the presence (absence) of diodes on the program matrix boards (PCB's 5 and 6). Visually, the diodes (Fig. 17) appear in a pattern similar to the timing diagram (Fig. 2). When the timing diagram is functionally altered, then PCB's 5 and/or 6 must be removed and diodes removed and/or soldered accordingly. Note that the 8 timing intervals mentioned above in 1.4 are selected channel by channel according to diodes (rows 12, 13, 14, 15 - binary code) on the program matrix boards.

1.6 PRINTED CIRCUIT BOARD LIST

PCB 1	Clock
PCB 2	Timing Matrix
PCB 3	Program Timer
PCB 4	Control
PCB 5	Program Matrix
PCB 6	Program Matrix
PCB 7	Buffer
PCB 8	Relay
PCB 9	Relay
Display Board	(Front Panel)
Relay Indicator	(Front Panel)

SOLIDSTATE PROGRAMMABLE-SEQUENCERS USING DIODE-MATRIX CIRCUITRY

The Programmable Sequencer is a self-contained electronic unit requiring only 110V 60 Hz supply and giving relay contact closures as outputs. Programming is internal -- by switches and replaceable diodes, with several front panel controls and status indicators. The Sequencer functionally provides a series of accurately-timed, parallel on-off steps. Packaging can be for laboratory or field use. The unit can be readily preset to control varied sequential experiments, and is especially useful when both long and short timings are needed.

SPECIFICATIONS

TIMING SOURCE: 60 Hz mains, Crystal clock optional.

OUTPUTS

Parallel relays : 12 Max. Both open and closed contacts.
Timed steps : 32 Max.
Choice of timing : 10 Max. (Repeated use at any step).
Minimum time interval : Limited by relay (.3 seconds).
Maximum time interval : 999 seconds (extension to min. & hr. possible)

CONTROLS

Internal : Functional : 32 x 16 diodes.
Timing memory : 10 x 16 DIP switches.
Front panel : Power On Switch.
Relay Enable Switch.
Run/halt Switch.
Manual Advance (to next step) Toggle.
Reset (to first step) Toggle.
Thumb wheel set <u>one</u> timing interval (0 to 99 sec.).

Power : 115 VAC ± 20% 60 Hz (See Timing Source) < 100 watts.
Physical : Standard Chassis (5" X 19" X 16")
Weight < 10 Kg.
Connectors : Line-cord input. Multipin output.
Environmental : -20 to +50°C non condensing.

FIGURE C-4: ELECTRONIC PROGRAMMABLE SEQUENCER USED FOR EXPERIMENTS

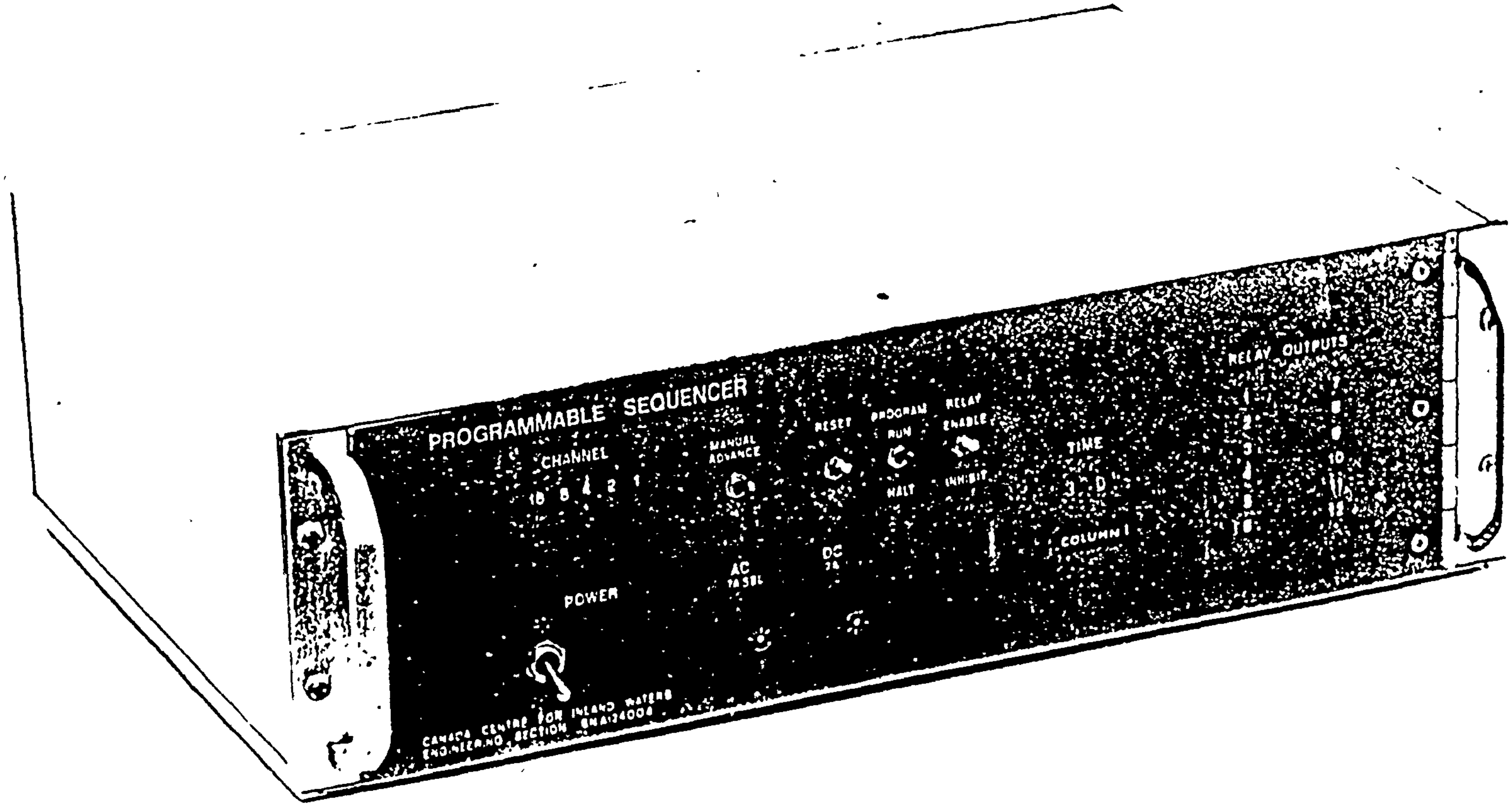
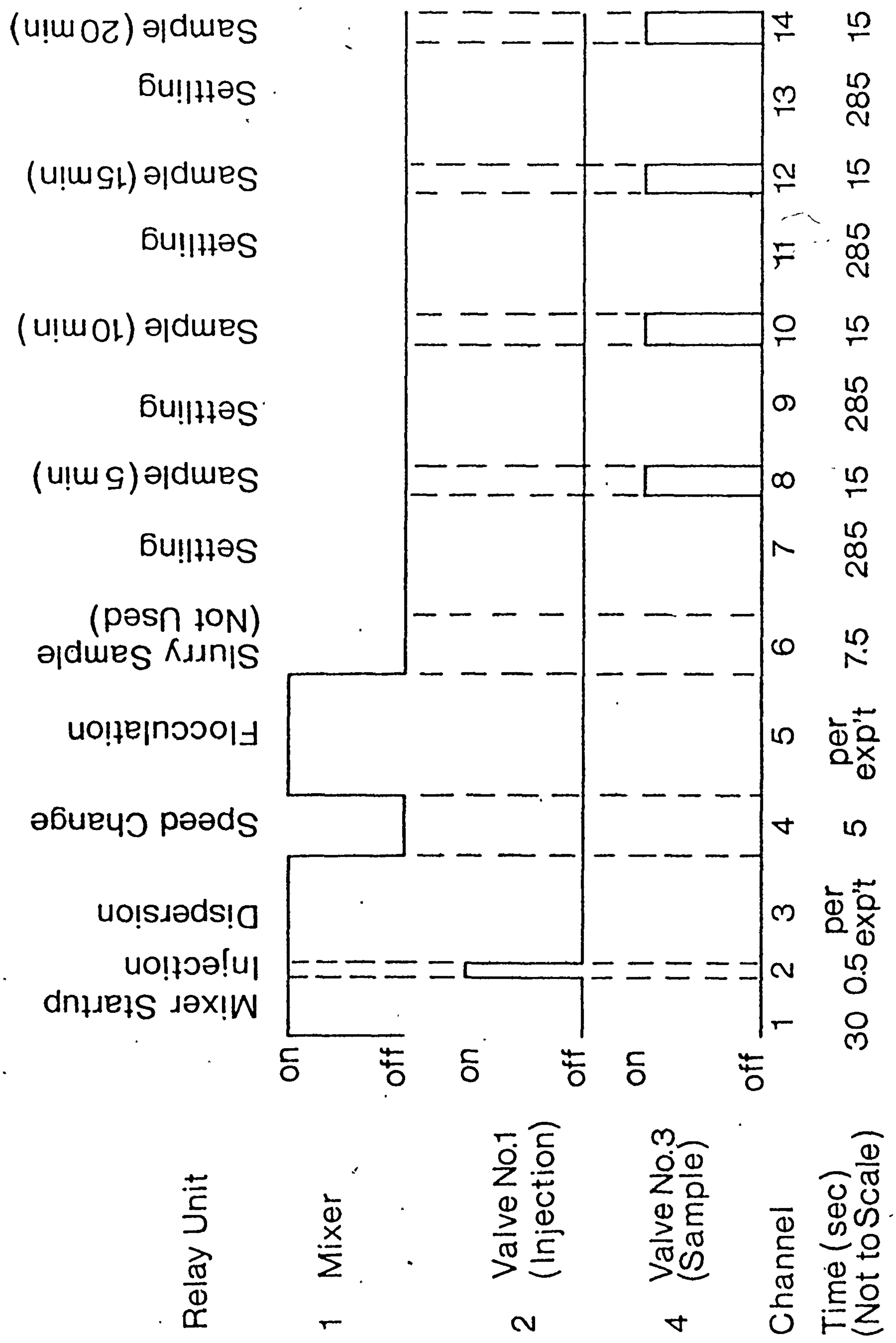


FIGURE C-5: TIMING SEQUENCE USED FOR EXPERIMENTS



APPENDIX D - POLYMER PROPERTIES: MEASUREMENT AND ALTERATION

Characterization of a polymeric flocculant implies knowing its chemical composition, molecular weight, and degree of charge. As discussed in Section 2.4.2, chemical composition was restricted to polyacrylamide for this research.

D.1 Molecular Weight

D.1.1 Expression and Measurement

The process used to manufacture a polymeric flocculant produces a distribution of molecular weights, shown typically in Figure D-1. The molecular weight averages most commonly used to characterize a polymer are the number average molecular weight, $\bar{M}_n$, and the weight average molecular weight, $\bar{M}_w$. The number average molecular weight is given by:

$$\bar{M}_n = \bar{r}_n \cdot M_o \qquad \text{(D-1)}$$

where $\bar{r}_n$ is the number average chain length of the polymer, and

M_o is the molecular weight of the monomer (polymer repeat unit).

By definition,

$$\bar{r}_n = \sum_{r=1}^{\infty} N(r) . r \qquad \text{(D-2)}$$

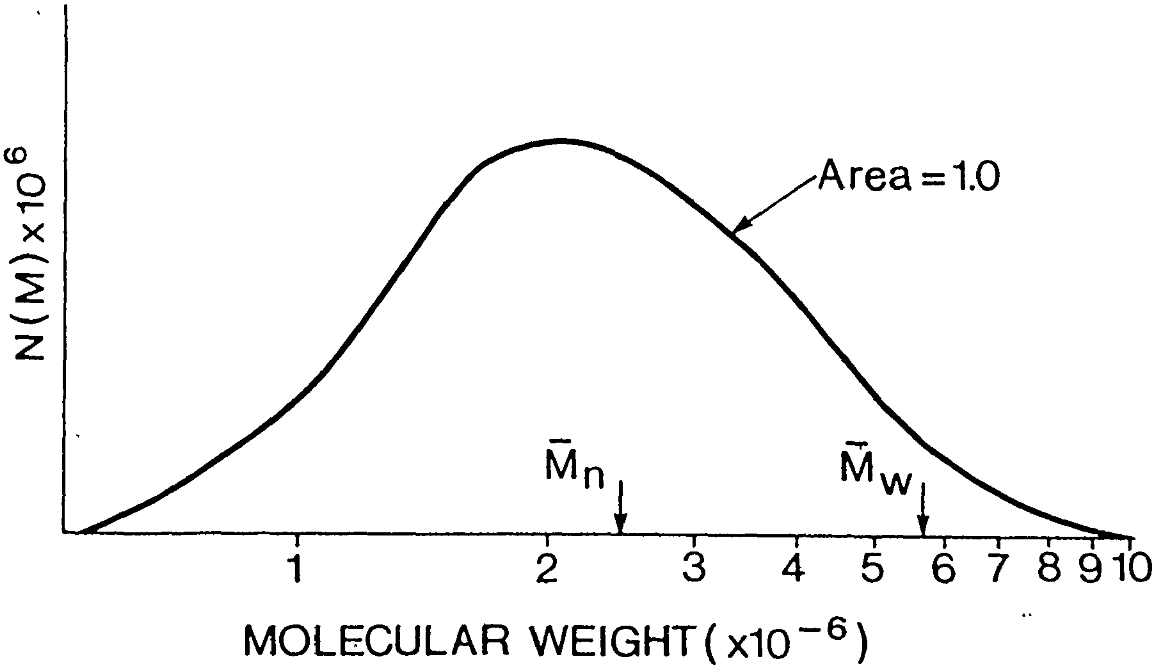


FIGURE D-1: TYPICAL POLYMER MOLECULAR WEIGHT DISTRIBUTION (MWD) where N(r) is the number fraction of polymer molecules having r monomer units.

Therefore $$\bar{M}_n = M_o \sum_{r=1}^{\infty} N(r).r \tag{D-3}$$

Similarly $$\bar{M}_w = M_o \sum_{r=1}^{\infty} W(r).r \tag{D-4}$$

where W(r) is the weight fraction of polymer molecules having r monomer units.

$\bar{M}_w$ will always be greater than $\bar{M}_n$ for any polymer.

In flocculation, $\bar{M}_w$ is a more useful average than $\bar{M}_n$ because polymer dosage is expressed as a weight. Since the largest chains are expected to be the most effective flocculants, a number characterizing the high molecular weight tail of the distribution is desirable. Since such a metric is not conventionally used, it was necessary to invent one. For this research, $\bar{M}_{w_{10}}$, the weight average molecular weight of the top 10% of the distribution, was used to compare polymers.

The most important tool available for the measurement of polymer molecular weight distribution is Gel Permeation Chromatography (GPC). Its principles and operational details have been well documented (Billmeyer and Altgelt, 1970; Lambert, 1971) and will only be discussed briefly here.

A typical GPC arrangement is shown schematically in Figure D-2. The pump forces a carrier fluid through the columns, which are packed with a porous gel. A solution of the polymer is injected into the apparatus between the pump and columns. The concentration of the solution after passing

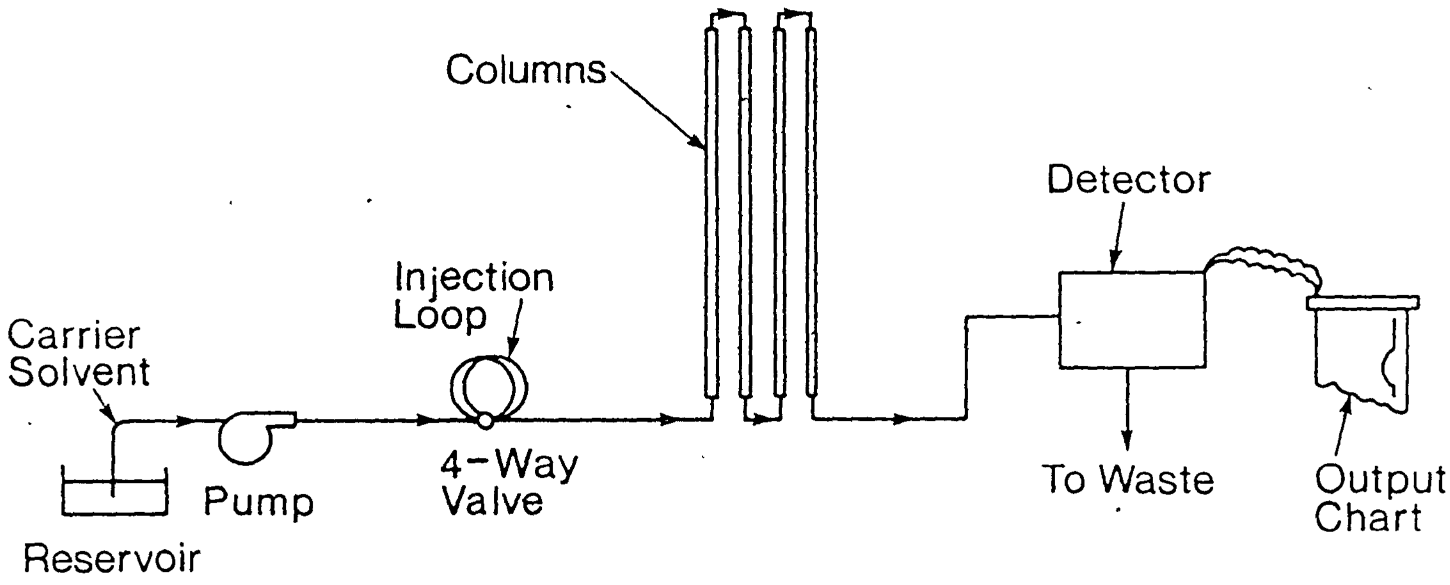


FIGURE D-2: SCHEMATIC DIAGRAM OF GPC APPARATUS through the columns is measured as a function of time by the detector. The elution time, or time to pass through the columns, is related to molecular weight. (Molecular size, actually, but for a given polydisperse polymer, molecular size is proportional to molecular weight).

The principle on which the GPC achieves separation is that as molecular size increases, the number of pores into which a molecule can diffuse decreases, and it passes more quickly through the column. The success of the separation depends on the distribution of pore sizes in relation to molecular sizes. For a given set of columns, separation can only be achieved over a given molecular size range. Molecules larger than the largest pores will be unable to diffuse into any pores and will elute together. Similarly, molecules smaller than the smallest pores will be able to diffuse into all pores and will elute together. Between these limits of resolution, the logarithm of molecular weight should decrease linearly with increasing elution volume.

Since GPC is a comparative technique and does not measure absolute size, calibration is required. This can be accomplished by injecting either monodisperse standards or a polymer with a known molecular weight distribution (MWD) or at least two known molecular weight averages to produce an effective calibration curve of the type shown in Figure D-3. The curve is valid for a particular instrument and column arrangement only for a particular period of time, since phenomena such as gradual plugging of the columns will

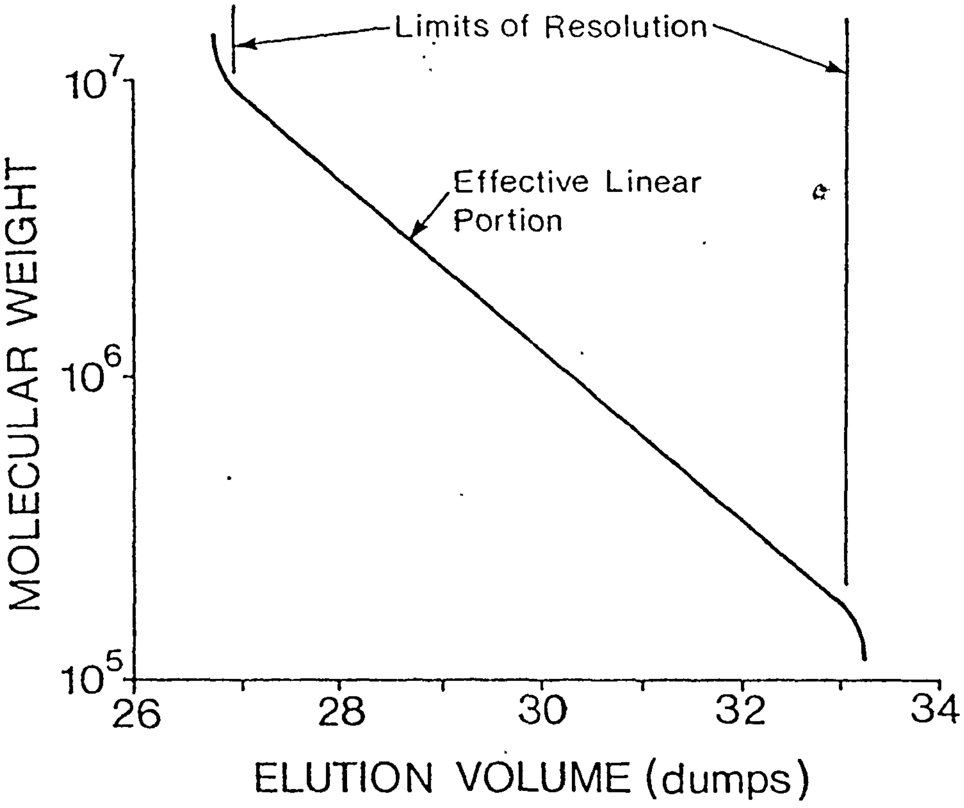


FIGURE D-3: TYPICAL GPC CALIBRATION CURVE cause it to shift.

The linear portion of the calibration curve can be represented by the equation:

$$M = D_1 \exp(-D_2 V) \qquad \text{(D-5)}$$

where M is molecular weight,
V is elution volume, and
D_1, D_2 are constants to be determined.

There are several methods of obtaining D_1 and D_2 from GPC data. One is to compute a normalized cumulative chromatogram, use a computer search routine for D_2 and then employ D_2 and one molecular weight average to obtain D_1. Another approach which can be used when the molecular weight distribution is known is to plot the cumulative MWD together with the cumulative chromatogram (Figure D-4). By using the link between these two functions which the cumulative distribution provides, data for molecular weight as a function of elution volume can be obtained. Equation D-5 can be fit to these data using a nonlinear least squares estimation programme to obtain estimates of D_1 and D_2. Although preparation of Figure D-4 requires curve fitting by eye, the cumulative chromatograph and MWD are well defined if at least 20 data points are available for each.

Equation D-5 must be fit in the form (e.g., exponential, logarithmic) for which the data have constant variance. For GPC calibration, the error in estimating M from the

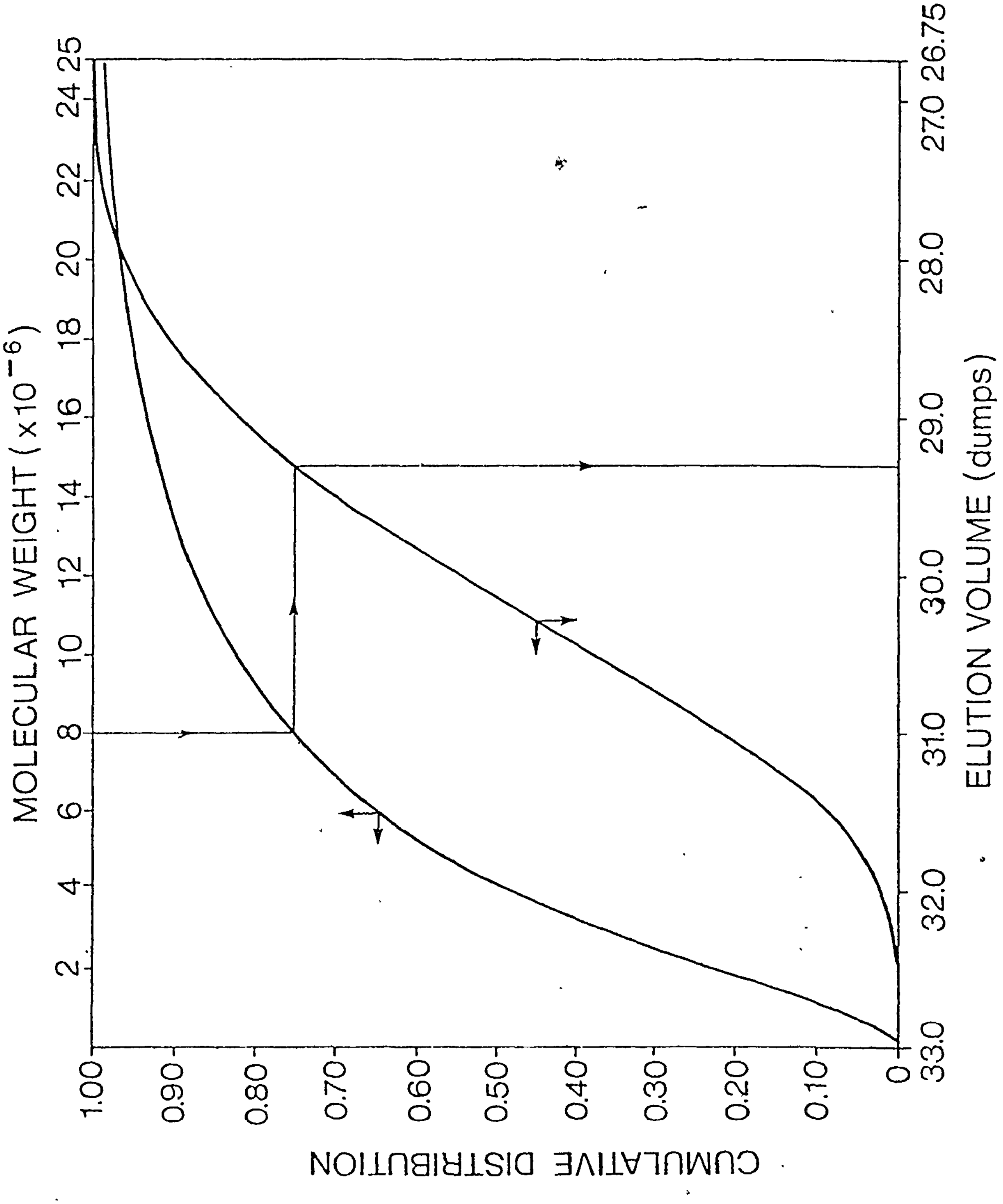


FIGURE D-4: CUMULATIVE DISTRIBUTION CURVES FOR POLYMER STANDARD C calibration curve is proportional to the magnitude of M, and it can therefore be shown (MacGregor, 1976) that Equation D-5 should be fit in the logarithmic form.

There is a problem in the fitting of expressions such as Equation D-5 (whether in logarithmic or exponential form) over a narrow range of the independent variable remote from the origin. A high correlation (usually ≈ -0.99) exists between D_1 and D_2, producing imprecise estimates of their values and yielding a wide confidence interval for M. To avoid this problem, the model can be reparameterized by addition and subtraction of the mean of the independent variable. For the exponential form:

$$M = D_1 \exp(-D_2 V) \qquad \text{(D-5)}$$

$$= D_1 \exp[-\{D_2(V-\bar{V} + \bar{V})\}]$$

$$= D_1 \exp(-D_2\bar{V}) \exp[-D_2(V-\bar{V})]$$

$$M = D_1' \exp[-D_2(V-\bar{V})] \qquad \text{(D-6)}$$

where $D_1' = D_1 \exp(-D_2\bar{V})$

In Equation D-6, the correlation between the two parameters (now D_1' and D_2) is virtually zero, allowing them and the value of M to be well defined. In physical terms D_1' is the molecular weight at the mean retention volume.

If the linear assumption for the calibration curve produces serious lack of fit in the model, a term in V^2 may be added to the exponent. The model then becomes, in reparameterized form,

$$M = D_1'' \exp\{-[D_2(V-\bar{V})+D_3(V^2-\bar{V}^2)]\} \qquad \text{(D-7)}$$

where $D_1'' = D_1 \exp(-D_2\bar{V}-D_3\bar{V}^2)$

(Although Equation D-7 was used for this research, later investigation revealed that expression of the quadratic model in this form did not eliminate the correlations between parameters.)

The polymer samples used in this research were analyzed on a GPC belonging to the Polymer Research Group at McMaster University. It was a Waters Model 301 and was equipped with five 4-foot columns of the following specifications: Bio-Glass, 2500 Å; CPG-10,2000 Å; Porasil DX, 400-800 Å; Porasil CX, 200-400 Å; CPG -125, 240-375 Å. The carrier solvent was water and the samples were run at room temperature, normally at a concentration of 0.02 percent by weight. (Occasionally a concentration of 0.03 percent was employed to increase peak height.)

The broad -MWD standard used to calibrate the instrument was Polyhall 402 (Standard C), a nonionic polyacrylamide. The MWD has been published by Abdel-Alim and Hamielec (1974) and is given in Table D-1. The polymer being characterized was Percol 720, also a nonionic polyacrylamide.

TABLE D-1

MOLECULAR WEIGHT DISTRIBUTION OF STANDARD C[1]

MOLECULAR WT. $M \times 10^{-6}$	DIFFERENTIAL MWD $W(M) \times 10^{8}$	CUMULATIVE MWD
0.10	2.22	
0.20	4.19	0.0032
0.40	7.43	0.0149
0.60	9.90	0.0323
0.80	11.73	0.0541
0.90	12.45	0.0662
1.00	13.05	0.0789
1.50	14.68	0.1490
2.00	14.77	0.2231
2.50	14.05	0.2954
3.00	12.93	0.3629
4.00	10.44	0.4797
5.00	8.25	0.5728
6.00	6.54	0.6464
7.00	5.26	0.7050
8.00	4.29	0.7526
10.00	2.98	0.8243
15.00	1.301	0.9254
20.00	0.549	0.9692
25.00	0.220	0.9873

$\bar{M}_n = 2.40 \times 10^6$, $\bar{M}_w = 5.83 \times 10^6$, $\bar{M}_w/\bar{M}_n = 2.43$

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[1] After Abdel-Alim and Hamielec (1974)

D.1.2 Alteration

Initially it was hoped to be able to separate the molecular weight distribution of the stock polymer (Percol 720) into narrow fractions and use these to establish the effect of molecular weight on flocculation. This separation is theoretically possible by addition of a nonsolvent to a solution of the polymer. The resulting decrease in the solvent power of the system causes the polymer to precipitate, beginning with the largest molecular weight chains (Cantow, 1967). Addition of further aliquots of nonsolvent with separation of the precipitated material after each addition should result in separation of the polymer into narrow molecular weight fractions.

Initial studies were conducted using propanol as a nonsolvent. In the initial fractionation attempts with an aqueous solution of Standard C, precipitated polymer adhered to the inside of the beaker containing the mixture, making quantitative recovery impossible. Nevertheless, the samples were analyzed on the GPC to determine what fractionation had occurred. The area under each chromatogram was obtained using Simpson's Rule and the heights scaled to give equal areas. The standardized chromatograms (Figure D-5) indicated that essentially no fractionation was being achieved. Because of this and the recovery problems, the use of propanol was abondoned.

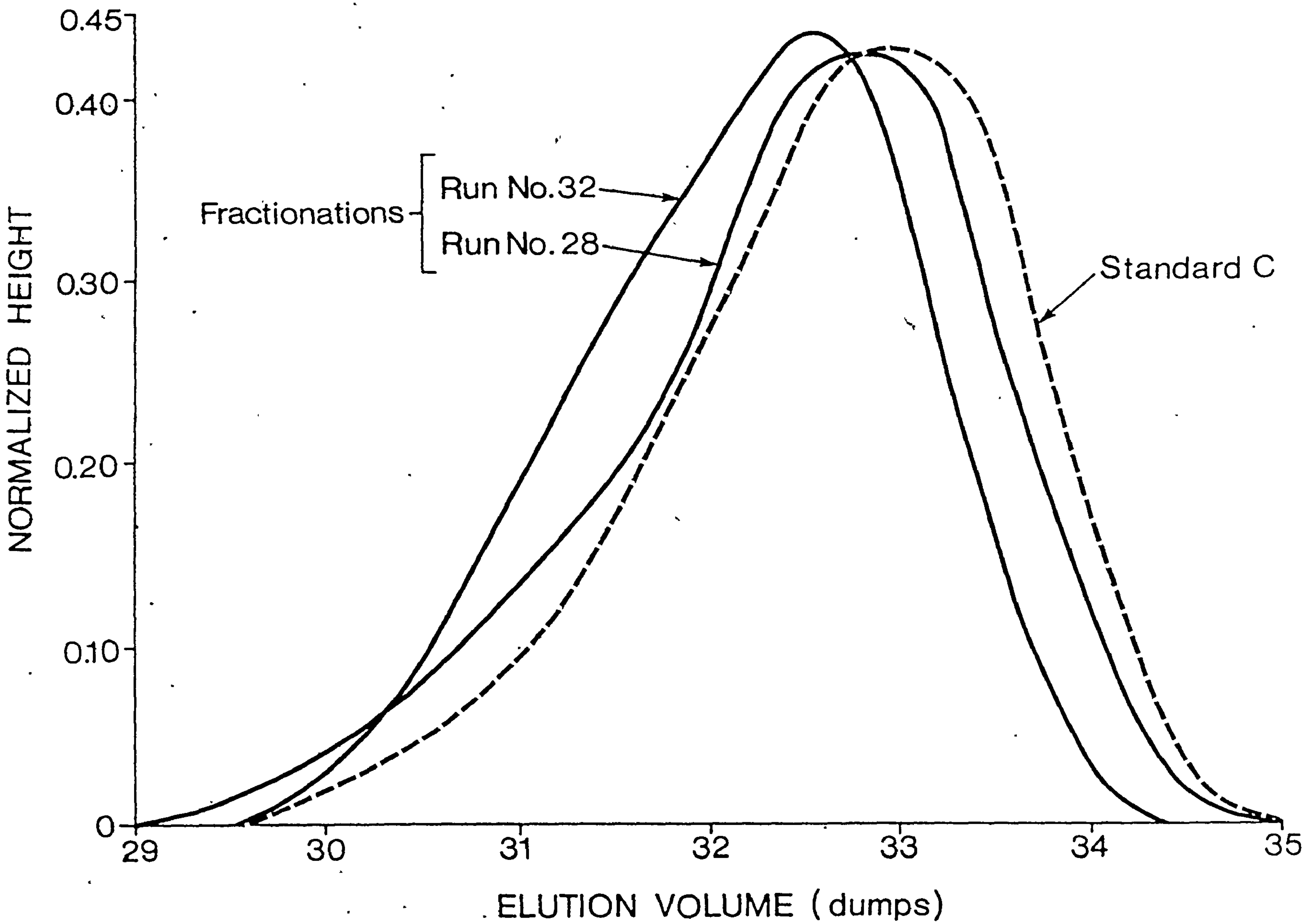

FIGURE D-5: NORMALIZED CHROMATOGRAMS FOR FRACTIONAL PRECIPITATION WITH PROPANOL

Methanol was tried as a nonsolvent since a preliminary test had indicated that the precipitate would not adhere to the walls of the container. An improved procedure was used, whereby after addition of the methanol and ensuing precipitation, the mixture was heated to re-dissolve the polymer. Subsequent cooling, with mixing, permitted polymer precipitation in the absence of local high methanol concentrations, and should have caused precipitation of the maximum molecular weight fraction. Fractionation was attempted for Percol 720, the stock polymer selected for use in the study. Initial fractionation attempts (as measured by GPC) were not encouraging. Various refinements to the procedure were tried, including slowing the rate of methanol addition, and controlling the volume of methanol very closely. For the last tests performed, the standardized chromatograms are shown in Figure D-6. Again, no substantial fractionation had occurred.

At this point it was decided to cease fractionation attempts and employ another method for obtaining different molecular weights. The method chosen, mechanical degradation of the polymer, has been described by Benedek _et al._ (1976). Degradation does not produce narrow molecular weight fractions, but breaks the largest chains, thereby shifting the molecular weight distribution towards lower values.

It was hoped to produce two lower distributions from the original polymer. Attempts were made to have the $\bar{M}_{w_{10}}$ values for the three samples equally spaced on an arithmetic scale.

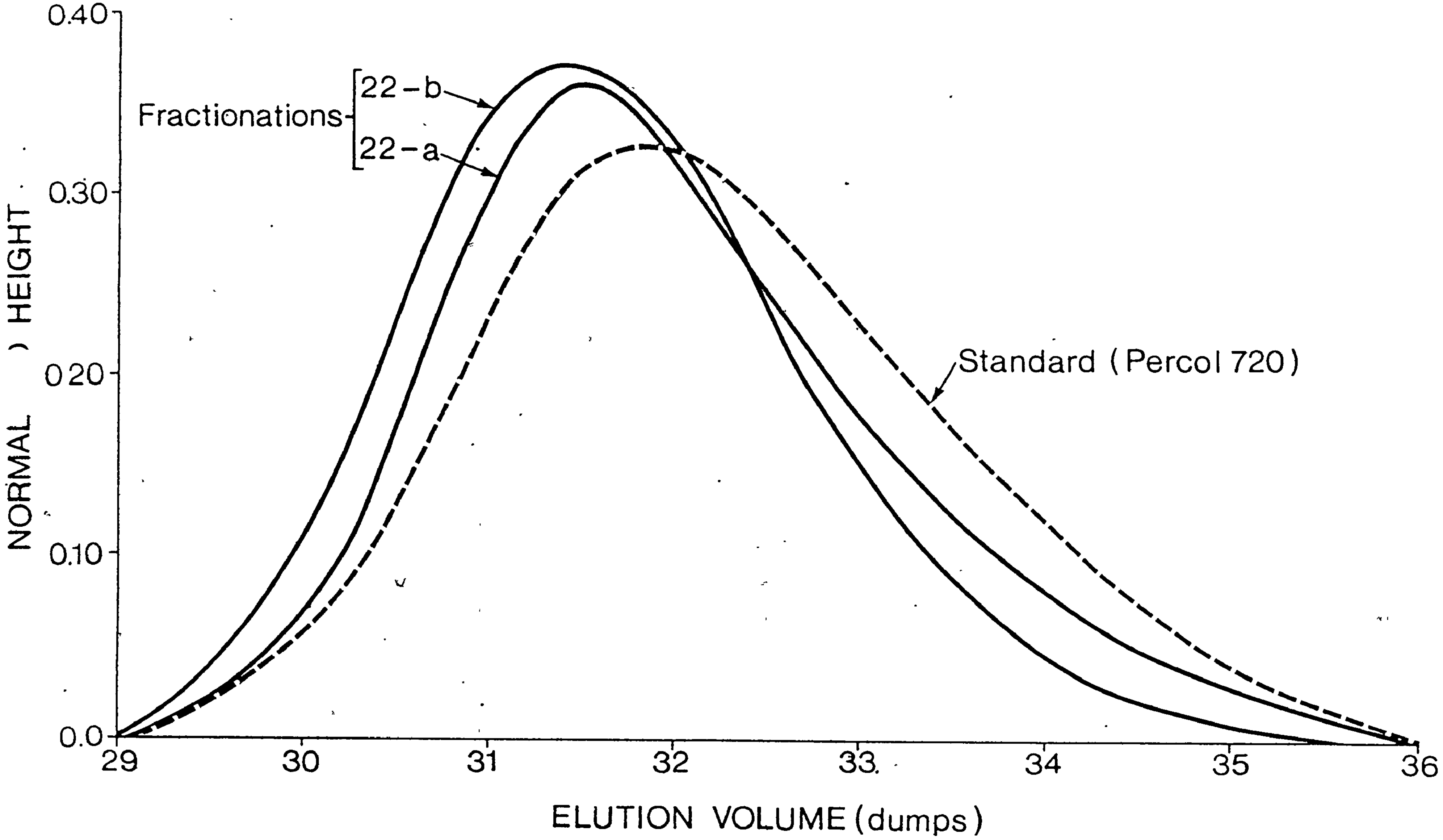

FIGURE D-6: NORMALIZED CHROMATOGRAMS FOR FRACTIONAL PRECIPITATION WITH METHANOL

Approximately 400 ml of Percol 720 solution (1.0 percent by weight) were agitated in a vessel at 1150 rpm using the ELB mixer described in Section 4.1. The vessel was 15.2 cm (6.0 in) in diameter and had four baffles, each set out 1.5 cm (0.6 in). Degradation was monitored qualitatively by withdrawing samples periodically and measuring their viscosity using a Brookfield viscometer. Viscosity decreased rapidly at first, probably because of untangling of polymer chains, and then began to level off after several hours. Shearing was accomplished using a 6.4 cm (2.5 in) diameter flat bladed turbine for the intermediate molecular weight sample and a 10.2 cm (4.0 in) turbine for the low molecular weight sample. Shearing times of 4 hr in the first case and 8 hr in the second case were selected after preliminary runs.

The initial chromatogram heights for these two samples plus undegraded Percol 720 are given in Table D-2 and the standardized chromatograms are shown in Figure D-7. Significant degradation of the high molecular weight tail is apparent.

To quantify the molecular weight reduction, it was necessary to obtain the GPC calibration curve using Standard C. To establish reproducibility, three chromatograms for Standard C were compared after standardization (Table D-3). The agreement was very good and one of these (Run 13) was used to obtain the calibration curve.

TABLE D-2

ORIGINAL CHROMATOGRAM HEIGHTS FOR PERCOL 720 BEFORE AND AFTER DEGRADATION

ELUTION VOLUME (Dumps)	SAMPLE		
	UNDEGRADED	"MIDDLE" MOL. WT.	"LOW" MOL.WT.
27.0	0.0	0.0	0.0
27.5	1.2	0.5	0.0
28.0	3.3	1.9	0.0
28.5	7.6	4.0	0.8
29.0	12.7	8.0	2.7
29.5	18.3	14.1	4.8
30.0	22.1	19.2	6.9
30.5	24.4	21.8	8.3
31.0	23.3	22.6	9.0
31.5	21.1	21.9	9.2
32.0	18.8	19.9	8.9
32.5	15.6	17.4	8.3
33.0	13.5	14.9	7.3
33.5	11.1	12.6	6.4
34.0	8.9	10.3	5.3
34.5	7.2	8.7	4.4
35.0	6.3	6.7	3.7
35.5	4.5	5.0	2.7
36.0	3.8	3.5	2.2
36.5	2.9	2.3	1.5
37.0	1.8	1.4	1.0
37.5	0.7	0.9	0.3
38.0	0.0	0.0	0.0

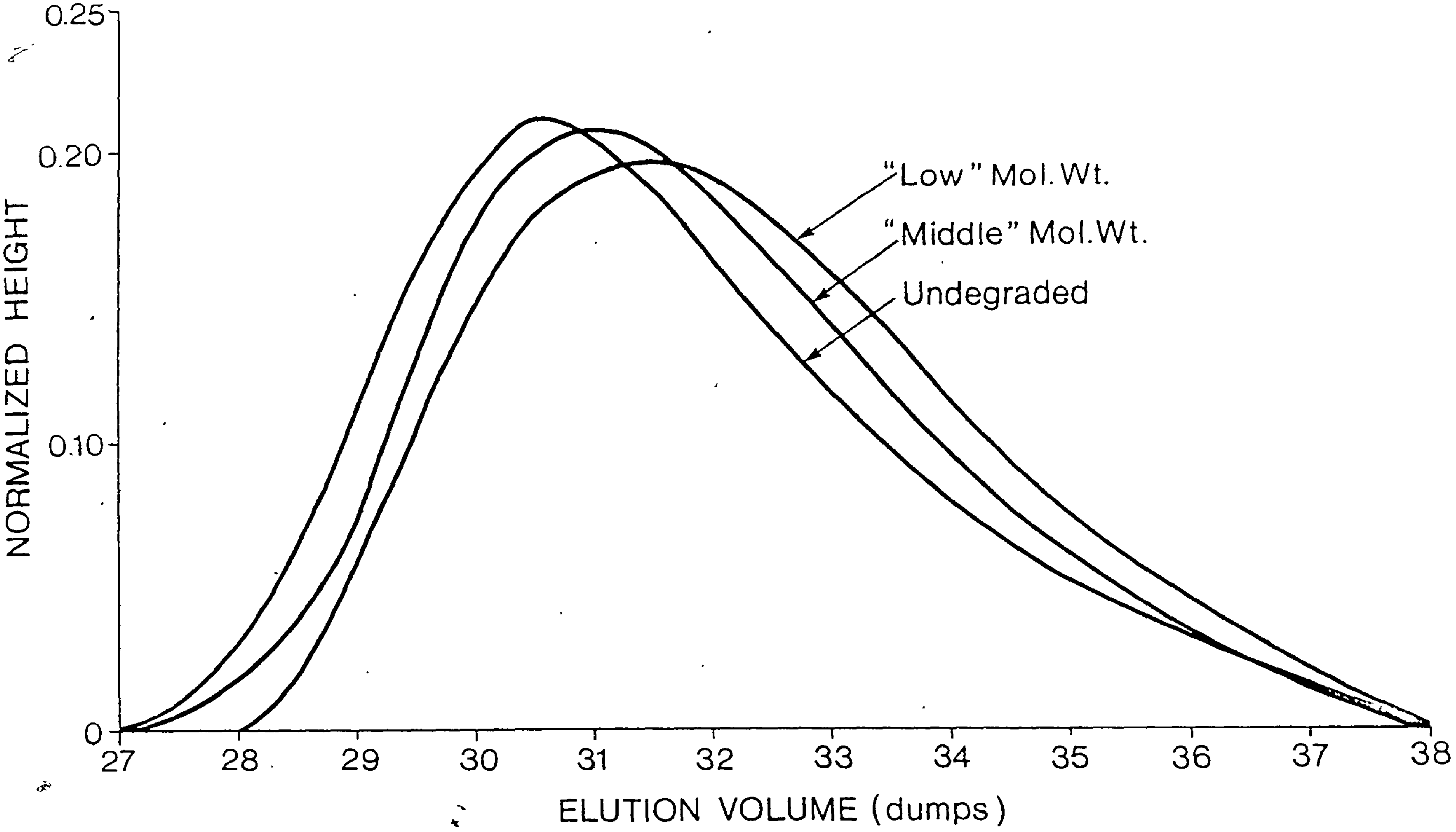

FIGURE D-7: NORMALIZED CHROMATOGRAMS FOR PERCOL 720 BEFORE AND AFTER DEGRADATION

TABLE D-3

STANDARDIZED CHROMATOGRAM HEIGHTS FOR STANDARD C

ELUTION VOLUME (DUMPS)	STANDARDIZED HEIGHTS		
	RUN 13	RUN 14	RUN 15
27.00	0.000	0.000	0.000
27.25	0.019	0.013	0.000
27.50	0.034	0.025	0.020
27.75	0.055	0.045	0.042
28.00	0.084	0.064	0.069
28.25	0.112	0.096	0.093
28.50	0.139	0.127	0.126
28.75	0.169	0.162	0.162
29.00	0.204	0.201	0.204
29.25	0.242	0.242	0.250
29.50	0.276	0.281	0.288
29.75	0.310	0.316	0.324
30.00	0.329	0.340	0.341
30.25	0.339	0.353	0.359
30.50	0.342	0.355	0.359
30.75	0.329	0.350	0.346
31.00	0.304	0.322	0.324
31.25	0.272	0.285	0.277
31.50	0.202	0.203	0.206
31.75	0.122	0.121	0.122
32.00	0.067	0.064	0.044
32.25	0.030	0.027	0.022
32.50	0.013	0.008	0.013
32.75	0.006	0.004	0.007
33.00	0.000	0.000	0.000

Because the MWD for Standard C was available, the least squares estimation procedure was employed to obtain the calibration curve. A sample run of the computer programme used is included in Appendix G. A linear "curve" was obtained first, using the reparameterized form of the model (Figure D-8). The approximate 95 percent confidence limits exclude parts of the curve drawn from the data. Because of this indication that the linear model was inadequate, the quadratic form (Equation D-7) was fit to give the curve with confidence limits shown in Figure D-9. This model provided a much better fit as indicated by comparison of Figures D-8 and D-9 and of the residual sums of squares.

The quadratic calibration curve was used to obtain molecular weight distributions for the three samples of Percol 720 - the original polymer and the two degraded samples. The MWD's were generated using an available computer programme (Appendix G). Unfortunately, because even the undegraded Percol had a much larger lower molecular weight tail than Standard C, the distributions included an unreasonably large proportion of very low molecular weight material. Despite its known inadequacy, the linear calibration was then used. Although it gave reasonable distributions (Figure D-10), the peaks occurred at lower molecular weights than expected for a flocculant, suggesting that the GPC column arrangement used was not ideal for this polymer. Since the high molecular weight tails of the distributions are difficult to distinguish

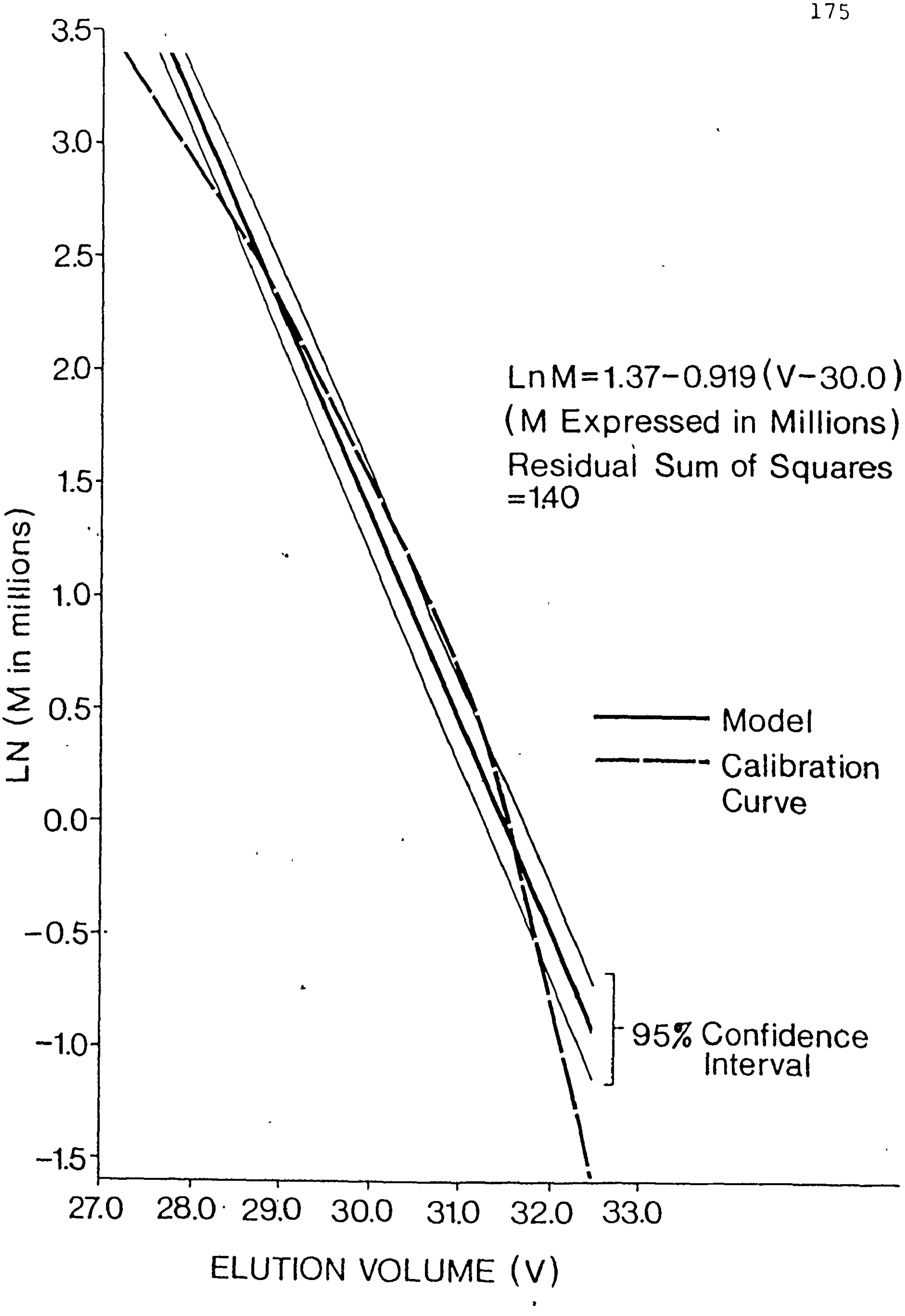

FIGURE D-8: REPARAMETERIZED LINEAR MODEL FOR CALIBRATION CURVE

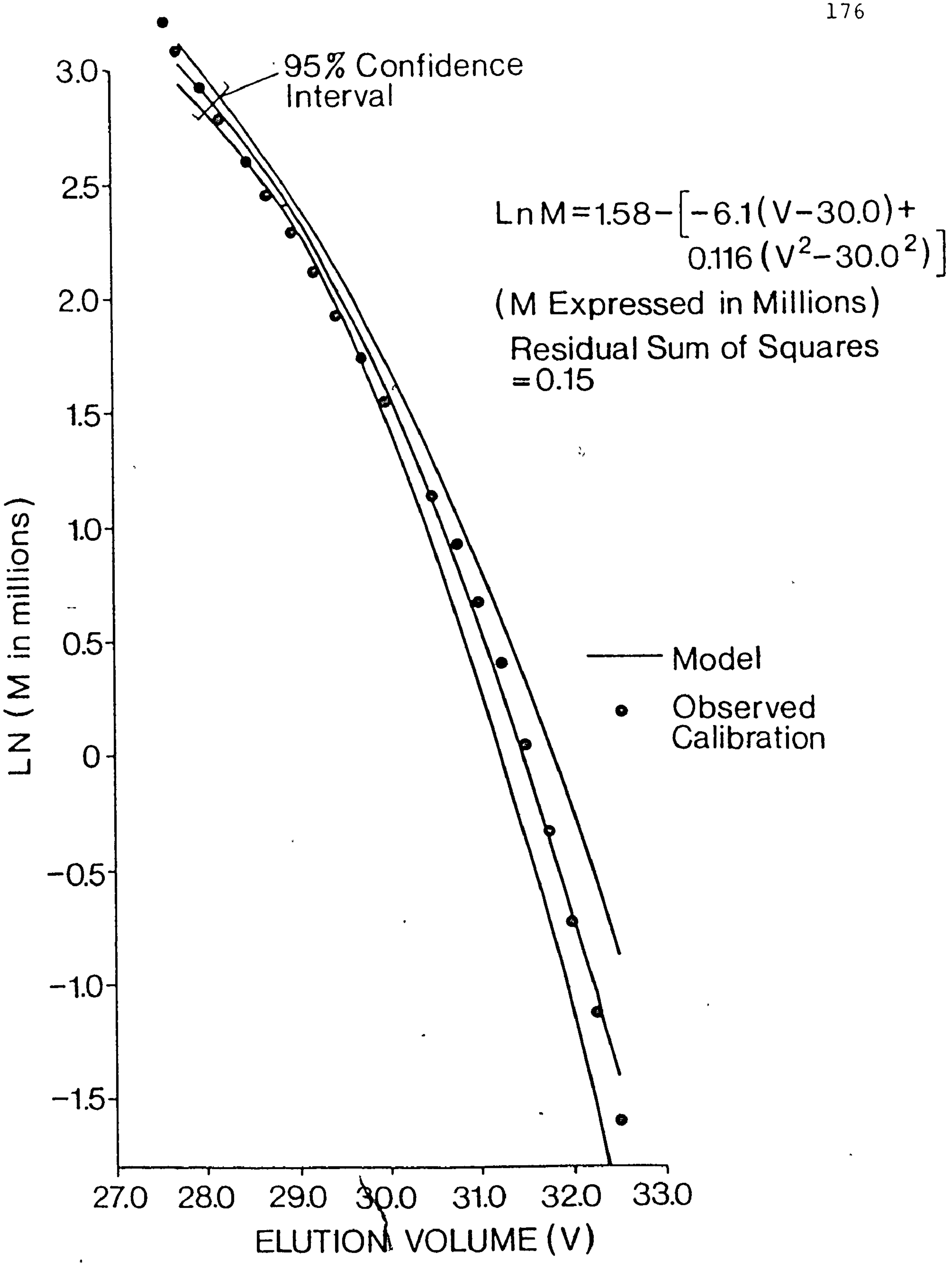

FIGURE D-9: QUADRATIC MODEL FOR CALIBRATION CURVE

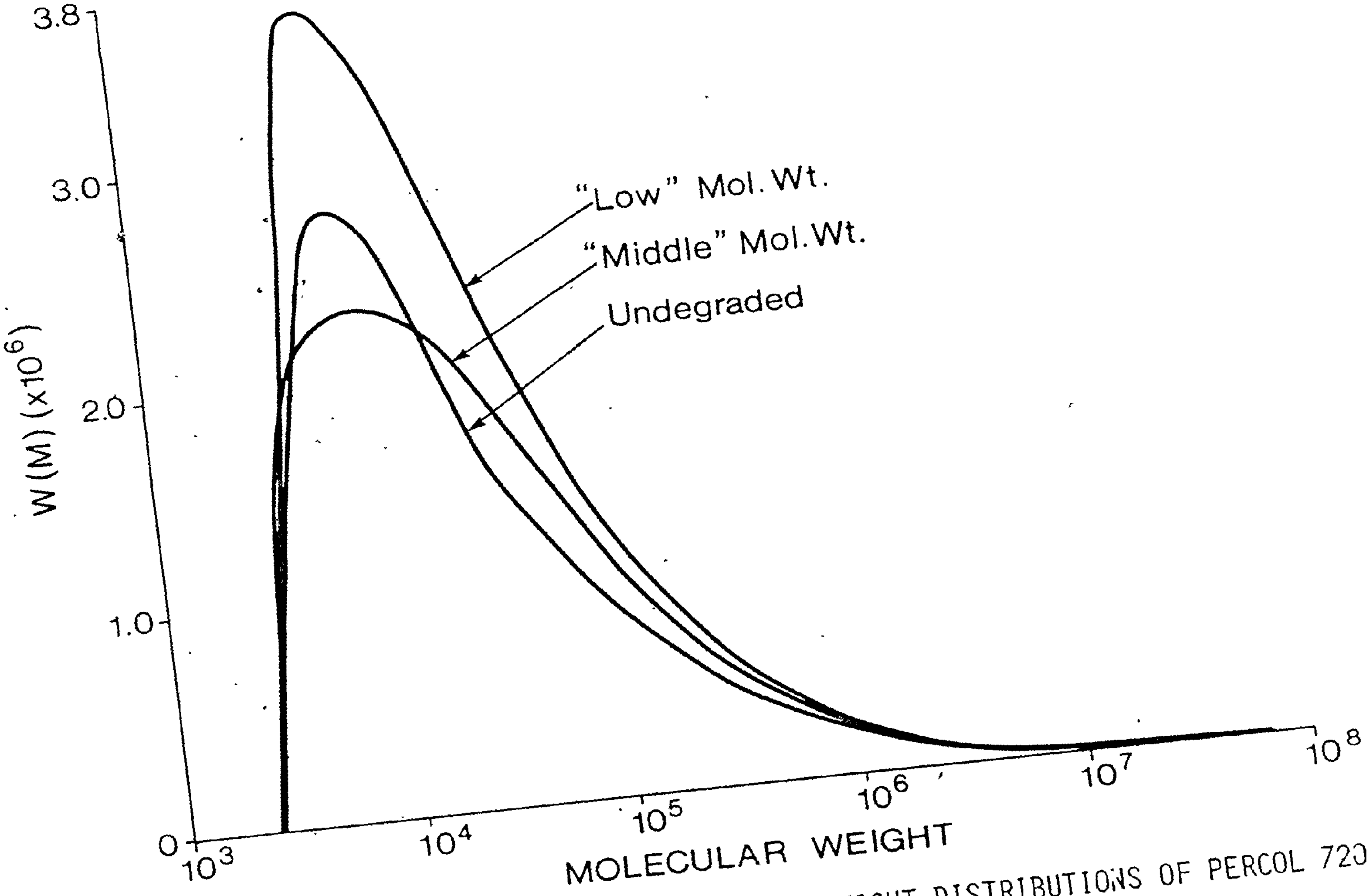

FIGURE D-10: COMPARISON OF MOLECULAR WEIGHT DISTRIBUTIONS OF PERCOL 720 BEFORE AND AFTER SHEARING (LINEAR CALIBRATION) in Figure D-10, they are shown on a larger scale in Figure D-11.

The change, owing to degradation, in $\bar{M}_{w_{10}}$, the weight average molecular weight of the upper 10 percent of the distribution, was calculated (Table D-4). Since this involved that part of the distribution where the quadratic calibration curve provided reasonable molecular weights, computations were made using it as well as using the linear model.

It is evident that substantial degradation of the longest chains occurred. The three $\bar{M}_{w_{10}}$ values are approximately equally spaced using the nonlinear calibration, but not using the linear calibration. Given the limitations of each calibration model, the probable non-ideal column arrangement and the inherent inaccuracies in measuring the tails of distributions, the results in Table D-4 must be regarded as approximate.

D.2 Charge

D.2.1 Expression

The charge on an anionic polyacrylamide (the only flocculant used in this research) can be expressed as the degree of hydrolysis. This is the fraction of amide groups on the polymer chain which have been converted to carboxyl groups. In the following example, the degree of hydrolysis is X/(X + Y).

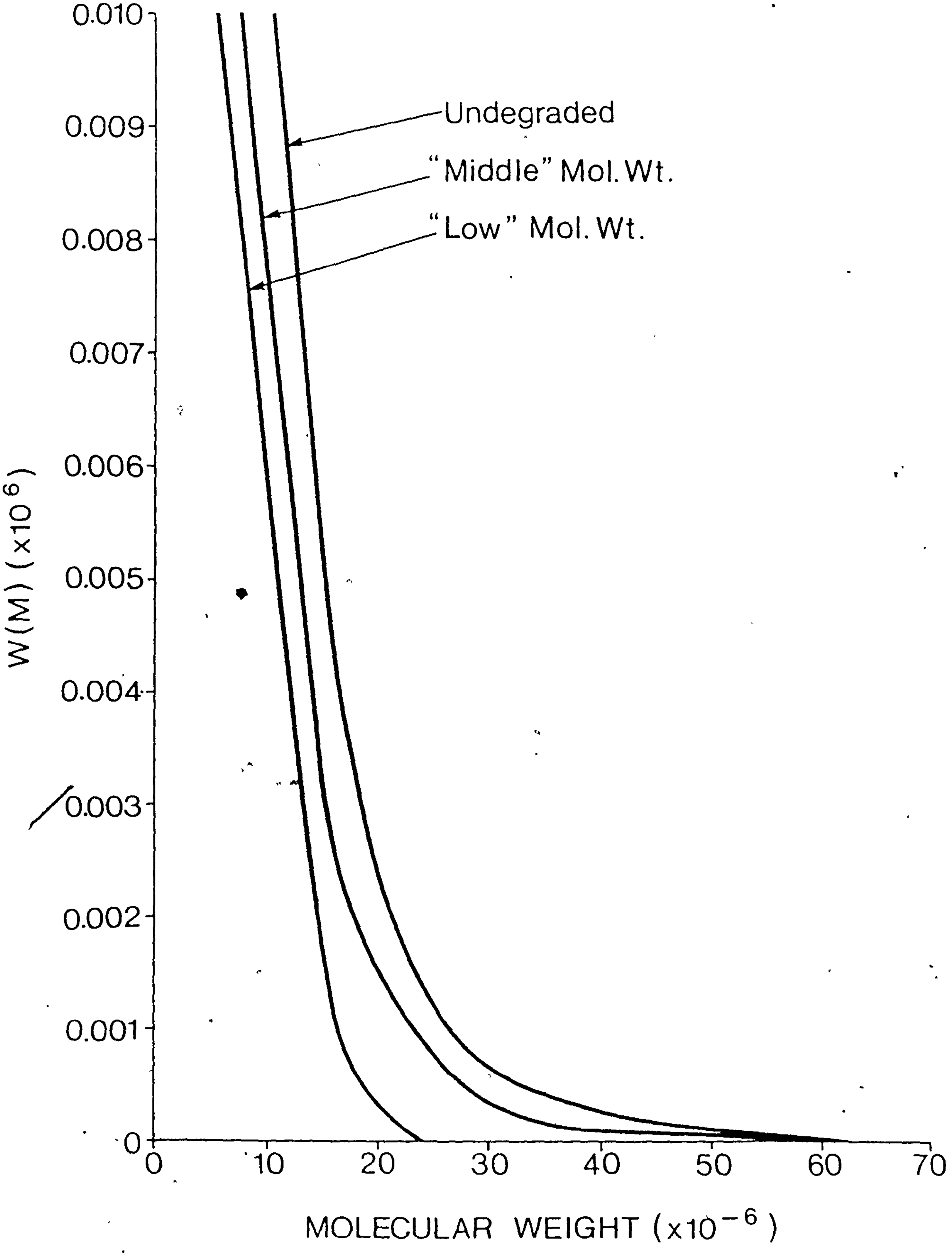

FIGURE D-11: COMPARISON OF UPPER PORTION OF MOLECULAR WEIGHT DISTRIBUTIONS OF PERCOL 720 BEFORE AND AFTER SHEARING (LINEAR CALIBRATION)

TABLE D-4

REDUCTION IN MOLECULAR WEIGHT OF PERCOL 720 THROUGH DEGRADATION

SAMPLE	CALIBRATION	
	LINEAR	NONLINEAR
Undegraded	14.5[1]	13.2
"Middle"Mol. Wt.	12.7	11.0
"Low"Mol. Wt.	7.1	8.3

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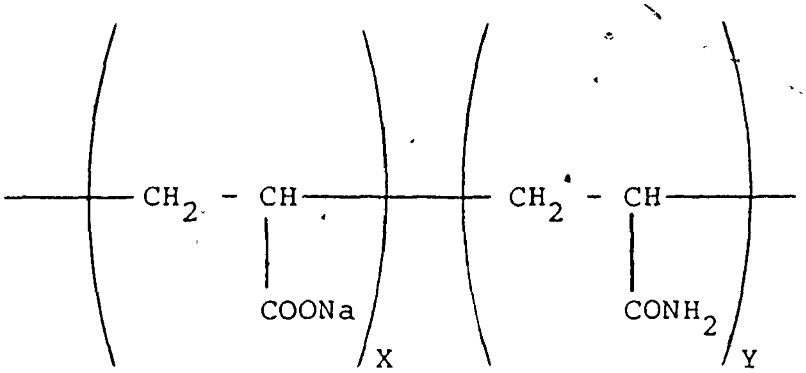
[1] Table entries are $\bar{M}_w$ x 10^{-6}
10

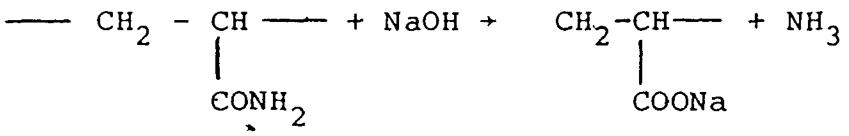


$$\left(-CH_2-\underset{COONa}{\underset{|}{CH}}-\right)_X\left(-CH_2-\underset{CONH_2}{\underset{|}{CH}}-\right)_Y$$

In aqueous solution, the carboxyl group dissociates, leaving a negative charge on the polymer. This serves to extend the polymer in solution, and can also act to neutralize positively charged colloidal particles.

D.2.2 Alteration

Commercially, anionic polyacrylamide is produced by copolymerization of polyacrylamide and polyacrylic acid. In the laboratory, nonionic polyacrylamide can be reacted with sodium hydroxide to produce the required degree of hydrolysis, according to the following reaction (Mukhopadhyay *et al.*, 1969):



$$-CH_2-\underset{CONH_2}{\underset{|}{CH}}- + NaOH \rightarrow CH_2-\underset{COONa}{\underset{|}{CH}}- + NH_3 \qquad (D-8)$$

The reaction is monitored by trapping the ammonia produced.

The apparatus used to carry out the hydrolysis is shown in Figure D-12. The procedure described below refers to Figure D-12 and is based on that used by Benedek *et al.* (1976). The modifications were introduced mainly to improve kinetic reproducibility so that specified degrees of hydrolysis could be produced routinely.

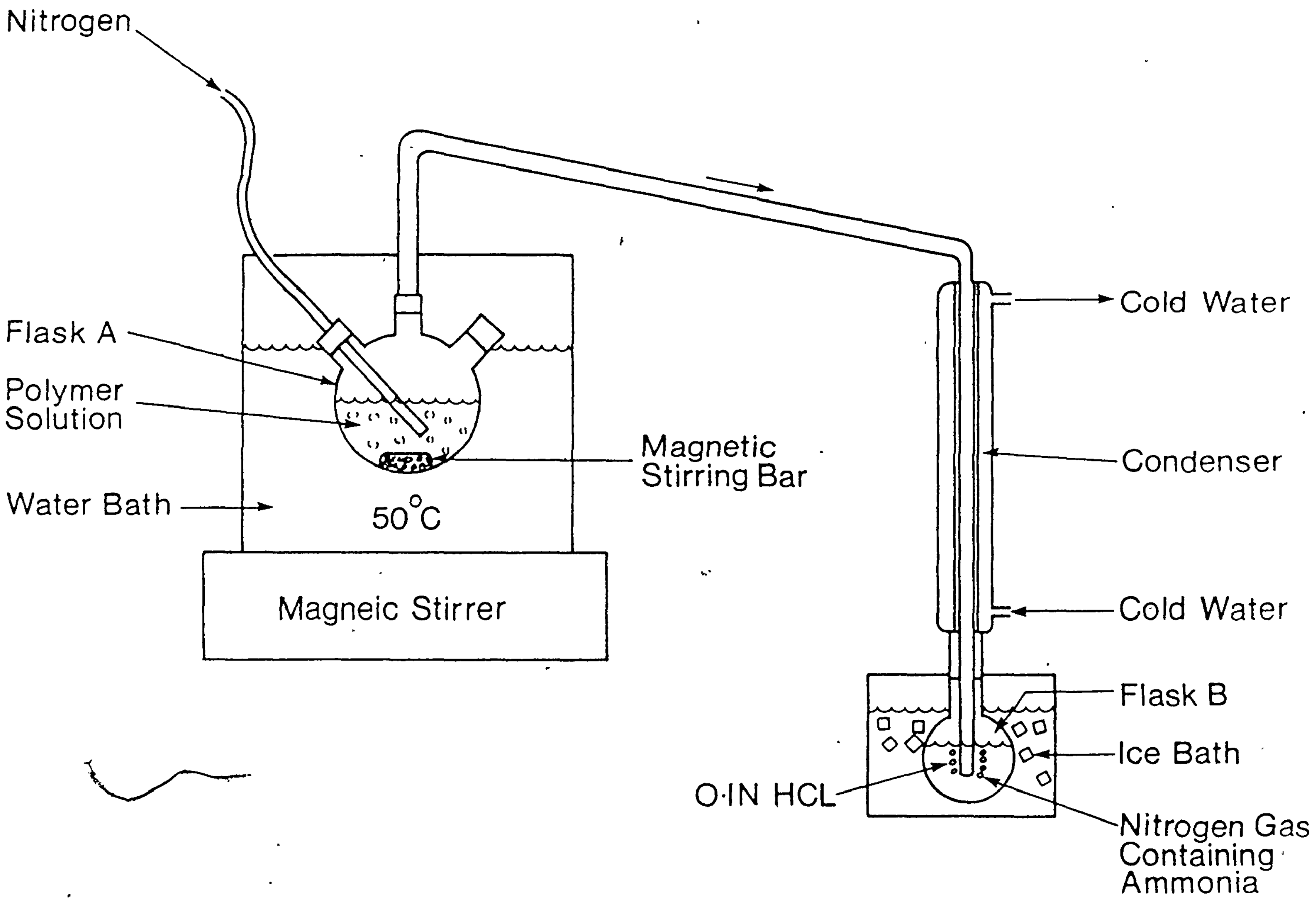


FIGURE D-12: APPARATUS FOR HYDROLYSIS OF POLYACRYLAMIDE

1. To 50 ml of 1.0 percent (by weight) of polyacrylamide (PAM) solution was added 20 ml of distilled water. This was placed in flask A. (The original procedure had called for 0.5 g of PAM to be dissolved in 70 ml of distilled water).

2. Flask A was then purged with nitrogen gas for 30 min., with mixing provided by a magnetic stirring bar. This purge removed oxygen which could degrade the polymer at the elevated temperatures used in the reaction. In a modification to the initial procedure, the nitrogen gas was first bubbled through a pyrogallol solution (0.5 percent by weight) to absorb any traces of oxygen.

3. While the purge was being carried out, a beaker containing 100 ml of 0.1 N NaOH was heated to 50°C in a water bath. (Although only 70 ml of NaOH was actually needed, 100 ml was used to allow for losses in transfer). Also at this time, 70 ml of 0.1 N HCl was placed in Flask B, which was then placed in the ice bath. The ammonia evolved in the reaction was trapped by the HCl and measured quantitatively by determining the HCl normality as a function of time.

4. At the end of 30 min. Flask A, still under agitation and nitrogen purge, was placed in the water bath at 50°C and the sodium hydroxide was placed in a 50°C oven.

Although the original procedure did not call for this preheating, it was done in an attempt to eliminate an initial lag period in the hydrolysis.

5. After 30 min., 70 ml of the preheated sodium hydroxide was poured into Flask A to begin the reaction. The heating, nitrogen purge and agitation were continued for the necessary length of time, as determined by monitoring the ammonia transported to Flask B by the nitrogen gas. The original reaction temperature, $60^{\circ}C$, was reduced to $50^{\circ}C$ to slow the reaction, allowing more time for monitoring the HCl normality and permitting closer control over the degree of hydrolysis produced.

6. Once the required degree of hydrolysis had been achieved, the reaction in Flask A was stopped by plunging it into an ice bath. The final normality of the HCl was determined, enabling calculation of the number of moles of NH_3 driven off and hence the degree of hydrolysis of the polymer. Sample calculations are given in Section D.2.3.

Prior to production of polymer for use, the production tolerance was set at one half percentage point (i.e.[4±0.5]%, [20±0.5]%). To facilitate production within this tolerance, an attempt was made to obtain the rate constant, K, for the following reaction equation;

$$\frac{-d[NH_2]}{dt} = K[R\text{-}NH_2]\,[NaOH] \qquad \text{(D-9)}$$

Since the initial concentrations of polymer and hydroxide were equal, the reaction was pseudo second-order. Reproducibility from batch to batch was poor, despite procedural modifications described above. It was felt that the problem may have been caused by a nonhomogeneous reaction mixture. Although the rate study had to be abandoned, increased expertise permitted successful production of the required degrees of hydrolysis. A listing of the "production" runs performed may be found in Table D-5. A fresh hydrolysis was performed monthly unless required more frequently.

The initial polymer recovery procedure, consisting of addition of large volumes of methanol to the polymer-sodium hydroxide solution and collection of the precipitate, proved to be impractical. An investigation showed that the slow addition of propanol while stirring the solution proved best. This involved making the 140 ml of polymer-sodium hydroxide solution up to about 1 litre with propanol over a period of about 3 hours. The resulting precipitated polymer was recovered by filtering the solution through the screen of a millipore filter apparatus. The residue was washed with propanol several times, dried to constant weight in a 50°C oven, ground with a mortar and pestle, weighed and prepared as a 0.5 percent solution by weight.

Despite careful drying, slightly more than 100 percent polymer recovery was normally obtained, a phenomenon attributed to the presence of some trapped water. In these cases, it was assumed that recovery was 100 percent.

TABLE D-5

TABULATION OF PRODUCTION HYDROLYSIS RUNS

DATE	% HYDROLYSIS TARGET	% HYDROLYSIS VALUE OBTAINED
Oct. 22/75	10	9.77
Oct. 28/75	5	5.13
Nov. 11/75 (degraded polymer)	10	10.43
Nov. 12/75 (degraded polymer)	5	4.96
Nov. 24/75 (degraded)	5	5.20
Nov. 25/75 (degraded)	10	9.59
Dec. 6/75	10	10.44
Jan. 8/76 (degraded)	5	5.31
Jan. 9/76 (degraded)	10	9.91
Jan. 13/76	12	12.61
Jan. 12/76	8	8.90
Jan. 19/76	4	4.40
Jan. 28/76	8	7.99
Feb. 4/76	2	2.25
Feb. 16/76	4	3.64
Feb. 16/76	6	6.42
March 9/76	4	3.57
March 17/76	8	8.34
March 22/76	6	6.45
March 23/76	2	1.51
March 25/76	19	18.83
March 31/76	50	35.00
April 2/76	4	4.18
April 7/76	↓	3.79
April 7/76		4.09
April 20/76		4.20
May 14/76		4.16
June 14/76		4.13
July 6/76		3.89
July 13/76		3.92
July 27/76		3.86
Aug. 6/76		3.98
Sept. 7/76		3.51
Sept. 30/76		3.54
Oct. 13/76		3.86
Oct. 26/76		3.83
Nov. 1/76		3.94
Nov. 1/76		4.10
Nov. 8/76		3.83
Nov. 23/76		4.04
Nov. 23/76		3.83
Dec. 6/76		3.60

D.2.3 Sample Calculation of Percent Hydrolysis

One determination of percent hydrolysis was performed during and at the end of each hydrolysis run. Both are shown in the following sample calculation.

Normality of NaOH = 9.276×10^{-2} N (determined for each run)

Normality of HCl = 0.1000 N.

After 30 min. of hydrolyzing:

Volume of 9.276×10^{-2} N NaOH required to neutralize 10.00 ml HCl to pH 7.00 = 10.53 ml

$$\therefore \text{Normality } (HCl_i) = \frac{(10.53)(9.276 \times 10^{-2})}{10.00} = 9.768 \times 10^{-2}$$

$$\therefore \text{No. moles/litre of acid (HCl) consumed} = 0.1000 - 9.768 \times 10^{-2}$$
$$= 2.32 \times 10^{-3}$$

Since 70.0 ml of HCl are present,

$$\text{moles/70.0 ml HCl consumed} = \frac{70.0(2.32 \times 10^{-3})}{1000} = 1.63 \times 10^{-4}$$

Since moles HCl consumed = moles NH_3 converted, and total moles NH_3 for 0.500 g PAM = 70.4×10^{-4}

$$\therefore \text{\% Hydrolysis} = \frac{1.63 \times 10^{-4}}{70.4 \times 10^{-4}} \times 100 = 2.31\text{\%}.$$

After 45 min of hydrolysis and reaction stopped:

Vol. of 9.276×10^{-2} N NaOH required to neutralize 10 ml of HCl to pH 7.00 = 10.32 ml

$$\therefore \text{Normality (HCl)} = \frac{9.276 \times 10^{-2}(10.32)}{10.00} = 9.573 \times 10^{-2}$$

$\therefore$ moles/l of HCl consumed since 30 min determination

$= 9.768 \times 10^{-2} - 9.573 \times 10^{-2} = 1.95 \times 10^{-3}$.

Since 10 mls were used for 30 min determination

moles/60 ml consumed $= \dfrac{60.0(1.95 \times 10^{-3})}{1000} = 1.17 \times 10^{-4}$

Since 1.63×10^{-4} moles of NH_3 were converted in the first 30 min, and 1.17×10^{-4} moles were converted from 30 to 45 min;

Total moles NH_3 converted $= (1.63+1.17)\times10^{-4}=2.80\times10^{-4}$

$\therefore$ Total % Hydrolysis $= \dfrac{2.80 \times 10^{-4}}{70.4 \times 10^{-4}} \times 100 = 3.98\%$.

APPENDIX E - OPTIMIZATION STUDIES: EXPERIMENTAL CONDITIONS AND RESULTS

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Experiment: 2.1 **Minewater:** 500 mg/l SO_4 - 150 mg/l Fe
2000 " - 600 "
8000 " - 2400 "

Objective: To investigate entire experimental region **Date:** Nov'75 - Jan'76

Design: Box and Behnken Design #5

Test No.	Treatment	Ionic Strength (mg/l SO_4)	POLYMER		DISPERSION			FLOC.	Supernatant Total Iron Conc'n
	a,b,c,d,e,f,g		$\bar{M}_{w_{10}}$ (10^6)	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Time (sec)	(mg/l)
1	0,0,0,1,1,1,0	2000	11.0	5	3	300	35	300	0.28
2	0,0,0,-1,1,1,0				0.33	300			0.76
3	0,0,0,1,-1,1,0				3	100			0.18
4	0,0,0,-1,-1,1,0				0.33	100	↓		0.47
5	0,0,0,1,1,-1,0				3	300	5		0.50
6	0,0,0,-1,1,-1,0				0.33	300			0.76
7	0,0,0,1,-1,-1,0				3	100			0.28
8	0,0,0,-1,-1,-1,0	↓			0.33	100	↓	↓	0.80
9	1,0,0,0,0,1,1,	8000			1	200	35	600	0.63
10	-1,0,0,0,0,1,1,	500					35		0.78
11	1,0,0,0,0,-1,1	8000					5		0.25
12	-1,0,0,0,0,-1,1	500					5	↓	1.01
13	1,0,0,0,0,1,-1	8000					35	0	0.26
14	-1,0,0,0,0,1,-1	500					35		3.10
15	1,0,0,0,0,-1,-1	8000					5		1.26
16	-1,0,0,0,0,-1,-1	500	↓			↓	5		10.78
17	0,1,0,0,1,0,1	2000	13.2			300	20	600	0.08
18	0,-1,0,0,1,0,1		8.3			300			0.06
19	0,1,0,0,-1,0,1		13.2			100			0.16
20	0,-1,0,0,-1,0,1		8.3			100		↓	0.09
21	0,1,0,0,1,0,-1		13.2			300		0	1.40
22	0,-1,0,0,1,0,-1		8.3			300			0.24
23	0,1,0,0,-1,0,-1		13.2			100			3.66
24	0,-1,0,0,-1,0,-1	↓	8.3		↓	100		↓	0.84
25	1,1,0,1,0,0,0,	8000	13.2		3	200		300	0.44
26	-1,1,0,1,0,0,0	500	13.2						0.28
27	1,-1,0,1,0,0,0	8000	8.3						0.04
28	-1,-1,0,1,0,0,0	500	8.3		↓				0.16
29	1,1,0,-1,0,0,0	8000	13.2		0.33				0.29
30	-1,1,0,-1,0,0,0	500	13.2						0.38
31	1,-1,0,-1,0,0,0	8000	8.3						0.28
32	-1,-1,0,-1,0,0,0	500	8.3	↓	↓			↓	1.22
33	0,0,1,1,0, 0,1	2000	11.0	10	3			600	0.16
34	0,0,-1,1,0,0,1			0	3				3.50
35	0,0,1,-1,0,0,1			10	0.33				0.43
36	0,0,-1,-1,0,0,1	↓	↓	0	0.33	↓	↓	↓	3.51

Experiment: 2.1 **Minewater:**
500 mg/l SO_4 - 150 mg/l Fe
2000 " - 600 "
8000 " - 2400 "

Objective: To investigate entire experimental region **Date:** Nov'75 - Jan'76

Design: Box and Behnken Design #5

Test No.	Treatment a,b,c,d,e,f,g	Ionic Strength (mg/l SO_4)	POLYMER $\bar{M}_{w10}$ (10^6)	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	DISPERSION Speed (rpm)	DISPERSION Time (sec)	FLOC. Time (sec)	Supernatant Total Iron Cond'n (mg/l)
37	0,0,1,1,0,0,-1	2000	11.0	10	3	200	20	0	0.84
38	0,0,-1,1,0,0,-1	↓	↓	0	3	↓	↓	↓	5.00
39	0,0,1,-1,0,0,-1	↓	↓	10	0.33	↓	↓	↓	1.88
40	0,0,-1,-1,0,0,-1	↓	↓	0	0.33	↓	↓	↓	3.28
41	1,0,1,0,1,0,0	8000	↓	10	1	300	↓	300	1.72
42	-1,0,1,0,1,0,0	500	↓	10	↓	↓	↓	↓	0.45
43	1,0,-1,0,1,0,0	8000	↓	0	↓	↓	↓	↓	2.51
44	-1,0,-1,0,1,0,0	500	↓	0	↓	↓	↓	↓	1.83
45	1,0,1,0,-1,0,0	8000	↓	10	↓	100	↓	↓	3.21
46	-1,0,1,0,-1,0,0	500	↓	10	↓	↓	↓	↓	1.06
47	1,0,-1,0,-1,0,0	8000	↓	0	↓	↓	↓	↓	3.06
48	-1,0,-1,0,-1,0,0	500	↓	0	↓	↓	↓	↓	1.29
49	0,1,1,0,0,1,0	2000	13.2	10	↓	200	35	↓	0.49
50	0,-1,1,0,0,1,0	↓	8.3	10	↓	↓	↓	↓	0.06
51	0,1,-1,0,0,1,0	↓	13.2	0	↓	↓	↓	↓	3.49
52	0,-1,-1,0,0,1,0	↓	8.3	0	↓	↓	↓	↓	1.27
53	0,1,1,0,0,-1,0	↓	13.2	10	↓	↓	5	↓	1.21
54	0,-1,1,0,0,-1,0	↓	8.3	10	↓	↓	↓	↓	0.23
55	0,1,-1,0,0,-1,0	↓	13.2	0	↓	↓	↓	↓	1.72
56	0,-1,-1,0,0,-1,0	↓	8.3	0	↓	↓	↓	↓	1.30
57	0,0,0,0,0,0,0	↓	11.0	5	↓	↓	20	↓	0.40
58	0,0,0,0,0,0,0	↓	↓	↓	↓	↓	↓	↓	0.29
59	0,0,0,0,0,0,0	↓	↓	↓	↓	↓	↓	↓	0.35
60	0,0,0,0,0,0,0	↓	↓	↓	↓	↓	↓	↓	0.53
61	0,0,0,0,0,0,0	↓	↓	↓	↓	↓	↓	↓	0.26
62	0,0,0,0,0,0,0	↓	↓	↓	↓	↓	↓	↓	0.33

EFFECTS[1] CALCULATED FROM THE DATA FOR EXPERIMENT 2.1

MODEL

$$\hat{y} = b_o + \sum_{i=1}^{7} b_i x_i + \sum_{i=1}^{7} b_{ii} x_i^2 + \sum_{i=1}^{6} \sum_{j=i+1}^{7} b_{ij} x_i x_j$$

$b_o = 0.360$

i	b_i	b_{ii}	b_{ij}					
			j=2	j=3	j=4	j=5	j=6	j=7
1	-0.349	0.583	0.141	0.121	0.134	-0.246	0.909	1.429
2	0.326	-0.473		-0.154	0.169	-0.214	0.156	-0.486
3	-0.835	1.035			-0.377	-0.261	-0.329	-0.107
4	-0.100	-0.077				0.009	0.001	-0.120
5	-0.188	-0.079					0.026	0.344
6	-0.347	0.306						1.101
7	-0.912	1.015						

---

[1] in mg/l

Exp.: 3.1.1 **Minewater:** 8000 mg/l SO_4^- **Date:** Dec.19/75
2400 mg/l Fe

Objective: To investigate all mixing and polymer variables

Design: 2^{6-2} **Defining Contrasts:** abce, bcdf, adef

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
		a	b	c	d	e	f	
1	f	10	0.33	300	5	55	300	0.13
2	aef	20	0.33	↓	↓	75	300	0.34
3	be	10	1	↓	↓	75	30	1.87
4	ab	20	1	↓	↓	55	↓	1.93
5	ce	10	0.33	600	↓	75	↓	0.39
6	ac	20	0.33	↓	↓	55	↓	0.42
7	bcf	10	1	↓	↓	55	300	0.18
8	abcef	20	1	↓	↓	75	300	0.13
9	d	10	0.33	300	20	55	30	0.37
10	ade	20	0.33	↓	↓	75	30	0.30
11	bdef	10	1	↓	↓	75	300	0.10
12	abdef	20	1	↓	↓	55	↓	0.20
13	cdef	10	0.33	600	↓	75	↓	0.15
14	acdf	20	0.33	↓	↓	55	↓	0.22
15	bcd	10	1	↓	↓	55	30	0.20
16	abcde	20	1	↓	↓	75	30	0.12

Exp.: 3.1.3	**Minewater:** 8000 mg/l SO_4- 2400 mg/l Fe						**Date:** Jan.12/76	
Objective: To investigate the path of steepest ascent								
Design: ------	**Defining Contrasts:** -----							

Test No.	Treatment	POLYMER Hyd. (%)	Dose (mg/g SO_4)	DISPERSION Speed (rpm)	Time (sec)	FLOCC'N Speed (rpm)	Time (sec)	Supernatant Total Iron Conc'n (mg/l)
A		16.3	0.67	450	13	65	165	0.03
B		16.3	0.44	600	21	65	330	0.09
C		16.3	0.20	750	29	65	495	0.33

Exp.: 3.1.5 **Minewater:** 8000 mg/l SO_4-
2400 mg/l Fe **Date:** Jan.16/76

Objective: To investigate polymer and mixing Variables

Design: 2^{6-2} **Defining Contrasts:** abce, bcdf, adef

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
1	f	8	0.5	450	12	65	165	0.14
2	aef	12	0.5	↓	↓	100	165	0.11
3	be	8	0.7	↓	↓	100	108	0.10
4	ab	12	0.7	↓	↓	65	↓	0.05
5	ce	8	0.5	550	↓	100	↓	0.10
6	ac	12	0.5	↓	↓	65	↓	0.09
7	bcf	8	0.7	↓	↓	65	165	0.13
8	abcef	12	0.7	↓	↓	100	165	0.17
9	d	8	0.5	450	16	65	108	0.08
10	ade	12	0.5	↓	↓	100	108	0.14
11	bdef	8	0.7	↓	↓	100	165	0.12
12	abdf	12	0.7	↓	↓	65	↓	0.15
13	cdef	8	0.5	550	↓	100	↓	0.07
14	acdf	12	0.5		↓	65	↓	0.17
15	bcd	8	0.7	↓	↓	65	108	0.07
16	abcde	12	0.7	↓	↓	100	108	0.07

Exp.: 3.1.7 **Minewater:** 8000 mg/l SO_4-
2400 mg/l Fe **Date:** Feb. 2/76

Objective: To investigate polymer hydrolysis and dosage

Design: 2^2 **Defining Contrasts:** -----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%) a	Dose (mg/g SO_4) b	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
1	(1)	4	0.3	550	12	100	120	0.13
2	a	8	0.3	↓	↓	↓	↓	0.15
3	ab	8	0.5					0.25
4	b	4	0.5					0.37

Exp.: 3.1.9 Minewater: 8000 mg/l SO_4- 2400 mg/l Fe Date: Feb.9/76

Objective: To investigate polymer hydrolysis and dosage

Design: 2^2 Defining Contrasts: -----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
1	(1)	2	0.1	550	12	100	120	0.17
2	a	4	0.1	↓	↓	↓	↓	0.18
3	ab	4	0.3	↓	↓	↓	↓	0.30
4	b	2	0.3	↓	↓	↓	↓	0.23

Exp.: 3.1.11 **Minewater:** 8000 mg/l SO_4- **Date:** Feb.26/76
3.1.11(repeat) 2400 mg/l Fe March 4/76

Objective: To obtain response surface for mixing near optimum

Design: Box and Behnken Design #2 **Defining Contrasts:** -----

Test No.	Treatment				POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)	
					Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	3.1.11	3111 repeat
	a	b	c	d			a	b	c	d		
1	1	1	0	0	4	0.1	750	18	80	90	0.44	0.57
2	-1	-1	0	0			250	6			0.42	0.87
3	1	-1	0	0			750	6			0.71	0.42
4	-1	1	0	0			250	18	↓	↓	0.35	0.36
5	0	0	1	1			500	12	12	135	0.13	0.21
6	0	0	-1	-1					40	45	0.45	1.41
7	0	0	1	-1					120	45	0.27	0.54
8	0	0	-1	1			↓		40	135	0.57	0.42
9	0	0	0	0					80	90	0.28	0.48
10	1	0	0	1			750			135	0.15	0.23
11	-1	0	0	-1			250			45	0.63	0.70
12	1	0	0	-1			750			45	0.79	0.36
13	-1	0	0	1			250	↓	↓	135	0.42	0.45
14	0	1	1	0			500	18	120	90	0.26	0.19
15	0	-1	-1	0				6	40		0.92	0.70
16	0	-1	1	0				6	120		0.20	0.24
17	0	1	-1	0				18	40		0.51	0.70
18	0	0	0	0			↓	12	80		0.32	0.42
19	1	0	1	0			750		120		0.21	0.28
20	-1	0	-1	0			250		40		0.93	1.16
21	1	0	-1	0			750		40		0.99	1.12
22	-1	0	1	0			250	↓	120	↓	0.23	0.49
23	0	1	0	1			500	18	80	135	0.22	0.18
24	0	-1	0	-1				6		45	0.38	0.97
25	0	1	0	-1				18		45	0.41	0.47
26	0	-1	0	1				6		135	0.38	0.25
27	0	0	0	0	↓	↓	↓	12	↓	90	0.30	1.16

Exp.: 3.1.13 **Minewater:** 8000 mg/l SO_4-
2400 mg/l Fe
Date: Mar.24/76

Objective: To investigate polymer properties near the optimum and a change of lime source

Design: 2^3 **Defining Contrasts:** -----

Test No.	Treatment	POLYMER			DISPERSION		FLOCC'N		Supernatant
		Lime c	Hyd. (%) a	Dose (mg/g SO_4) b	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Total Iron Conc'n (mg/l)
1	(1)	BDH	6	0.3	550	12	100	60	0.44
2	a	BDH	8	0.3	↓	↓	↓	↓	0.22
3	b	BDH	6	0.5					0.30
4	ab	BDH	8	0.5					0.28
5	c	Fisher	6	0.3					0.22
6	ac	Fisher	8	0.3					0.20
7	bc	Fisher	6	0.5					0.28
8	abc	Fisher	8	0.5					0.17

Exp.: 3.1.2 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** Dec.16/75

Objective: To investigate all mixing and polymer variables

Design: 2^{6-2} **Defining Contrasts:** abce, bcdf, adef

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%) a	Dose (mg/g SO_4) b	Speed (rpm) c	Time (sec) d	Speed (rpm) e	Time (sec) f	
1	f	10	1	300	30	35	1200	0.04
2	aef	20	1	↓	↓	55	1200	0.05
3	be	10	3	↓	↓	55	600	0.07
4	ab	20	3	↓	↓	35	↓	0.12
5	ce	10	1	600	↓	55	↓	0.07
6	ac	20	1	↓	↓	35	↓	0.20
7	bcf	10	3	↓	↓	35	1200	0.13
8	abcef	20	3	↓	↓	55	1200	0.07
9	d	10	1	300	60	35	600	0.07
10	ade	20	1	↓	↓	55	600	0.05
11	bdef	10	3	↓	↓	55	1200	0.01
12	abdef	20	3	↓	↓	35	↓	0.02
13	cdef	10	1	600	↓	55	↓	0.02
14	acdf	20	1	↓	↓	35	↓	0.11
15	bcd	10	3	↓	↓	35	600	0.10
16	abcde	20	3	↓	↓	55	600	0.07

Exp.: 3.1.4 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** Jan.14/76

Objective: To investigate the path of steepest ascent

Design: ----- **Defining Contrasts:** -----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
A1		10	2	450	45	45	900	<0.01
B1		10	2	325	56	54	1122	<0.01
C1		8	2	200	67	63	1344	0.04

Exp.: 3.1.6 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** Jan.23/76

Objective: To investigate polymer and mixing variables

Design: 2^{6-2} **Defining Contrasts:** abce, bcdf, adef

Test No.	Treatment	POLYMER Hyd. (%) a	POLYMER Dose (mg/g SO_4) b	DISPERSION Speed (rpm) c	DISPERSION Time (sec) d	FLOCC'N Speed (rpm) e	FLOCC'N Time (sec) f	Supernatant Total Iron Conc'n (mg/l)
1	f	4	0.5	325	45	45	1440	0.08
2	aef	12	0.5	↓	↓	55	1440	0.07
3	be	4	2	↓	↓	55	900	0.08
4	ab	12	2	↓	↓	45	↓	0.07
5	ce	4	0.5	450	↓	55	↓	0.12
6	ac	12	0.5	↓	↓	45	↓	0.08
7	bcf	4	2	↓	↓	45	1440	0.08
8	abcef	12	2	↓	↓	55	1440	0.04
9	d	4	0.5	325	72	45	900	0.08
10	ade	12	0.5	↓	↓	55	900	0.10
11	bdef	4	2	↓	↓	55	1440	0.08
12	abdf	12	2	↓	↓	45	↓	0.11
13	cdef	4	0.5	450	↓	55	↓	0.08
14	acdf	12	0.5	↓	↓	45	↓	0.07
15	bcd	4	2	↓	↓	45	900	0.10
16	abcde	12	2	↓	↓	55	900	0.08

Exp.: 3.1.8 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** Feb. 4/76

Objective: To investigate polymer hydrolysis and dosage and rapid mix time

Design: 2^3 **Defining Contrasts:** -----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%) a	Dose (mg/g SO_4) b	Speed (rpm) c	Time (sec)	Speed (rpm)	Time (sec)	
1	1	2	0.1	100	38	40	750	1.43
2	a	4	0.1	↓	↓	↓	↓	1.16
3	b	2	0.5	↓	↓	↓	↓	0.36
4	ab	4	0.5	↓	↓	↓	↓	0.56
5	c	2	0.1	300	↓	↓	↓	0.36
6	ac	4	0.1	↓	↓	↓	↓	0.36
7	bc	2	0.5	↓	↓	↓	↓	0.23
8	abc	4	0.5	↓	↓	↓	↓	0.06

Exp.: 3.1.10 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** Feb.12/76

Objective: To obtain response surface for mixing variables near optimum

Design: Box and Behnken Design #2 **Defining Contrasts:** -----

Test No.	Treatment				POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
					Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
	a	b	c	d			a	b	c	d	
1	1	1	0	0	4	0.5	450	68	45	900	0.09
2	-1	-1	0	0	↓	↓	150	23	↓	↓	0.26
3	1	-1	0	0	↓	↓	450	23	↓	↓	0.09
4	-1	1	0	0	↓	↓	150	68	↓	↓	0.18
5	0	0	1	1	↓	↓	300	45	67.5	1350	0.13
6	0	0	-1	-1	↓	↓	↓	↓	22.5	450	0.21
7	0	0	1	-1	↓	↓	↓	↓	67.5	450	0.11
8	0	0	-1	1	↓	↓	↓	↓	22.5	1350	0.08
9	0	0	0	0	↓	↓	↓	↓	45	900	0.08
10	1	0	0	1	↓	↓	450	↓	↓	1350	0.12
11	-1	0	0	-1	↓	↓	150	↓	↓	450	0.22
12	1	0	0	-1	↓	↓	450	↓	↓	450	0.10
13	-1	0	0	1	↓	↓	150	↓	↓	1350	0.18
14	0	1	1	0	↓	↓	300	68	67.5	900	0.12
15	0	-1	-1	0	↓	↓	↓	23	22.5	↓	0.24
16	0	-1	1	0	↓	↓	↓	23	67.5	↓	0.13
17	0	1	-1	0	↓	↓	↓	68	22.5	↓	0.18
18	0	0	0	0	↓	↓	↓	45	45	↓	0.08
19	1	0	1	0	↓	↓	450	↓	67.5	↓	0.10
20	-1	0	-1	0	↓	↓	150	↓	22.5	↓	0.31
21	1	0	-1	0	↓	↓	450	↓	22.5	↓	0.10
22	-1	0	1	0	↓	↓	150	↓	67.5	↓	0.22
23	0	1	0	1	↓	↓	300	68	45	1350	0.08
24	0	-1	0	-1	↓	↓	↓	23	↓	450	0.13
25	0	1	0	-1	↓	↓	↓	68	↓	450	0.12
26	0	-1	0	1	↓	↓	↓	23	↓	1350	0.13
27	0	0	0	0	↓	↓	↓	45	↓	900	0.06

Exp.: 3.1.12 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** Feb.20/76

Objective: To obtain response surface for hydrolysis, dosage and pH near optimum.

Design: Box and Behnken Design #1 **Defining Contrasts:** -----

Test No.	Trmt.	POLYMER			DISPERSION		FLOCC'N		Supernatant
		pH	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Total Iron Conc'n (mg/l)
	a b c	c		a	b				
1	1 1 0	9.5	6	0.75	372	49	45.2	1044	0.06
2	-1 -1 0	↓	2	0.25	↓	↓	↓	↓	0.11
3	1 -1 0		6	0.25					0.12
4	-1 1 0		2	0.75					0.06
5	1 0 1	10.5	6	0.50					0.14
6	-1 0 -1	8.5	2	↓					0.06
7	1 0 -1	8.5	6						0.09
8	-1 0 1	10.5	2						0.16
9	0 1 1	10.5	4	0.75					0.11
10	0 -1 -1	8.5	↓	0.25					0.09
11	0 -1 1	10.5		0.25					0.15
12	0 1 -1	8.5		0.75					0.04
13	0 0 0	9.5		0.50					0.04
14	0 0 0	9.5		0.50					0.07
15	0 0 0	9.5		0.50					0.09

Exp.: 3.1.12a **Minewater:** 500 mg/l SO_4- **Date:** March 11/76
150 mg/l Fe

Objective: To obtain response surface for hydrolysis and dosage near optimum

Design: 3^2 with midpoint replicates **Defining Contrasts:** -----

Test No.	Treatment		POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
	a	b	Hyd. (%) a	Dose (mg/g SO_4) b	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
1	-1	-1	2	0.25	372	49	45.2	1044	0.13
2	0	-1	4	↓	↓	↓	↓	↓	0.15
3	1	-1	6	↓	↓	↓	↓	↓	0.15
4	-1	0	2	0.5	↓	↓	↓	↓	0.19
5	0	0	4	↓	↓	↓	↓	↓	0.18
6	1	0	6	↓	↓	↓	↓	↓	0.11
7	-1	1	2	0.75	↓	↓	↓	↓	0.32
8	0	1	4	↓	↓	↓	↓	↓	0.16
9	1	1	6	↓	↓	↓	↓	↓	0.14
10	0	0	4	0.5	↓	↓	↓	↓	0.15
11	0	0	4	0.5	↓	↓	↓	↓	0.20

EQUATIONS OF RESPONSE SURFACES FOR IRON NEAR OPTIMA (FIGURE 5-2)

1. Low Strength Minewater-Mixing (Exp't 3.1.10)

$$\begin{aligned}\hat{y} - 0.073 &- 0.064\,x_1 - 0.018\,x_2 - 0.026\,x_3 - 0.014\,x_4\\ &+ 0.058x_1^2 + 0.031\,x_2^2 + 0.053\,x_3^2 + 0.013\,x_4^2\\ &+ 0.020\,x_1x_2 + 0.022x_1x_3 + 0.015\,x_1x_4\\ &+ 0.012x_2x_3 - 0.010\,x_2x_4 + 0.038\,x_3x_4.\ \text{mg/l}\end{aligned}$$

x_1 = Rapid mix speed x_2 = Rapid mix time

x_3 = Flocc'n speed x_4 = Flocc'n time

Total sum of squares = 0.1087 $(\text{mg/l})^2$
Residual sum of squares = 0.0074 $(\text{mg/l})^2$

2. Low Strength Minewater - Polymer (Exp't 3.1.12)

$$\begin{aligned}\hat{y} = 0.067 &+ 0.002\,x_1 - 0.025\,x_2 + 0.035\,x_3\\ &+ 0.018\,x_1^2 + 0.003\,x_2^2 + 0.028\,x_3^2\\ &- 0.002\,x_1x_2 - 0.012\,x_1x_3 + 0.002\,x_2x_3\ \ \text{mg/l}\end{aligned}$$

x_1 = Hydrolysis x_2 = Dosage x_3 = pH

Total sum of squares = 0.0207 $(\text{mg/l})^2$
Residual sum of squares = 0.0014 $(\text{mg/l})^2$

In Figure 5-2, x_3 was set equal to zero, i.e. pH was 9.5.

3. High Strength Minewater-Mixing (Exp't 3.1.11)

$$\begin{aligned}\hat{y} = 0.320 &- 0.022\ x_1 - 0.068\ x_2 - 0.256\ x_3 - 0.040\ x_4 \\ &+ 0.118\ x_1^2 - 0.057\ x_2^2 + 0.116\ x_3^2 - 0.065\ x_4^2 \\ &- 0.050\ x_1x_2 - 0.020\ x_1x_3 + 0.038\ x_1x_4 \\ &+ 0.118\ x_2x_3 - 0.048\ x_2x_4 - 0.065\ x_3x_4 \quad \text{mg/l}\end{aligned}$$

x_1 = Rapid mix speed

x_2 = Rapid mix time

x_3 = Flocc'n speed

x_4 = Flocc'n time

Total sum of squares = 1.457 $(\text{mg/l})^2$

Residual sum of squares = 0.2799 $(\text{mg/l})^2$

4. High Strength Minewater - Polymer (Exp't 3.1.13)

Since this was a two-level design, an equation was not fitted. Plotted contours are based on observed values.

Exp.: 3.1.17 **Minewater:** 8000 mg/l SO_4^-
2400 mg/l Fe **Date:** Apr. 1/76

Objective: To investigate the effect of hydrolysis

Design: One factor varied **Defining Contrasts:** -----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
1		0	0.5	550	12	100	120	1.58
2		0	↓	↓	↓	↓	↓	1.16
3		0						2.12
4		2						0.31
5		4						0.32
6		6						0.24
7		6						0.23
8		6						0.21
9		8						0.20
10		18						0.09
11		34.5						0.09
12		34.5						0.11
13		34.5						0.14

Exp.: 3.1.19 **Minewater:** 8000 mg/SO_4- 2400 mg/l Fe **Date:** Apr. 9/76

Objective: To investigate the effect of rapid mix speed

Design: One factor varied **Defining Contrasts:** -----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
1		4	0.5	50	12	100	120	0.60
2				50				0.60
3				50				0.15
4				100				0.34
5				300				0.16
6				500				0.11
7				500				0.18
8				500				0.18
9				700				0.06
10				900				0.09
11				1100				0.09
12				1100				0.11
13		↓	↓	1100	↓	↓	↓	0.05

Exp.: 3.1.21 **Minewater:** 8000 mg/l SO_4- **Date:** Apr.12/76
2400 mg/l Fe

Objective: To investigate the effect of rapid mix time

Design: One factor varied **Defining Contrasts:**

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
1		4	0.5	550	2	100	120	0.58
2		↓	↓	↓	2	↓	↓	0.44
3		↓	↓	↓	2	↓	↓	0.32
4		↓	↓	↓	4	↓	↓	0.24
5		↓	↓	↓	7	↓	↓	0.18
6		↓	↓	↓	12	↓	↓	0.13
7		↓	↓	↓	12	↓	↓	0.11
8		↓	↓	↓	22	↓	↓	0.11
9		↓	↓	↓	42	↓	↓	0.08
10		↓	↓	↓	77	↓	↓	0.10
11		↓	↓	↓	↓	↓	↓	0.11
12		↓	↓	↓	↓	↓	↓	0.11
13		↓	↓	↓	↓	↓	↓	0.10

Exp.: 3.1.23 **Minewater:** 8000 mg/l SO_4- **Date:** Apr.15/76
2400 mg/l Fe

Objective: To investigate the effect of flocculation time

Design: One factor varied **Defining Contrasts:** -----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Total Iron Conc'n (mg/l)
1		4	0.5	550	12	100	6.9	0.42
2							6.9	0.46
3							6.9	1.40
4							17.9	0.37
5							46.4	0.29
6							120	0.22
7							120	0.16
8							120	0.17
9							311	0.12
10							804	0.18
11							2080	0.17
12							2080	0.25
13		↓	↓	↓	↓	↓	2080	0.20

Exp.: 3.1.25 **Minewater:** 8000 mg/l SO_4- 2400 mg/l Fe **Date:** Apr.13/76

Objective: To investigate the effect of flocculation speed

Design: One factor varied **Defining Contrasts:** -----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Total Iron Conc'n (mg/l)
1		4	0.5	550	12	25	120	0.68
2						25		0.51
3						25		0.62
4						39.7		0.63
5						63		0.38
6						100		0.31
7						100		0.20
8						100		0.30
9						159		0.26
10						252		0.20
11						400		0.31
12						400		0.36
13						400		0.34

Exp.: 3.1.16 Minewater: 500 mg/l SO_4- 150 mg/l Fe Date: Mar.29/76

Objective: To investigate the effect of dosage

Design: One factor varied Defining Contrasts:-----

Test No.	Treatment	POLYMER		DISPERSION		FLOCC'N		Supernatant
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Total Iron Conc'n (mg/l)
1		4	0.001	372	49	45.2	1044	2.05
2		↓	0.001	↓	↓	↓	↓	3.90
3		↓	0.01	↓	↓	↓	↓	3.40
4		↓	0.032	↓	↓	↓	↓	0.92
5		↓	0.10	↓	↓	↓	↓	0.43
6		↓	0.32	↓	↓	↓	↓	0.15
7		↓	1.0	↓	↓	↓	↓	0.06
8		↓	10	↓	↓	↓	↓	0.05
9		↓	10	↓	↓	↓	↓	0.09
10		↓	32	↓	↓	↓	↓	0.29

Exp.: 3.2.3 **Minewater:** 8000 mg/l SO_4-
2400 mg/l Zn **Date:** Feb.24/76

Objective: To obtain response surface for hydrolysis and dosage

Design: 3^2 **Defining Contrasts:** -----

Test No.	Treatment		POLYMER		DISPERSION		FLOCC'N		Supernatant Total Zinc Conc'n (mg/l)
			Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
	a	b	a	b					
1	-1	-1	2	0.1	500 ↓	12 ↓	80 ↓	90 ↓	0.23
2	0	-1	4	0.1					0.30
3	1	-1	6	0.1					0.31
4	-1	0	2	0.3					0.27
5	0	0	4	0.3					0.27
6	1	0	6	0.3					0.28
7	-1	1	2	0.5					0.23
8	0	1	4	0.5					0.27
9	1	1	6	0.5					0.25

Exp.: 3.2.2 **Minewater:** 500 mg/l SO_4- 150 mg/l Zn **Date:** Feb.27/76

Objective: To obtain response surface for hydrolysis and dosage

Design: 3^2 **Defining Contrasts:** -----

Test No.	Treatment a	Treatment b	POLYMER Hyd. (%) a	POLYMER Dose (mg/g SO_4) b	DISPERSION Speed (rpm)	DISPERSION Time (sec)	FLOCC'N Speed (rpm)	FLOCC'N Time (sec)	Supernatant Total Zinc Conc'n (mg/l)
1	-1	-1	2	0.25	372	45.2	49	1044	0.27
2	0	-1	4	0.25	↓	↓	↓	↓	0.28
3	1	-1	6	0.25	↓	↓	↓	↓	0.29
4	-1	0	2	0.50	↓	↓	↓	↓	0.26
5	0	0	4	0.50	↓	↓	↓	↓	0.25
6	1	0	6	0.50	↓	↓	↓	↓	0.33
7	-1	1	2	0.75	↓	↓	↓	↓	0.27
8	0	1	4	0.75	↓	↓	↓	↓	0.29
9	1	1	6	0.75	↓	↓	↓	↓	0.24

Exp.: 3.3.1 **Minewater:** 8000 mg/l SO_4-
2400 mg/l Cu **Date:** Mar.31/76

Objective: To obtain response surface for hydrolysis and dosage

Design: 3^2 **Defining Contrasts:** -----

Test No.	Treatment		POLYMER		DISPERSION		FLOCC'N		Supernatant Tot.Copper Conc'n (mg/l)
			Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	
	a	b	a	b					
1	-1	-1	2	0.1	550	12	100	120	4.65*
2	0	-1	4	0.1	↓	↓	↓	↓	5.10
3	1	-1	6	0.1					3.22
4	-1	0	2	0.3					3.60
5	0	0	4	0.3					4.28
6	1	0	6	0.3					6.62
7	-1	1	2	0.5					3.52
8	0	1	4	0.5					4.05
9	1	1	6	0.5					6.91

*It is the dissolved portion which makes these results so high. See results for exp'ts 3.3.5 and 3.3.9.

Exp.: 3.3.2 **Minewater:** 500 mg/l SO_4-
150 mg/l Cu **Date:** March 2/76

Objective: To obtain response surface for hydrolysis and dosage

Design: 3^2 **Defining Contrasts:** -----

Test No.	Treatment		POLYMER		DISPERSION		FLOCC'N		Supernatant
			Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Tot. Copper Conc'n (mg/l)
	a	b	a	b					
1	-1	-1	2	0.25	372	45.2	49	1044	0.21
2	0	-1	4	0.25	↓	↓	↓	↓	0.28
3	1	-1	6	0.25	↓	↓	↓	↓	0.19
4	-1	0	2	0.5	↓	↓	↓	↓	0.20
5	0	0	4	0.5	↓	↓	↓	↓	0.19
6	1	0	6	0.5	↓	↓	↓	↓	0.13
7	-1	1	2	0.75	↓	↓	↓	↓	0.24
8	0	1	4	0.75	↓	↓	↓	↓	0.17
9	1	1	6	0.75	↓	↓	↓	↓	0.16

Exp.: 3.1.37
3.1.39

Minewater: 8000 mg/l SO_4-
2400 mg/l Fe

Date: July 20/76
July 29/76

Objective: Replicate midpoint

Design: 3 replicates

Test No.	POLYMER		DISPERSION		FLOCC'N		Supernatant Particulate Metal Concentration (mg/l)		
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Fe	Zn	Cu
Exp't 3.1.37									
1	4	0.5	550	12	100	120	0.14		
2	↓	↓	↓	↓	↓	↓	0.12		
3							0.12		
Exp't 3.1.39									
1	4	0.5	550	12	100	120	0.17		
2	↓	↓	↓	↓	↓	↓	0.08		
3							0.18		

Exp.: 3.1.28a
3.1.30
Minewater: 500 mg/l SO_4-
150 mg/l Fe
Date: July 16/76
July 29/76
Objective: Replicate midpoint

Design: 3 replicates

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	DISPERSION Speed (rpm)	DISPERSION Time (sec)	FLOCC'N Speed (rpm)	FLOCC'N Time (sec)	Supernatant Particulate Metal Concentration (mg/l) Fe	Zn	Cu
Exp't 3.1.28a									
1	4	0.5	372	49	45	1044	0.03		
2	↓	↓	↓	↓	↓	↓	0.04		
3							0.02		
Exp't 3.1.30									
1	4	0.5	372	49	45	1044	0.13		
2	↓	↓	↓	↓	↓	↓	0.15		
3							0.10		

Exp.: 3.2.5
3.2.7

Minewater: 8000 mg/l SO_4-
2400 mg/l Zn

Date: July 21/76
July 22/76

Objective: To replicate midpoint

Design: 3 replicates

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	DISPERSION Speed (rpm)	DISPERSION Time (sec)	FLOCC'N Speed (rpm)	FLOCC'N Time (sec)	Supernatant Particulate Metal Concentration (mg/l) Fe	Zn	Cu
Exp't 3.2.5									
1	4	0.5	550	12	100	120		0.32	
2	↓	↓	↓	↓	↓	↓		0.23	
3								0.16	
Exp't 3.2.7									
1	4	0.5	550	12	100	120		0.28	
2	↓	↓	↓	↓	↓	↓		0.26	
3								0.23	

Exp.: 3.2.2a
3.2.8

Minewater: 500 mg/l $SO_4^=$
150 mg/l Zn

Date: Mar. 9/76
July. 29/76

Objective: To replicate midpoint

Design: 3 replicates

Test No.	POLYMER		DISPERSION		FLOCC'N		Supernatant Particulate Metal Concentration (mg/l)		
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Fe	Zn	Cu
Exp't 3.2.2a									
1	4	0.5	372	49	45	1044		0.32	
2	↓	↓	↓	↓	↓	↓		0.22	
3								0.12	
Exp't 3.2.8									
1	4	0.5	372	49	45	1044		0.21	
2	↓	↓	↓	↓	↓	↓		0.06	
3								0.06	

Exp.: 3.3.5
3.3.9

Minewater: 8000 mg/l SO_4-
2400 mg/l Cu

Date: July 21/76
Aug. 5/76

Objective: Replicate midpoint

Design: 3 replicates

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	DISPERSION Speed (rpm)	DISPERSION Time (sec)	FLOCC'N Speed (rpm)	FLOCC'N Time (sec)	Supernatant Particulate Metal Concentration (mg/l) Fe	Zn	Cu
Exp't 3.3.5									
1	4	0.5	550	12	100	120			0.60
2	↓	↓	↓	↓	↓	↓			0.10
3									0.12
Exp't 3.3.9									
1	4	0.5	550	12	100	120			0.65
2	↓	↓	↓	↓	↓	↓			0.45
3									0.43

Exp.: 3.3.2a
3.3.6
Minewater: 500 mg/l SO_4- 150 mg/l Cu
Date: Mar. 9/76 July 29/76
Objective: To replicate midpoint

Design: 3 replicates

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	DISPERSION Speed (rpm)	DISPERSION Time (sec)	FLOCC'N Speed (rpm)	FLOCC'N Time (sec)	Supernatant Particulate Metal Concentration (mg/l) Fe	Zn	Cu
Exp't 3.3.2a									
1	4	0.5	372	49	45	1044			0.33
2	↓	↓	↓	↓	↓	↓			0.34
3									0.38
Exp't 3.3.6									
1	4	0.5	372	49	45	1044			0.12
2	↓	↓	↓	↓	↓	↓			0.12
3									0.13

Exp.: 4.3
4.7
Objective: To replicate midpoint
Design: 3 replicates

Minewater: 8000 mg/l SO_4-
1200 mg/l Cu +
1200 mg/l Zn

Date: July 22/76
July 26/76

Test No.	POLYMER Hyd. (%)	Dose (mg/g SO_4)	DISPERSION Speed (rpm)	Time (sec)	FLOCC'N Speed (rpm)	Time (sec)	Supernatant Particulate Metal Concentration (mg/l) Fe	Zn	Cu
Exp't 4.3									
1	4	0.5	550	12	100	120		0.31	0.08
2	↓	↓	↓	↓	↓	↓		0.26	0.02
3								0.30	0.12
Exp't 4.7									
1	4	0.5	550	12	100	120		0.23	0.12
2	↓	↓	↓	↓	↓	↓		0.13	0.01
3								0.12	0.01

Exp.: 4.5
4.9
Minewater: 8000 mg/l SO_4-
1200 mg/l Fe +
1200 mg/l Zn
Date: July 21/76
Aug. 18/76
Objective: To replicate midpoint

Design: 3 replicates

Test No.	POLYMER Hyd. (%)	 Dose (mg/g SO_4)	DISPERSION Speed (rpm)	 Time (sec)	FLOCC'N Speed (rpm)	 Time (sec)	Supernatant Particulate Metal Concentration (mg/l) Fe	 Zn	 Cu
Exp't 4.5									
1	4	0.5	550	12	100	120	0.01	0.13	
2	↓	↓	↓	↓	↓	↓	0.04	0.13	
3							0.01	0.14	
Exp't 4.9									
1	4	0.5	550	12	100	120	0.02	0.03	
2	↓	↓	↓	↓	↓	↓	0.01	0.01	
3							0.01	0.03	

Exp.: 4.4
Minewater: 500 mg/l SO_4- 75 mg/l Cu + 75 mg/l Zn
Date: July 19/76
Objective: To replicate midpoint
Design: 3 replicates

Test No.	POLYMER		DISPERSION		FLOCC'N		Supernatant Particulate Metal Concentration (mg/l)		
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Fe	Zn	Cu
1	4	0.5	372	49	45	1044		0.46	0.01
2	4	0.5	372	49	45	1044		0.27	0.02
3	4	0.5	372	49	45	1044		0.06	0.01

Exp.: 4.6
Minewater: 500 mg/l SO_4- 75 mg/l Fe + 75 mg/l Zn
Date: July 16/76

Objective: To replicate midpoint

Design: 3 replicates

Test No.	POLYMER		DISPERSION		FLOCC'N		Supernatant Particulate Metal Concentration (mg/l)		
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Speed (rpm)	Time (sec)	Fe	Zn	Cu
1	4	0.5	372	49	45	1044	0.01	0.24	
2	4	0.5	372	49	45	1044	0.01	0.01	
3	4	0.5	372	49	45	1044	0.02	0.06	

APPENDIX F - MECHANISTIC MODELLING STUDIES: EXPERIMENTAL CONDITIONS AND RESULTS

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Exp.: 3.1.27 **Minewater:** 8000 mg/l SO_4- 2400 mg/l Fe **Date:** May 3/76

Objective: Initial response surface - single stage mixing

Design: 3^2 with replicates

Test No.	Treatment a	Treatment b	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm) a	MIXING Time (sec) b	Supernatant Total Iron Conc'n (mg/l)
1	-1	-1	4	0.5	100	10	1.23*
2	0	-1			300	10	0.28*
3	+1	-1			500	10	0.25
4	-1	0			100	54	0.51*
5	0	0			300	54	0.17*
6	+1	0			500	54	0.18
7	-1	+1			100	98	0.38*
8	0	+1			300	98	0.11*
9	+1	+1			500	98	0.33
10	+1	-1			500	10	0.21
11	+1	-1	↓	↓	500	10	0.23

*These results were used later in modelling

Exp.: 3.1.29 **Minewater:** 8000 mg/l SO_4- 2400 mg/l Fe **Date:** May 19/76

Objective: Path of steepest ascent - single stage mixing

Design:

Test No.	Treatment	POLYMER		MIXING		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1		4	0.5	350	59	0.32
2		↓	↓	350	70	0.25
3				400	70	0.41
4				300	70	0.23
5				350	81	0.18

Exp.: 3.1.31 Minewater: 8000 mg/l $SO_4^=$ Date: June 8/76
2400 mg/l Fe

Objective: Path of steepest ascent - single stage mixing

Design:

Test No.	Treatment	POLYMER		MIXING		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1		4	0.5	295	124	0.16
2		↓	↓	290	150	0.19
3		↓	↓	285	176	0.17
4		↓	↓	280	202	0.25
5		↓	↓	275	228	0.20

Exp.: 3.1.33 **Minewater:** 8000 mg/l SO_4- 2400 mg/l Fe **Date:** June 22/76

Objective: Path of steepest ascent - single stage mixing

Design:

Test No.	Treatment	POLYMER		MIXING		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1		4	0.5	260	300	0.20
2		↓	↓	240	400	0.20
3		↓	↓	220	500	0.21
4		↓	↓	200	600	0.21
5		↓	↓	180	700	0.17

Exp.: 3.1.35 **Minewater:** 8000 mg/l SO_4 - 2400 mg/l Fe **Date:** July 12/76

Objective: Response surface near optimum - single stage mixing

Design: 3^2

Test No.	Treatment a	Treatment b	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm) a	MIXING Time (sec) b	Supernatant Total Iron Conc'n (mg/l)
1	-1	-1	4	0.5	100	125	0.54
2	0	-1			280	125	0.30
3	+1	-1			460	125	0.52
4	-1	0			100	175	0.71
5	0	0			280	175	0.48
6	+1	0			460	175	0.92
7	-1	+1			100	225	0.73
8	0	+1			280	225	0.84
9	+1	+1	↓	↓	460	225	0.78

Exp.: 3.1.37 **Minewater:** 8000 mg/l SO_4-
2400 mg/l Fe
Date: Aug. 3/76

Objective: Path of steepest ascent - single stage mixing

Design:

Test No.	Treatment	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Total Iron Conc'n (mg/l)
1		4	0.5	280	125	0.33
2		4	0.5	280	175	0.29
3		4	0.5	280	225	0.31

Exp.: 3.1.18 **Minewater:** 500 mg/l SO_4-
150 mg/l Fe **Date:** May 4/76

Objective: Initial response surface - single stage mixing

Design: 3^2

Test No.	Treatment a	Treatment b	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm) a	MIXING Time (sec) b	Supernatant Total Iron Conc'n (mg/l)
1	-1	-1	4	0.5	45	50	2.04
2	0	-1	↓	↓	209	50	1.71* **
3	+1	-1	↓	↓	372	50	0.77 **
4	-1	0	↓	↓	45	224	1.88
5	0	0	↓	↓	209	224	0.66* **
6	+1	0	↓	↓	372	224	1.47 **
7	-1	+1	↓	↓	45	398	0.86
8	0	+1	↓	↓	209	398	0.59* **
9	+1	+1	↓	↓	372	398	3.50 **

* ** These results were used later in modelling

Exp.: 3.1.20 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** May 18/76

Objective: Path of steepest ascent - single stage mixing

Design:

Test No.	Treatment	POLYMER		MIXING		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1		4	0.5	200	450	0.43* **
2				190	500	0.62 **
3				180	550	0.50 **
4				170	600	0.46 **
5		↓	↓	160	650	0.51 **

*
** These results were used later in modelling

Exp.: 3.1.22 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** June 7/76

Objective: Path of steepest ascent - single stage mixing

Design:

Test No.	Treatment	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Total Iron Conc'n (mg/l)
1		4	0.5	100	1070	0.22 **
2				140	790	0.28 **
3				130	860	0.23 **
4				90	1140	0.29
5		↓	↓	110	1000	0.21 **

** These results were used later in modelling

Exp.: 3.1.24 **Minewater:** 500 mg/l SO_4- 150 mg/l Fe **Date:** June 21/76

Objective: Path of steepest ascent - single stage mixing

Design:

Test No.	Treatment	POLYMER		MIXING		Supernatant Total Iron Conc'n (mg/l)
		Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1		4	0.5	70	1250	0.21
2		↓	↓	60	1323	0.14
3		↓	↓	50	1400	0.13
4		↓	↓	40	1480	0.30
5		↓	↓	30	1550	0.22

Exp.: 3.1.26 Minewater: 500 mg/l SO_4-
150 mg/l Fe
Date: July 12/76

Objective: Response surface near optimum - single stage mixing

Design: 3^2

Test No.	Treatment		POLYMER		MIXING		Supernatant Total Iron Conc'n (mg/l)
	a	b	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm) a	Time (sec) b	
1	-1	-1	4	0.5	45	850	0.62
2	0	-1	↓	↓	129	850	0.87 **
3	+1	-1			372	850	7.63 **
4	-1	0			45	1031	0.70
5	0	0			129	1031	0.69 **
6	+1	0			372	1031	9.20 **
7	-1	+1			45	1250	0.19
8	0	+1			129	1250	1.10 **
9	+1	+1			372	1250	9.60 **

** These results were used later in modelling

Exp.: 3.1.28 Minewater: 500 mg/l SO_4- 150 mg/l Fe Date: Aug.3/76

Objective: Path of steepest ascent - single stage mixing

Design:

Test No.	Treatment	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Total Iron Conc'n (mg/l)
1		4	0.5	129	850	0.29 **
2		4	0.5	129	1031	0.27 **
3		4	0.5	129	1250	0.45 **

** These results were used later in modelling

Exp.: 6.1 **Minewater:** 2103 mg/l SO_4- 631 mg/l Zn **Date:** June 16/76

Objective: Model Discrimination

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1	4	0.5	209	1000	0.35
2	↓	↓	↓	↓	0.40
3	↓	↓	↓	↓	0.26
4	↓	↓	↓	↓	0.36

Exp.: 6.2
6.2a
6.2c

Minewater: 500 mg/l SO4-
150 mg/l Zn

Date: June 29/76
July 14/76
July 15/76

Objective: Determine variance

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Particulate Zinc Concentration (mg/l)
Exp't 6.2					
1	4	0.5	45	5	1.70
2			45	50	0.80
3			110	1000	0.38
1a			45	5	2.15
2a			45	50	1.03
3a			110	1000	0.22
Exp't 6.2a					
1			45	5	1.70
2			45	50	1.37
3			110	1000	0.55
Exp't 6.2c					
1			45	5	1.64
2			45	50	1.20
3			110	1000	0.48
1a			45	5	1.62
2a			45	50	1.28
3a			110	1000	0.75

Exp.: 6.3 **Minewater:** 527 mg/l SO_4- 158 mg/l Zn **Date:** June 30/76

Objective: Model discrimination

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Particulate Zinc Concentration (mg/l)
1	4	0.5	209	1000	0.39
2	4	0.5	209	1000	0.32

Exp.: 6.4 Minewater: 8373 mg/l SO_4- 2512 mg/l Zn Date: July 16/76

Objective: Model discrimination

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Particulate Zinc Concentration (mg/l)
1	4	0.5	209	251	0.02
2	4	0.5	209	251	0.08

Exp.: 6.5 Minewater: 5285 mg/l SO4-
1585 mg/l Zn
Date: July 26/76

Objective: Model discrimination

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose ($mg/g\ SO_4$)	Speed (rpm)	Time (sec)	
1	4	0.5	209	10	0.47
2	4	0.5	209	10	0.44

Exp.: 6.7 Minewater: 1327 mg/l SO_4- Date: Aug. 18/76
398 mg/l Zn

Objective: Model discrimination

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Particulate Zinc Concentration (mg/l)
1	4	0.5	209	16	0.03
2	4	0.5	209	16	0.06

Exp.: 6.11 **Minewater:** 333 mg/l SO_4- 100 mg/l Zn **Date:** Sept.20/76

Objective: Model discrimination

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1	4	0.5	209	25	0.59
2	4	0.5	209	25	0.70
3	4	0.5	209	25	1.10

Exp.: 6.12 Minewater: 1327 mg/l SO_4- 398 mg/l·Zn Date: Sept.20/76

Objective: Model discrimination

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1	4	0.5	209	10	0.29
2	4	0.5	209	10	0.43
3	4	0.5	209	10	0.44

Exp.: 6.13 Minewater: 333 mg/l SO_4- 100 mg/l Zn Date: Sept.27/76

Objective: Model discrimination

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1	4	0.5	209	10	1.19
2	4	0.5	209	10	1.58
3	4	0.5	209	10	1.78

Exp.: 6.14
6.15
6.16
Minewater: 333 mg/l SO_4-
100 mg/l Zn
Date: Oct. 15/76
Oct. 18/76
Oct. 25/76

Objective: Parameter estimation

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Particulate Zinc Concentration (mg/l)
Exp't 6.14					
1	4	0.5	209	10	1.08
2	↓	↓	↓	↓	1.85
3	↓	↓	↓	↓	1.86
Exp't 6.15					
1	↓	↓	↓	↓	0.90
2	↓	↓	↓	↓	1.94
3	↓	↓	↓	↓	2.40
Exp't 6.16					
1	↓	↓	↓	↓	1.12
2	↓	↓	↓	↓	1.46
3	↓	↓	↓	↓	1.57

Exp.: 6.17
6.18
6.19

Minewater: 8373 mg/l SO_4^{-}
2512 mg/l Zn

Date: Oct. 25/76
Oct. 29/76
Oct. 29/76

Objective: Parameter estimation

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
Exp't 6.17					
1	4	0.5	209	10	0.08
2	↓	↓	↓	↓	0.01
3	↓	↓	↓	↓	0.10
Exp't 6.18					
1	↓	↓	↓	63	0.10
2	↓	↓	↓	↓	0.07
3	↓	↓	↓	↓	0.08
Exp't 6.19					
1	↓	↓	↓	398	0.10
2	↓	↓	↓	↓	0.08
3	↓	↓	↓	↓	0.03

Exp.: 6.21 **Minewater:** 6637 mg/l SO_4 **Date:** Nov. 4/76
1991 mg/l Zn

Objective: Parameter estimation

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1	4	0.5	209	32	0.01
2	4	0.5	209	32	0.05
3	4	0.5	209	32	0.04

Exp.: 6.22 **Minewater:** 10571 mg/l SO_4- **Date:** Nov. 4/76
6.23 3155 mg/l Zn Nov. 4/76

Objective: Parameter estimation

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
Exp't	6.22				
1	4	0.5	209	50	0.09
2	↓	↓	↓	50	0.04
3	↓	↓	↓	50	0.06
Exp't	6.23				
1	↓	↓	↓	199	0.02
2	↓	↓	↓	199	0.03
3	↓	↓	↓	199	0.01

Exp.: 6.24 Minewater: 1333 mg/l SO_4- Date: Nov. 25/76
400 mg/l Zn

Objective: To obtain data for model confirmation

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1	4	0.5	209	25	0.46
2	↓	↓	↓	35	0.38
3	↓	↓	↓	50	0.24
4	↓	↓	↓	75	0.20

Exp.: 6.25 **Minewater:** 667 mg/l SO_4- 200 mg/l Zn **Date:** Nov. 25/76

Objective: To obtain data for model confirmation

Test No.	POLYMER		MIXING		Supernatant Particulate Zinc Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	
1	4	0.5	209	25	0.37
2	↓	↓	↓	35	0.38
3	↓	↓	↓	50	0.46
4	↓	↓	↓	75	0.38

Exp.: 3.1.49 **Minewater:** 200 mg/l SO_4-
600 mg/l Fe **Date:** Dec. 7/76

Objective: To obtain data for model fitting (Table 5-18)

Test No.	POLYMER		MIXING		Supernatant Particulate Metal Concentration (mg/l)
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Fe
1	4	1.67	100	10	4.25
2	↓	↓	100	100	1.32
3			100	150	0.89
5			209	100	0.39
7			300	10	1.52
8			300	100	0.21

The additional data used in Table 5-18 are from the following sources:

N_o=150 -tests marked with an asterisk in Expt's 3.1.18 and 3.1.20 (single stage mixing). These total conc'ns were converted to particulate conc'ns by subtracting a mean dissolved concentration of 0.10 mg/l.

N_o=2400-tests marked with an asterisk in Exp't 3.1.27 (single stage mixing). Total to particulate conversion as above.

N_o=3922-results from Exp't SCL-2.

Exp.: SCL-2[1]
SCL-3

Minewater: Synthetic Crotch Lake:
9819 mg/l SO_4
3922 mg/l Fe

Date: Nov. 9/76

Objective: To determine effect of metal type

Test No.	POLYMER		MIXING		Supernatant Particulate Metal Concentration (mg/l)	
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Fe	Cu
SCL-2						
1	4	1.67	209	10	1.10	
2				20	0.62	
3				50	0.42	
4				100	0.36	
SCL-3						
1	4	1.67	209	10	0.73	
2				20	0.34	
3				50	0.12	
4				100	0.04	

[1] In Exp't SCL-2 all iron was initially Fe^{+3}

In Exp't SCL-3 half the iron was initially Fe^{+2}

Exp.: 3.1.47 Minewater: 500 mg/l SO_4- Date: Dec. 8/76
150 mg/l Fe

Objective: To obtain data for floc breakup modelling

Test No.	POLYMER		MIXING		Supernatant Particulate Metal Concentration (mg/l)	
	Hyd. (%)	Dose (mg/g SO_4)	Speed (rpm)	Time (sec)	Fe	Cu
1	4	0.5	129	850	0.58	
2			372	850	6.19	
3			129	1031	0.93	
4			372	1031	8.75	
5			129	1250	0.68	
6			372	1250	9.26	
7			220	800	1.86	
8			220	1200	3.52	
9			220	1600	4.72	
10			250	600	1.70	
11			310	400	2.10	
12				800	4.71	
13				1200	6.37	
14	↓	↓	↓	1600	7.55	

The additional data used for floc breakup modelling (Figure 5-11) were obtained from the following single stage mixing experiments: 3.1.18, 3.1.20, 3.1.22, 3.1.26, 3.1.28. The values used are indicated by double asterisks in those listings. They were converted from total to particulate metal concentrations by subtracting a mean dissolved metal concentration of 0.10 mg/l.

Exp.: 3.51
3.36
3.53
3.55

Minewater: as indicated

Date: Dec. 2/76
Dec.20/76

Objective: To obtain copper data for modelling

Test No.	POLYMER Hyd. (%)	POLYMER Dose (mg/g SO_4)	MIXING Speed (rpm)	MIXING Time (sec)	Supernatant Particulate Metal Concentration (mg/l) Fe	Supernatant Particulate Metal Concentration (mg/l) Cu
Exp't 3.51 (Minewater: 2000 mg/l SO_4-600 mg/l Cu)						
1	4	1.67	209	10		3.89
2				100		1.50
3				30		2.72
4	↓	↓	↓	60		2.26
Exp't 3.53 (Minewater: 2000 mg/l SO_4-600 mg/l Cu)						
1	4	1.67	209	20		3.04
Exp't 3.36 (Minewater: 500 mg/l SO_4-150 mg/l Cu)						
1	4	1.67	209	20		3.02
Exp't 3.55 (Minewater: 8000 mg/l SO_4-2400 mg/l Cu)						
1	4	1.67	209	20		0.96

Exp.: Q-1 **Minewater:** 494 mg/l SO_4 **Date:** Oct. 27/76
64 mg/l Fe
(Actual Quirke #2)

Objective: To obtain data for model confirmation

Test No.	POLYMER		MIXING		Supernatant Partic. Metal Concentration (mg/l)			
	Hyd. (%)	Dose (mg/g Me)	Speed (rpm)	Time (sec)	Fe	Zn	Cu	Total
1	4	1.67*	209	10	1.69			
2	↓	↓	↓	100	0.58			
3	↓	↓	↓	30	0.69			
4	↓	↓	↓	1000	1.02			

* equivalent to 0.5 mg/g SO_4
when Me/SO_4 = 0.3

Exp.: CL-1 **Minewater:** Crotch Lake (Actual) **Date:** Oct.27/76
9819 mg/l SO_4
3922 mg/l Fe

Objective: To obtain data for model confirmation

Test No.	POLYMER		MIXING		Supernatant Partic. Metal Concentration (mg/l)			
	Hyd. (%)	Dose (mg/g Me)	Speed (rpm)	Time (sec)	Fe	Zn	Cu	Total
2	4	1.67	209	100	0.01			
3	4	1.67	209	10	3.50			
4	4	1.67	209	20	0.80			

*equivalent to 0.5 mg/g SO_4 when $Me/SO_4 = 0.3$

Exp.: G-1 **Minewater:** GECo 2142 mg/l SO_4 **Date:** Nov. 9/76
(Actual) 149 mg/l Fe
205 mg/l Zn
13 mg/l Cu

Objective: To obtain data for model confirmation

Test No.	POLYMER Hyd. (%)	Dose (mg/g Me)	MIXING Speed (rpm)	Time (sec)	Supernatant Partic. Metal Concentration (mg/l) Fe	Zn	Cu	Total
1	4	1.67	209	10	0.36	0.80	0.06	1.22
2	↓	↓	↓	20	0.20	0.56	0.04	0.80
3	↓	↓	↓	100	0.02	0.15	<0.01	0.17
4	↓	↓	↓	70	0.07	0.28	0.02	0.37

*equivalent to 0.5 mg/g SO_4 when $Me/SO_4 = 0.3$

Exp.: B-1 **Minewater:** Actual Brunswick #6 **Date:** Nov.18/76

4454 mg/l SO_4
644 mg/l Fe
390 mg/l Zn
37 mg/l Cu
186 mg/l Mn

Objective: To obtain data for model confirmation

Test No.	POLYMER		MIXING		Supernatant Partic. Metal Concentration (mg/l)			
	Hyd. (%)	Dose (mg/g Me)	Speed (rpm)	Time (sec)	Fe	Zn	Cu	Total
1	4	1.67	209	10	0.91	0.55	<0.01	1.46
2	↓	↓	↓	100	0.01	0.02	↓	0.03
3	↓	↓	↓	20	0.54	0.33	↓	0.87
4	↓	↓	↓	50	0.16	0.10	↓	0.26

*equivalent to 0.5 mg/g SO_4 when $Me/SO_4 = 0.3$

PARAMETER ESTIMATES[1] AT EACH STAGE OF DISCRIMINATION FOR SIMPLE AGGREGATION MODELS

EXP'T NO.	MODEL			
	Von Smoluchowski	Argaman-Kaufman	LaMer-Healy	LaMer-Healy (Modified)
1	----	----	----	----
2	0.3080×10^{-5}	0.6506×10^{-5}	0.7263×10^{-3}	0.3766×10^{-4}
3	"	"	0.7206×10^{-3}	"
4	"	"	0.1180×10^{-1}	"
5	"	"	0.3684×10^{-1}	0.8134×10^{-4}
6	0.5640×10^{-5}	0.1073×10^{-4}	0.3547×10^{-1}	0.8327×10^{-4}
7	0.9782×10^{-5}	0.2076×10^{-4}	0.3063×10^{-1}	0.2000×10^{-3}
8	"	"	"	"
9	0.2176×10^{-4}	0.4519×10^{-4}	0.2262×10^{-1}	0.2839×10^{-3}

---

[1] For the models as they appear in Table 3-1

PARAMETER ESTIMATES FOR DISCRIMINATION WITH FLOC BREAKUP MODELS

1. The parameter estimates did not change during discrimination since all data were at hand initially.
2. The parameters are for the models as they appear in Table 3-1 (von Smoluchowski model) and Table 3-2 (other models).

Von Smoluchowski Model

$$K' = 0.2176 \times 10^{-4}$$

Argaman-Kaufman Model

$K_7 = 0.2296 \times 10^{-4}$ $K_9 = 0.3639 \times 10^{0}$

LaMer-Healy Model

$K_{11} = 0.2304 \times 10^{-3}$ $K_{12} = 0.2139 \times 10^{+5}$

LaMer-Healy Model (Modified)

$K_5 = 0.2152 \times 10^{-3}$ $K_{14} = 0.1411 \times 10^{-3}$

FLOC DENSITY AS A FUNCTION OF MINEWATER STRENGTH

MINEWATER STRENGTH Fe (mg/l)	SO$_4$ (mg/l)	NO. DENSITY MEASUREMENTS	FLOC DENSITY (g/cm^3) $\bar{x}$	σ
20	100	6	0.9992	0.000612
200	1000	15	1.000587	0.000414
2000	10000	6	1.0140	0.001095

APPENDIX G - COMPUTER PROGRAMMES

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```
C-------------LINEAR LEAST SQUARES AND CANONICAL REDUCTION--UP TO 5 VARIABLE
C-------------50 OBSERVATIONS AND 5 RESPONSES
C-------------NVAR=NO. OF INDEPENDENT VARIABLES
C-------------NRESP=NO. OF DEPENDENT VARIABLES OR RESPONSES
C-------------NY=NO. OF OBSERVATIONS IN EACH RESPONSE
C-------------REQUIRES SUBROUTINE EIGEN IN THE CCIW PROGTAMME
C-------------LIBRARY
C-------------WRITTEN BY J F MACGREGOR
C-------------MODIFIED TO RUN AT CCIW BY P.M HUCK  JAN 1976
      DIMENSION XPRIM(25,50),XX(25,25),XY(25,5),Y(50,5),BETA(5,5),B1(5),
     1          A(15),R(25),RES(50),YCA(50)
      READ(60,2) EXPTNO
      READ(60,1)NVAR,NY,NRESP
      NP1=NVAR+1
      NB=NP1*(NP1+1)/2
      NVAR1=NVAR-1
         DO 5 I=2,NP1
    5    READ(60,10)(XPRIM(I,J),J=1,NY)
         DO 7 J=1,NRESP
    7    READ(60,10)(Y(I,J),I=1,NY)
         DO 6 J=1,NY
    6    XPRIM(1,J)=1.0
C-------------
C-------------INCLUDE ANY X OR Y TRANSFORMATIONS HERE
C-------------
C-------------SET UP REMAINDER OF XPRIME MATRIX
      DO 15 I=1,NVAR
         DO 15 J=1,NY
            M=NP1+I
   15 XPRIM(M,J)=XPRIM(I+1,J)*XPRIM(I+1,J)
      L=0
      DO 20 I=2,NVAR
         II=I+1
         DO 20 J=II,NP1
             L=L+1
             DO 21 K=1,NY
                 M=NP1+NVAR+L
   21        XPRIM(M,K)=XPRIM(I,K)*XPRIM(J,K)
   20 CONTINUE
      WRITE(61,3) EXPTNO
      WRITE(61,23)
      DO 24 J=1,NY
   24 WRITE(61,25)(XPRIM(I,J),I=1,NB)
C-------------SOLVE NORMAL EQUATIONS
C-------------CALCULATE XPRIME-Y MATRIX
      DO 40 I=1,NB
         DO 40 J=1,NB
             SUMXX=0.0
             DO 41 K=1,NY
   41        SUMXX=XPRIM(I,K)*XPRIM(J,K)+SUMXX
   40 XX(I,J)=SUMXX
      WRITE(61,42)
      DO 43 I=1,NB
   43 WRITE(61,53)(XX(I,J),J=1,NB)
      DO 45 J=1,NRESP
         DO 45 I=1,NB
             SUMXY=0.0
             DO 46 K=1,NY
   46        SUMXY=SUMXY+XPRIM(I,K)*Y(K,J)
   45 XY(I,J)=SUMXY
C-------------FIND LEAST SQUARES PARAMETERS
      K=NRESP
      CALL MATINV(XX,NB,XY,K,DET,25)
      WRITE(61,50)
      DO 56 I=1,NB
   56 WRITE(61,51)(I,(XY(I,J),J=1,NRESP))
      WRITE(61,52)
      DO 55 I=1,NB
   55 WRITE(61,53)(XX(I,J),J=1,NB)
      WRITE(61,54)DET,K
      DO 65 KK=1,NRESP
         WRITE(61,66)KK
C-------------CALCULATE RESIDUALS AND SSR
        SSR=0.0
         DO 60 J=1,NY
             SUM=0.0
             DO 61 I=1,NB
   61        SUM=SUM+XY(I,KK)*XPRIM(I,J)
```

<u>NOTE:</u> A programme similar to this was used for Exp't 2.1, which had 7 independent variables.

```
            YCA(J)=SUM
            RES(J)=Y(J,KK)-YCA(J)
            SSR=SSR+RES(J)*RES(J)
   60     CONTINUE
          WRITE(61,62)
          WRITE(61,63)(Y(J,KK),YCA(J),RES(J),J=1,NY)
          WRITE(61,64)SSR
C-------------
C-------------CANONICAL ANALYSIS
C-------------
C------------- SET UP BETA MATRIX
      DO 200 I=1,NVAR
      M=NP1+I
  200 BETA(I,I)=XY(M,KK)
      L=0
      DO 201 I=1,NVAR1
         II=I+1
         DO 201 J=II,NVAR
            L=L+1
            M=NP1+NVAR+L
            BETA(I,J)=XY(M,KK)/2.0
            BETA(J,I)=BETA(I,J)
  201 CONTINUE
C-------------LOCATE CENTRE CONDITIONS
      DO 205 I=1,NVAR
  205 B1(I)=-XY(I+1,KK)/2.0
      K=1
      CALL MATINV(BETA,NVAR,B1,K,DET,5)
      BXS=0.0
      DO 206 K=1,NVAR
  206 BXS=BXS+XY(K+1,KK)*B1(K)
      YS=XY(1,KK)+BXS*0.5
      WRITE(61,210)
      WRITE(61,211) YS,(I,B1(I),I=1,NVAR)
C-------------
C-------------CALCULATE EIGENVALUES AND EIGENVECTORS
C-------------USE IS MADE OF THE FACT THAT THE SAME TRANSFORMATION TAKES
C-------------BOTH A AND A-INVERSE INTO ITS CANONICAL FORM
      L=0
      DO 300 J=1,NVAR
         DO 300 I=1,J
         L=L+1
  300 A(L)=BETA(I,J)
      CALL EIGEN(A,R,NVAR,0)
      L=0
      DO 301 J=1,NVAR
         DO 301 I=1,NVAR
            L=L+1
  301 BETA(I,J)=R(L)
C-------------BETA NOW CONTAINS EIGENVECTORS
C-------------A NOW CONTAINS THE INVERSE EIGENVALUES ON DIAGONAL
      WRITE(61,220)
      DO 230 K=1,NVAR
         I=K*(K+1)/2
         A(I)=1.0/A(I)
  230 WRITE(61,221) K,A(I)
      WRITE(61,222)
      DO 223 I=1,NVAR
  223 WRITE(61,224) (BETA(I,J),J=1,NVAR)
   65 CONTINUE
    1 FORMAT(3I5)
    2 FORMAT(2A4)
    3 FORMAT(1H1,≠EXPERIMENT NUMBER     ≠,2A4)
   10 FORMAT(8F10.5)
   20 FORMAT(1H1,40X,≠X MATRIX≠,//)
   25 FORMAT(1H0,F9.3,11F10.3/12F10.3)
   42 FORMAT(1H1,20X,≠XPRIME-X MATRIX≠//)
   50 FORMAT(1H1,10X,≠PARAMETERS≠//)
   51 FORMAT(1H0,5X,I2,5(8X,E12.4))
   52 FORMAT(//≠1≠,20X,≠XPRIME-X INVERSE≠//)
   53 FORMAT(1H0,E14.3,7E15.3/8E15.3)
   54 FORMAT(///1H0,≠DETERMINANT=≠E16.5,10X,≠NO. OF DEPENDENT ROWS = ≠I4
     1)
   62 FORMAT(1H0,14X,≠Y(J)≠,16X,≠YCA(J)≠,15X,≠RESIDUALS≠/)
   63 FORMAT(≠0≠,3(10X,E12.3))
   64 FORMAT(//1H0,≠RESIDUAL SUM OF SQUARES = ≠,F15.4)
   65 FORMAT(1H1,10X,≠ANALYSIS OF RESPONSE NUMBER ≠I2///)
  210 FORMAT(1H1,10X,17HCENTRE CONDITIONS//)
```

```
0157        211 FORMAT(10X,3HYS=E15.4//(1H0,4X,3HXS(I2,3H) =E15.4))
0158        220 FORMAT(////19X,11HEIGENVALUES/)
0159        221 FORMAT(1H0,10X,I2,5X,E12.4)
0160        222 FORMAT(////10X,32HEIGENVECTORS (STORED COLUMNWISE)/)
0161        224 FORMAT (1H0,5(5X,E10.3))
0162            STOP
0163            END

   USASI FORTRAN DIAGNOSTIC RESULTS FOR FTN.MAIN

         NO ERRORS
```

```
      SUBROUTINE MATINV(A,NVAR,B,NB,DETERM,MA)
      DIMENSION A(MA,MA),B(MA,NB),INDEX(50,2)
      EQUIVALENCE (T,SWAP,PIVOT),(K,L1)
C
C     INITIALIZATION
C
      DETERM=1.0
      DO 20 J=1,50
   20 INDEX(J,1)=0
C
C     SEARCH FOR PIVOT ELEMENT
C
      I=0
      IRANK=0
   40 AMAX=-1.
      DO 105 J=1,NVAR
      IF (INDEX(J,1)) 105,60,105
   60 DO 100 K=1,NVAR
      IF (INDEX(K,1)) 100,80,100
   80 T= ABS(A(J,K))
      IF (T-AMAX) 100,100,85
   85 IROW=J
      ICOLUM=K
      AMAX=T
  100 CONTINUE
  105 CONTINUE
      IF(AMAX) 720,720,110
  110 INDEX (ICOLUM,1)=IROW
C
C     INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
C
      IF (IROW-ICOLUM) 140,310,140
  140 DETERM=-DETERM
      DO 200 L=1,NVAR
      SWAP=A(IROW,L)
      A(IROW,L)=A(ICOLUM,L)
  200 A(ICOLUM,L)=SWAP
      DO 250 L=1, NB
      SWAP=B(IROW,L)
      B(IROW,L)=B(ICOLUM,L)
  250 B(ICOLUM,L)=SWAP
      I=I+1
      INDEX(I,2)=ICOLUM
  310 PIVOT=A(ICOLUM,ICOLUM)
      DETERM=PIVOT*DETERM
      IRANK=IRANK+1
C
C     DIVIDE PIVOT ROW BY PIVOT ELEMENT
C
      A(ICOLUM,ICOLUM)=1.0
      PIVOT=A(ICOLUM,ICOLUM)/PIVOT
      DO 350 L=1,NVAR
  350 A(ICOLUM,L)=A(ICOLUM,L)*PIVOT
      DO 370 L=1,NB
  370 B(ICOLUM,L)=B(ICOLUM,L)*PIVOT
C
C     REDUCE NON-PIVOT ROWS
C
      DO 550 L1=1,NVAR
      IF (L1-ICOLUM) 400,550,400
  400 T=A(L1,ICOLUM)
      A(L1,ICOLUM)=0.0
      DO 450 L=1,NVAR
  450 A(L1,L)=A(L1,L)-A(ICOLUM,L)*T
      DO 500 L=1,NB
  500 B(L1,L)=B(L1,L)-B(ICOLUM,L)*T
  550 CONTINUE
      GO TO 40
C
C     INTERCHANGE COLUMNS
C
  630 ICOLUM=INDEX(I,2)
      IROW=INDEX(ICOLUM,1)
      DO 705 K=1,NVAR
      SWAP=A(K,IROW)
      A(K,IROW)=A(K,ICOLUM)
  705 A(K,ICOLUM)=SWAP
      I=I-1
```

```
      720 IF(I) 740,740,630                                         MAT
     740  NB=NVAR-IRANK                                             MAT
          RETURN                                                    MAT
          END                                                       MAT

   USASI FORTRAN DIAGNOSTIC RESULTS FOR MATINV

        NO ERRORS

IB,PDIF
```

```
EXPERIMENT NUMBER   3127

                X MATRIX

 1.000    -1.000    -1.000     1.000     1.000     1.000
 1.000     0.000    -1.000     0.000     1.000     0.000
 1.000     1.000    -1.000     1.000     1.000    -1.000
 1.000    -1.000     0.000     1.000     0.000     0.000
 1.000     0.000     0.000     0.000     0.000     0.000
 1.000     1.000     0.000     1.000     0.000     0.000
 1.000    -1.000     1.000     1.000     1.000    -1.000
 1.000     0.000     1.000     0.000     1.000     0.000
 1.000     1.000     1.000     1.000     1.000     1.000

          XPRIME-X MATRIX

 0.900E+01    0.000E+00    0.000E+00    0.600E+01    0.600E+01    0.000E+00
 0.000E+00    0.600E+01    0.000E+00    0.000E+00    0.000E+00    0.000E+00
 0.000E+00    0.000E+00    0.600E+01    0.000E+00    0.000E+00    0.000E+00
 0.600E+01    0.000E+00    0.000E+00    0.600E+01    0.400E+01    0.000E+00
 0.600E+01    0.000E+00    0.000E+00    0.400E+01    0.600E+01    0.000E+00
 0.000E+00    0.000E+00    0.000E+00    0.000E+00    0.000E+00    0.400E+01
```

```
PARAMETERS

   1          0.1078E+00
   2         -0.2267E+00
   3         -0.1567E+00
   4          0.2833E+00
   5          0.1333E+00
   6          0.2325E+00

           XPRIME-X INVERSE

    0.556E+00      0.000E+00      0.000E+00     -0.333E+00     -0.333E+00      0.000E+00
    0.000E+00      0.167E+00      0.000E+00      0.000E+00      0.000E+00      0.000E+00
    0.000E+00      0.000E+00      0.167E+00      0.000E+00      0.000E+00      0.000E+00
   -0.333E+00      0.000E+00      0.000E+00      0.500E+00      0.000E+00      0.000E+00
   -0.333E+00      0.000E+00      0.000E+00      0.000E+00      0.500E+00      0.000E+00
    0.000E+00      0.000E+00      0.000E+00      0.000E+00      0.000E+00      0.250E+00

DETERMINANT=     0.5184E+04          NO. OF DEPENDENT ROWS =
```

```
ANALYSIS OF RESPONSE NUMBER 1

     Y(J)                  YCA(J)               RESIDUALS

  0.123E+01             0.114E+01             0.897E-01
  0.280E+00             0.398E+00            -0.118E+00
  0.250E+00             0.222E+00             0.281E-01
  0.510E+00             0.618E+00            -0.108E+00
  0.200E+00             0.108E+00             0.922E-01
  0.180E+00             0.164E+00             0.156E-01
  0.380E+00             0.362E+00             0.181E-01
  0.110E+00             0.844E-01             0.256E-01
  0.133E+01             0.137E+01            -0.436E-01

RESIDUAL SUM OF SQUARES =         0.0460

    CENTRE CONDITIONS

    YS=      0.5061E-01

  XS( 1) =   0.2475E+00
  XS( 2) =   0.3717E+00

        EIGENVALUES

    1       0.6999E-01
    2       0.3467E+00

  EIGENVECTORS (STORED COLUMNWISE)

  0.478E+00     0.878E+00
 -0.878E+00     0.478E+00

STOP
```

```
C-------------X IS THE MATRIX OF EXPERIMENTAL CONDITIONS
C-------------Y IS THE VECTOR OF OBSERVED VALUES
C-------------N IS THE OBSERVATION NUMBER
C-------------THE PROGRAMME IS SET UP TO PASS TWO MODELS OVER THE SAME
C-------------DATA
C-------------P M HUCK NOV 18/75     REVISED JULY 7/76
      EXTERNAL MODE
      DIMENSION F(10),          Y(10),DIFF(3),SIGNS(3),TH(3),SCRAT(374)
      COMMON X(10,3)
      DATA NPROB/2/,NOB/10/,NP/03/,EPS1/0./,            MIT/20/,FLAM/10./,F
     1NU/10./
      DATA EPS2/10.0E-05/
  100  FORMAT(I5,3F10.0,F12.2)
  101 FORMAT(1H1,15X,≠INPUT DATA≠,//4X,≠N≠,6X,≠NO≠,7X,≠G≠,7X,≠T≠,9X,≠Y≠)
  102  FORMAT(1H0,I5,3F8.0,F12.2)
  104 FORMAT(6E10.4)
C-------------READ IN EXPERIMENTAL CONDITIONS AND OBSERVED VALUES AND PRINT
C-------------THEM OUT
      WRITE(61,101)
      DO 6 K=1,NOB
      READ (60,100) N,(X(K,I),I=1,3),Y(K)
      WRITE(61,102) N,(X(K,I),I=1,3),Y(K)
    6 CONTINUE
C-------------INITIALIZE VALUES OF VECTORS DIFF AND SIGNS
      DO 9 K=1,NP
      DIFF(K)=.01
      SIGNS(K)=2.
    9 CONTINUE
C-------------CALL UWHAUS ONCE FOR EACH MODEL
C-------------FOR THIS RUN, ONLY ONE MODEL IS ENTERTAINED
      LMN=1
      IF(LMN.EQ.1)GO TO 990
C-------------READ INITIAL PARAMETER ESTIMATE FOR FIRST MODEL
      READ(60,104) (TH(I),I=1,NP)
      NPROB=1
      CALL UWHAUS(NPROB,MODE, NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT,FLAM,
     1FNU,SCRAT)
  990 CONTINUE
C-------------READ INITIAL PARAMETER ESTIMATE FOR SECOND MODEL
      READ(60,104) (TH(I),I=1,NP)
      NPROB=2
      CALL UWHAUS(NPROB,MODE, NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,MIT,FLAM,
     1FNU,SCRAT)
      STOP
      END
```

```
USASI FORTRAN DIAGNOSTIC RESULTS FOR FTN.MAIN

      NO ERRORS
```

```
FORTRAN(2.3)/MASTER      INTEGER WORD SIZE = 1 , * OPTION IS  OFF , O OPTION IS   OF

      SUBROUTINE MODE (NPROB,TH,F,NOB,NP)
C-------------THIS SUBROUTINE COMPUTES VALUES OF THE MODEL(S)
C-------------P M HUCK NOV 18/75     REVISED JULY 27/76
      DIMENSION TH(1),F(1)
      COMMON X(10,3)
C-------------FOR THE MODEL WITH FLOC BREAKUP, NPROB=1
C-------------FOR THE MODEL WITHOUT FLOC BREAKUP NPROB=2
      GO TO (10,20),NPROB
   10 DO 1 I=1,NOB
      F(I)=   X(I,1)/((TH(1)*(X(I,1)        )*X(I,2)*(X(I,3)**TH(2)))+1.)
     1   +TH(3)*(X(I,1)**(-1.))+X(I,2)*(X(I,3))
    1 CONTINUE
      GO TO 40
   20 DO 2 I=1,NOB
      F(I)=   X(I,1)/((TH(1)*(X(I,1)**TH(2))*(X(I,2)        )*(X(I,3)**
     1    TH(3)))+1.)
    2 CONTINUE
   40 CONTINUE
      RETURN
      END

USASI FORTRAN DIAGNOSTIC RESULTS FOR MODE

     NO ERRORS
```

```
FORTRAN(2.3)/MASTER      INTEGER WORD SIZE = 1 , * OPTION IS  OFF  , D OPTION IS   OF
```

```
      SUBROUTINE UWHAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,
     1  MIT, FLAM, FNU, SCRAT)
      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  HAUS59(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)  )
      RETURN
      END
```

```
   USASI FORTRAN DIAGNOSTIC RESULTS FOR UWHAUS

        NO ERRORS
```

```
      SUBROUTINE HAUS59(NPRBO, MODEL, NBO, Y,NQ,TH,DIFZ,SIGNS,EP1S,EP2S,
     1MIT,FLAM,FNU,    Q,P,E,PHI,TB,F,R,A,D,DELZ)
C                          FORTRAN II VERSION
C                             H. J. WERTZ
C     ADAPTED FOR THE CDC 6400   (J. E. MACGREGOR)
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)
      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
       PRINT 1000, NPROB, NOB, NP, NSCRAC
      PRINT 1001
       CALL GASS60(1, NP, TH, TEMP, TMEP)
      PRINT 1002
       CALL GASS60(1, NP, DIFZ, TEMP, TEMP)
      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)
      PRINT 1003, SSQ
C
C                                                      BEGIN ITERATION
C
  100 GA = GA / FNU
      INTCNT = 0
      PRINT 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
      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)
      153   A(JI) = A(IJ)
     C                                                    A= SCALED MOMENT MATRIX
            II = - NP
            DO 155 I=1,NP
            P(I)=D(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)
            PRINT 1041, DET, TEMP
      170   DO 220 I = 1, NP
            P(I) = PHI(I) *STEP / E(I)
            TB(I) = TH(I) + P(I)
      220   CONTINUE
            PRINT 7000
     7000   FORMAT(30H0TEST POINT PARAMETER VALUES      )
            PRINT 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)
            PRINT 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   PRINT 1007
            DO 669 I=1,NP
     669    TH(I)=TB(I)
             CALL GASS60(1, NP, TH, TEMP, TEMP)
            PRINT 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
            PRINT 1009, EPS2
            GO TO 280
      265   IF(ABS(SUMB - SSQ) - EPS1*SSQ) 266, 265, 270
      266   PRINT 1010, EPS1
            GO TO 280
     270    SSQ=SUMB
            NIT=NIT+1
```

```
      IF(NIT - MIT) 100, 100, 280
 2700 PRINT 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 PRINT 1011
      PRINT 2001, (F(I), I = 1, NOB)
      PRINT 1012
      PRINT 2001, (R(I), I = 1, NOB)
      SSQ=SUMB
      IDF=NOB-NP
      PRINT 1015
      I=0
       CALL MATIN(D, NP, P, I, DET)
      DO 7592 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 GASS60(3, NP, TEMP, TEMP, A)
      PRINT 1016
       CALL GASS60(1, NP, E, TEMP, TEMP)
      IF(IDF) 341, 410, 341
  341 SDEV = SSQ / IDF
      PRINT 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
      PRINT 1039
       CALL GASS60(2, NP, TB, P, TEMP)
      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
      R(K)=F(K)+TEMP
  415 F(K)=F(K)-TEMP
      PRINT 1008
      IE=0
      DO 425 I=1,NOB,10
      IE=IE+10
      IF(NOB-IE) 430,435,435
  430 IE=NOB
  435 PRINT 2001, (R(J), J = I, IE)
  425 PRINT 2006, (F(J), J = I, IE)
  410 PRINT 1033, NPROB
      RETURN
   99 PRINT 1034
      GO TO 410
10000FORMAT(38H1NON-LINEAR ESTIMATION, PROBLEM NUMBER   I3,// I5,
     1  14H OBSERVATIONS, I5, 11H PARAMETERS  I14, 17H SCRATCH REQUIRED)
 1001 FORMAT(/25H0INITIAL PARAMETER VALUES  )
 1002 FORMAT(/54H0PROPORTIONS USED IN CALCULATING DIFFERENCE QUOTIENTS )
 1003 FORMAT(/25H0INITIAL SUM OF SQUARES =    F12.4)
 1004 FORMAT(////45X,13HITERATION NO.  I4)
 1007 FORMAT(/32H0PARAMETER VALUES VIA REGRESSION  )
 1008 FORMAT(////54H0APPROXIMATE CONFIDENCE LIMITS FOR EACH FUNCTION VAL
     1UE    )
```

```
      10090FORMAT(/62H0ITERATION STOPS - RELATIVE CHANGE IN EACH PARAMETER LE
          1SS THAN   E12.4)
      10100FORMAT(/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   )
      10390FORMAT(/71H0INDIVIDUAL CONFIDENCE LIMITS FOR EACH PARAMETER (ON LI
          1NEAR HYPOTHESIS)    )
      10400FORMAT(/9H0LAMBDA =E10.3,40X,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(/10E12.4)
      2006 FORMAT(10E12.4)
           END
```

```
FORTRAN12.31/MASTER     INTEGER WORD SIZE = 1 , * OPTION IS OFF , O OPTION IS OF

   USASI FORTRAN DIAGNOSTIC RESULTS FOR HAUS59
 LINE    S    ERRNUM                          MESSAGE
 0057    I    5154     DO PARAMETER MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.

LLOWING ARE COMMON BLOCK NAMES OR NAMES NOT ASSIGNED STORAGE
```

```
          SUBROUTINE MATIN(A, NVAR, B, NB, DET)
          DIMENSION A(NVAR, 1), B(NVAR, 1)
          COMMON/GASPAR/DUMIES(7), PIVOTM
           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
```

```
    USASI FORTRAN DIAGNOSTIC RESULTS FOR MATIN

       NO ERRORS

LLOWING ARE COMMON BLOCK NAMES OR NAMES NOT ASSIGNED STORAGE
PAR
```

```
FORTRAN(2.3)/MASTER     INTEGER WORD SIZE = 1 , * OPTION IS  OFF , O OPTION IS  OF

                 SUBROUTINE GASS60(ITYPE, NQ, A, B, C)
                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     PRINT 500, (J,J=LOW,LUP)
                GO TO (40,50,80),ITYPE
         40     PRINT 600,(A(J),J=LOW,LUP)
                GO TO 100
         50     PRINT 600, (B(J),J=LOW,LUP)
                GO TO 40
         80     DO 90 I=LOW,LUP
         90     PRINT 720,I,(C(J,I),J=LOW,I)
                LOW2=LUP+1
                IF(LOW2 .GT. NP) GO TO 100
                DO 95 I=LOW2,NP
         95     PRINT 720,I,(C(J,I),J=LOW,LUP)
        100      LOW = LOW + 10
                 LUP = LUP + 10
                 NR = NR - 1
                 GO TO 10
        500     FORMAT(/I8,9I12)
        600     FORMAT(10E12.4)
        720     FORMAT(1H0,I3,1X,F7.4,9F12.4)
          1     CONTINUE
                RETURN
                END

   USASI FORTRAN DIAGNOSTIC RESULTS FOR GASS60

        NO ERRORS

REFERENCED STATEMENT LABELS

1
```

```
INPUT DATA
    N     N0      G       T        Y
    1    600.    194.     10.     3.89
    2    600.    194.     30.     2.72
    3    600.    194.     60.     2.26
    4    600.    194.    100.     1.50
    5    150.    194.     20.     3.02
    6    150.    194.     20.     3.08
    7    600.    194.     20.     3.34
    8    600.    194.     20.     3.49
    9   2400.    194.     20.     0.96
   10   2400.    194.     20.     0.73

NON-LINEAR ESTIMATION, PROBLEM NUMBER  2
 10 OBSERVATIONS,    3 PARAMETERS            74 SCRATCH REQUIRED

INITIAL PARAMETER VALUES
      1           2           3
 0.1445E+03  0.1247E+01  0.3461E+00

PROPORTIONS USED IN CALCULATING DIFFERENCE QUOTIENTS
      1           2           3
 0.1000E-01  0.1000E-01  0.1000E-01

INITIAL SUM OF SQUARES =  0.4415E+01
```

```
                                        ITERATION NO.    1
DETERMINANT =  0.4087E+01       ANGLE IN SCALED COORD. =11.10DEGREES
 TEST POINT PARAMETER VALUES
  0.1446E-03  0.1247E+01  0.3462E+00
 TEST POINT SUM OF SQUARES =  0.4415E+01

PARAMETER VALUES VIA REGRESSION
      1           2           3
  0.1446E-03  0.1247E+01  0.3462E+00

 LAMBDA = 0.100E+01                          SUM OF SQUARES AFTER REGRESSION =  0.4414653E+01


                                        ITERATION NO.    2
DETERMINANT =  0.4016E-01       ANGLE IN SCALED COORD. =67.11DEGREES
 TEST POINT PARAMETER VALUES
  0.1442E-03  0.1247E+01  0.3460E+00
 TEST POINT SUM OF SQUARES =  0.4415E+01

PARAMETER VALUES VIA REGRESSION
      1           2           3
  0.1442E-03  0.1247E+01  0.3460E+00

LAMBDA = 0.100E+00                           SUM OF SQUARES AFTER REGRESSION =  0.4414632E+01


                                        ITERATION NO.    3
DETERMINANT =  0.1648E-02       ANGLE IN SCALED COORD. =12.82DEGREES
 TEST POINT PARAMETER VALUES
  0.1456E-03  0.1247E+01  0.3450E+00
 TEST POINT SUM OF SQUARES =  0.4415E+01

PARAMETER VALUES VIA REGRESSION
      1           2           3
  0.1456E-03  0.1247E+01  0.3450E+00

LAMBDA = 0.100E-01                           SUM OF SQUARES AFTER REGRESSION =  0.4414604E+01
```

```
                                                 ITERATION NO.    4
DETERMINANT =  0.5690E-03        ANGLE IN SCALED COORD. =64.71DEGREES

TEST POINT PARAMETER VALUES
 0.1465E-03  0.1246E+01  0.3438E+00

TEST POINT SUM OF SQUARES =  0.4415E+01
DETERMINANT =  0.1649E-02        ANGLE IN SCALED COORD. =63.81DEGREES

TEST POINT PARAMETER VALUES
 0.1460E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

PARAMETER VALUES VIA REGRESSION

      1           2           3
 0.1460E-03  0.1246E+01  0.3443E+00

LAMBDA = 0.100E-01                                        SUM OF SQUARES AFTER REGRESSION =  0.4414601E+01


                                                 ITERATION NO.    5
DETERMINANT =  0.5693E-03        ANGLE IN SCALED COORD. =52.63DEGREES

TEST POINT PARAMETER VALUES
 0.1468E-03  0.1246E+01  0.3437E+00

TEST POINT SUM OF SQUARES =  0.4415E+01
DETERMINANT =  0.1649E-02        ANGLE IN SCALED COORD. =51.28DEGREES

TEST POINT PARAMETER VALUES
 0.1467E-03  0.1246E+01  0.3440E+00

TEST POINT SUM OF SQUARES =  0.4415E+01
DETERMINANT =  0.4217E-01        ANGLE IN SCALED COORD. =48.21DEGREES

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

PARAMETER VALUES VIA REGRESSION

      1           2           3
 0.1461E-03  0.1246E+01  0.3443E+00

LAMBDA = 0.100E+00                                        SUM OF SQUARES AFTER REGRESSION =  0.4414599E+01
```

```
                                                ITERATION NO.   6
DETERMINANT =  0.1650E-02       ANGLE IN SCALED COORD. =11.77DEGREES

TEST POINT PARAMETER VALUES
 0.1463E-03  0.1246E+01  0.3439E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1462E-03  0.1246E+01  0.3441E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1462E-03  0.1246E+01  0.3442E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3442E+01

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES

 0.1461E-03  0.1246E+01 -0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01
```

```
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES

 0.1461E-03  0.1246E+01  0.3443E+00
TEST POINT SUM OF SQUARES =  0.4415E+01
TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00
```

```
TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1451E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

TEST POINT PARAMETER VALUES
 0.1461E-03  0.1246E+01  0.3443E+00

TEST POINT SUM OF SQUARES =  0.4415E+01

PARAMETER VALUES VIA REGRESSION
      1           2           3
 0.1461E-03  0.1246E+01  0.3443E+00

LAMBDA = 0.100E-01                                   SUM OF SQUARES AFTER REGRESSION =  0.4414599E+01

ITERATION STOPS - RELATIVE CHANGE IN EACH PARAMETER LESS THAN  0.1000E-03
```

```
FINAL FUNCTION VALUES
 0.3236E+01  0.2255E+01  0.1778E+01  0.1492E+01  0.3574E+01  0.3574E+01  0.2591E+01  0.2591E+01  0.1848E+01  0.1848E+01

RESIDUALS
 0.6042E+00  0.4651E+00  0.4824E+00  0.8354E-02 -0.5544E+00 -0.4944E+00  0.4488E+00  0.8988E+00 -0.8882E+00 -0.1118E+01

CORRELATION MATRIX
      1          2          3
 1  1.0000
 2 -0.7409     1.0000
 3 -0.6471    -0.0215     1.0000

NORMALIZING ELEMENTS
     1          2          3
 0.1721E-03  0.1517E+00  0.2574E+00

VARIANCE OF RESIDUALS =  0.6307E+00,   7 DEGREES OF FREEDOM

INDIVIDUAL CONFIDENCE LIMITS FOR EACH PARAMETER (ON LINEAR HYPOTHESIS)
     1          2          3
 0.4134E-03  0.1487E+01  0.7531E+00
-0.1272E-03  0.1305E+01 -0.6458E-01

APPROXIMATE CONFIDENCE LIMITS FOR EACH FUNCTION VALUE
 0.4459E+01  0.2843E+01  0.2631E+01  0.2492E+01  0.4621E+01  0.4621E+01  0.3142E+01  0.3142E+01  0.2653E+01  0.2653E+01
 0.2102E+01  0.1667E+01  0.9241E+00  0.4913E+00  0.2528E+01  0.2528E+01  0.2040E+01  0.2040E+01  0.1043E+01  0.1043E+01

END OF PROBLEM NO.  2

   STOP
```

main program may then either prepare a new problem (see the example in Section 6.2.2), or terminate. The observed function values and independent variable values are not modified during the estimation procedure; consequently, they may be used for another problem, *e.g.*, to try a different model on the same data.

2.1.2 GAUSHAUS Calling Sequence. (UWHAUS IS CALLED GAUSHAUS IN THIS WRITEUP)

GAUSHAUS is called from the main program with a FORTRAN statement of the form

```
CALL GAUSHAUS (NPROB, FOF, NOB, Y, NP, TH, DIFF, SIGNS, EPS1, EPS2, MIT,
               FLAM, FNU, SCRAT)
```

NPROB	is a TYPE INTEGER constant or variable which is the problem number. It is reproduced at the top of the first page of output produced by GAUSHUAS. Other uses are explained in Section 2.1.4.1.
FOF	is the name of the User-supplied subroutine which computes the values of the model. (See Section 2.1.3.) *FOF* must be declared an external symbol in the main program. (*i.e.*, the main program must have in it, before any executable statements, the FORTRAN statement: EXTERNAL FOF.)
NOB	is a TYPE INTEGER constant or variable which is the number of observations. It corresponds to " n " of Sections 1.0 and 3.0.
Y	is a TYPE REAL one-dimensional array containing the vector of observed function values (*i.e.*, *Y(I)* is the *Ith* observed function value, *I=1,...,NOB.*) The main program stores the observed function values in this array.
NP	is a TYPE INTEGER constant or variable which is the number of unknown parameters. It corresponds to " p " of Sections 1.0 and 3.0. *NP* must satisfy *NP* > 0. *NP* ≤ *NOB*, and *NP* ≤ 50.
TH	is a TYPE REAL one-dimensional array containing a vector of parameter values. (*i.e.*, *TH(J)* is the *Jth* parameter value, *J=1,...,NP.*) As can be seen from Section 3.0, a vector, $\underline{\theta}^{(0)}$,

of starting guesses for $\underline{\theta}$ is needed; these starting guesses must be stored in array *TH* before GAUSHAUS is called. During the execution of GAUSHAUS, the most current parameter estimates are kept in this array. When GAUSHAUS returns control to the main program, this array will contain the final parameter estimates computed by GAUSHAUS. It is very important to obtain reasonable starting guesses for the parameters, *e.g.*, by plotting the data, by using previously reported results from similar experiments, *etc.*. Not only will computation time be decreased by a good choice of starting values, but there is also the possibility (since non-linear least squares estimates are not in general unique) of converging to a more reasonable estimate. (See also Box and Hunter (1965).)

DIFF is a TYPE REAL one-dimensional array containing a vector of proportions in $\underline{\theta}$, for use in computing the difference quotients of the model function values. The derivatives, $\frac{\partial f(\underline{\theta},\underline{\xi}_u)}{\partial \theta_i}$, of Section 3.0 are approximated by difference quotients within the program:

$$\frac{\partial f(\underline{\theta},\underline{\xi}_u)}{\partial \theta_i} = \frac{f(\theta_1,\ldots,\theta_i+\Delta\theta_i,\ldots,\theta_p,\underline{\xi}_u) - f(\underline{\theta},\underline{\xi}_u)}{(\theta_i+\Delta\theta_i) - \theta_i}$$

Thus at any point in the calculations, the denominator of the above difference quotient would be expressed as:

*(TH(I)+DIFF(I)*TH(I)) - TH(I) = DIFF(I)*TH(I).*

Setting *DIFF(I) = .01 (I=1,...,NP)* has worked well in many cases. In any case, *DIFF(I)* must satisfy $0<|DIFF(I)|<1$ *(I=1,...,NP)*.

Note that this method of calculating the differences prohibits using a starting guess of zero for any parameter. It is unlikely that any parameter will ever be exactly zero during the course of the calculations.

SIGNS is a TYPE REAL one-dimensional array containing a vector indicating the existence of a priori sign restrictions on each of the parameters. Occasionally mathematical models are used such that there is an a priori restriction on one or more of the parameters. If *SIGNS (I)* is set equal to any positive quantity, GAUSHAUS will not allow the *Ith* parameter to change its sign during the calculations; thus the *Ith* parameter, *TH(I)*, retains the same sign as the starting guess for that parameter. If *SIGNS (I) = 0*, this feature is disabled for the *Ith* parameter. If the User desires a restriction such as $\theta_i > 1$, he may replace θ_i in the model with $\phi_i + 1$ (where $\phi_i = \theta_i - 1$), and set the restriction $\phi_i > 0$.

EPS1 is a TYPE REAL constant or variable which is the sum of squares convergence criterion and is used to terminate the calculations based on the relative change in the sum of squares from one iteration to the next iteration. More precisely, if at the completion of the ith iteration, it is true that

$$\left| \frac{S(\underline{\theta}^{(i)}) - S(\underline{\theta}^{(i-1)})}{S(\underline{\theta}^{(i-1)})} \right| \leq EPS1,$$

then the calculations are terminated. (Here, as in Section 3.0, $S(\underline{\theta}^{(i)})$ denotes the sum of squares after the i^{th} iteration.) Roughly, this means that if $EPS1 = 10^{-k}$, the calculations will be stopped if the sum of squares for the $(i-1)^{st}$ and i^{th} iterations agree to k decimal places. If *EPS1* is set equal to zero, this feature is disabled.

EPS2 is a TYPE REAL constant or variable which is the parameter convergence criterion and is used to terminate the calculations based on the relative change in the parameter values from one iteration to the next iteration. Suppose that after the i^{th} iteration, the value of the j^{th} parameter is $\theta_j^{(i)}$ $(j=1,\ldots,p)$. If, at the completion of the i^{th} iteration, the following holds:

- 12 -

$$\left| \frac{\theta_j^{(i)} - \theta_j^{(i-1)}}{\theta_j^{(i-1)}} \right| < EPS2$$

for <u>all</u> $j=1,\ldots,p$, then the calculations are terminated. Roughly, this means that if *EPS2* $= 10^{-k}$, the calculations will be stopped if the value of each parameter after the i^{th} iteration agrees to k decimal places with the value of the same parameter after the $(i-1)^{st}$ iteration. This feature is disabled if *EPS2* is set to zero.

MIT is a TYPE INTEGER constant or variable (where $0 < MIT < 1000$) which is the maximum number of iterations to be performed during the current call to GAUSHAUS. If the calculations have not been terminated for some other reason, they will be terminated when the number of iterations equals *MIT*.

FLAM is a TYPE REAL constant or variable which is a starting value for λ of Section 3.0. Marquardt (1963) has suggested using .01 for this initial value of λ. However, frequently situations have been encountered where it was more appropriate to use as high a value as $\lambda^{(0)} = 1$ in order to control the initial iterations properly.

FNU is a TYPE REAL constant or variable which is the value of ν of Section 3.0. Marquardt (1963) recommends $\nu = 10$. *FNU* must satisfy $FNU \geq 1$.

SCRAT is an array ~~optional parameter~~ used to specify temporary storage for use by GAUSHAUS, ~~when automatic storage allocation is not desired~~. When present in the calling sequence, *SCRAT* must be the name of an array in which are available the number of storage locations given by the expression:
5*NP + NP^2 + 2*NOB + NP*NOB. (This expression is explained in Section 2.5.) The contents of these locations will be destroyed during execution of GAUSHAUS. ~~If SCRAT is not~~

```
C------------THIS PROGRAMME COMPUTES D, THE BOX-HILL CRITERION FOR MODEL
C------------DISCRIMINATION, OVER A SPECIFIED RANGE OF POSSIBLE EXPERI-
C------------MENTAL CONDITIONS (THE OPERABILITY REGION)
C------------IT IS CURRENTLY WRITTEN FOR TWO INDEPENDENT VARIABLES
C------------AND IT PRINTS A GRID OF COMPUTED D VALUES
C------------INPUT DATA CONSIST OF
C------------     RANGE AND INCREMENT FOR EACH INDEPENDENT VARIABLE
C------------     ( MIN,  MAX,  INC)
C------------     PARAMETER ESTIMATES (TH) FROM PROGRAMME UWHAUS
C------------     VARIANCE (SIGSQR)
C------------     MODEL PROBABILITIES FROM PREVIOUS RUN (PPR)
C------------     OBSERVED EXPERIMENTAL VALUE (Y)
C------------     EXPERIMENTAL CONDITIONS
C------------           INITIAL PARTICLE CONCENTRATION, ZI1 (RNO)
C------------           TIME, ZI2 (T)
C------------           VELOCITY GRADIENT,  ZI3 (G)
C------------     EXPERIMENT NUMBER (N)
C------------     NINVAR IS THE NUMBER OF INDEPENDENT VARIABLES
C------------PY IS THE PROBABILITY OF Y(N) GIVEN M(I)
C------------PR IS THE NEW PROBABILITY OF EACH MODEL
C------------N1,N2 ARE THE NUMBER OF SETTINGS OF EACH INDEPENDENT VARIABLE
C------------TO BE EXAMINED
C------------NMOD IS THE NUMBER OF MODELS BEING ENTERTAINED
C------------NOB IS THE NUMBER OF OBSERVATIONS
C------------NM1 IS THE NUMBER OF OBSERVATIONS MINUS ONE
C------------X(I) IS THE MATRIX OF DERIVATIVES OF MODEL I WITH RESPECT
C------------TO ITS PARAMETERS
C------------XP(I) CONTAINS ALL OF X(I) EXCEPT THE MOST RECENT DERIVATIVE
C------------XPX IS THE XPRIME-X MATRIX AND IS STORED TEMPORARILY IN XXX
C------------SIGMSQ IS (SIGMA(I))**2.
C------------PR(I) IS THE NEW PROBABILITY OF MODEL I
C------------YHAT(I) IS THE PREDICTED RESPONSE OF MODEL I
C------------DIJ IS THE QUANTITY COMPUTED FOR EACH PAIR OF MODELS
C------------NP(I) IS THE NUMBER OF PARAMETERS IN MODEL I
C------------NNPMAX IS THE MAXIMUM NUMBER OF PARAMETERS IN ANY MODEL
C------------LL AND MM ARE WORK VECTORS REQUIRED BY LIBRARY S/R MINV
C------------THESE DIMENSIONS DO NOT CHANGE UNLESS THE SEARCH REGION CHANGE
C------------DIMENSION D(N1INC+1,N2INC+1),Z1(N1INC+1),Z2(N2INC+1)
      DIMENSION D(11,11), Z1(11),Z2(11)
C------------THESE DIMENSIONS DO NOT CHANGE UNLESS EITHER THE NUMBER OF
C------------MODELS OR THE MODELS THEMSELVES CHANGE
C------------DIMENSION NP(NMOD ),XN(1,NPMAX),XPX(NPMAX,NPMAX),XNXPX(1,NPMAX
C------------         TH(NMOD,NPMAX),LL(NPMAX),MM(NPMAX),YHAT(NMOD),
C------------         SIGMSQ(NMOD),PR(NMOD),PPR(NMOD),PY(NMOD),
C------------         ZED(NINVAR),DIJ(NMOD,NMOD),XNP(NPMAX,1)
C------------         XXX(NPMAX,NPMAX)
      DIMENSION NP(4),XN(1,1),XPX(1,1),XNXPX(1,1),TH(4,1),LL(1),MM(1),
     1YHAT(4),SIGMSQ(4),PR(4),PPR(4),PY(4),ZED(   3),DIJ(4,4),XNP(1,1),
     2XXX(1,1)
C------------THESE DIMENSIONS CHANGE WITH THE NUMBER OF OBSERVATIONS
C------------DIMENSION Y(NOB),ZI(NOB,NINVAR        ),X(NOB,NPMAX),
C------------         XSTORE(NMOD,NOB,NPMAX),XP(NM1,NPMAX)
      DIMENSION Y(9),ZI(9,3),X(9,1),XSTORE(4,9,1),XP(8,1)
      COMMON /C3/SIGSQR
      COMMON /C4/ G
      COMMON /COM5/ RNOMIN,RNOMAX,TMIN,TMAX,N1INC,N2INC
      COMMON /C7/ XXPXX(1,1)
C------------READ AND WRITE INPUT DATA
      READ(60,101)SIGSQR
      READ(60,100) NINVAR
      READ (60,101) NMOD,NPMAX
      READ(60,103)(NP(I),I=1,NMOD)
      DO 4 I=1,NMOD
      NPI=NP(I)
    4 READ(60,105)(TH(I,J),J=1,NPI)
      READ (60,7)   RNOMIN,RNOMAX,TMIN,TMAX,N1INC,N2INC,G
      READ (60,102) PPR
      READ (60,100) NOB
      WRITE (61,109)
      WRITE(61,110) NOB,NINVAR,NMOD,NPMAX,SIGSQR,PPR
      WRITE(61,111)
      DO 6 I=1,NMOD
      NPI=NP(I)
      WRITE(61,112) I,NPI,(TH(I,J),J=1,NPI)
    6 CONTINUE
      WRITE(61,113)
      DO 3 I=1,NOB
      READ (60,104) N,(ZI(I,K),K=1,3),Y(I)
```

Note: In obtaining Table 5-15, a modified programme was used in which $(X'X)^{-1}$ was calculated on the basis of all data rather than updated.

```
      WRITE(61,114) N,(ZI(I,K),K=1,3),Y(I)
    3 CONTINUE
      WRITE (61,8)
      WRITE(61,9)    RNOMIN,RNOMAX,TMIN,TMAX,N1INC,N2INC,G
C------------UPDATE MODEL PROBABILITIES
      N1I1=N1INC+1
      N2I1=N2INC+1
      NM1=NOB-1
      CALL       PROB1(NOB,Y,ZI,NP,X,XSTORE,XPX,XNXPX,TH,LL,MM,YHAT,
     1SIGMSQ,PR,PPR,PY,NMOD,NINVAR,NPMAX,ZED,XN,XNP,XXX,XP,NM1)
      PRINT 206
      WRITE(61,204) (YHAT(J),J=1,NMOD),(PY(J),J=1,NMOD),(PR(J),J=1,NMOD)
C------------EVALUATE D OVER OPERABILITY REGION TO PERMIT SELECTION OF
C------------CONDITIONS FOR NEXT EXPERIMENT
      CALL       DEVAL3 (NOB,Z1,Z2,ZED,D,DIJ,X,XSTORE,XN,XPX,XNXPX,
     1TH,YHAT,NP,PR,LL,MM,SIGMSQ,NMOD,NINVAR,NPMAX,N1I1,N2I1,XNP,XXX)
    7 FORMAT(4F10.0,2I5,F10.0)
    8 FORMAT(1H0,///4X,≠RNOMIN≠,4X,≠RNOMAX≠,6X,≠TMIN≠,6X,≠TMAX≠,3X,
     1≠N1INC≠,2X,≠N2INC≠,4X,≠NEW G≠)
    9 FORMAT(1H0,4F10.0,2I7,F10.0)
  100 FORMAT(2I5)
  101 FORMAT(E10.3,I5)
  102 FORMAT(4E10.4)
  103 FORMAT(5I5)
  104 FORMAT(I5,3F10.0,F12.2)
  105 FORMAT(5E10.4)
  109 FORMAT(1H1,30X,≠INPUT DATA≠,///3X,≠NOB≠,2X,≠NINVAR≠,2X,≠NMOD≠,
     12X,≠NPMAX≠,      2X,≠SIGSQR≠,5X,≠PRIOR MODEL PROBABILITIES≠)
  110 FORMAT(1H0,4I5,E10.3,     5X,4E11.4)
  111 FORMAT(1H0,10X,≠MODEL NO.≠,5X,≠NO. PARAMETERS≠,5X,≠PARAMETER ESTIM
      1ATES FROM UWHAUS≠)
  112 FORMAT(1H0,10X,I5,10X,I5,12X,3(2X,E10.4))
  113 FORMAT(1H0,///4X,≠N≠,7X,≠NO≠,9X,≠G≠,9X,≠T≠,11X,≠Y≠)
  114 FORMAT(1H0,I5,3F10.0,F12.2)
  204 FORMAT(1H0,8(1X,E10.3),4(    E11.4))
  205 FORMAT(1H0,///4X,    ≠YHAT(1)≠,4X,≠YHAT(2)≠,4X,≠YHAT(3)≠,4X,≠YHAT(4
     1)≠,        5X,≠PY(1)≠,6X,≠PY(2)≠,6X,≠PY(3)≠,6X,≠PY(4)≠,6X,≠PR(1)≠,
     2      6X,≠PR(2)≠,6X,≠PR(3)≠,6X,≠PR(4)≠)
      STOP
      END
```

```
   USASI FORTRAN DIAGNOSTIC RESULTS FOR FTN.MAIN

          NO ERRORS

LOWING ARE COMMON BLOCK NAMES OR NAMES NOT ASSIGNED STORAGE

          C4              COM6           C7
```

```
      SUBROUTINE PROB1(NOB,Y,ZI,NP,X,XSTORE,XPX,XNXPX,TH,LL,MM,YHAT,
     1SIGMSQ,PR,PPR,PY,NMOD,NINVAR,NPMAX,ZED,XN,XNP,XXX,XP,NM1)
C-------------THIS S/R UPDATES MODEL PROBABILITIES AFTER THE MOST RECENT
C-------------OBSERVATION(S)
C-------------P M HUCK JUNE 24/76   REV SEPT 21/76
      DIMENSION     LL(1),MM(1),YHAT(1),SIGMSQ(1),PR(1),PPR(1),PY(1),Y(1)
     1,NP(1),ZED(1)
      DIMENSION     ZI(NOB,NINVAR),XSTORE(NMOD,NOB,NPMAX),X(NOB,NPMAX),
     1      XPX(NPMAX,NPMAX),XNXPX(1,NPMAX),TH(NMOD,NPMAX),XN(1,NPMAX),
     2      XNP(NPMAX,1),XXX(NPMAX,NPMAX),XP(NM1,NPMAX)
      COMMON /C3/SIGSQR
C-------------COMPUTE SIGMA(I)**2. FOR EACH MODEL
      DO 35 I=1,NMOD
      NPI=NP(I)
C-------------RE-EVALUATE THE X*X MATRIX USING THE MOST RECENT PARAMETER
C-------------ESTIMATES
C-------------STORE THE X MATRIX FOR USE LATER IN THE PROGRAMME
      DO 18 K=1,NM1
      DO 10 L=1,NINVAR
      ZED(L)=ZI(K   ,L)
   10 CONTINUE
      CALL DERIV3(K   ,ZED,I,X,TH,NOB,NMOD,NPI)
      DO 20 L=1,NPI
      XSTORE(I,K,L)=X(K,L)
      XP(K,L)=X(K,L)
   20 CONTINUE
   18 CONTINUE
C-------------FORM THE XPRIME-X MATRIX
      CALL GASO11(XP,XXX,NM1,NPI,0)
C-------------CHANGE THE STORAGE MODE OF XXX FROM SYMMETRIC TO GENERAL
C-------------AS REQUIRED BY S/R MINV
      CALL GASO41 (XXX,XPX,NPI,1,0)
C-------------INVERT THE XPRIME-X MATRIX
      CALL MINV(XPX,NPI,DET,LL,MM)
C-------------THE ORIGINAL MATRIX IS DESTROYED AND XPX IS NOW THE INVERSE
C-------------OF XPX
C-------------EVALUATE THE DERIVATIVE AT THE MOST RECENT EXPERIMENTAL
C-------------CONDITIONS AND STORE IT
      DO 19 L=1,NINVAR
      ZED(L)=ZI(NOB,L)
   19 CONTINUE
      CALL DERIV3(NOB,ZED,I,X,TH,NOB,NMOD,NPI)
      DO 22 L=1,NPI
   22 XSTORE(I,NOB,L)=X(NOB,L)
C-------------EVALUATE SIGMA(I)**2.
      DO 27 L=1,NPI
   27 XN(1,L)=X(NOB,L)
      CALL SIGSQ1  (NPI,XN,XNP,XPX,XNXPX,SIGMSQ,I)
   35 CONTINUE
C-------------EVALUATE YHAT FOR EACH MODEL
      DO 33 L=1,NINVAR
      ZED(L)=ZI(NOB,L)
   33 CONTINUE
      CALL YHCAL3(NOB,ZED,YHAT,TH,NMOD,NPMAX)
C-------------EVALUATE P(Y/M(I))
      DO 30 I=1,NMOD
   30 PY(I)=(1./SQRT(2.*3.14159*(SIGSQR+SIGMSQ(I))))*EXP(-(1./(2.*
     1(SIGSQR + SIGMSQ(I))))*((ABS(Y(NOB)-YHAT(I)))**2.))
C-------------CALCULATE MODEL PROBABILITIES
      SUM=0.
      DO 40 I=1,NMOD
   40 SUM=SUM+PPR(I)*PY(I)
      DO 50 I=1,NMOD
   50 PR(I)=(PPR(I)*PY(I))/SUM
      RETURN
      END
```

```
FORTRAN(2.3)/MASTER     INTEGER WORD SIZE = 1 , * OPTION IS  OFF , O OPTION IS  OF

   USASI FORTRAN DIAGNOSTIC RESULTS FOR PROB1
LINE    S    ERRNUM                          MESSAGE
0022    I     5152      DO CONTROL VARIABLE MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.
0022    I     5154      DO PARAMETER MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.
0042    I     5152      DO CONTROL VARIABLE MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.
0042    I     5154      DO PARAMETER MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.
0048    I     5152      DO CONTROL VARIABLE MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.

LLOWING ARE COMMON BLOCK NAMES OR NAMES NOT ASSIGNED STORAGE
```

```
      SUBROUTINE DEVAL3 (NOB,Z1,Z2,ZED,D,DIJ,X,XSTORE,XN,XPX,XNXPX,
     1TH,YHAT,NP,PR,LL,MM,SIGMSQ,NMOD,NINVAR,NPMAX,N1I1,N2I1,XNP,XXX)
C-------------THIS S/R SETS UP A GRID IN THE OPERABILITY REGION AND
C-------------EVALUATES D ON THAT GRID
C-------------P M HUCK JUNE 9/76     REV AUG 9/76
      DIMENSION Z1(1),Z2(1),YHAT(1),ZED(1),
     1NP(1),PR(1),LL(1),MM(1),SIGMSQ(1)
      DIMENSION    D(N1I1,N2I1),DIJ(NMOD,NMOD),X(NOB,NPMAX),
     1    XSTORE(NMOD,NOB,NPMAX),XN(1,NPMAX),XPX(NPMAX,NPMAX),XNXPX(1,
     2  NPMAX),TH(NMOD,NPMAX),XNP(NPMAX,1),XXX(NPMAX,NPMAX)
      COMMON /C4/ G
      COMMON /COM6/ RNOMIN,RNOMAX,TMIN,TMAX,N1INC,N2INC
C-------------UPDATE THE XPRIME-X MATRIX TO INCLUDE THE DERIVATIVE AT
C-------------THE MOST RECENT EXPERIMENTAL CONDITIONS
      DO 17 I=1,NMOD
      NPI=NP(I)
      DO 15 K=1,NOB
      DO 15 L=1,NPI
   15 X(K,L)=XSTORE(I,K,L)
      CALL GAS011(X,XXX,NOB,NPI,0)
C-------------CHANGE THE STORAGE MODE OF XXX FROM SYMMETRIC TO GENERAL
C-------------AS REQUIRED BY S/R MINV
      CALL GAS041 (XXX,XPX,NPI,1,0)
      CALL MINV(XPX,NPI,DET,LL,MM)
C-------------PRINT UPDATED XPRIME-X MATRIX
      WRITE(61,22) I
      DO 19 K=1,NPI
   19 WRITE(61,24)  (XPX(K,L),L=1,NPI)
   17 CONTINUE
C-------------SET UP GRID OF POINTS (EQUALLY SPACED ON LOG SCALE) AT WHICH
C-------------TO EVALUATE D
      B1=(ALOG(RNOMAX)-ALOG(RNOMIN))/N1INC
      B2=(ALOG(TMAX)-ALOG(TMIN))/N2INC
C-------------EVALUATE D FOR EACH POINT ON GRID
      PRINT 10
      N1INC1=N1INC+1
      N2INC1=N2INC+1
      DO 40 I=1,N1INC1
      DO 39 J=1,N2INC1
      Z1(I)=RNOMIN*EXP((I-1)*B1)
      Z2(J)=TMIN*EXP((J-1)*B2)
C-------------CALCULATE YHAT FOR EACH MODEL AT THE CHOSEN CONDITIONS
      ZED(1)  =Z1(I)
      ZED(2)  =G
      ZED(3)  =Z2(J)
      CALL YHCAL3(1,ZED,YHAT,TH,NMOD,NPMAX)
C-------------CALCULATE SIGMA(I)**2. FOR EACH MODEL AT THE CHOSEN CONDITIONS
      DO 25 II=1,NMOD
      NPI=NP(II)
      CALL DERIV3(1,ZED,II,X,TH,NOB,NMOD,NPI)
      DO 27 L=1,NPI
   27 XN(1,L)=X(1,L)
      CALL SIGSQ1 (NPI,XN,XNP,XPX,XNXPX,SIGMSQ,II)
   25 CONTINUE
      WRITE(61,1)Z1(I),Z2(J),(YHAT(K),K=1,NMOD)
C-------------EVALUATE DIJ FOR ALL PAIRS OF MODELS
      CALL DEE1(D,DIJ,SIGMSQ,YHAT,NMOD,N1I1,N2I1)
C-------------EVALUATE D AT PROPOSED EXPERIMENTAL CONDITIONS
      SUM=0.
      DO 20 K=1,NMOD
      K1=K+1
      DO 20 L=K1 ,NMOD
   20 SUM=SUM+PR(K)*PP(L)*DIJ(K,L)
      D(I,J)=SUM
   39 CONTINUE
      WRITE(61,11)
   40 CONTINUE
      WRITE(61,13)
      WRITE(61,21) (Z1(I),I=1,N1INC1)
      DO 50 J=1,N2INC1
   50 WRITE(61,23)Z2(J),(D(I,J),I=1,N1INC1)
    1 FORMAT(1H0,2F10.0,+F10.2)
   10 FORMAT(1H1,5X,≠CONC≠,6X,≠TIME≠,3X,≠YHAT(1)≠,3X,≠YHAT(2)≠,3X,≠YHAT(
     13)≠,3X,≠YHAT(4)≠)
   11 FORMAT(1H0,/)
   13 FORMAT(1H1,10X,≠COMPUTED D VALUES....≠,//)
   21 FORMAT(1H0,1X,≠CONCEN≠,11F11.0,//7X,≠T≠)
   22 FORMAT(1H0,//10X,    ≠UPDATED XPRIME-X-INVERSE MATRIX FOR MODEL NUM
```

```
     1BER=',I3)
  23 FORMAT(1H0,F6.0,11E11.3)
  24 FORMAT(1H0,3(2X,E10.4))
     RETURN
     END
```

```
FORTRAN(2.3)/MASTER   INTEGER WORD SIZE = 1 , T OPTION IS  OFF , O OPTION IS  OF

   USASI FORTRAN DIAGNOSTIC RESULTS FOR DEVAL3.
LINE    S   ERRNUM                          MESSAGE
0050    I    5152     DO CONTROL VARIABLE MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.
0050    I    5154     DO PARAMETER MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.
0053    I    5152     DO CONTROL VARIABLE MAY BE REDEFINED IN EXTERNAL SUBPROGRAM.

LLOWING ARE COMMON BLOCK NAMES OR NAMES NOT ASSIGNED STORAGE
          COM6
```

```
      SUBROUTINE SIGSQ1(NPI,XN,XNP,XPX,XNXPX,SIGMSQ,I)
C-------------THIS S/R EVALUATES SIGMA(I)**2., GIVEN XN,   XPX AND SIGSQR
C-------------XPX IS ACTUALLY XPX-INVERSE
C-------------P M HUCK JUNE 7/76   REV AUG 9/76
      DIMENSION SIGMSQ(1)
      DIMENSION   XN(1 ,NPI),XPX(NPI,NPI),XNXPX(1,NPI),XNP(NPI,1)
      COMMON /C3/SIGSQR
      COMMON /C7/ XXPXX(1,1)
C-------------PREMULTIPLY XPX BY XN
      CALL GAS003(XN,XPX,XNXPX,1,NPI,NPI)
C-------------TRANSPOSE XN
      DO 60 K=1,NPI
   60 XNP(K,1)=XN(1,K)
C-------------POSTMULTIPLY XNXPX BY XNP, THE TRANSPOSE OF XN
      CALL GAS003(XNXPX,XNP,XXPXX,1,NPI,1)
      SIGMSQ(I)=XXPXX(1,1)*SIGSQR
      RETURN
      END

  USASI FORTRAN DIAGNOSTIC RESULTS FOR SIGSQ1

        NO ERRORS

LLOWING ARE COMMON BLOCK NAMES OR NAMES NOT ASSIGNED STORAGE

        C7
```

```
FORTRAN(2.3)/MASTER     INTEGER WORD SIZE = 1 , *-OPTION IS OFF , D-OPTION IS OF

              SUBROUTINE DEE1(D,DIJ,SIGMSQ,YHAT,NMOD,N1I1,N2I1)
        C-------------THIS S/R CALCULATES DIJ FOR ALL PAIRS OF MODELS
        C-------------P M HUCK JUNE 9/76   REV AUG 5/76
              DIMENSION                 SIGMSQ(1),YHAT(1)
              DIMENSION     D(N1I1,N2I1),DIJ(NMOD,NMOD)
              COMMON /C3/SIGSQR
              DO 20 I=1,NMOD
              I1=I+1
              DO 20 J=I1 ,NMOD
              DIJ(I,J)=0.5*((((ABS(SIGMSQ(I)-SIGMSQ(J)))**2.)/((SIGSQR+
             1SIGMSQ(I))*(SIGSQR+SIGMSQ(J))))+(((ABS(YHAT(I)-YHAT(J)))**2.)*
             2((1./(SIGSQR+SIGMSQ(I)))+(1./(SIGSQR+SIGMSQ(J))))))
           20 CONTINUE
              RETURN
              END

    USASI FORTRAN DIAGNOSTIC RESULTS FOR DEE1

          NO ERRORS

LOWING ARE COMMON BLOCK NAMES OR NAMES NOT ASSIGNED STORAGE
```

```
      SUBROUTINE DERIV3(M,ZED,I,X,TH,NOB,NMOD,NPI)
C-------------THIS S/R COMPUTES MODEL DERIVATIVES (X VALUES)
C-------------P M HUCK JUNE 22/76    REV AUG 11/76
      DIMENSION   ZED(1),X(NOB,NPI),TH(NMOD,NPI)
      Q=ZED(1)*ZED(2)*ZED(3)
C-------------EVALUATE THE DERIVATIVE FOR  THE APPROPRIATE MODEL
      GO TO (10,20,30,35),I
C-------------VON SMOLUCHOWSKI MODEL
   10 X(M,1)=-ZED( 1)*Q*EXP(-TH(1,1)*Q)
      GO TO 40
C-------------ARGAMAN-KAUFMAN MODEL
   20 X(M,1)=-((ZED( 1)-1.)*ZED( 1)*Q*EXP(-TH(2,1)*Q))/
     1((1.+((ZED( 1)-1.)*EXP(-TH(2,1)*Q)))**2.)
      GO TO 40
C-------------LA MER-HEALY MODEL (MODIFIED BY PMH)
   30 X(M,1)=-SQRT(ZED (1))*Q*EXP(-TH(3,1)*Q/SQRT(ZED( 1)))
      GO TO 40
C-------------LA MER-HEALY MODEL (UNMODIFIED)
   35 X(M,1)=-(ZED(1)**1.5)*ZED(3)/      ((1.+TH(4,1)*SQRT(ZED(1))*
     1ZED(3))**2.)
   40 CONTINUE
C              IF DERIVATIVE IS LESS THAN 10E-100, SET IT EQUAL TO ZERO
C-------------TO AVOID EXPONENT UNDERFLOW PROBLEM.  THIS HAS NO EFFECT ON
C-------------CALCULATIONS
      P=10.**(-100.)
      DO 70 L=1,NPI
      IF(ABS(X(M,L)).LT.P        ) GO TO 50
      GO TO 60
   50 CONTINUE
      WRITE(61,200) I,M,L,X(M,L)
      X(M,L)=0.0
   60 CONTINUE
   70 CONTINUE
  200 FORMAT(1H0,10X,≠FOR MODEL ≠,I2,≠ X(≠,I1,≠,≠,I1,≠) WAS≠,E12.4,≠ AND
     1 WAS SET EQUAL TO ZERO≠)
      RETURN
      END
```

USASI FORTRAN DIAGNOSTIC RESULTS FOR DERIV3

NO ERRORS

```
FORTRAN(2.3)/MASTER    INTEGER WORD SIZE = 1 , * OPTION IS OFF , O OPTION IS OF

            SUBROUTINE YHCAL3(M,ZED,YHAT,TH,NMOD,NPMAX)
      C-------------THIS S/R COMPUTES YHAT FOR EACH MODEL
      C-------------P M HUCK JUNE 22/76    REV AUG 5/76
            DIMENSION ZED(1), YHAT(1)
            DIMENSION   TH(NMOD,NPMAX)
            Q=ZED(1)*ZED(2)*ZED(3)
      C-------------VON SMOLUCHOWSKI MODEL
            YHAT(1)=ZED( 1)*EXP(-TH(1,1)*Q)
      C-------------ARGAMAN-KAUFMAN MODEL
            YHAT(2)=(ZED( 1)*(ZED( 1)-1.)*EXP(-TH(2,1)*Q))/
           1(1.+((ZED( 1)-1.)*EXP(-TH(2,1)*Q)))
      C-------------LA MER-HEALY MODEL (MODIFIED BY PMH)
            YHAT(3)=ZED( 1)*EXP(-TH(3,1)*Q/SQRT(ZED( 1)))
      C-------------LA MER-HEALY MODEL (UNMODIFIED)
            YHAT(4)=ZED(1)/(1.+TH(4,1)*SQRT(ZED(1))*ZED(3))
            RETURN
            END

   USASI FORTRAN DIAGNOSTIC RESULTS FOR YHCAL3

           NO ERRORS

3,PDIR
```

```
                        INPUT DATA
NOB  NINVAR  NMOD  NPMAX  SIGSQR     PRIOR MODEL PROBABILITIES
 9     3      4     1     0.046    0.9733E+00 0.5386E-04 0.2855E-16 0.2661E-01
        MODEL NO.      NO. PARAMETERS     PARAMETER ESTIMATES FROM UNHAUS .
            1               1              0.2176E-04
            2               1              0.4319E-04
            3               1              0.2839E-03
            4               1              0.4388E+01

 N        NO         G          T          Y
 1       150.       194.       50.        1.71
 2       531.       194.      1000.       0.26
 3       158.       194.      1000.       0.35
 4      2512.       194.       251.       0.05
 5      1585.       194.        10.       0.45
 6       398.       194.        16.       0.26
 7       398.       194.        10.       0.39
 8       100.       194.        25.       0.80
 9       100.       194.        10.       1.52

PNOMIN    PNOMAX       TMIN       TMAX   N1INC  N2INC     NEW G
  100.    10000.         10.      1000.    10     10       194.
        FOR MODEL  1 X(2,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
        FOR MODEL  1 X(3,1) WAS -0.1038-279 AND WAS SET EQUAL TO ZERO
        FOR MODEL  1 X(4,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
        FOR MODEL  2 X(2,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
        FOR MODEL  2 X(3,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
        FOR MODEL  2 X(4,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
        FOR MODEL  3 X(2,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
        FOR MODEL  3 X(3,1) WAS -0.8371-292 AND WAS SET EQUAL TO ZERO
        FOR MODEL  3 X(4,1) WAS -0.7562-291 AND WAS SET EQUAL TO ZERO

 YHAT(1)    YHAT(2)    YHAT(3)    YHAT(4)     PY(1)      PY(2)      PY(3)      PY(4)      PR(1)      PR(2)      PR(3)      PR(4)
0.147E+01 0.152E+01 0.406E+00 0.227E+00 0.827E-02 0.333E-05 0.606E-01 0.523E-07 0.1000E+01 0.5893E-07 0.2151E-15 0.1723E-26
                                                          UPDATED XPRIME-X-INVERSE MATRIX FOR MODEL NUMBER  3
      UPDATED XPRIME-X-INVERSE MATRIX FOR MODEL NUMBER  1      0.1614E-07
0.1233E-10

                                                          UPDATED XPRIME-X-INVERSE MATRIX FOR MODEL NUMBER  4
      UPDATED XPRIME-X-INVERSE MATRIX FOR MODEL NUMBER  2      0.1642E+02
0.1157E-10
```

```
CONC     TIME   YHAT(1)    YHAT(2)    YHAT(3)    YHAT(4)
100.      10.     1.47       1.52       0.41       0.23
100.      16.     0.12       0.01       0.02       0.14
100.      25.     0.00       0.00       0.00       0.09
100.      40.     0.00       0.00       0.00       0.06
100.      63.     0.00       0.00       0.00       0.04
100.     100.     0.00       0.00       0.00       0.02
100.     158.     0.00       0.00       0.00       0.01
100.     251.     0.00       0.00       0.00       0.01
    FOR MODEL  2 X(1,1) WAS -0.2033-140 AND WAS SET EQUAL TO ZERO
100.     398.     0.00       0.00       0.00       0.01
    FOR MODEL  1 X(1,1) WAS -0.2578-106 AND WAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) WAS -0.7125-229 AND WAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) WAS -0.1466-142 AND WAS SET EQUAL TO ZERO
100.     631.     0.00       0.00       0.00       0.00
    FOR MODEL  1 X(1,1) WAS -0.8974-174 AND WAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) WAS -0.1239-230 AND WAS SET EQUAL TO ZERO
100.    1000.     0.00       0.00       0.00       0.00

158.      10.     0.20       0.02       0.15       0.23
158.      16.     0.00       0.00       0.00       0.18
158.      25.     0.00       0.00       0.00       0.11
158.      40.     0.00       0.00       0.00       0.07
158.      63.     0.00       0.00       0.00       0.05
158.     100.     0.00       0.00       0.00       0.03
158.     158.     0.00       0.00       0.00       0.02
    FOR MODEL  2 X(1,1) WAS -0.5126-140 AND WAS SET EQUAL TO ZERO
158.     251.     0.00       0.00       0.00       0.01
    FOR MODEL  1 X(1,1) WAS -0.4087-106 AND WAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) WAS -0.1796-228 AND WAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) WAS -0.2025-111 AND WAS SET EQUAL TO ZERO
158.     398.     0.00       0.00       0.00       0.01
    FOR MODEL  1 X(1,1) WAS -0.1422-173 AND WAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) WAS -0.2448-181 AND WAS SET EQUAL TO ZERO
158.     631.     0.00       0.00       0.00       0.00
    FOR MODEL  1 X(1,1) WAS -0.1323-260 AND WAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) WAS -0.2881-292 AND WAS SET EQUAL TO ZERO
158.    1000.     0.00       0.00       0.00       0.03
```

```
251.      10.     0.01      0.03      0.04      0.36
251.      16.     0.00      0.00      0.00      0.23
251.      25.     0.00      0.00      0.00      0.14
251.      40.     0.00      0.00      0.00      0.09
251.      63.     0.00      0.00      0.00      0.06
251.     100.     0.00      0.00      0.00      0.04
    FOR MODEL  2 X(1,1) HAS -0.1291-139 AND HAS SET EQUAL TO ZERO
251.     158.     0.00      0.00      0.00      0.02
    FOR MODEL  1 X(1,1) HAS -0.6427-106 AND HAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) HAS -0.4523-228 AND HAS SET EQUAL TO ZERO
251.     251.     0.00      0.00      0.00      0.01
    FOR MODEL  1 X(1,1) HAS -0.2254-173 AND HAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) HAS -0.3683-142 AND HAS SET EQUAL TO ZERO
251.     398.     0.00      0.00      0.00      0.01
    FOR MODEL  1 X(1,1) HAS -0.2098-280 AND HAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) HAS -0.3113-230 AND HAS SET EQUAL TO ZERO
251.     631.     0.00      0.00      0.00      0.01
    FOR MODEL  1 X(1,1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
251.    1000.     0.00      0.00      0.00      0.00

398.      10.     0.00      0.00      0.01      0.45
398.      16.     0.00      0.00      0.00      0.29
398.      25.     0.00      0.00      0.00      0.18
398.      40.     0.00      0.00      0.00      0.11
398.      63.     0.00      0.00      0.00      0.07
    FOR MODEL  2 X(1,1) HAS -0.3247-139 AND HAS SET EQUAL TO ZERO
398.     100.     0.00      0.00      0.00      0.03
    FOR MODEL  1 X(1,1) HAS -0.1026-105 AND HAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) HAS -0.1138-227 AND HAS SET EQUAL TO ZERO
398.     158.     0.00      0.00      0.00      0.03
    FOR MODEL  1 X(1,1) HAS -0.3573-173 AND HAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) HAS -0.5088-111 AND HAS SET EQUAL TO ZERO
398.     251.     0.00      0.00      0.00      0.02
    FOR MODEL  1 X(1,1) HAS -0.3324-280 AND HAS SET EQUAL TO ZERO
    FOR MODEL  2 X(1,1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
    FOR MODEL  3 X(1,1) HAS -0.6148-181 AND HAS SET EQUAL TO ZERO
398.     398.     0.00      0.00      0.00      0.01
```

```
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.7238-292 AND WAS SET EQUAL TO ZERO
334.      631.       0.00       0.00       0.00       0.01
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
338.     1000.       0.00       0.00       0.00       0.00

631.       10.       0.00       0.00       0.00       0.57
631.       16.       0.00       0.00       0.00       0.36
631.       25.       0.00       0.00       0.00       0.23
631.       40.       0.00       0.00       0.00       0.14
      FOR MODEL  2 X(1,1) WAS -0.8163-139 AND WAS SET EQUAL TO ZERO
631.       63.       0.00       0.00       0.00       0.09
      FOR MODEL  1 X(1,1) WAS -0.1627-105 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.2861-227 AND WAS SET EQUAL TO ZERO
631.      100.       0.00       0.00       0.00       0.06
      FOR MODEL  1 X(1,1) WAS -0.5552-173 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
631.      158.       0.00       0.00       0.00       0.04
      FOR MODEL  1 X(1,1) WAS -0.3259-280 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.9251-142 AND WAS SET EQUAL TO ZERO
631.      251.       0.00       0.00       0.00       0.02
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.7819-230 AND WAS SET EQUAL TO ZERO
631.      398.       0.00       0.00       0.00       0.01
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
631.      631.       0.00       0.00       0.00       0.01
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
631.     1000.       0.00       0.00       0.00       0.01

1000.      10.       0.00       0.00       0.00       0.72
1000.      16.       0.00       0.00       0.00       1.46
1000.      25.       0.00       0.00       0.00       0.23
      FOR MODEL  2 X(1,1) WAS -0.2052-138 AND WAS SET EQUAL TO ZERO
```

```
1000.      40.      0.00      0.00      0.00      0.18
     FOR MODEL  1 X(1,1) WAS -0.2578-105 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.7190-227 AND WAS SET EQUAL TO ZERO
1000.      63.      0.00      0.00      0.00      0.11
     FOR MODEL  1 X(1,1) WAS -0.8974-173 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
1000.     100.      0.00      0.00      0.00      0.07
     FOR MODEL  1 X(1,1) WAS -0.8350-280 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.1278-110 AND WAS SET EQUAL TO ZERO
1000.     158.      0.00      0.00      0.00      0.05
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.1544-180 AND WAS SET EQUAL TO ZERO
1000.     251.      0.00      0.00      0.00      0.03
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.1818-291 AND WAS SET EQUAL TO ZERO
1000.     398.      0.00      0.00      0.00      0.02
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
1000.     631.      0.00      0.00      0.00      0.01
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
1000.    1000.      0.00      0.00      0.00      0.01

1585.      10.      0.00      0.00      0.00      0.91
1585.      16.      0.00      0.00      0.00      0.57
     FOR MODEL  2 X(1,1) WAS -0.5155-138 AND WAS SET EQUAL TO ZERO
1585.      25.      0.00      0.00      0.00      0.36
     FOR MODEL  1 X(1,1) WAS -0.4087-105 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.1807-226 AND WAS SET EQUAL TO ZERO
1585.      40.      0.00      0.00      0.00      0.23
     FOR MODEL  1 X(1,1) WAS -0.1422-172 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
1585.      63.      0.00      0.00      0.00      0.14
     FOR MODEL  1 X(1,1) WAS -0.1323-279 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
1585.     100.      0.00      0.00      0.00      0.03
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
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      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.2324-141 AND WAS SET EQUAL TO ZERO
1535.      158.      0.00      0.00      0.00      0.06
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.1964-229 AND WAS SET EQUAL TO ZERO
1535.      251.      0.00      0.03      0.00      0.04
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
1535.      398.      0.00      0.00      0.00      0.02
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
1535.      631.      0.00      0.03      0.00      0.01
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
1535.     1000.      0.00      0.05      0.00      0.01

2512.       10.      0.00      0.00      0.00      1.14
      FOR MODEL  2 X(1,1) WAS -0.1295-137 AND WAS SET EQUAL TO ZERO
2512.       16.      0.00      0.03      0.00      0.72
      FOR MODEL  1 X(1,1) WAS -0.6477-105 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.4539-226 AND WAS SET EQUAL TO ZERO
2512.       25.      0.00      0.00      0.00      0.45
      FOR MODEL  1 X(1,1) WAS -0.2254-172 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
2512.       40.      0.00      0.03      0.00      0.29
      FOR MODEL  1 X(1,1) WAS -0.2698-279 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
2512.       63.      0.00      0.03      0.00      0.15
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.3210-110 AND WAS SET EQUAL TO ZERO
2512.      100.      0.00      0.00      0.00      0.11
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.3879-180 AND WAS SET EQUAL TO ZERO
2512.      158.      0.00      0.00      0.00      0.07
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
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      FOR MODEL  3 X(1,1) WAS -0.4567-291 AND WAS SET EQUAL TO ZERO
2512.      251.      0.00      0.00      0.00      0.05
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
2512.      398.      0.00      0.00      0.00      0.03
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
2512.      531.      0.00      0.00      0.00      0.02
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
2512.     1000.      0.00      0.00      0.00      0.01

      FOR MODEL  2 X(1,1) WAS -0.3254-137 AND WAS SET EQUAL TO ZERO
3931.       10.      0.00      0.00      0.00      1.44
      FOR MODEL  1 X(1,1) WAS -0.1026-164 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.1140-225 AND WAS SET EQUAL TO ZERO
3931.       16.      0.00      0.00      0.00      0.91
      FOR MODEL  1 X(1,1) WAS -0.3573-172 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
3931.       25.      0.00      0.00      0.00      0.57
      FOR MODEL  1 X(1,1) WAS -0.3324-279 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
3931.       40.      0.00      0.00      0.00      0.36
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
3931.       63.      0.00      0.00      0.00      0.23
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.5837-141 AND WAS SET EQUAL TO ZERO
3931.      100.      0.00      0.00      0.00      0.14
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.4934-229 AND WAS SET EQUAL TO ZERO
3931.      158.      0.00      0.00      0.00      0.09
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
      FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
3931.      251.      0.00      0.00      0.00      0.05
      FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
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     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
3931.      398.      0.00      0.00      0.00      0.04
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
3931.      531.      0.00      0.00      0.00      0.02
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
3931.     1000.      0.00      0.00      0.00      0.01

     FOR MODEL  1 X(1,1) WAS -0.1627-104 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.2865-225 AND WAS SET EQUAL TO ZERO
6310.       10.      0.00      0.00      0.00      1.81
     FOR MODEL  1 X(1,1) WAS -0.5662-172 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
6310.       16.      0.00      0.00      0.00     -1.14
     FOR MODEL  1 X(1,1) WAS -0.5259-279 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
6310.       25.      0.00      0.00      0.00      0.72
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
6310.       40.      0.00      0.00      0.00      0.45
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.5063-110 AND WAS SET EQUAL TO ZERO
6310.       63.      0.00      0.00      0.00      0.29
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.9744-180 AND WAS SET EQUAL TO ZERO
6310.      100.      0.00      0.00      0.00      0.18
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.1147-290 AND WAS SET EQUAL TO ZERO
6310.      158.      0.00      0.00      0.00      0.11
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
6310.      251.      0.00      0.00      0.00      0.07
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
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          FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
 6310.      398.      0.00      0.00      0.00      0.05
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
 6310.      631.      0.00      0.00      0.00      0.03
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
 6310.     1000.      0.00      0.00      0.00      0.02

          FOR MODEL  1 X(1,1) WAS -0.8974-172 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
10000.       10.      0.00      0.00      0.00      2.29
          FOR MODEL  1 X(1,1) WAS -0.8350-279 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
10000.       16.      0.00      0.00      0.00      1.44
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
10000.       25.      0.00      0.00      0.00      0.91
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
10000.       40.      0.00      0.00      0.00      0.57
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  3 X(1,1) WAS -0.1466-140 AND WAS SET EQUAL TO ZERO
10000.       63.      0.00      0.00      0.00      0.36
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  3 X(1,1) WAS -0.1239-228 AND WAS SET EQUAL TO ZERO
10000.      100.      0.00      0.00      0.00      0.23
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
10000.      158.      0.00      0.00      0.00      0.14
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
10000.      251.      0.00      0.00      0.00      0.09
          FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
          FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
```

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10000.    398.    0.20    0.03    0.00    0.06
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
10000.    631.    0.20    0.03    0.00    0.04
     FOR MODEL  1 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  2 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
     FOR MODEL  3 X(1,1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
10000.   1000.    0.00    0.03    0.00    0.02


    COMPUTED Q VALUES....

CONCEN     100.       158.       251.       398.       631.       1000.      1585.      2512.      3981.      6310.      10000.
  T
   10.  0.113E+06  0.437E+04  0.118E+02  0.444E-03  0.110E-05  0.166E-05  0.248E-05  0.366E-05  0.539E-05  0.796E-05  0.119E-04
   16.  0.214E+04  0.539E+01  0.175E-03  0.299E-06  0.466E-06  0.721E-06  0.110E-05  0.166E-05  0.248E-05  0.366E-05  0.539E-05
   25.  0.203E+01  0.714E-04  0.770E-07  0.121E-06  0.191E-06  0.299E-06  0.467E-06  0.721E-06  0.110E-05  0.166E-05  0.248E-05
   40.  0.285E-04  0.195E-07  0.308E-07  0.487E-07  0.770E-07  0.122E-06  0.191E-06  0.300E-06  0.467E-06  0.721E-06  0.110E-05
   63.  0.490E-08  0.776E-08  0.123E-07  0.195E-07  0.308E-07  0.488E-07  0.771E-07  0.122E-06  0.191E-06  0.300E-06  0.639+301
  100.  0.195E-08  0.309E-08  0.490E-08  0.776E-08  0.123E-07  0.195E-07  0.308E-07  0.488E-07  0.172+308  0.122E-06  0.191E-05
  158.  0.777E-09  0.123E-08  0.195E-08  0.309E-08  0.490E-08  0.776E-08  0.272+307  0.195E-07  0.308E-07  0.488E-07  0.771E-07
  251.  0.309E-09  0.490E-09  0.777E-09  0.123E-08  0.632+306  0.309E-08  0.490E-08  0.776E-08  0.123E-07  0.195E-07  0.308E-07
  398.  0.123E-09  0.195E-09  0.684+305  0.490E-09  0.777E-09  0.123E-08  0.195E-08  0.309E-08  0.490E-08  0.776E-08  0.123E-07
  631.  0.639+297  0.777E-10  0.123E-09  0.195E-09  0.309E-09  0.490E-09  0.777E-09  0.123E-08  0.195E-08  0.309E-08  0.490E-08
 1000.  0.195E-10  0.309E-10  0.490E-10  0.777E-10  0.123E-09  0.195E-09  0.309E-09  0.490E-09  0.777E-09  0.123E-08  0.195E-08

STOP
```

```
      C-------------THIS PROGRAMME DETERMINES OPTIMUM EXPERIMENTAL CONDITIONS
      C-------------FOR PRECISE PARAMETER ESTIMATION USING THE XPRIME-X CRITERION
      C-------------THE VALUE OF XPRIME-X IS COMPUTED
      C-------------OVER THE POSSIBLE EXPERIMENTAL RANGE (OPERABILITY REGION) OF
      C-------------TWO INDEPENDENT VARIABLES
      C-------------AS THE PROGRAMME IS PRESENTLY WRITTEN, THESE INDEPENDENT
      C-------------VARIABLES ARE INITIAL PARTICLE CONCENTRATION (Z1 OR RNO)
      C-------------AND TIME (Z2 OR T), IN MG/L AND SEC RESPECTIVELY
      C-------------G, THE VELOCITY GRADIENT, IS ALSO AN INDEPENDENT VARIABLE
      C-------------BUT IS NOT VARIED
      C-------------THE PROGRAMME COMPUTES THE OPTIMUM CONDITIONS FOR ONE
      C-------------ADDITIONAL RUN
      C-------------INPUT DATA ARE
      C-------------          XPX--THE LATEST VALUE OF THE XPRIME-X INVERSE MATRIX
      C-------------          FROM UWHAUS (THIS IS INVERTED BY THIS PROGRAMME,TO
      C-------------          OBTAIN XPRIME-X)
      C-------------          TH--THE MOST RECENT PARAMETER ESTIMATE(S)
      C-------------          RNOMIN/RNOMAX,TMIN/TMAX--MINIMUM/MAXIMUM VALUES TO BE
      C-------------          CONSIDERED FOR RNO AND T
      C-------------          N1INC,N2INC--THE NUMBER OF INCREMENTS OF THE TWO
      C-------------          INDEPENDENT VARIABLES, WITHIN THEIR RESPECTIVE RANGES
      C-------------          G THE VELOCITY GRADIENT
      C-------------          NP--THE NUMBER OF PARAMETERS IN THE MODEL
      C-------------NINVAR IS THE NUMBER OF INDEPENDENT VARIABLES (INCLUDING G)
      C-------------YHAT IS THE PREDICTED VALUE AT GIVEN CONDITIONS
      C-------------XN IS THE DERIVATIVE(S) OF THE MODEL WITH RESPECT TO ITS
      C-------------PARAMETER(S), EVALUATED AT CHOSEN CONDITIONS
      C-------------XNPXN IS XN MULTIPLIED BY ITSELF
      C-------------XNX IS USED TO STORE XNPXN TEMPORARILY
      C-------------XPLUS IS XPX+XNPXN
      C-------------LL AND MM ARE WORK VECTORS REQUIRED BY LIBRARY S/R MINV
      C-------------D OR XCRIT IS THE DETERMINANT OF XPLUS
      C-------------THESE DIMENSIONS CHANGE ONLY IF THE OPERABILITY REGION CHANGES
      C-------------DIMENSION Z1(N1INC+1),Z2(N2INC+1),XCRIT(N1INC+1,N2INC+1),
      C-------------            YHAT(N1INC+1,N2INC+1),ZED(NINVAR)
            DIMENSION Z1(11),Z2(11),XCRIT(11,11),YHAT(11,11),ZED(3)
      C-------------THESE DIMENSIONS CHANGE IF THE MODEL CHANGES
      C-------------DIMENSION TH(NP),XN(1,NP),XNX(NP,NP),XNPXN(NP,NP),XPX(NP,NP),
      C-------------            XPLUS(NP,NP),LL(NP),MM(NP)
            DIMENSION TH(2),XN(1,2),XNX(2,2),XNPXN(2,2),XPX(2,2),XPLUS(2,2),
           1 LL(2),MM(2)
            READ( 60,7) RNOMIN,RNOMAX,TMIN,TMAX,N1INC,N2INC,G
            WRITE(61, 5)
            WRITE(61,9) RNOMIN,RNOMAX,TMIN,TMAX,N1INC,N2INC,G
            READ (60,102) NP
            READ (60,104) (TH(I),I=1,NP)
            WRITE(61, 8)
            WRITE(61,112) NP,(TH(I),I=1,NP)
            WRITE(61,10)
            DO 6 I=1,NP
            READ (60,106) (XPX(I,J),J=1,NP)
            WRITE(61,118) (XPX(I,J),J=1,NP)
          6 CONTINUE
      C-------------INVERT XPRIME-X INVERSE TO FORM XPRIME-X
            CALL MINV(XPX,NP,DD,LL,MM)
            WRITE(61,12)
            DO 16 I=1,NP
         16 WRITE(61,118) (XPX(I,J),J=1,NP)
            WRITE(61,14)
      C-------------SET UP GRID OF POINTS (EQUALLY SPACED ON LOG SCALE) AT WHICH
      C-------------TO EVALUATE XPRIME-X CRITERION
            N1INC1=N1INC+1
            N2INC1=N2INC+1
            B1=(ALOG(RNOMAX)-ALOG(RNOMIN))/N1INC
            B2=(ALOG(  TMAX)-ALOG(  TMIN))/N2INC
      C-------------EVALUATE YHAT AND XPRIME-X CRITERION FOR EACH POINT ON GRID
            DO 40 I=1,N1INC1
            DO 39 J=1,N2INC1
            Z1(I)=RNOMIN*EXP((I-1)*B1)
            Z2(J)=TMIN*EXP((J-1)*B2)
      C-------------CALCULATE YHAT AT THE CHOSEN CONDITIONS
            ZED(1)=Z1(I)
            ZED(2)=G
            ZED(3)=Z2(J)
            CALL YHCAL4(ZED,YCAL,TH)
            YHAT(I,J)=YCAL
      C-------------EVALUATE THE DERIVATIVE(S) AT THE CHOSEN CONDITIONS
            CALL DERIV4(ZED,XN,TH,NP)
```

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FORTRAN(2.3)/MASTER   INTEGER WORD SIZE = 1 , A OPTION IS OFF , D OPTION IS OF

C-------------EVALUATE XNPRIME-XN (XNX)
         CALL GAS011(XN,XNX,1,NP,0)
C-------------CHANGE THE STORAGE MODE OF XNX FROM SYMMETRIC TO GENERAL
         CALL GAS041(XNX,XNPXN,NP,1,0)
C-------------ADD XNPXN TO XPX
         CALL GAS001(XPX,XNPXN,XPLUS,NP,NP)
C-------------EVALUATE THE DETERMINANT, D
         CALL MINV(XPLUS,NP,D,LL,MM)
C-------------D IS THE CRITERION FOR THE CHOSEN CONDITIONS
         XCRIT(I,J)=D
      39 CONTINUE
      40 CONTINUE
C-------------PRINT PREDICTED YHAT VALUES TO INDICATE TRIALS WHICH WILL
C-------------GIVE MEASURABLE RESULTS
         WRITE (61,114)
         WRITE(61,21)Z1
         DO 50 J=1,N2INC1
      50 WRITE(61,23)Z2(J),(YHAT(I,J),I=1,N1INC1)
C-------------PRINT THE XPRIME-X CRITERION
         WRITE (61,116)
         WRITE(61,21)Z1
         DO 60 J=1,N2INC1
      60 WRITE(61,23)Z2(J),(XCRIT(I,J),I=1,N1INC1)
       5 FORMAT(1H1,20X,≠INPUT DATA....≠,////2X,≠RNOMIN≠,2X,≠RNOMAX≠,
        13X,≠TMIN≠,4X,≠TMAX≠,3X,≠N1INC≠,3X,≠N2INC≠,5X,≠G≠)
       7 FORMAT(4F10.0,2I5,F10.0)
       8 FORMAT(1H0,//8X,≠NP≠,2X,≠PARAMETER ESTIMATES≠)
       9 FORMAT(1H0,4F8.0,I7,1X,I7,1X,F8.0)
      10 FORMAT(1H0,//10X,≠XPRIME-X INVERSE≠)
      12 FORMAT(1H0,//15X,≠XPRIME-X≠)
      14 FORMAT(1H0,//20X,≠DERIVATIVES SET EQUAL TO ZERO TO AVOID UNDERFLOW
        1...≠)
      21 FORMAT(1H0,1X,≠CONCEN≠,11E11.0,//7X,≠I≠)
      23 FORMAT(1H0,F8.0,11E11.3)
     102 FORMAT(I5)
     104 FORMAT(4E10.4)
     106 FORMAT(4E10.4)
     112 FORMAT(1H0,5X,I5,4E12.4)
     114 FORMAT(1H1,10X,≠COMPUTED Y VALUES (YHAT)....≠)
     116 FORMAT(1H1,10X,≠COMPUTED XPRIME-X VALUES (XCRIT)....≠)
     118 FORMAT(1H0,5X,4E12.4)
         STOP
         END

    USASI FORTRAN DIAGNOSTIC RESULTS FOR FTN.MAIN

          NO ERRORS
```

```
FORTRAN(2.3)/MASTER      INTEGER WORD SIZE = 1 , * OPTION IS OFF , 0 OPTION IS   OF

          SUBROUTINE YHCAL4(ZED,YCAL,TH)
    C-------------THIS S/R COMPUTES YHAT
    C-------------P M HUCK  OCT 8/76
          DIMENSION ZED(1),TH(1)
          YCAL    =(ZED( 1)*(1.-TH(  2))*EXP(-TH(  1)*SQRT(ZED( 1))*ZED( 3)))
         1      +(TH(  2)*ZED( 1))
          RETURN
          END

  USASI FORTRAN DIAGNOSTIC RESULTS FOR YHCAL4

       NO ERRORS
```

```
FORTRAN(2.3)/MASTER     INTEGER WORD SIZE = 1 , * OPTION IS  OFF , 0 OPTION IS  0

                SUBROUTINE DERIV4(ZED,X,TH,NP)
         C-------------THIS S/R COMPUTES MODEL DERIVATIVES (X VALUES)
         C-------------P M HUCK - OCT 8/76
                DIMENSION ZED(1),TH(1),X(1,2)
                Q=SQRT(ZED( 1)*ZED( 3))
                X(1,1)=-Q*     ZED( 1) *(1.-TH(  2))*EXP(-TH(  1)*Q)
                X(1,2)=ZED( 1)*(1.-EXP(-TH(  1)*Q))
         C-------------IF DERIVATIVE IS LESS THAN 10E-100, SET IT EQUAL TO ZERO
         C-------------TO AVOID EXPONENT UNDERFLOW PROBLEM IN CALCULATION OF
         C-------------XNPRIME-XN MATRIX.  THIS CHANGE HAS NO EFFECT ON
         C-------------CALCULATIONS
                P=10.**(-100.)
                DO 70 L=1,NP
                IF(ABS(X(1,L)).LT.P) GO TO 50
                GO TO 60
             50 CONTINUE
                WRITE(61,200) ZED(1),ZED(3),L,X(1,L)
                X(1,L)=0.0
             60 CONTINUE
             70 CONTINUE
            200 FORMAT(1H0,10X,≠FOR CONCEN =≠,F8.0,≠  AND TIME =≠,F5.0,≠X(≠,I1,≠)
               1WAS≠,     E12.4,≠ AND WAS SET EQUAL TO ZERO≠)
                RETURN
                END

    USASI FORTRAN DIAGNOSTIC RESULTS FOR DERIV4

           NO ERRORS

I3,PDIR
```

```
                    INPUT DATA....

RHOMIN  RHOMAX   TMIN    TMAX   N1INC   N2INC     G
  100.  10000.    10.   1000.     10      10     194.

    IP  PARAMETER ESTIMATES
      2  0.4106E-01  0.6568E-14

      XPRIME-X INVERSE
     0.9567E-05  0.2422E-07
     0.2422E-07  0.3508E-07

          XPRIME*X
     0.1047E+06 -0.7229E+05
    -0.7229E+05  0.2856E+08

          DERIVATIVES SET EQUAL TO ZERO TO AVOID UNDERFLOW...
      FOR CONCEN =    100.  AND TIME = 631.X(1) HAS -0.1936-106 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    100.  AND TIME =1000.X(1) HAS -0.4772-172 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    158.  AND TIME = 631.X(1) HAS -0.2847-135 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    158.  AND TIME =1000.X(1) HAS -0.5408-218 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    251.  AND TIME = 398.X(1) HAS -0.4862-106 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    251.  AND TIME = 631.X(1) HAS -0.1199-171 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    251.  AND TIME =1000.X(1) HAS -0.3544-276 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    398.  AND TIME = 398.X(1) HAS -0.7150-135 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    398.  AND TIME = 631.X(1) HAS -0.1610-217 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    398.  AND TIME =1000.X(1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    631.  AND TIME = 251.X(1) HAS -0.1221-105 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    631.  AND TIME = 398.X(1) HAS -0.3011-171 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    631.  AND TIME = 631.X(1) HAS -0.2397-275 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =    631.  AND TIME =1000.X(1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1000.  AND TIME = 251.X(1) HAS -0.1796-134 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1000.  AND TIME = 398.X(1) HAS -0.4343-217 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1000.  AND TIME = 631.X(1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1000.  AND TIME =1000.X(1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1585.  AND TIME = 158.X(1) HAS -0.3068-105 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1585.  AND TIME = 251.X(1) HAS -0.7562-171 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1585.  AND TIME = 398.X(1) HAS -0.6022-275 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1585.  AND TIME = 631.X(1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   1585.  AND TIME =1000.X(1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   2512.  AND TIME = 158.X(1) HAS -0.4511-134 AND HAS SET EQUAL TO ZERO
      FOR CONCEN =   2512.  AND TIME = 251.X(1) HAS -0.1016-216 AND HAS SET EQUAL TO ZERO.
      FOR CONCEN =   2512.  AND TIME = 398.X(1) HAS -0.0000E+00 AND HAS SET EQUAL TO ZERO
```

```
FOR CONCEN =   2512.  AND TIME = 631.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   2512.  AND TIME =1000.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   3981.  AND TIME = 100.X(1) WAS -0.7706-105 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   3981.  AND TIME = 158.X(1) WAS -0.1900-170 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   3981.  AND TIME = 251.X(1) WAS -0.1513-274 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   3981.  AND TIME = 398.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   3981.  AND TIME = 631.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   3981.  AND TIME =1000.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   6310.  AND TIME = 100.X(1) WAS -0.1133-133 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   6310.  AND TIME = 158.X(1) WAS -0.2551-216 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   6310.  AND TIME = 251.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   6310.  AND TIME = 398.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   6310.  AND TIME = 631.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =   6310.  AND TIME =1000.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =  10000.  AND TIME =  63.X(1) WAS -0.1936-104 AND WAS SET EQUAL TO ZERO
FOR CONCEN =  10000.  AND TIME = 100.X(1) WAS -0.4772-170 AND WAS SET EQUAL TO ZERO
FOR CONCEN =  10000.  AND TIME = 158.X(1) WAS -0.3800-274 AND WAS SET EQUAL TO ZERO
FOR CONCEN =  10000.  AND TIME = 251.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =  10000.  AND TIME = 398.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =  10000.  AND TIME = 631.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
FOR CONCEN =  10000.  AND TIME =1000.X(1) WAS -0.0000E+00 AND WAS SET EQUAL TO ZERO
```

```
     COMPUTED Y VALUES (YHAT).....
CONCEN     100.       158.       251.       398.       631.       1000.      1585.      2512.      3981.      6310.      10000.
  T
   10.  0.165E+01  0.912E+00  0.391E+00  0.136E+00  0.624E-01  0.680E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
   16.  0.155E+00  0.543E-01  0.248E-01  0.271E-01  0.415E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
   25.  0.983E-02  0.109E-01  0.165E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
   40.  0.558E-02  0.104E-01  0.155E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
   63.  0.637E-02  0.104E-01  0.165E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
  100.  0.657E-02  0.104E-01  0.165E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
  158.  0.657E-02  0.104E-01  0.155E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
  251.  0.657E-02  0.104E-01  0.165E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
  398.  0.657E-02  0.104E-01  0.165E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
  631.  0.657E-02  0.104E-01  0.165E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00
 1000.  0.657E-02  0.104E-01  0.165E-01  0.261E-01  0.414E-01  0.657E-01  0.104E+00  0.165E+00  0.261E+00  0.414E+00  0.657E+00


     COMPUTED XPRIME-X VALUES (XCRIT).......
CONC'N     100.       158.       251.       398.       631.       1000.      1585.      2512.      3981.      6310.      10000.
  T
   10.  0.376E+13  0.335E+13  0.309E+13  0.301E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
   16.  0.3[illegible]E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
   25.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
   40.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
   63.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
  100.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
  158.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
  251.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
  398.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
  631.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
 1000.  0.299E+13  0.299E+13  0.299E+13  0.300E+13  0.303E+13  0.309E+13  0.325E+13  0.365E+13  0.464E+13  0.715E+13  0.135E+14
STOP
```

```
C
C
C     HT(I) --- I-TH POINT CHROMATOGRAM HEIGHT FROM BASE-LINE
C     EV(I) --- I-TH POINT ELUTION(RETENTION) VOLUME BY COUNT
C     FV(I) --- HT(I) NORMALIZED WITH RESPECT TO AREA UNDER CURVE
C     FW(I) --- I-TH POINT WEIGHT FRACTION
C     M(I)  --- I-TH POINT MOLECULAR WEIGHT CALCULATED FROM CALIBRATION CURV
C     MNOO --- RESOLUTION UNCORRECTED NO. AVE. MOL. WT.
C     MWOO --- RESOLUTION UNCORRECTED WT. AVE. MOL. WT.
C     MZOO --- RESOLUTION UNCORRECTED  Z- AVE. MOL. WT.
C     POO --- RESOLUTION UNCORRECTED POLYDISPERSITY
C     DMDV(I) --- DERIVATIVE D(M)/D(V)
C     NDP --- NO. OF DATA POINT
C     V0 --- ELUTION VOLUME OF THE FIRST POIINT = EV(1)
C     VF --- ELUTION VOLUME OF THE LAST POINT = EV(NDP)
C     CINC --- INCLEMENT OF DATA POINT BY COUNT
C
C
C
      REAL   MZ, MN, MW, HT(300), FV(300), EV(300), FW(300), MZP100,
     1      M(300), YMN(300), YMW(300), YMZ(300), MNOO, MWOO, MZOO,
     2       DMDV(300),YMZP1(300),CUMFW(300),CUMFV(300)
C
      FUNCM(V)=D1*EXP(-(D2*V+D3*V**2+D4*V**3+D5*V**4))
      FUNCD(V)=D2+2.0*D3*V+3.0*D4*V**2+4.0*D5*V**3
C
      READ(60,500)NCURVE
      READ(60,505)D1,D2,D3,D4,D5
      DO 200 NC=1,NCURVE
      READ(60,501)NHEAD,POLID,DATE,PH
      READ(60,503)NDP, V0, VF, CINC
      READ(60,504)(HT(I),I=1,NDP)
C
      WRITE(61,600)NHEAD
      WRITE(61,601)POLID
      WRITE(61,602)DATE
      WRITE(61,603)PH
      WRITE(61,609)NDP
      WRITE(61,610)CINC
      WRITE(61,616)D1,D2,D3,D4,D5
C
      DO 100 I=1,NDP
      EV(I)=V0+CINC*FLOAT(I-1)
      M(I)=FUNCM(EV(I))
      DMDV(I)=M(I)*FUNCD(EV(I))
  100 CONTINUE
C
      CALL SIMPSON(EV,HT,CINC,NDP,AINTHT)
      DO 105 I=1,NDP
      FV(I)=HT(I)/AINTHT
      FW(I)=FV(I)/DMDV(I)
  105 CONTINUE
C
      CUMFW(1)=0.
      CUMFV(1)=0.
      DO77 I=2,NDP
      AREAFV=0.5*(EV(I)+EV(I-1))*CINC
      CUMFV(I)=CUMFV(I-1)+AREAFV
      AREAFW=0.5*(FW(I)+FW(I-1))*(M(I-1)-M(I))
      CUMFW(I)=CUMFW(I-1)+AREAFW
   77 CONTINUE
      DO88 I=1,NDP
      CUMFV(I)=1.-CUMFV(I)
      CUMFW(I)=1.-CUMFW(I)
   88 CONTINUE
C
      WRITE(61,620)
      WRITE(61,635)
      WRITE(61,621)
      WRITE(61,622)(I, EV(I), HT(I), FV(I), CUMFV(I), M(I), FW(I), CUMFW
     1(I), I=1,NDP)
      WRITE(61,635)
      WRITE(61,662)
      WRITE(61,625)AINTHT
      WRITE(61,635)
      WRITE(61,624)
C
      DO 120  I=1,NDP
```

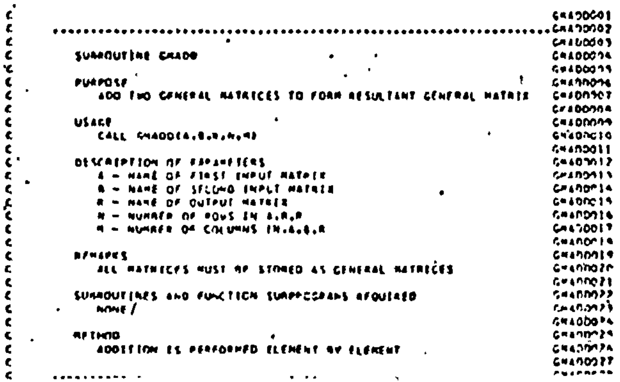
```
            YMN(I)=FV(I)/M(I)
            YMW(I)=FV(I)*M(I)
            YMZ(I)=YMW(I)*M(I)
            YMZP1(I)=FV(I)*(M(I)**3)
    120     CONTINUE
            CALL SIMPSON(EV,YMN,CINC,NOP,AINTYMN)
            CALL SIMPSON(EV,YMW,CINC,NOP,AINTYMW)
            CALL SIMPSON(EV,YMZ,CINC,NOP,AINTYMZ)
            CALL SIMPSON(EV,YMZP1,CINC,NOP,AMZP1)
            MNOO=1.0/AINTYMN
            MWOO=AINTYMW
            POO=MWOO/MNOO
            MZOO=AINTYMZ/MWOO
            MZP100=AMZP1/(MZOO*MWOO)
      C
            WRITE(61,630)MNOO
            WRITE(61,631)MWOO
            WRITE(61,632)MZOO
            WRITE(61,680)MZP100
            WRITE(61,634)POO
            WRITE(61,635)
      C
      200   CONTINUE
      C
      C
      500   FORMAT(I10)
       501  FORMAT(A5,A10,A10,F5.2)
      503   FORMAT(I10,3F10.2)
      504   FORMAT(16F5.0)
       505  FORMAT(5E15.4)
       600  FORMAT(1H1,30X,*+++GPC RUN NO.*,A5,*+++*//)
       601  FORMAT(10X,*POLYMER SAMPLE ID...........................*,A10)
       602  FORMAT(10X,*DATE.......................................*,A10)
       603  FORMAT(10X,*PH OF SOLVENT..............................*,F5.2)
      609   FORMAT(10X, *NO. OF DATA POINTS READ -----------*, I5)
      610   FORMAT(10X, *INTERVAL OF DATA POINT BY COUNT ---*, F6.3)
      616   FORMAT(10X,*CALIBRATION CURVE*,8X,*M=D1.EXP(-(D2.V+D3.V.V+D4.V.V.V
           1+D5.V.V.V.V))*/40X,*D1=*,E11.4,3X,*D2=*,E11.4,3X,*D3=*,E11.4/
           1 40X,*D4=*,E11.4,3X,*D5=*,E11.4)
      620   FORMAT(1H0, 10X, * ... GPC DATA ... */)
       621  FORMAT(3X,*I*,5X,*EV(I)*,8X,*HT(I)*,11X,*FV(I)*,10X,*CUM FV(I)*,9X
           1,*MOL. WT.*,11X,*W(M)*,11X,*CUM W(M)*/)
       622  FORMAT(I4,3X,F6.2,7X,F6.2,6X,E11.4,6X,E11.4,6X,E11.4,6X,E11.4,6X,E
           111.4)
      624   FORMAT(1H0, 10X,*COMPARISONS ASSUMING INFINITE RESOLUTION*/)
       625  FORMAT(20X,*AREA UNDER CURVE = *,E10.3/)
      630   FORMAT(15X,*MN(T) = *,7X,    10X,*MN(OO) = *,F9.0,10X,*MN(T)/MN(OO)
           1 = *)
      631   FORMAT(15X,*MW(T) = *,7X,  10X,*MW(OO) = *, F9.0,10X,*MW(T)/MW(OO)
           1 = *)
      632   FORMAT(15X,*MZ(T) = *,7X,  10X,*MZ(OO) = *,F9.0,10X,*MZ(T)/MZ(OO)
           1= *)
      680   FORMAT(13X,*MZ+1(T) = *,15X,*MZ+1(OO) = *,F9.0)
      634   FORMAT(16X,*P(T) = *,6X,  12X,*P(OO) = *, F6.3/)
      635   FORMAT(121(1H*))
      662   FORMAT(1H1,10X,*NORMALIZED CHROMATOGRAM*/)
            STOP
            END

USASI FORTRAN DIAGNOSTIC RESULTS FOR FTN.MAIN

      NO ERRORS

LOWING ARE COMMON BLOCK NAMES OR NAMES NOT ASSIGNED STORAGE

      MN        MW        V
```

```
FORTRAN(2.3)/MASTER    INTEGER WORD SIZE = 1 , * OPTION IS  OFF , D OPTION IS  OF

      C
      C
            SUBROUTINE SIMPSON(X,Y,DELX,N,AINTY)
            DIMENSION X(300),Y(300),YN(300)
      C *** THIS SUBPROGRAM EVALUATE ZERO MOMENT OF DISTRIBUTION Y=F(X),
      C
      C
      C     ASSUME NO. OF DATA POINT IS ODD
            NE=0
            IF((N/2)*2.NE.N) GO TO 3
      C     IT WAS EVEN, THUS CHANGE NE
            NE=1
            N=N+1
            Y(N)=0.0
            X(N)=X(N-1)+DELX
        3   CONTINUE
            NM1=N-1
            NM2=N-2
            SUMODD=0.0
            SUMEVEN=0.0
            DO 4 I=2,NM1,2
            SUMEVEN=SUMEVEN+Y(I)
        4   CONTINUE
            DO 5 I=3,NM2,2
            SUMODD=SUMODD+Y(I)
        5   CONTINUE
            SUM=Y(1)+4.0*SUMEVEN+2.0*SUMODD+Y(N)
            AINTY=DELX*SUM/3.0
            IF(NE.LT.1) RETURN
            N=N-1
            OMAKE=DELX*Y(N)/2.0
            AINTY=AINTY-OMAKE
            RETURN
            END

 USASI FORTRAN DIAGNOSTIC RESULTS FOR SIMPSON

      NO ERRORS
```

```
                    ***GPC RUN NO. PAM ***

POLYMER SAMPLE ID..............................  RC MIOM4
DATE...........................................  E8 18,76
PH OF SOLVENT..................................  0.00
NO. OF DATA POINTS READ -----------         23
INTERVAL OF DATA POINT BY COUNT --- 0.500
CALIBRATION CURVE          M=D1.EXP(-(D2.V+D3.V.V+D4.V.V.V+D5.V.V.V.V))
                                 D1= 0.3655E+19   D2= 0.9190E+00   D3= 0.0000E+00
                                 D4= 0.0000E+00   D5= 0.0000E+00

    ... GPC DATA ...

****************************************************************************************************
  I     V(I).      HT(I)        FV(I)         CUM FV(I)        MOL. WT.         W(M)          CUM W(M)

  1    27.00        0.00      0.0000E+00     0.1000E+01     0.6120E+08     0.0000E+00     0.1000E+01
  2    27.50        5.00      0.4590E-02     0.9989E+00     0.3865E+08     0.1292E-09     0.9985E+00
  3    28.00       19.00      0.1745E-01     0.9933E+00     0.2441E+08     0.7774E-09     0.9921E+00
  4    28.50       40.00      0.3672E-01     0.9798E+00     0.1542E+08     0.2591E-08     0.9769E+00
  5    29.00       80.00      0.7346E-01     0.9523E+00     0.9739E+07     0.8206E-08     0.9463E+00
  6    29.50      141.00      0.1294E+00     0.9016E+00     0.6151E+07     0.2290E-07     0.8935E+00
  7    30.00      192.00      0.1763E+00     0.8252E+00     0.3885E+07     0.4937E-07     0.8166E+00
  8    30.50      218.00      0.2001E+00     0.7310E+00     0.2454E+07     0.8875E-07     0.7396E+00
  9    31.00      226.00      0.2075E+00     0.6291E+00     0.1550E+07     0.1457E-06     0.6038E+00
 10    31.50      219.00      0.2010E+00     0.5270E+00     0.9789E+06     0.2235E-06     0.4384E+00
 11    32.00      199.00      0.1827E+00     0.4311E+00     0.6182E+06     0.3215E-06     0.4002E+00
 12    32.50      174.00      0.1597E+00     0.3455E+00     0.3905E+06     0.4451E-06     0.3129E+00
 13    33.00      149.00      0.1368E+00     0.2713E+00     0.2466E+06     0.6035E-06     0.2374E+00
 14    33.50      126.00      0.1157E+00     0.2082E+00     0.1558E+06     0.8080E-06     0.1733E+00
 15    34.00      103.00      0.9456E-01     0.1557E+00     0.9838E+05     0.1146E-05     0.1291E+00
 16    34.50       87.00      0.7989E-01     0.1121E+00     0.6214E+05     0.1399E-05     0.7583E-01
 17    35.00       67.00      0.6151E-01     0.7673E-01     0.3925E+05     0.1705E-05     0.4030E-01
 18    35.50       50.00      0.4590E-01     0.4988E-01     0.2479E+05     0.2015E-05     0.1343E-01
 19    36.00       35.00      0.3213E-01     0.3037E-01     0.1566E+05     0.2233E-05    -0.5991E-02
 20    36.50       23.00      0.2111E-01     0.1706E-01     0.9889E+04     0.2323E-05    -0.1313E-01
 21    37.00       14.00      0.1285E-01     0.8568E-02     0.6245E+04     0.2239E-05    -0.2744E-01
 22    37.50        9.00      0.8262E-02     0.3289E-02     0.3944E+04     0.2279E-05    -0.3264E-01
 23    38.00        0.00      0.0000E+00     0.1224E-02     0.2491E+04     0.0000E+00    -0.3430E-01
****************************************************************************************************


      NORMALIZED CHROMATOGRAM
           AREA UNDER CURVE =  0.109E+04
****************************************************************************************************

      COMPARISONS ASSUMING INFINITE RESOLUTION

          MN(T) =                    MN(00) =     118422.          MN(T)/MN(00) =
          MW(T) =                    MW(00) =    2311650.          MW(T)/MW(00) =
          MZ(T) =                    MZ(00) =    9288951.          MZ(T)/MZ(00) =
        MZ+1(T) =                  MZ+1(00) =   18527670.
           P(T) =                     P(00) =     19.520
****************************************************************************************************

 STOP
```

CLASSIFICATION: Matrix Operations		NO.: 04.06/2
NAME: GAS001	LANGUAGE: Fortran	DATE:
AUTHOR:	SOURCE EMR Library	
MACHINE: CDC3170	OP.SYS.: MASTER	
MEMORY REQUIREMENTS:	SPECIAL CONFIGURATION:	See: P.LIB.AUX.LIB.

CALL GAS001 (A, B, R, N, M)



```
C                                                                    GMAD0001
C     .............................................................. GMAD0002
C                                                                    GMAD0003
C        SUBROUTINE GMADD                                            GMAD0004
C                                                                    GMAD0005
C        PURPOSE                                                     GMAD0006
C           ADD TWO GENERAL MATRICES TO FORM RESULTANT GENERAL MATRIX GMAD0007
C                                                                    GMAD0008
C        USAGE                                                       GMAD0009
C           CALL GMADD(A,B,R,N,M)                                    GMAD0010
C                                                                    GMAD0011
C        DESCRIPTION OF PARAMETERS                                   GMAD0012
C           A - NAME OF FIRST INPUT MATRIX                           GMAD0013
C           B - NAME OF SECOND INPUT MATRIX                          GMAD0014
C           R - NAME OF OUTPUT MATRIX                                GMAD0015
C           N - NUMBER OF ROWS IN A,B,R                              GMAD0016
C           M - NUMBER OF COLUMNS IN A,B,R                           GMAD0017
C                                                                    GMAD0018
C        REMARKS                                                     GMAD0019
C           ALL MATRICES MUST BE STORED AS GENERAL MATRICES          GMAD0020
C                                                                    GMAD0021
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED               GMAD0022
C           NONE                                                     GMAD0023
C                                                                    GMAD0024
C        METHOD                                                      GMAD0025
C           ADDITION IS PERFORMED ELEMENT BY ELEMENT                 GMAD0026
C                                                                    GMAD0027
C     ..........                                                     [illegible]
```

General Matrix

- N * M elements in storage

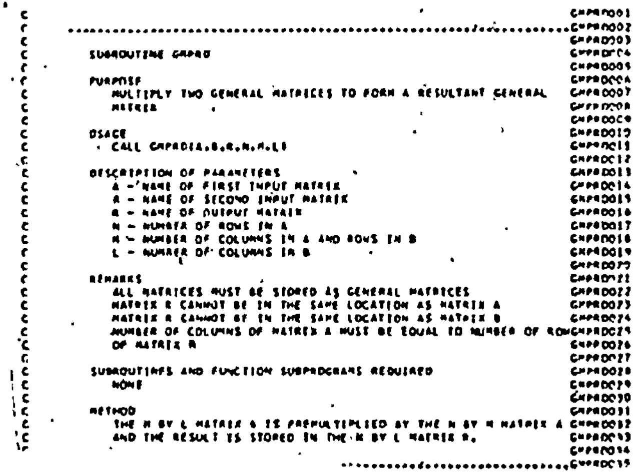
eg

$$\begin{array}{c|cccc} & M= 1 & 2 & 3 & 4 \\ \hline N=1 & 1 & 5 & 9 & 13 \\ 2 & 2 & 6 & 10 & 14 \\ 3 & 3 & 7 & 11 & 15 \\ 4 & 4 & 8 & 12 & 16 \end{array}$$

4 * 4 = 16 elements

CLASSIFICATION: Matrix Operations
NO.: 04.06/4
NAME: GAS003
LANGUAGE: Fortran
DATE:
AUTHOR:
SOURCE EMR Library
MACHINE: CDC3170
OP.SYS.: MASTER
MEMORY REQUIREMENTS:
SPECIAL CONFIGURATION:
See: P.LIB.AUX.LIB.

CALL GAS003 (A, B, R, N, M, L)



```
C                                                                       GMPRD001
C     ..................................................................GMPRD002
C                                                                       GMPRD003
C        SUBROUTINE GMPRD                                               GMPRD004
C                                                                       GMPRD005
C        PURPOSE                                                        GMPRD006
C           MULTIPLY TWO GENERAL MATRICES TO FORM A RESULTANT GENERAL   GMPRD007
C           MATRIX                                                      GMPRD008
C                                                                       GMPRD009
C        USAGE                                                          GMPRD010
C           CALL GMPRD(A,B,R,N,M,L)                                     GMPRD011
C                                                                       GMPRD012
C        DESCRIPTION OF PARAMETERS                                      GMPRD013
C           A - NAME OF FIRST INPUT MATRIX                              GMPRD014
C           B - NAME OF SECOND INPUT MATRIX                             GMPRD015
C           R - NAME OF OUTPUT MATRIX                                   GMPRD016
C           N - NUMBER OF ROWS IN A                                     GMPRD017
C           M - NUMBER OF COLUMNS IN A AND ROWS IN B                    GMPRD018
C           L - NUMBER OF COLUMNS IN B                                  GMPRD019
C                                                                       GMPRD020
C        REMARKS                                                        GMPRD021
C           ALL MATRICES MUST BE STORED AS GENERAL MATRICES             GMPRD022
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX A         GMPRD023
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX B         GMPRD024
C           NUMBER OF COLUMNS OF MATRIX A MUST BE EQUAL TO NUMBER OF ROWGMPRD025
C           OF MATRIX B                                                 GMPRD026
C                                                                       GMPRD027
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                  GMPRD028
C           NONE                                                        GMPRD029
C                                                                       GMPRD030
C        METHOD                                                         GMPRD031
C           THE M BY L MATRIX B IS PREMULTIPLIED BY THE N BY M MATRIX A GMPRD032
C           AND THE RESULT IS STORED IN THE N BY L MATRIX R.            GMPRD033
C                                                                       GMPRD034
C                                 ..................................GMPRD035
                                                                        GMPRD036
```

General Matrix

- N * M elements in storage

eg

M=	1	2	3	4
N=1	1	5	9	13
2	2	6	10	14
3	3	7	11	15
4	4	8	12	16

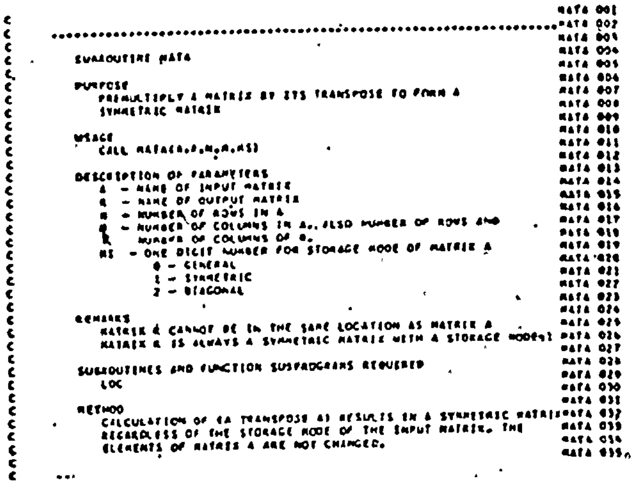
4 * 4 = 16 elements

CLASSIFICATION: Matrix Operations	NO.: 04.06/12

NAME: GAS011	LANGUAGE: Fortran	DATE:

AUTHOR:	SOURCE EMR Library
MACHINE: CDC3170	OP.SYS.: MASTER
MEMORY REQUIREMENTS:	SPECIAL CONFIGURATION:

CALL GAS011 (A, R, N, M, MS)



```
C                                                                       MATA 001
C     ..................................................................MATA 002
C                                                                       MATA 003
C        SUBROUTINE MATA                                                MATA 004
C                                                                       MATA 005
C        PURPOSE                                                        MATA 006
C           PREMULTIPLY A MATRIX BY ITS TRANSPOSE TO FORM A             MATA 007
C           SYMMETRIC MATRIX                                            MATA 008
C                                                                       MATA 009
C        USAGE                                                          MATA 010
C           CALL MATA(A,R,N,M,MS)                                       MATA 011
C                                                                       MATA 012
C        DESCRIPTION OF PARAMETERS                                      MATA 013
C           A  - NAME OF INPUT MATRIX                                   MATA 014
C           R  - NAME OF OUTPUT MATRIX                                  MATA 015
C           N  - NUMBER OF ROWS IN A                                    MATA 016
C           M  - NUMBER OF COLUMNS IN A. ALSO NUMBER OF ROWS AND        MATA 017
C                NUMBER OF COLUMNS OF R.                                MATA 018
C           MS  - ONE DIGIT NUMBER FOR STORAGE MODE OF MATRIX A         MATA 019
C                  0 - GENERAL                                          MATA 020
C                  1 - SYMMETRIC                                        MATA 021
C                  2 - DIAGONAL                                         MATA 022
C                                                                       MATA 023
C        REMARKS                                                        MATA 024
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX A         MATA 025
C           MATRIX R IS ALWAYS A SYMMETRIC MATRIX WITH A STORAGE MODE=1 MATA 026
C                                                                       MATA 027
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                  MATA 028
C           LOC                                                         MATA 029
C                                                                       MATA 030
C        METHOD                                                         MATA 031
C           CALCULATION OF (A TRANSPOSE A) RESULTS IN A SYMMETRIC MATRIXMATA 032
C           REGARDLESS OF THE STORAGE MODE OF THE INPUT MATRIX. THE     MATA 033
C           ELEMENTS OF MATRIX A ARE NOT CHANGED.                       MATA 034
C                                                                       MATA 035
C
C     ...
```

General Matrix

- N * M elements in storage

eg	M= 1	2	3	4
N=1	1	5	9	13
2	2	6	10	14
3	3	7	11	15
4	4	8	12	16

4 * 4 = 16 elements

Symmetric Matrix

- N * (N + 1) / 2 elements in storage

eg	M= 1	2	3	4
N= 1	1.	2	4	7
2	(2)	3	5	8
3	(4)	(5)	6	9
4	(7)	(8)	(9)	10

4 * (4+1)/2
= 10 elements

Diagonal Matrix

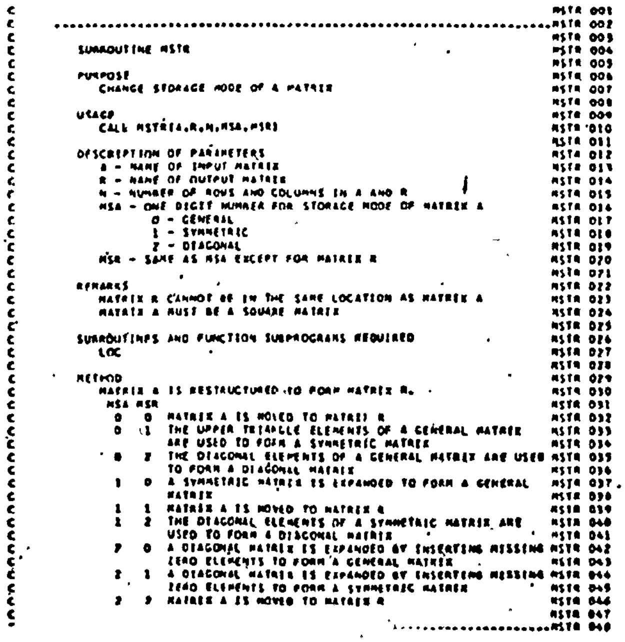
- N elements in storage

eg	M= 1	2	3	4
N= 1	1	(0)	(0)	(0)
2	(0)	2	(0)	(0)
3	(0)	(0)	3	(0)
4	(0)	(0)	(0)	4

4 elements

CLASSIFICATION: Matrix Operations		NO.: 04.06/42	
NAME: GAS041	LANGUAGE: Fortran	DATE:	
AUTHOR:	SOURCE EMR Library		
MACHINE: CDC3170	OP.SYS.: MASTER	See: P.LIB.AUX.LIB.	
MEMORY REQUIREMENTS:	SPECIAL CONFIGURATION:		

CALL GAS041 (A, R, N, MSA, MSR)



```
C                                                                       MSTR 001
C     ..................................................................MSTR 002
C                                                                       MSTR 003
C        SUBROUTINE MSTR                                                MSTR 004
C                                                                       MSTR 005
C        PURPOSE                                                        MSTR 006
C           CHANGE STORAGE MODE OF A MATRIX                             MSTR 007
C                                                                       MSTR 008
C        USAGE                                                          MSTR 009
C           CALL MSTR(A,R,N,MSA,MSR)                                    MSTR 010
C                                                                       MSTR 011
C        DESCRIPTION OF PARAMETERS                                      MSTR 012
C           A - NAME OF INPUT MATRIX                                    MSTR 013
C           R - NAME OF OUTPUT MATRIX                                   MSTR 014
C           N - NUMBER OF ROWS AND COLUMNS IN A AND R                   MSTR 015
C           MSA - ONE DIGIT NUMBER FOR STORAGE MODE OF MATRIX A         MSTR 016
C                  0 - GENERAL                                          MSTR 017
C                  1 - SYMMETRIC                                        MSTR 018
C                  2 - DIAGONAL                                         MSTR 019
C           MSR - SAME AS MSA EXCEPT FOR MATRIX R                       MSTR 020
C                                                                       MSTR 021
C        REMARKS                                                        MSTR 022
C           MATRIX R CANNOT BE IN THE SAME LOCATION AS MATRIX A         MSTR 023
C           MATRIX A MUST BE A SQUARE MATRIX                            MSTR 024
C                                                                       MSTR 025
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                  MSTR 026
C           LOC                                                         MSTR 027
C                                                                       MSTR 028
C        METHOD                                                         MSTR 029
C           MATRIX A IS RESTRUCTURED TO FORM MATRIX R.                  MSTR 030
C            MSA MSR                                                    MSTR 031
C             0   0  MATRIX A IS MOVED TO MATRIX R                      MSTR 032
C             0   1  THE UPPER TRIANGLE ELEMENTS OF A GENERAL MATRIX    MSTR 033
C                    ARE USED TO FORM A SYMMETRIC MATRIX                MSTR 034
C             0   2  THE DIAGONAL ELEMENTS OF A GENERAL MATRIX ARE USED MSTR 035
C                    TO FORM A DIAGONAL MATRIX                          MSTR 036
C             1   0  A SYMMETRIC MATRIX IS EXPANDED TO FORM A GENERAL   MSTR 037
C                    MATRIX                                             MSTR 038
C             1   1  MATRIX A IS MOVED TO MATRIX R                      MSTR 039
C             1   2  THE DIAGONAL ELEMENTS OF A SYMMETRIC MATRIX ARE    MSTR 040
C                    USED TO FORM A DIAGONAL MATRIX                     MSTR 041
C             2   0  A DIAGONAL MATRIX IS EXPANDED BY INSERTING MISSING MSTR 042
C                    ZERO ELEMENTS TO FORM A GENERAL MATRIX             MSTR 043
C             2   1  A DIAGONAL MATRIX IS EXPANDED BY INSERTING MISSING MSTR 044
C                    ZERO ELEMENTS TO FORM A SYMMETRIC MATRIX           MSTR 045
C             2   2  MATRIX A IS MOVED TO MATRIX R                      MSTR 046
C                                                                       MSTR 047
C     ..................................................................MSTR 048
```

CLASSIFICATION: Matrix Operations	NO.: 04.06/58
NAME: MINV	LANGUAGE: Fortran
DATE:	
AUTHOR:	SOURCE EMR Library
MACHINE: CDC3170	OP.SYS.: MASTER
MEMORY REQUIREMENTS:	SPECIAL CONFIGURATION: See P.LIB. AUX.LIB.

CALL MINV (A, N, D, L, M)

```
C
C        ..............................................................MINV 001
C                                                                      MINV 002
C        SUBROUTINE MINV                                               MINV 003
C                                                                      MINV 004
C        PURPOSE                                                       MINV 005
C           INVERT A MATRIX                                            MINV 006
C                                                                      MINV 007
C        USAGE                                                         MINV 008
C           CALL MINV(A,N,D,L,M)                                       MINV 009
C                                                                      MINV 010
C        DESCRIPTION OF PARAMETERS                                     MINV 011
C           A - INPUT MATRIX, DESTROYED IN COMPUTATION AND REPLACED BY MINV 012
C               RESULTANT INVERSE.                                     MINV 013
C           N - ORDER OF MATRIX A                                      MINV 014
C           D - RESULTANT DETERMINANT                                  MINV 015
C           L - WORK VECTOR OF LENGTH N                                MINV 016
C           M - WORK VECTOR OF LENGTH N                                MINV 017
C                                                                      MINV 018
C        REMARKS                                                       MINV 019
C           MATRIX A MUST BE A GENERAL MATRIX                          MINV 020
C                                                                      MINV 021
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                 MINV 022
C           NONE                                                       MINV 023
C                                                                      MINV 024
C        METHOD                                                        MINV 025
C           THE STANDARD GAUSS-JORDAN METHOD IS USED. THE DETERMINANT  MINV 026
C           IS ALSO CALCULATED. A DETERMINANT OF ZERO INDICATES THAT   MINV 027
C           THE MATRIX IS SINGULAR.                                    MINV 028
C                                                                      MINV 029
C                                                                      MINV 030
C        ..............................................................MINV 031
```

General Matrix

- N * M elements in storage

eg

$$\begin{array}{c|cccc} & M=1 & 2 & 3 & 4 \\ \hline N=1 & 1 & 5 & 9 & 13 \\ 2 & 2 & 6 & 10 & 14 \\ 3 & 3 & 7 & 11 & 15 \\ 4 & 4 & 8 & 12 & 16 \end{array}$$

4 * 4 = 16 elements

CLASSIFICATION: Matrix Operations		NO.: 04.06/59
NAME: EIGEN	LANGUAGE: Fortran	DATE:
AUTHOR:	SOURCE EMR Library	
MACHINE: CDC3170	OP.SYS.: MASTER	
MEMORY REQUIREMENTS:	SPECIAL CONFIGURATION: see P.LIB.AUX.LIB	

CALL EIGEN (A, R, N, MV)

This subroutine computes the eigenvalues and eigenvectors of a real symmetric matrix.

Given a symmetric matrix A of order N, eigenvalues are to be developed in the diagonal elements of the matrix. A matrix of eigenvectors R is also to be generated.

An identity matrix is used as a first approximation of R.

The initial off-diagonal norm is computed:

$$\nu_I = \left\{ \sum_{i \le k} 2A_{ik}^2 \right\}^{1/2} \tag{1}$$

ν_I = initial norm

A = input matrix (symmetric)

This norm is divided by N at each stage to produce the threshold.

The final norm is computed:

$$\nu_F = \frac{\nu_I \times 10^{-6}}{N} \tag{2}$$

This final norm is set sufficiently small that the requirement that any off-diagonal element A_{lm} shall be smaller than ν_F in absolute magnitude defines the convergence of the process.

An indicator is initialized. This indicator is later used to determine whether any off-diagonal elements have been found that are greater than the present threshold.

Each off-diagonal element is selected in turn and a transformation is performed to annihilate the off-diagonal (pivotal) element, as shown by the following equations:

$$\lambda = -A_{lm} \tag{3}$$

$$\mu = 1/2\,(A_{ll} - A_{mm}) \tag{4}$$

$$\omega = \text{sign}\,(\mu)\,\frac{\lambda}{\sqrt{\lambda^2 + \mu^2}} \tag{5}$$

$$\sin\theta = \frac{\omega}{\sqrt{2(1 + \sqrt{1 - \omega^2})}} \tag{6}$$

$$\cos\theta = \sqrt{1 - \sin^2\theta} \tag{7}$$

$$B = A_{il}\cos\theta - A_{im}\sin\theta \tag{8}$$

$$C = A_{il}\sin\theta + A_{im}\cos\theta \tag{9}$$

$$B = R_{il}\cos\theta - R_{im}\sin\theta \tag{10}$$

$$R_{im} = R_{il}\sin\theta + R_{im}\cos\theta \tag{11}$$

$$R_{il} = B \tag{12}$$

$$\begin{aligned} A_{ll} &= A_{il}\cos^2\theta + A_{mm}\sin^2\theta \\ &\quad - 2A_{lm}\sin\theta\cos\theta \end{aligned} \tag{13}$$

$$\begin{aligned} A_{mm} &= A_{ll}\sin^2\theta + A_{mm}\cos^2\theta \\ &\quad + 2A_{lm}\sin\theta\cos\theta \end{aligned} \tag{14}$$

$$\begin{aligned} A_{lm} &= (A_{ll} - A_{mm})\sin\theta\cos\theta \\ &\quad + A_{lm}(\cos^2\theta - \sin^2\theta) \end{aligned} \tag{15}$$

The above calculations are repeated until all of the pivotal elements are less than the threshold.

```
C
C                                                                       EIGEN001
C        ..................................................................EIGEN002
C        SUBROUTINE EIGEN                                               EIGEN003
C                                                                       EIGEN004
C        PURPOSE                                                        EIGEN005
C           COMPUTE EIGENVALUES AND EIGENVECTORS OF A REAL SYMMETRIC    EIGEN006
C           MATRIX                                                      EIGEN007
C                                                                       EIGEN008
C        USAGE                                                          EIGEN009
C           CALL EIGEN(A,R,N,MV)                                        EIGEN010
C                                                                       EIGEN011
C        DESCRIPTION OF PARAMETERS                                      EIGEN012
C           A - ORIGINAL MATRIX (SYMMETRIC), DESTROYED IN COMPUTATION.  EIGEN013
C               RESULTANT EIGENVALUES ARE DEVELOPED IN DIAGONAL OF      EIGEN014
C               MATRIX A IN DESCENDING ORDER.                           EIGEN015
C           R - RESULTANT MATRIX OF EIGENVECTORS (STORED COLUMNWISE,    EIGEN016
C               IN SAME SEQUENCE AS EIGENVALUES)                        EIGEN017
C           N - ORDER OF MATRICES A AND R                               EIGEN018
C           MV- INPUT CODE                                              EIGEN019
C                   0   COMPUTE EIGENVALUES AND EIGENVECTORS            EIGEN020
C                   1   COMPUTE EIGENVALUES ONLY (R NEED NOT BE         EIGEN021
C                       DIMENSIONED BUT MUST STILL APPEAR IN CALLING    EIGEN022
C                       SEQUENCE)                                       EIGEN023
C                                                                       EIGEN024
C        REMARKS                                                        EIGEN025
C           ORIGINAL MATRIX A MUST BE REAL SYMMETRIC (STORAGE MODE=1)   EIGEN026
C           MATRIX A CANNOT BE IN THE SAME LOCATION AS MATRIX R         EIGEN027
C                                                                       EIGEN028
C        SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED                  EIGEN029
C           NONE                                                        EIGEN030
C                                                                       EIGEN031
C        METHOD                                                         EIGEN032
C           DIAGONALIZATION METHOD ORIGINATED BY JACOBI AND ADAPTED     EIGEN033
C           BY VON NEUMANN FOR LARGE COMPUTERS AS FOUND IN 'MATHEMATICALEIGEN034
C           METHODS FOR DIGITAL COMPUTERS', EDITED BY A. RALSTON AND    EIGEN035
C           H.S. WILF, JOHN WILEY AND SONS, NEW YORK, 1962, CHAPTER 7   EIGEN036
C                                                                       EIGEN037
C        ..................................................................EIGEN038
```

APPENDIX H - ABBREVIATIONS AND SYMBOLS

The following abbreviations and symbols are used in the body of the thesis. Additional symbols which are used in the appendices are defined where they first occur.

A : exponent in mechanistic model

A_L : linear effect of variable A(analysis of variance)

A_Q : quadratic effect of variable A (analysis of variance)

a : exponent in mechanistic model

AB : interaction between variables A and B (analysis of variance)

AWWA : American Water Works Association

B : exponent in mechanistic model

B : floc breakup constant

B_{ii} : coefficient for empirical model in canonical form

B_L : linear effect of variable B (analysis of variance)

B_Q : quadratic effect of variable B (analysis of variance)

b : exponent in mechanistic model

b : equilibrium constant for the adsorption-desorption reaction (Langmuir isotherm)

b_i, b_{ii}, b_{ij} : coefficients in empirical model

C : exponent in mechanistic model

calc : calculated

CI : confidence interval

cm : centimetres

conc'n : concentration

D : exponent in mechanistic model

D : diameter (impeller)

D : model discrimination criterion

d : particle diameter

d.f. : degrees of freedom

E : exponent in mechanistic model

e : base of natural logarithms

ELB : trade name of mixing device employed

EPA : Environmental Protection Agency

F : variance ratio

floc : flocculation

flocc'n : flocculation

G : root mean square velocity gradient

G* : optimum root mean square velocity gradient

g : grams

g_c : gravitational constant

H : theoretical impeller head

i : subscript

in : inches

j : subscript

K,K' : constants in mechanistic models

K_X : constant in mechanistic models

$K_1, K_2, \ldots K_{17}$: constants in mechanistic models

K_1', K_{17}' : constants in mechanistic models

K_1^*, K_2^* : constants in mechanistic models

K_P : performance parameter characterizing stirring arrangement

K_s : coefficient relating particle diffusion coefficient to turbulence energy spectrum

k_1, k_2, k_3 : constants in mechanistic models

l : litre

ln : natural logarithm

M_i : the ith model

m : upper limit in summation

m : number of dimensions for response surface

mg : milligrams

mg/l : milligrams per litre

min : minutes

N : normality (acid or base)

N : number or weight of primary (unflocculated) particles

N_F : number of flocs

N_o : initial number or weight of primary (unflocculated) particles

N_p : power number

n : rotational speed (impeller)

n : number of data points

oz : ounce

P : activity of polymer in solution (Langmuir isotherm)

P : power (mixing)

PFTR : plug flow tubular reactor

Pr : probability

PSA : Path of Steepest Ascent

Q : discharge

R : radius of primary particle

R : polymer chain to which functional group is attached

R_F : radius of floc

r : radial distance

RM : rapid mix

rms : root mean square

rpm : revolution per minute

S : entropy

sec : seconds

t : student's t statistic

t : flocculation or rapid mix time

tab : tabulated

$\overline{u^2}$: mean square velocity fluctuation

X_i : independent variable in empirical model (canonical form)

$\underline{X}$: matrix of experimental conditions

$\underline{X}'$: transpose of matrix of experimental conditions

x_i : independent variable in empirical model

$\bar{x}$: mean

$\hat{Y}$: predicted metal concentration (empirical model in canonical form)

$\hat{y}$: predicted metal concentration (empirical model)

Y_s : predicted metal concentration at stationary conditions (empirical model in canonical form)

α : significance level

δ : parameter in floc breakup model

ϵ : total power dissipated per unit mass of fluid

η : collision efficiency

θ : fraction of adsorbent surface covered by adsorbed polymer segments

µm : micron

ν : kinematic viscosity

π : pi (3.14159 .....)

ρ : fluid density

Σ : summation

σ : standard deviation

ω : angular velocity

$\propto$: proportional to

$^{\circ}$: degrees (angular measure)