National Library of Canada
Canadian Theses Service
Ottawa, Canada
K1A 0N4

Bibliothèque nationale du Canada
Services des thèses canadiennes

CANADIAN THESES

THÈSES CANADIENNES

NOTICE

The quality of this microfiche is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Previously copyrighted materials (journal articles, published tests, etc.) are not filmed.

Reproduction in full or in part of this film is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30. Please read the authorization forms which accompany this thesis.

AVIS

La qualité de cette microfiche dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

Les documents qui font déjà l'objet d'un droit d'auteur (articles de revue, examens publiés, etc.) ne sont pas microfilmés.

La reproduction, même partielle, de ce microfilm est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30. Veuillez prendre connaissance des formules d'autorisation qui accompagnent cette thèse.

THIS DISSERTATION
HAS BEEN MICROFILMED
EXACTLY AS RECEIVED

LA THÈSE A ÉTÉ
MICROFILMÉE TELLE QUE
NOUS L'AVONS REÇUE

NL 339 (r 86/01)

Canada

ABSTRACT

The effects of a number of operating variables upon the properties of the precipitation of uranium from aqueous solution using hydrogen peroxide were evaluated. The reaction studied was

$$UO_2(SO_4)_3^{4-} + 2H_2O + H_2O_2 \rightarrow UO_4 \cdot 2H_2O + 3SO_4^{2-} + 2H^+$$

The operating variables studied were; 1) the initial uranium concentration, 2) the amount of hydrogen peroxide added, 3) the precipitation pH, 4) sulphate concentration in the solution, 5) the residence time in the precipitator. The effects of these operating variables upon the following precipitation properties were evaluated; 1) filtercake yield, 2) amount of uranium precipitated, 3) concentration of uranium in the barrens, 4) the conversion, 5) uranium content of the cake, 6) sulphur content of the cake, 7) particle size, 8) particle size distribution.

The effects of the operating variables upon the responses were determined by obtaining the parameters of an empirical model of the form

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \ldots + \beta_{12} x_1 x_2 + \ldots + \beta_{45} x_4 x_5 + \ldots + \beta_{55} x_5^2$$

A two level fractional factorial design was used as the basis for two experimental plans to screen out any insignificant effects. These two experimental plans were; 1) a central composite design and 2) the fractional factorial design with added centrepoints. The adequacy of the resultant models was evaluated using a quantitative lack of fit test. In general, the models describing the system responses derived from the central composite design did not pass this test. For the fractional factorial design with centrepoints, most of the response variables were adequately modelled.

The resultant models indicated that the responses were primarily dependent upon the initial uranium content of the solution although the filtercake yield and uranium content of the barrens also depended upon the pH. Along with being affected by the initial uranium concentration, the amount of uranium precipitated was found to be affected by the amount of hydrogen peroxide added and the total sulphate in the solution. The concentration of uranium in the barrens was not adequately modelled by either experimental design, however, the resultant parameter values were consistent with what would be expected from a mass balance on the uranium. The amount of uranium precipitated and the uranium concentration of the barrens varied in opposite directions as the operating variables were changed.

Overall, the results indicated that the responses could be adequately represented by simple linear equations.

The experimental design techniques may be useful in an actual uranium mill that may be considering a changeover to the hydrogen peroxide precipitation method.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. J. A. Golding and Mr. G. M. Ritcey for their guidance and supervision throughout his work. Special thanks are also extended to the technical staff of the Department of Chemical Engineering of the University of Ottawa for the assistance that they offered and to the personnel of CANMET for their chemical and particle size analyses.

The author's deepest thanks go to his wife, Carol, for her patience and love throughout the work and a special thanks for her typing skills.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

NOMENCLATURE

A	Surface Area of a Crystal, cm^2
C	Concentration of the crystallizing species in the bulk solution, moles/l
C_i	Concentration of the crystallizing species at the liquid-solid interface, moles/l
C^*	Solubility of the crystallizing species, moles/l
$\underline{C}$	Variance-Covariance matrix of the parameter estimates
c.v.	Coefficient of Variation
D_p	Particle Diameter, μm
e_u	Residual value for run u
$\underline{e}$	Matrix of Residual Values
F_{ν_1,ν_2}	Value of F-distribution for ν_1 and ν_2 degrees of freedom
GR	Galvanometer Reading of the fluorimeter
k_d	Diffusion mass transfer coefficient, Eq. 2.3.1 $(g\cdot l)/(sec)(cm^2)(mol)$
k_{obs}	Observed reaction rate constant Eq. 2.2.6 $(mole)^{-1}(time)^{-1}$
k_r	Surface reaction mass transfer coefficient, Eq. 2.3.2 $(g\cdot l)/(sec)(cm^2)(mol)$
K_{dec}	Decomposition rate of H_2O_2, $(moles)(time)^{-.33}$
K_G	Overall mass transfer coefficient, $(g\cdot l)/(sec)(cm^2)(mol)$

$K_{H_2O_2}$	Equilibrium constant Eq. 2.2.3
K_0	Initial value of $K_{H_2O_2}$
$\overline{L}$	Mean particle size, μm
$\overline{L}'$	Adjustable mean length parameter in a log-normal distribution, μm
$L_{.50}$	Median particle size, μm
m	Mass of a crystal Equations 2.2.11 - 2.2.13, g
m	Number of centrepoint runs for the factorial design
n	Number of experimental runs
p	Number of parameters in the linear equation
Q	Ratio of extra sum of squares to the estimated variance
r	Radius of a crystal, cm
R	Ratio of error due to lack of fit to the pure error variance
SSR	Sum of squares of the residuals
t	Time, sec
t_ν	Value of t-distribution for ν degrees of freedom
U_0	Initial uranium concentration , g/l
v	Volume of solution taken for second dilution step in fluorimetry analysis, ml
V_{1D}	Volume of solution after first dilution in fluorimetry analysis, ml
V_{2D}	Volume of solution after second dilution in fluorimetry analysis, ml

x_i	Coded value of independent variable i in the linear equations
x_{iu}	Coded value of independent variable i for run u
X_i	Actual value of the independent variable i
$\underline{X}$	Matrix of the independent variables
y_u	Measured response for experimental run u
Y	Dependent variable in the linear equation
$\underline{Y}$	Vector of measured responses

GREEK SYMBOLS

β_i	Parameter associated with main effect i in the linear equation $i = 0,1,2,\ldots,5$
β_{ii}	Parameter associated with a quadratic effect i $i = 1,2,\ldots,5$
β_{ij}	Parameter associated with an interaction effect between variables i and j $i,j = 1,2,\ldots,5,\ i \neq j$
$\hat{\beta}$	Parameter value estimated from linear least squares
$\underline{\hat{\beta}}$	Vector of estimated parameter values
ε	Random error associated with a measured response
ν	Degrees of freedom for a t-distribution
ν_1	Degrees of freedom in the numerator of an F-distribution
ν_2	Degrees of freedom in the denominator of an F-distribution

ρ	Density of a crystal, g/cm^3
σ^1	Adjustable dispersion parameter in a log-normal distribution
$\hat{\sigma}^2$	Estimated variance

SUPERSCRIPTS

T	Transpose of a matrix
*	Solubility value, Equations 2.2.12 - 2.2.15
*	Alternative set of independent variables in the linear equations, Cases 2 and 4

SUBSCRIPTS

B	Blank in Equation A3.1
S	Sample in Equation A3.1
u	Run number
U	Standard in Equation A3.2
$_0$	Initial value
$_0$	Value of y-intercept in the linear equations
$_1$	Initial Uranium Content
$_2$	Amount of H_2O_2
$_3$	pH
$_4$	Sulphate Level
$_5$	Time
c.p.	Centrepoint

1. INTRODUCTION

The precipitation of uranium from aqueous solutions to form yellowcake is an important step towards the final fuel used in nuclear reactors. It is necessary for the yellowcake to be of high purity, have good filtration characteristics, and to dry readily. Yellowcake should also have good material handling characteristics. A number of methods for obtaining yellowcake from a uranium solution are in use. Of the precipitation methods available, the precipitation of uranium with ammonia to form ammonium diuranate is the one most frequently used in North America. Ammonium diuranate is generally of high quality, however, specifications that must be met regarding impurity levels are becoming more stringent. Also, the ores presently being processed are of a lower grade than those processed in the past. This has led mill operators to consider hydrogen peroxide precipitation as an alternative since this precipitation method yields a high purity product under a wide range of conditions. In order to convert from one precipitation method to another, it is necessary to know how the properties of the uranium solution affect the characteristics of the precipitation. Some of the critical factors include:

1) the initial uranium concentration
2) the H_2O_2/U molar ratio
3) the excess sulphate in the solution

4) the precipitation pH

5) the residence time in the precipitator.

Other variables that could be considered are the mixing characteristics, temperature and impurity levels in the solution. These variables were not studied in this work, but could be part of the experimental design in an actual plant.

Most of the research in hydrogen peroxide precipitation of uranium has been directed towards determining how the above factors affect the barrens concentration (i.e. uranium concentration of the filtrate). One of the objectives of this study was to extend this work to determine how other characteristics of the precipitation were affected by the operating variables. These characteristics include filtercake yield, uranium content of the cake, the amount of uranium precipitated, the sulphur content of the cake, and the particle size and size distribution of the precipitate. Filtercake yield differs from the amount of uranium precipitated by the fact that the filtercake will contain impurities such as hydrated water and some residual moisture which would later be removed in drying operations. The amount of uranium precipitated is a measure of the efficiency of the reaction.

If hydrogen peroxide precipitation is to be considered by a uranium mill without any major changes being made to the rest of the process, it would be of particular importance to evaluate the effects of process variables upon the precipitation properties. A method which will measure the effects of process variables upon a group of response variables is experimental design. In this study, two different experimental designs were used. Both experimental designs used a 2^5 factorial design as a basis: one design being a central composite design, the other being the factorial design with the centrepoints included. This method of experimentation involves fitting experimental data to an empirical linear model which allows for the screening out of unimportant variables. The disadvantages of the experimental design methods employed in this study are the inabilities to extrapolate beyond the experimental points and to derive the parameters in a complex mechanistic model. These experimental designs are also limited to data which can be well described by a simply polynomial (i.e. the data is not highly non-linear in nature). The effectiveness of the resultant linear equations in describing system behaviour has been evaluated to determine whether the possibility exists of employing these methods for describing the system in an actual uranium mill.

2. LITERATURE SURVEY

2.1 The Production of Yellowcake

There are a number of different processing methods used for the production of yellowcake. The choice of one method over another depends primarily upon the uranium species in the ore, impurities such as vanadium and molybdenum which may be present, and the cost and availability of the precipitating reagents.

No matter which process is chosen, the operations are similar. The differences lie in the chemicals which are used for any of the steps and whether ion exchange or solvent extraction is used. These steps include; 1) grinding of the ore, 2) leaching of the ore, 3) solvent extraction or ion exchange of the uranium from the leach solution, 4) stripping of the organic phase in solvent extraction or elution of the ionic exchange resin, 5) precipitation of the uranium from the strip solution, 6) separation of the yellowcake by thickening and filtration, 7) drying of the precipitate, 8) calcination to form U_3O_8. A typical process flowsheet is provided in Figure 2.1. A number of authors have written extensively upon current uranium milling practices with the emphasis being upon the solvent extraction or ion exchange circuits (1-4). A brief overview of current practices is given below.

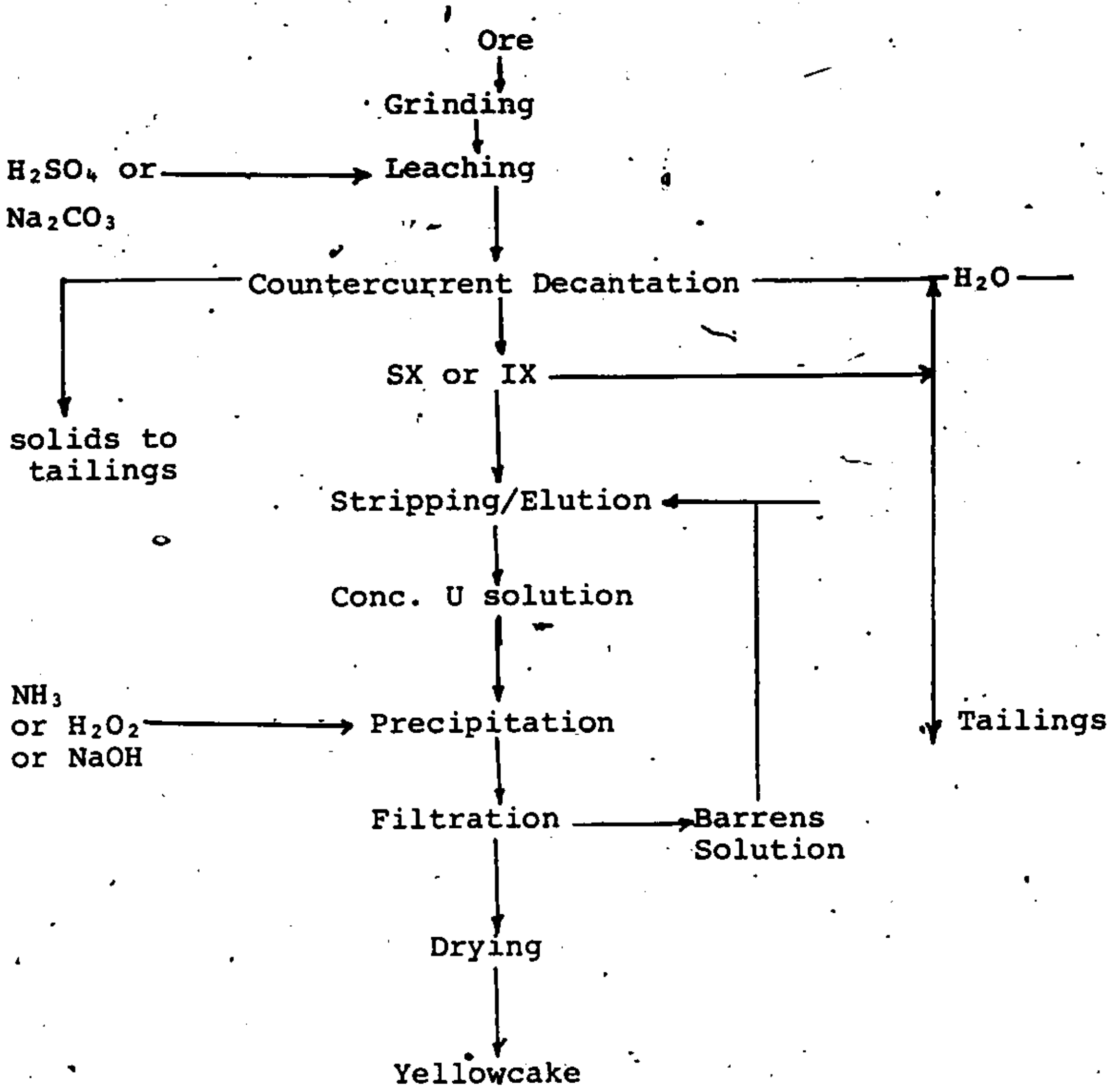

Figure 2.1: Process Flow Sheet for a Typical Uranium Milling Process

2.1.1 Leaching

The ore is leached either by an acid leach using H_2SO_4 to form $UO_2(SO_4)_3^{4-}$ or by an alkaline leach with Na_2CO_3 to give $UO_2(CO_3)_3^{4-}$ in solution. Acid-leaching is never performed when the concentration of calcium carbonate in the ore exceeds 6% by weight (3). The concentration of acid required in the leach solution varies depending upon the type of ore being processed. For example, at the Mary Kathleen Mill in Australia, the leach is carried out using concentrated H_2SO_4 (98.5%) due to a high silica content in the ore which tends to consume the acid (5). Concentrations of the same order may also be required if the ore contains asphalts which also tend to consume acid (3). Less concentrated acids can be used if these contaminants are not present. The Purlex process for instance, contains 3.5 g H_2SO_4/l and 20 g SO_4^{2-}/l in the leach solution (6).

An interesting aspect of alkaline leaching is the fact that the uranium is sometimes precipitated directly from the leach solution. The reason being that no organic solvent has been developed to efficiently extract the uranyl carbonate ion under the possible conditions of high salt content which may occur at elevated pH's (7). The grade of the yellowcake can be as high as 70 - 75% on a U_3O_8 basis, however, the presence of impurities such as vanadium or molybdenum in unacceptable quantities may require that the concentrate undergo further processing, e.g. by dissolving the precipitate in H_2SO_4 followed by reprecipitation with NH_3 or H_2O_2.

2.1.2 Solvent Extraction and Ion Exchange

Uranium is extracted from the leach liquor by either solvent extraction or ion exchange. Older mills use strong-base ion exchange although solvent extraction is gaining appeal since the process may be run as a continuous circuit, and the kinetics of extraction are faster than those for ion exchange.

Strong-base ion exchange involves the following processes depending upon the leach solution present:

$$2R_2SO_4 + UO_2(SO_4)_3^{4-} \rightleftarrows R_4UO_2(SO_4)_3 + 2SO_4^{2-} \qquad (2.1.1)$$

and

$$UO_2(SO_4)_2^{2-} + R_2SO_4 \rightleftarrows R_2UO_2(SO_4)_2 + SO_4^{2-} \qquad (2.1.2)$$

for acid leach solutions or;

$$4RX + UO_2(CO_3)_3^{4-} \rightleftarrows R_4UO_2(CO_3) + 4X^- \qquad (2.1.3)$$

for alkaline leach solutions at low salt content.

Boydell (2) has summarized the common elution reagents used with strong-base ion exchange. The elution reagents, the uranium species with which they are used, and concentrations are given in Table 2.1.

Table 2.1

Elution Reagents for Strong-Base Ion-Exchange Resins (8)

Reagent	Concentration (g/l)	Absorbed species
HNO_3	25	$UO_2(SO_4)_3^{4-}$
$(NH_4)NO_3$	50-75	
SO_4^{2-}		
H_2SO_4	105-120	$UO_2(SO_4)_3^{4-}$
NaCl	50-55	$UO_2(SO_4)_3^{4-}$
H_2SO_4	10	
NaCl	60	$UO_2(SO_4)_3^{4-}$
NaCl	90-110	$UO_2(CO_3)_3^{4-}$
$NaHCO_3$	4	
$NaHCO_3$	50-80	$UO_2(CO_3)_3^{4-}$
$(NH_4)_2CO_3$	70-120	

Example

$$R_4UO_2(SO_4)_3 + 4NaCl \rightleftarrows 4RCl + 4Na^+ + UO_2(SO_4)_3^{4-}$$

Weak-base ion exchange is not employed to any large extent. The chemistry of these systems is the same as that for solvent extraction. Weak-base ion exchange resins are more selective to absorbing uranium over some of the common impurities such as vanadium and iron compared to strong-base ion exchange. For this reason, they offer an advantage as far as purity of the product is concerned. However, the reaction kinetics are much slower than for strong-base ion exchange resulting in the need for greater residence times. Some of the weak-base elution reagents used are summarized in Table 2.2.

Solvent extraction has gained considerable attention as an alternative to ion exchange. It offers the advantages of being run as a continuous circuit and having fast extraction kinetics. Solvent extraction can be used with leach liquors when the concentration of uranium is greater than 0.1g/l. However, if there are significant levels of molybdenum present, ion exchange is preferred (10). The most common extraction reagents are tertiary amines in kerosene as the organic solvent. The extraction process has the following general reactions:

$$2(R_3NH)_2SO_4 + UO_2(SO_4)_3^{4-} \rightleftharpoons (R_3NH)_4UO_2(SO_4)_3 + 2SO_4^{2-} \quad (2.1.4)$$

$$(R_3NH)_2SO_4 + UO_2SO_4 \rightleftharpoons (R_3NH)_2\,UO_2(SO_4)_2 \quad (2.1.5)$$

Molybdenum if present, may be a problem because it is preferentially extracted over uranium within the operating

Table 2.2

Elution Reagents for Weak-Base Ion-Exchange Resins (9)

Reagent	Concentration (g/ltr)
HNO_3	< 5
$(NH_4)NO_3$	60
H_2SO_4	45
$(NH_4)_2SO_4$	480
NaCl pH 1.9	60-70

conditions of the process (11). Thus, molybdenum will be carried throughout the milling process and appear as a contaminant in the uranium precipitate. The strip reagents used in conjunction with solvent extraction include:

$NH_3/(NH_4)_2SO_4$, $NaCl$, Na_2CO_3, or NH_4Cl (2)

2.1.3 Precipitation Practice

The precipitation of uranium from the eluate or strip liquor is carried out in several different ways. The most common practices follow.

a) Precipitation with NaOH

When an alkaline leach has been used, the uranium is usually precipitated with NaOH according to the following reaction:

$$2UO_2(CO_3)_3^{4-} + 14NaOH \rightarrow Na_2U_2O_7\downarrow + 6Na_2CO_3 + 8OH^- + 3H_2O \quad (2.1.6)$$

The disadvantage of this method is that the final product may have impurity levels that do not meet refiners' standards. For this reason, one or more of the following purification steps are needed (3).

i) The removal of vanadium by roasting:

$$Na_2U_2O_7 + NaVO_3 + Na_2CO_3 \rightarrow Na_2U_2O_7 + VO_3^- + CO_3^{2-} + 3Na^+ \quad (2.1.7)$$

ii) The removal of sodium by metathesis:

$$Na_2U_2O_7 + (NH_4)_2SO_4 \rightarrow (NH_4)_2U_2O_7 + 2Na^+ + SO_4^{2-} \quad (2.1.8)$$

iii) Conversion to ammonium diuranate or precipitation with hydrogen peroxide:

$$Na_2U_2O_7 + 6H_2SO_4 \rightarrow 2UO_2(SO_4)_3^{4-} + 2Na^+ + 2H_2O \qquad (2.1.9)$$

then

$$2UO_2(SO_4)_3^{4-} + 6NH_3 \rightarrow (NH_4)_2U_2O_7\downarrow + 4SO_4^{2-} \qquad (2.1.10)$$

or

$$UO_2(SO_4)_3^{4-} + H_2O_2 + 2H_2O \rightarrow UO_4\cdot 2H_2O\downarrow + 3SO_4^{2-} + 2H^+ \qquad (2.1.11)$$

b) Ammonia Precipitation

The recovery of uranium by the addition of ammonia is governed by equation 2.1.10 given above. Care must be taken when using ammonia that the ammonia concentration does not fall below the required stoichiometric amount. This leads to the formation of uranium sulphate which would result in a final product with unacceptably high sulphate levels. Ammonia precipitation, at present, is the most commonly used method in North America.

c) Hydrogen Peroxide Precipitation

Uranium precipitation using hydrogen peroxide has become the subject of widespread interest. This is due to the high purity of the product, and the favourable physical properties resulting in ease of thickening and filtration operations. As may be seen in Table 2.3, peroxide precipitation can be carried out at lower temperatures and the retention time in the precipitator is generally much less than for

Table 2.3

Operating Conditions of Uranium Precipitation Processes and Physical Properties of the Precipitate.

	Sodium Diuranate	Ammonium Diuranate	Uranium Peroxide	Ref.
Operating Temperature	50-80°C(from leach) 20-30°C(from strip)	50-85°C	20-25°C	[3]
Precipitation Time	6-12h (from leach) 2-4h (from strip)	2-6h	2-8h	[3]
Reagent Addition	5-6kgNaOH/kgU_3O_8(leach) 3-4kgNaOH/kgU_3O_8(strip)	0.22kgNH_3/kgU_3O_8	0.18-.25kgH_2O_2/kgU_3O_8	[3]
Filtration Rate (kg/h per m^2 of filter area)	15-40	25-125	45-1000	[3]
Filter cake (% solids)	30-50	30-50	40-70	[3]
Thickening				
Underflow density (% solids)	35-40	15-30	30-50	[3]
Settling Rate	ND	2-4 cm/min	4-6 cm/min	[3]
Effective particle size (μ)	ND	10-12	12-15	[3]
Specific Gravity of Solid	ND	2.8	5.7	[12]
Purity (% U_3O_8)	ND	85-89	90-95	[12]

other processes. The precipitates also have much higher settling and filtration rates.

2.2 Research in Uranium Precipitation

Research in uranium precipitation is limited by the fact that the results depend heavily upon the characteristics of the system under study. Some of the results of research in uranium precipitation are as follows.

The precipitation of uranium by ammonia from aqueous solutions has been studied with varying results (13-17). Tomazic et. al (13) studied the system $UO_2(NO_3)_2$ $-NH_4OH-NH_4NO_3$. It was found that precipitation will occur only at certain levels of pH, and ammonia concentrations. Precipitation depended upon the initial ratio of $NH_4OH/UO_2(NO_3)_2$. It was observed that there was a sudden pH drop upon the initiation of the reaction.

For the same system, Stuart and Whateley (14) used infra red spectrophotometry and thermal analysis to discover that the formula for ammonium diuranate is only approximate. They found that rather than being $(NH_4)_2U_2O_7$, ammonium diuranate had a continuous ratio of $NH_3:U$ in its structure and the reaction between $UO_2(OH)_2$ and NH_3 was as follows:

$$UO_2(OH)_2 + xNH_4^+ \rightarrow UO_2(OH)_{2-x}(O^-NH_4^+)_x + xH^+ \qquad (2.2.1)$$

Merino (15), studied the precipitation of ammonium diuranate with the purpose of determining how operating conditions in the precipitator affected the thickening, filtering, stirring, pumping and drying properties of the yellowcake. The temperature of the precipitator was varied, continuous and batch precipitators were used, and both NH_4OH and gaseous NH_3 were used. It was observed that adjusting the operating variables to make the properties of the suspension more suitable for further processing such as settling and filtration could adversely affect the U_3O_8 content of the final product.

Rodriguez (16) investigated the recovery of uranium from the Purlex process using ammonia. It was observed that sulphate levels in the cake can be kept within the refiners' specification limits by manipulating the precipitation temperature and keeping it between 30-40°C. It was recommended that the product be calcined at 700°C.

Bryson (17) studied the electrolytic precipitation of ammonium diuranate from sulphate solutions. The reaction took place in the cathode department of an electrolytic cell. He discovered that the precipitation and settling rates of the ammonium diuranate were correlated with the current consumption. The two factors, however, were found to be inversely correlated. In other words, to increase the settling rate, the current had to be decreased, but a decrease in yield resulted.

In the case of uranium peroxide precipitation, the research has been concerned with reducing the concentration of uranium in the barrens solution (12, 18-22). In some studies, however, the kinetics of the reaction have been considered (19, 20). Brown (12) studied the effect of a number of operating conditions upon the barrens of the process. He recognized the fact that operating conditions in individual mills vary and developed a theoretical model to predict the barrens concentration for given concentrations of sulphate and chloride, pH, and precipitation time. The model was based upon the chemical equilibria created between $UO_2{}^{2+}$ with $SO_4{}^{2-}$ and Cl^-. The model that was given to describe the barrens concentration using a U_3O_8 basis was:

$$U_3O_8\,(g/l) = \frac{(10^{-pH})^2 \left[1 + 710\frac{[SO_4]^2}{96} + \frac{0.88\,[Cl]}{35.5}\right]}{\frac{3}{810 \times 34}\,[H_2O_2] \cdot K_{H_2O_2}} \qquad (2.2.2)$$

Brown also expressed $K_{H_2O_2}$ and $[H_2O_2]$ as functions of time (12).

$$K_{H_2O_2} = K_o + t^2/(1 + 0.0075t^2) \qquad (2.2.3)$$

$$[H_2O_2] = [H_2O_2]_0 \; [1 - K_{dec} \; \sqrt[3]{t-.67} \;] \left[\frac{[U_3O_8]_0 - [U_3O_8]_t}{[U_3O_8]_0} \right] \quad (2.2.4)$$

where K_{dec} was a decomposition constant for H_2O_2.

By performing a number of batch precipitations, the theoretical model was compared with an empirical model based upon the interactions of the variables upon the barrens concentration. It was noted that the theoretical model tended to underestimate the barrens concentration and that the empirical model agreed more closely with the experimental data. The empirical model was not given.

Shabbir and Tame (18) performed batch tests on the same system to measure the effect of a different set of variables upon the barrens and purity. A synthetic stock solution was prepared with molybdenum and vanadium included to determine how purity was influenced by their presence. The effect of temperature upon the barrens concentration and Mo and V levels in the precipitate was measured. The effect of pH upon the same two variables was measured. It was concluded that the reaction required more than the stoichiometric amount of peroxide, the precipitation was dependent upon pH, while the vanadium content of the cake was lowered if the reaction pH was increased to 5. Increased temperature resulted in an increase in the reaction rate, but an increase in the vanadium and molybdenum concentrations in the cake was also observed. It was also observed that increased sulphate levels slowed down the rate of reaction.

Using a spectrophotometer to measure the change of U(IV) concentration with time, Bhattacharyya, et. al. (19, 20) studied the kinetics of the reaction

$$U(IV) + H_2O_2 \rightarrow U(VI) + 2H^+ \qquad (2.2.5)$$

in the presence of both sulphate and chloride.
Their results indicated that the reaction could be described by the biomolecular rate equation

$$\frac{-d}{dt} [U(IV)] = k_{obs} [U(IV)] [H_2O_2] \qquad (2.2.6)$$

$k_{obs} = f([H^+]^{-1.3})$ for hydrochloric acid medium

$k_{obs} = f([H^+]^{-.55})$ for sulphuric acid medium.

It was also found that k_{obs} was a function of equilibrium constants of uranium/sulphate or uranium/chloride complexes suspected of participating in the reaction mechanism.

The implication of these studies was that the rate of particle growth of the uranium precipitate would depend upon the concentration of sulphate, uranium, and peroxide and the pH since this growth would be dependent upon the concentration of U(VI).

2.3 Crystal Growth

The kinetics of the growth of a precipitate is usually discussed in the literature dealing with crystallization since it has a lot in common with crystal growth (23). The differences between precipitation and crystallization arise in the method of obtaining supersaturation. In the case of a crystallization process, a saturated solution becomes supersaturated either by cooling the solution, thereby reducing the solubility or by removal of some of the solvent by evaporation. In precipitation operations, the supersaturation is achieved by transforming the desired product from a soluble species to an insoluble one by means of a chemical reaction. The uranium recovery reactions fall into this category.

The size and size distribution of the solid produced by either of these methods is important when it comes to further processing of these materials especially in solid/liquid separations such as settling and filtration rates which are dependent upon the particle size. For this reason, considerable research has been carried out into finding methods to predict and control the crystal size distribution (CSD). The general equations used to analyze crystallization/precipitation reactions are as follows:

Crystal growth is a mass transfer operation and as such is dependent upon the surface area and a concentration gradient. The mechanism involves; 1) a migration of a molecule from the bulk solution to the interface between the solution and particle with diffusion through this interface, 2) a surface "reaction" (absorption) of the particle upon the crystal surface.

1) $$\frac{dm}{dt} = k_d A(C - C_i) \qquad (2.3.1)$$

2) $$\frac{dm}{dt} = k_r A(C_i - C^*) \qquad (2.3.2)$$

Combining the two equations yields

$$\frac{dm}{dt} = k_d A(C - C_i) = k_r A(C_i - C^*)$$

$$= K_G A(C - C^*) \qquad (2.3.3)$$

where $$\frac{1}{K_G} = \frac{1}{k_d} + \frac{1}{k_r} \qquad (2.3.4)$$

This equation may be written in terms of the radial growth of a crystal by dividing both sides of the equation by the particle density and the surface area, hence, for a spherical crystal

$$\frac{dr}{dt} = \frac{K_G}{\rho}(C - C^*) \qquad (2.3.5)$$

Therefore, depending upon whether data are collected in terms of the mass deposited over time or the actual particle sizes are measured, the crystal growth rate may be measured. The particle size analysis has the advantage, however, of providing the crystal size distribution which is needed for determining nucleation rates.

The crystal size distribution of a crystallization process is primarily a result of the nucleation rate (i.e. the rate of formation of new crystals). Randolph and Larson (24) have developed a population balance method of determining the nucleation rate based upon the effect of residence time upon the CSD with the use of an MSMPR (mixed suspension-mixed product removal) continuous crystallizer. Misra and White (25) have adapted the population balance method for use with a batch crystallizer taking into account the dynamic nature of supersaturation with time.

Precipitation offers unique problems in this kind of analysis because of the fact that the supersaturation ratio S(=C/C*) is virtually infinity since C* is close to zero. For this reason, the radius of a stable nucleus can be quite small and a large number of nuclei can form compared to a crystallization operation. This can lead to the formation of a large number of small particles, depending upon the speed of the chemical reaction. In this instance, crystal growth does not have the chance to occur. Instead, one obtains a number of small uniform particles not much larger than nuclei. If these particles are small enough, they may agglomerate due to attraction forces between the particles. This phenomenon has been observed in precipitation processes and should not be confused with crystal growth. Whether crystal growth or agglomeration occurs, the particle size of the precipitate is time dependent.

3. EXPERIMENTAL

3.1 Experimental Design

A factorial design approach was used to determine the location of the experimental runs. The particular factorial design used was a half fraction of a 2^5 design with time confounded with the other variables listed in Table 3.1. Centrepoints and axial points were also run as given by Bacon (26) to yield an orthogonal central composite design so that any quadratic effects of the main variables could be measured. The experimental design points are given in Table 3.2. Experimental runs 1 through 16 correspond to the 2^5 fractional factorial design points, runs 17 through 26 were the axial points and runs 27 through 36 were the centrepoints of the design. (Due to difficulties in obtaining the desired pH, the experimental pH's were not those of the design, but are those given in brackets). An explanation of the factorial design technique and least square analysis has been given in Appendix II. The experiments were run in a randomized order.

In analyzing the data, two different experimental plans were used. Experimental Plan I consisted of using all 36 points for the analysis (i.e. full central composite design) and Experimental Plan II in which only the fractional factorial design points and centrepoints were used in the

Table 3.1

Design Region of Operating Variables

Initial Uranium Content, X_1 (g/l)	Initial Fraction of Stoichiometric Ratio, X_2 (g mol U/g mol H_2O_2)	Precipitation pH, X_3	Excess Sulphate, X_4 (g/l)	Time, X_5 (hr)
10.0	.75	2.40	0	1
12.5	1.50	2.85	4.4	2
15.0	2.25	3.30	8.8	3
17.5	3.00	3.75	13.2	4
20.0	3.75	4.20	17.6	5

Table 3.2

The Operating Values of the Experimental Runs

Run Number	X_1	X_2	X_3	$(pH_{expt.})$	X_4	X_5
1	12.5	1.50	2.85	(2.83)	4.4	4
2	17.5	1.50	2.85	(1.81)	4.4	2
3	12.5	3.00	2.85	(2.11)	4.4	2
4	17.5	3.00	2.85	(3.07)	4.4	4
5	12.5	1.50	3.75	(7.20)	4.4	2
6	17.5	1.50	3.75	(7.85)	4.4	4
7	12.5	3.00	3.75	(7.84)	4.4	4
8	17.5	3.00	3.75	(5.00)	4.4	2
9	12.5	1.50	2.85	(3.26)	13.2	2
10	17.5	1.50	2.85	(1.79)	13.2	4
11	12.5	3.00	2.85	(2.60)	13.2	4
12	17.5	3.00	2.85	(2.92)	13.2	2
13	12.5	1.50	3.75	(6.80)	13.2	4
14	17.5	1.50	3.75	(8.34)	13.2	2
15	12.5	3.00	3.75	(3.32)	13.2	2
16	17.5	3.00	3.75	(4.65)	13.2	4
17	10.0	2.25	3.30	(8.90)	8.8	3
18	20.0	2.25	3.30	(3.22)	8.8	3
19	15.0	.75	3.30	(3.72)	8.8	3
20	15.0	3.75	3.30	(3.63)	8.8	3
21	15.0	2.25	2.40	(1.55)	8.8	3
22	15.0	2.25	4.20	(4.29)	8.8	3
23	15.0	2.25	3.30	(3.09)	0	3
24	15.0	2.25	3.30	(7.67)	17.6	3
25	15.0	2.25	3.30	(3.65)	8.8	1
26	15.0	2.25	3.30	(3.50)	8.8	5
27	15.0	2.25	3.30	(2.94)	8.8	3
28	15.0	2.25	3.30	(4.74)	8.8	3
29	15.0	2.25	3.30	(4.22)	8.8	3
30	15.0	2.25	3.30	(4.28)	8.8	3
31	15.0	2.25	3.30	(6.60)	8.8	3
32	15.0	2.25	3.30	(5.40)	8.8	3
33	15.0	2.25	3.30	(3.29)	8.8	3
34	15.0	2.25	3.30	(3.80)	8.8	3
35	15.0	2.25	3.30	(3.09)	8.8	3
36	15.0	2.25	3.30	(4.25)	8.8	3

analysis. Plan I which contained the axial points would be useful if any quadratic effects of the main variables are present. In the absence of quadratic effects, Plan II should yield comparable results with fewer runs. Experimental Plan II is a more economical design since only 26 runs are involved. It would be the more desirable plan to use in practice because of the fewer runs involved. If it is suspected that after performing the runs of Plan II, that quadratic effects may be important, then the axial runs may be performed afterwards.

To reduce the correlations among the parameter estimates, the operating variables presented in Table 3.2 were coded in the following manner.

$$x_1 = \frac{X_1 - 15}{2.5} \tag{3.1}$$

$$x_2 = \frac{X_2 - 3.25}{.75} \tag{3.2}$$

$$x_3 = \frac{X_3 - 4.3669}{3.675} \tag{3.3}$$

$$x_4 = \frac{X_4 - 8.8}{4.4} \tag{3.4}$$

$$x_5 = \frac{X_5 - 1}{1} \tag{3.5}$$

The coded values of the operating variables are presented in Table 3.3.

Table 3.3

Coded Values of the Operating Variables

Run Number	x_1	x_2	x_3	x_4	x_5
1	-1	-1	-.4182	-1	1
2	1	-1	-.6958	-1	-1
3	-1	1	-.6141	-1	-1
4	1	1	-.3529	-1	1
5	-1	-1	-.7709	-1	-1
6	1	-1	.9478	-1	1
7	-1	1	.9450	-1	1
8	1	1	.1722	-1	-1
9	-1	-1	-.3012	1	-1
10	1	-1	-.7012	1	1
11	-1	1	-.4808	1	1
12	1	1	-.3937	1	-1
13	-1	-1	.6620	1	1
14	1	-1	1.0811	1	-1
15	-1	1	-.2849	1	-1
16	1	1	.0770	1	1
17	-2	0	1.2335	0	0
18	2	0	-.3125	0	0
19	0	-2	-.1765	0	0
20	0	2	-.2010	0	0
21	0	0	-.7670	0	0
22	0	0	-.0214	0	0
23	0	0	-.3479	-2	0
24	0	0	.8983	2	0
25	0	0	-.1955	0	-2
26	0	0	-.2364	0	2
27	0	0	-.3887	0	0
28	0	0	.1011	0	0
29	0	0	-.0404	0	0
30	0	0	-.0241	0	0
31	0	0	.6072	0	0
32	0	0	.2807	0	0
33	0	0	-.2935	0	0
34	0	0	-.1547	0	0
35	0	0	-.3479	0	0
36	0	0	-.0323	0	0

It was also noted that possibly, the responses could be better correlated with different forms of x_2, x_3, and x_4, denoted by x_2*, x_3*, and x_4*. For example, rather than using pH, $[H^+]$ was used. Since pH is a logarithmic form of $[H^+]$, the nonlinear nature of pH may affect the analysis. Using the molar ratio of H_2O_2 to Uranium may also yield misleading results. For example, a molar ratio of 1.50 would require different amounts of H_2O_2 to be added depending upon whether the initial solution contained 12.5g U/l or 17.5g U/l. This would lead to 2 actual levels of peroxide being added (i.e. to get a molar ratio of 1.50 for a 12.5 g/l solution add 2.68 g H_2O_2/l for a 17.5 gU/l solution, add 3.75 gH_2O_2/l). Because of the different amounts of H_2O_2 added to achieve an equivalent molar ratio, there were actually 9 different levels of hydrogen peroxide added. The excess sulphate was that amount of sulphate added to the system over and above that needed to form $UO_2(SO_4)_3^{4-}$ whereas, the total sulphate was the excess plus this stoichiometric amount. There were actually 11 levels of total sulphate as opposed to the 5 levels of excess sulphate. The coding used to transform these three operating variables were as follows:

$$x_2^* = \frac{(H_2O_2)_0 - 4.82}{6.42} \quad (3.6)$$

$$x_3^* = \frac{[H^+] - .0022224}{.0140917} \quad (3.7)$$

$$x_4^* = \frac{(\text{Total } SO_4) - 27.33}{8.8} \quad (3.8)$$

The coded values for x_2^*, x_3^* and x_4^* have been presented in Table 3.4.

With this in mind, four different cases were evaluated to determine which (if any) of these representations may yield different results. These were:

Case 1 The data were analyzed with the original variables x_1, x_2, x_3, x_4, and x_5.

Case 2 The data were analyzed using $[H^+]$ rather than pH, i.e. the effects of x_1, x_2, x_3^*, x_4, and x_5.

Case 3 For this case x_2 and x_4 were replaced in Case 1 with x_2^*, and x_4^* respectively to analyze the effects of x_1, x_2^*, x_3, x_4^* and x_5.

Case 4 The three variables x_2, x_3, and x_4 were all replaced with x_2^*, x_3^*, and x_4^* to analyze the effects of x_1, x_2^*, x_3^*, x_4^* and x_5.

Table 3.4

The Alternative Values for Cases 2, 3, and 4

Run Number	H_2O_2 Concentration (g/l)	Coded x_2^*	H^+ Concentration (mol/l)	Coded x_3^*	Total SO_4^{2-} (g/l)	Coded x_4^*
1	2.68	-.3333	1.4791×10^{-3}	- .0527447	19.84	- .8511
2	3.75	-.1667	1.5488×10^{-2}	.9413789	26.02	- .1489
3	5.36	.0833	7.7625×10^{-3}	.3131398	19.84	- .8511
4	7.50	.4167	8.5114×10^{-4}	- .0973073	26.02	- .1489
5	2.68	-.3333	6.3096×10^{-8}	- .1577010	19.84	- .8511
6	3.75	-.1667	1.4125×10^{-8}	- .1577054	26.02	- .1489
7	5.36	.0833	1.4454×10^{-8}	- .1577054	19.84	- .8511
8	7.50	.4167	1.0000×10^{-5}	- .1575282	26.02	- .1489
9	2.68	-.3333	5.4954×10^{-4}	- .1187095	28.64	.1489
10	3.75	-.1667	1.6218×10^{-2}	.9931746	34.82	.8511
11	5.36	.0833	2.5119×10^{-3}	.0205422	28.64	.1489
12	7.50	.4167	1.2023×10^{-3}	- .0723907	34.82	.8511
13	2.68	-.3333	1.5849×10^{-7}	- .1576952	28.64	.1489
14	3.75	-.1667	4.5709×10^{-9}	- .1577061	34.82	.8511
15	5.36	.0833	4.7863×10^{-4}	- .1237415	28.64	.1489
16	7.50	.4167	2.2387×10^{-5}	- .1561178	34.82	.8511
17	3.21	-.2500	1.2589×10^{-9}	- .1577063	21.15	- .7023
18	6.43	.2500	6.0258×10^{-4}	- .1149471	33.51	.7023
19	1.61	-.5000	1.9055×10^{-4}	- .1438360	27.33	0
20	8.04	.5000	2.3442×10^{-4}	- .1410711	27.33	0
21	4.82	0	2.8184×10^{-2}	1.8422936	27.33	0
22	4.82	0	5.1286×10^{-5}	- .1540670	27.33	0
23	4.82	0	8.1283×10^{-4}	- .1000257	18.53	-1
24	4.82	0	2.1380×10^{-8}	- .1577049	36.13	1
25	4.82	0	2.2387×10^{-4}	- .1418198	27.33	0
26	4.82	0	3.1623×10^{-4}	- .1352660	27.33	0
27	4.82	0	1.1482×10^{-3}	- .0762305	27.33	0
28	4.82	0	1.8197×10^{-5}	- .1564151	27.33	0
29	4.82	0	6.0256×10^{-5}	- .1534305	27.33	0
30	4.82	0	5.2481×10^{-5}	- .1539822	27.33	0
31	4.82	0	2.5119×10^{-7}	- .1576886	27.33	0
32	4.82	0	3.9811×10^{-6}	- .1574239	27.33	0
33	4.82	0	5.1286×10^{-4}	- .1213124	27.33	0
34	4.82	0	1.5849×10^{-4}	- .1464596	27.33	0
35	4.82	0	8.1283×10^{-4}	- .1000257	27.33	0
36	4.82	0	5.6234×10^{-5}	- .1537159	27.33	0

3.2 Experimental Procedure

The chemicals used in the experimental procedure were those listed in Table 3.5. The uranium source was a blend of scrap yellowcake from previous experimental investigations. The blended yellowcake was analyzed for uranium content which was found to be 67.86% U by weight.

The required amount of yellowcake for any given run was dissolved in the stoichiometric amount of sulphuric acid to form $UO_2(SO_4)_3^{4-}$. The excess amount of H_2SO_4 required by the design was also added at this stage. A small amount of distilled water was added to the solution to utilize the heat of reaction to facilitate in the dissolution of the uranium. After complete dissolution of the solids, the solution was transferred to a 1 litre volumetric flask and diluted with distilled water. The solution was then transferred to a 4 litre beaker and the mixer was started. The mixer used was a variable speed mixer with a propellor type impeller having 1" blades. Magnesium oxide was added to increase the pH to approximately 3.0 followed by the rapid addition of the experimental amount of 30% hydrogen peroxide. Magnesium oxide was then added to adjust the pH. The suspension was then continually stirred at 175 rpm (stirrer Reynolds Number was approximately 1500) throughout the time of the run.

Table 3.5

Summary of Chemicals Used

Chemical	Supplier	Grade
H_2SO_4	Anachemia	Reagent, 98% H_2SO_4
30% H_2O_2	Anachemia	Reagent, 31% H_2O_2
MgO Powder	Baker	Reagent, 97.4% MgO
pH Buffers 2.00±.02 4.00±.02 7.00±.02 9.00±.02	Fisher	

After the required time had passed, the suspension was filtered through a Buchner funnel using Whatman 42 filter paper. The filtrate was sent to the analytical chemistry department at CANMET to determine the uranium in the barrens solution. The filtercake was air dried for two to three days then weighed on a Mettler balance to give the filtercake yield. The cake was then sent for analysis to determine the uranium, magnesium and sulphur contents of the cake.

pH Measurement

The pH was measured using a Fisher Accumet Model 420 pH/Ion Meter. For the experimental runs, the pH meter was calibrated using a buffer solution of pH 2.00 and the digestion pH was noted. After filtration, the pH of the solution was again measured by calibrating the pH meter using a pH standard closer to the noted pH. The pH determined at this point was considered to be the precipitation pH.

The Determination of the Uranium Values

The uranium contents of the cake and of the filtrate were determined by the analytical chemistry division of CANMET. The analytical method used was fluorimetry (27). This method is described in Appendix III.

Particle Size Analysis

The particle size analyses of the samples were carried out using image analysis techniques by CANMET personnel. A small sample for each run was mounted upon a microscope slide in emulsion oil and placed under a microscope. An image of the field was transmitted to a computer which performed the analysis. Eight to ten fields were analyzed for each sample. The resultant data were presented in terms of the percentage of the sample which would be retained by a sieve of the given size.

?

4. RESULTS AND DISCUSSION

4.1 Analysis of Results

The experimental results including the particle size analyses are presented in Appendix I. Each set of data has been analyzed using least squares by fitting the data to the linear equation;

$$\hat{Y} = \hat{\beta}_0 + \hat{\beta}_1 x_1 + \hat{\beta}_2 x_2 + \ldots + \hat{\beta}_{12} x_1 x_2 + \hat{\beta}_{13} x_1 x_3 + \ldots + \hat{\beta}_{45} x_4 x_5 + \hat{\beta}_{11} x_1^2 + \ldots + \hat{\beta}_{55} x_5^2 \qquad (4.1)$$

for the central composite design (Experimental Plan I) for each of the four cases presented in Chapter 3. For the fractional factorial design with centrepoints (Plan II), the quadratic effects were dropped from equation 4.1 (e.g. $\hat{\beta}_{11} x_1^2$ to $\hat{\beta}_{55} x_5^2$), hence, only the main effects and 2 variable interaction effects were analyzed. Only cases 1 and 3 were used for the analysis. The resultant parameter values from the least squares analysis of equation 4.1 were evaulated for their significance by calculating their 80, 90 and 95% confidence intervals. The reason for calculating the 80 and 90% confidence intervals was because of the correlation among the parameter values (i.e. the value of one parameter affected the value of another). This correlation was caused by the fact that the experimental precipitation pH was not the same as the design precipitation pH. Due to this correlation, it was felt that certain significant terms may be dropped prematurely. In other words, the joint confidence region of the parameters may have been of such a nature to cause significant terms to have a value close to zero for the given least squares estimates. The 80 and 90% confidence intervals are narrower than the 95% confidence interval, and therefore may exclude zero from the interval. Hence, some parameters that were plausibly zero at 95% were not plausibly zero at 80 or 90%. In all, three sets of parameter values were initially calculated (one for each initial confidence interval). Any parameter values that were plausibly zero (i.e. the value of zero was contained within the interval) were dropped from equation 4.1. The resultant equations (one for each initial confidence interval) were then subjected to the regression analysis. At this point, and for any further iterations, only the 95% confidence intervals of the parameters were calculated. The procedure was continued until no more parameters were deemed insignificant. The procedure for calculating the confidence intervals is given in Appendix II. The results of the regression analyses indicated that some additional terms did appear in the final equation for the initial 80 and 90% confidence intervals. In other words, more than one model could occur for any one of the four cases examined (i.e. for different initial confidence intervals). If more than one model existed, the need for additional terms was evaluated by calculating the ratio, Q, where Q is given by (28)

$$Q = \frac{1}{\hat{\sigma}^2}\,\frac{(\text{SSR from Model A}) - (\text{SSR from Model B})}{(\text{Number of parameters in Model B}) - (\text{Number of Parameters in Model A})} \qquad (4.2)$$

where $\hat{\sigma}^2 = \text{SSR}/(n-p)$ for the model with the most terms (Model B). The ratio, Q, was compared with $F_{0.05,\nu_1,\nu_2}$ where ν_1 was the difference in the number of parameters of models A and B and ν_2 was the value of n-p for model B. If Q was larger than F, then the need for the extra terms was considered significant (i.e. the extra terms were needed). This was a significance test of the null hypothesis that all of the true values of the additional parameters of model B were zero.

The models were also tested for lack of fit to determine whether they accurately described the data. This was done using a quantitative lack of fit test by calculating the ratio, R, where R is given by (29)

$$R = \frac{(\text{SSR} - \nu_2\hat{\sigma}^2)/(n-p-\nu_2)}{\hat{\sigma}^2_{c.p.}} \qquad (4.3)$$

where $\hat{\sigma}^2_{c.p.}$ was the estimated variance at the centrepoints assuming the possible effect of pH or $[H^+]$ in this region was negligible and ν_2 was the degrees of freedom associated with $\hat{\sigma}^2_{c.p.}$. The variances used for calculating the ratio, R, have been given in Table 4.1. It was recognized that these

Table 4.1

Means and Variances of the Response Variables at the Design Centrepoint

Variable	Mean	$\hat{\sigma}^2$
Filtercake Yield (g)	23.899	.324
Uranium Precipitated (g)	14.435	.149
Uranium Content of the Cake (wt%)	60.409	1.452
Barrens (g/l)	.0023	1.489×10^{-5}
Conversion (%)	98.440	1.457
Sulphur (wt%)	.216	.007
Mean Particle Size (μm)	8.884	7.094
Particle Size Distribution	.388	.006

variance estimates were not good estimates of the pure error variance since the pH varied from run to run. However, the actual pure error variance would be a much smaller value. Any model which did not pass the lack of fit test with the variance estimate that was used, would not pass the lack of fit test with a better estimate of the pure error variance. The ratio, R, was compared with $F_{0.05,\nu_1,\nu_2}$ to determine whether a quantitative lack of fit was evident. This was a significance test of the null hypothesis that the bias due to model inadequacy is zero (i.e. the error caused by lack of fit was not significantly greater than the pure error).

The results of the analyses are presented in the ensuing tables for each of the responses. The parameter values given are those for the coded variables. The stars signify that the parameter value was estimated using the alternative set of operating variables (e.g. $x_2{}^*$ instead of x_2). The ensuing figures were drawn by calculating the responses with the given parameters using the coded form of the significant variables although these variables were presented in their actual form in the figures.

4.2 Filtercake Yield

The models describing filtercake yield for Experimental Plan I have been given in Table 4.2. Cases 1 and 3 in which pH was a variable gave similar results which indicated that the original uranium and peroxide concentrations (x_1 and x_2) were important. Cases 2 and 4 each gave two different models depending upon which initial confidence interval was investigated. In both cases, testing the need for the extra terms resulting from different initial confidence intervals indicated that they were important. However, all models for all cases failed the quantitative lack of fit test indicating that the data were not well represented by the equations. This was primarily due to the response at the point at which the peroxide concentration was below the stoichiometric amount. Plots of the models for Cases 1, 2 and 3 in Figures 4.1, 4.2 and 4.3 confirmed this. The plots also indicated that the only obvious effect was that of the original uranium content of the solution.

The point at which the peroxide level was below the stoichiometric amount (Run 19) was dropped and the effect of only the initial uranium content upon filtercake yield was re-evaluated for the remaining 35 runs. The resultant equation passed the lack of fit test. A plot of the equation has been presented (Figure 4.4). The equation

Table 4.2

Plausible Models for the Filtercake Yield for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	24.126± .658	79.988	2.50
		β_1	3.916± .658		
		β_2	1.150± .658		
		β_{22}	-1.019± .658		
2/1	95	β_0	23.40	517.904	14.979
2/2	80,90	β_0	24.126± .765	111.705	3.39
		β_1	3.916± .765		
		β_{22}	-1.091± .765		
3/1	all	β_0	24.009± .707	91.680	2.865
		β_1	3.426± .788		
		β_2*	2.603±1.410		
		β_{22}*	2.885±1.945		
4/1	80	β_0	23.991± .788	113.262	3.539
		β_1	4.191± .802		
		β_3*	-1.819±1.605		
		β_{22}*	-2.803±2.177		
4/2	90,95	β_0	23,895± .832	132.140	4.004
		β_1	4.046± .841		
		β_{22}*	-2.345±2.272		

Q-test Results

Model A	Model B	Q	F
2/1	2/2	60.0	3.30
4/2	4/1	5.33	4.15

R-test Results

Case/Model	R	F
1/1	10.36	2.91
2/2	14.01	2.90
3/1	11.91	2.91
4/1	14.81	2.91

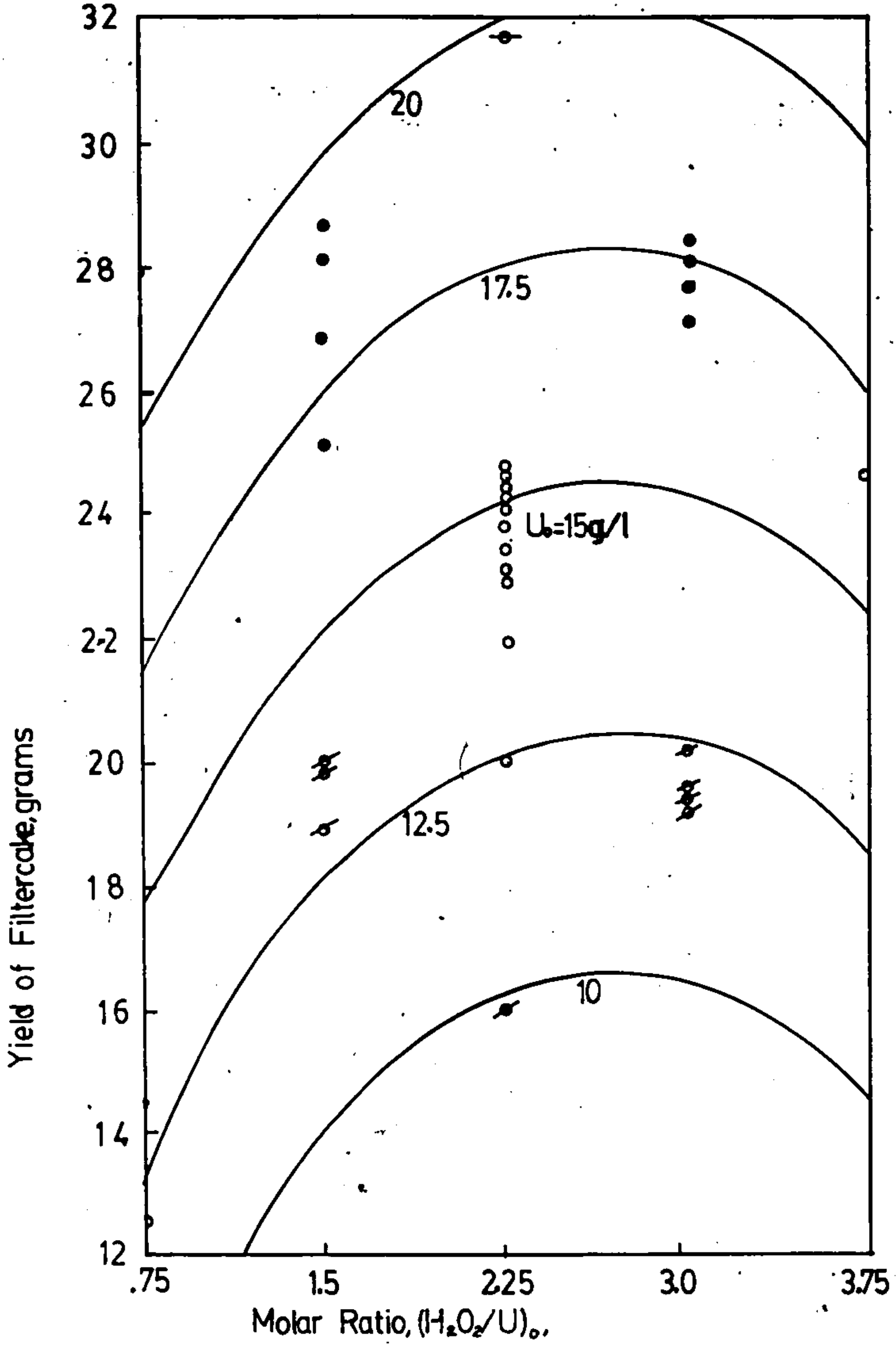

Figure 4.1: Resultant Model for Filtercake Yield for Plan I - Model 1/1 (-o- - U_0=20g/l, ● -U_0=17.5g/l, o-U_0=15g/l, ø-U_0=12.5g/l, ø-U_0=10g/l)

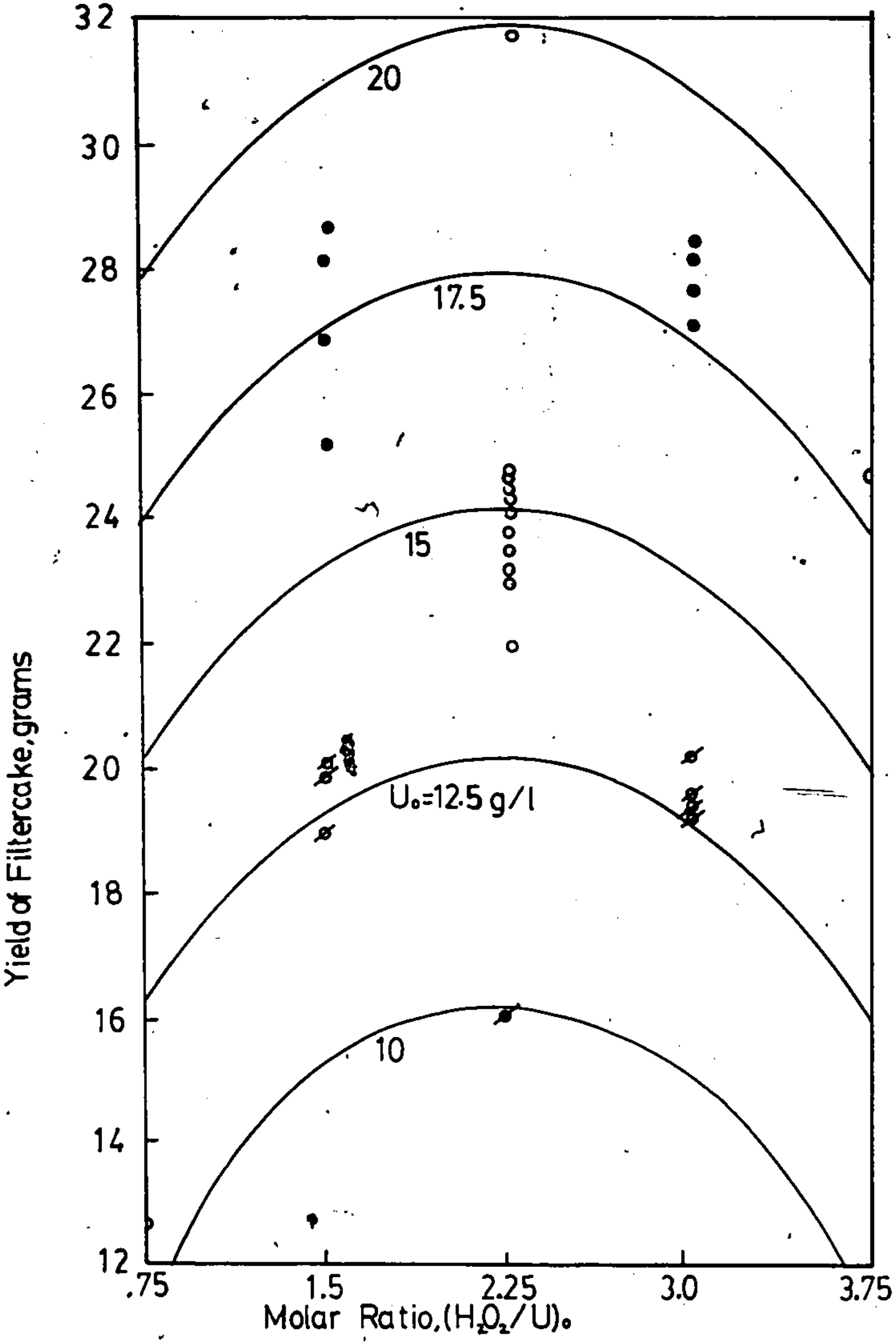

Figure 4.2: Resultant Model for Filtercake Yield for Plan I - Model 2/2 (Refer to Figure 4.1 for the Legend)

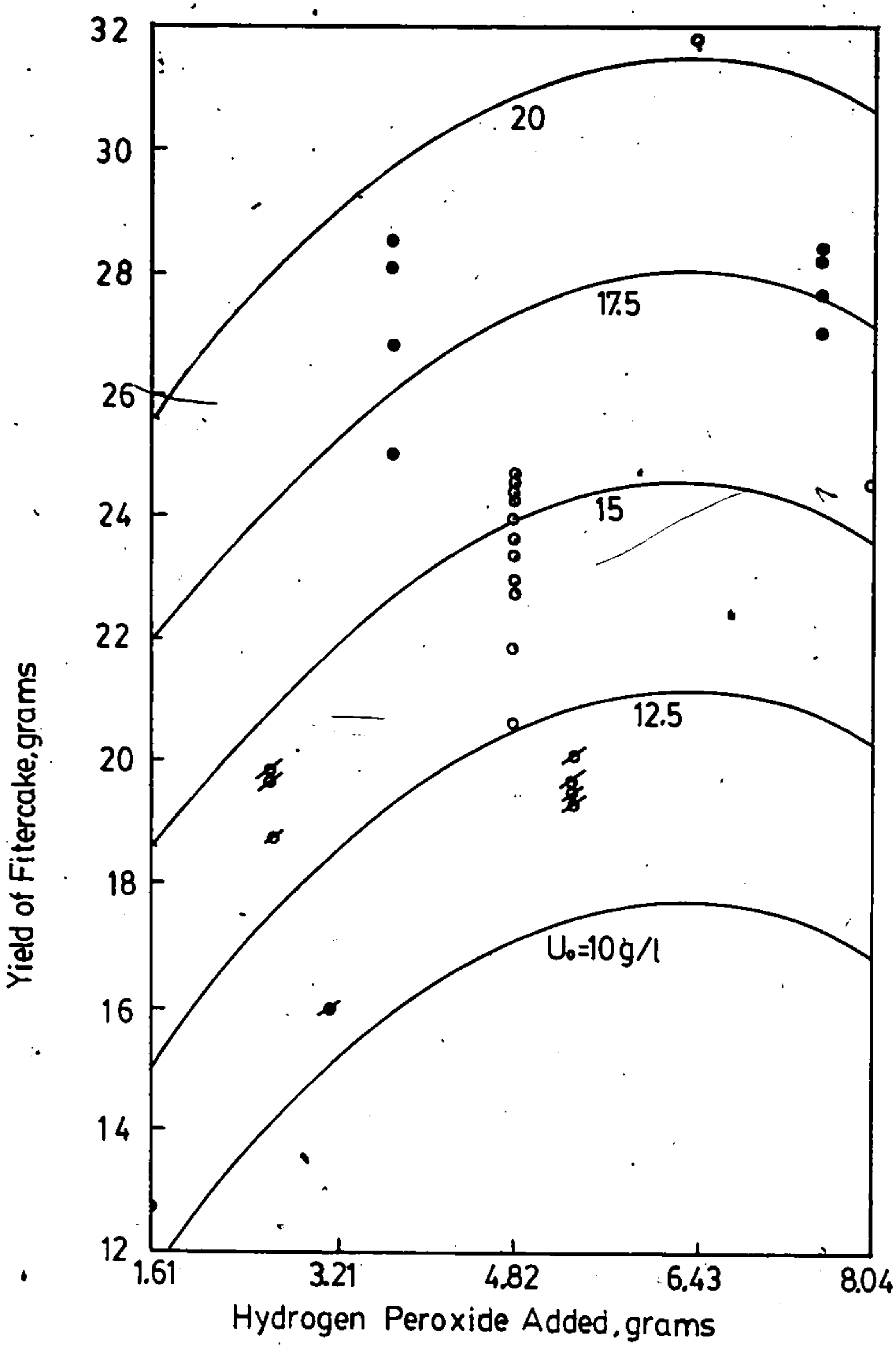

Figure 4.3: Resultant Model for Filtercake Yield for Plan I - Model 3/1 (Refer to Figure 4.1 for the Legend)

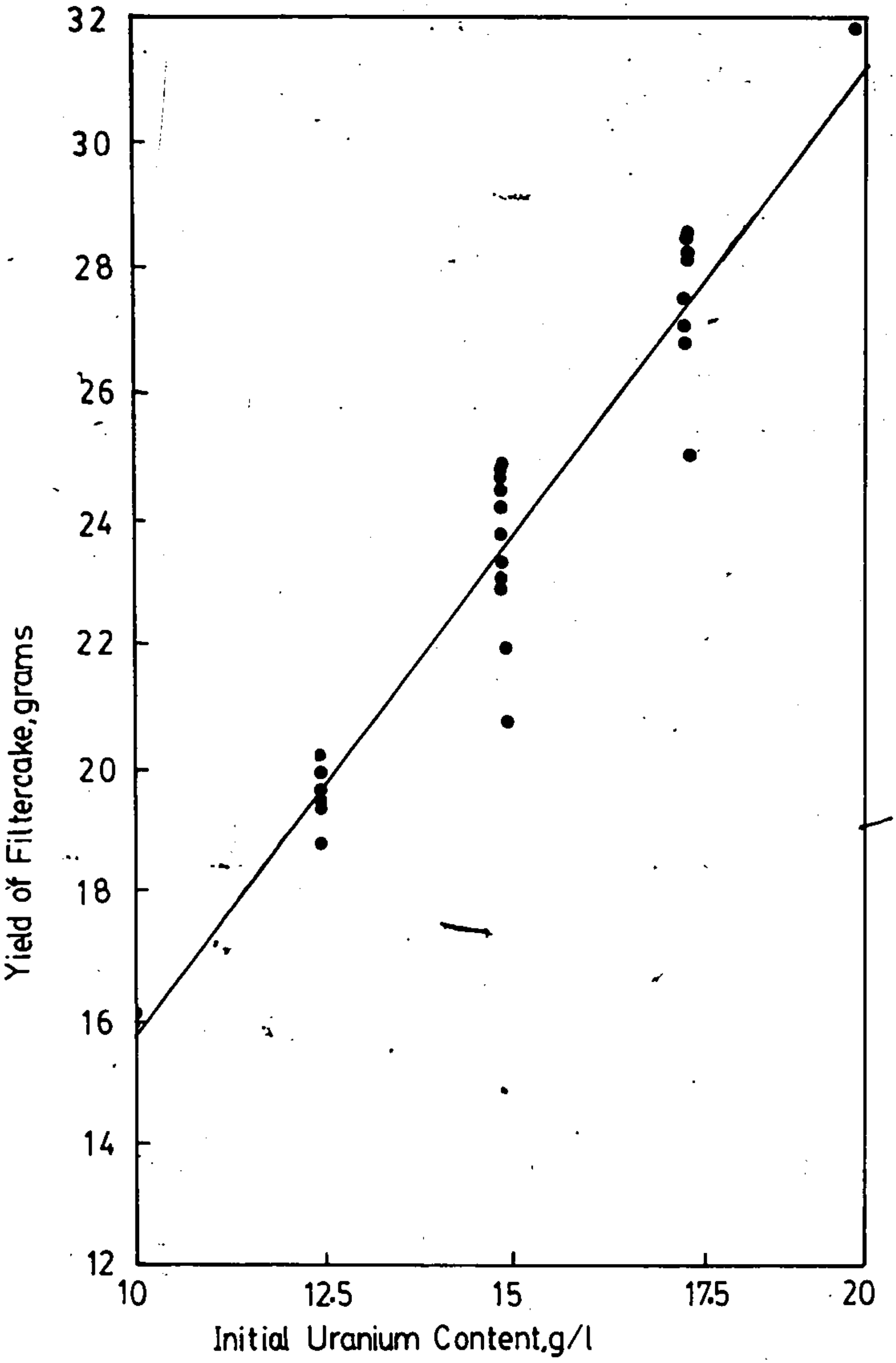

Figure 4.4: Effect of Initial Uranium Concentration upon the Filtercake Yield Excluding Run Number 19.

fit the data quite well although there was a wide variation of filtercake yield observed at the experimental points. This could be attributed to the experimental error and the effects of pH and peroxide levels observed when just the factorial design points and the centrepoints were analyzed.

The parameter values calculated for this equation were not significantly different than those given for the effect of the initial uranium content for Experimental Plan II given in Table 4.3. This indicated that the plausible models for Experimental Plan II could be applicable for the entire design region as long as sufficient peroxide was added to the solution.

For Experimental Plan II, all models passed the lack of fit test. Again, the models for any case which yielded extra terms indicated that the need for these terms was significant. Therefore, for Case 1, both the original uranium concentration and the pH were important and for Case 3, the above two variables were important in addition to the initial peroxide level. The best models for Cases 1 and 3 were compared to test the need of peroxide level. It was found that the peroxide level was important. Hence, the filtercake yield within the factorial design region was dependent upon the original uranium content in the solution, the initial peroxide concentration and the pH. Plots of

Table 4.3

Plausible Models for the Filtercake Yield for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	90	β_0	23.717±.317	14.739	.614
		β_1	3.903±.404		
1/2	95	β_0	23.731±.276	10.66	.463
		β_1	3.915±.352		
		β_3	.777±.529		
3/1	90	β_0	23.711±.257	8.774	.399
		β_1	3.911±.335		
		β_2*	.347±.335		
		β_3	.873±.504		
3/2	95	β_0	23.717±.317	14.739	.614
		β_1	3.903±.404		

Q-test Results

Model A	Model B	Q	F
1/1	1/2	8.81	4.28
3/2	3/1	7.47	3.40

R-test Results

Case/Model	R	F
1/2	1.71	3.02
3/1	1.39	3.04

filtercake yield as a function of initial uranium content and pH are presented in Figures 4.5 and 4.6.

An interesting observation of this analysis was that different initial confidence intervals within each case could yield different final results for significant parameters. For Case 1, the initial 90% confidence interval did not yield pH as a significant parameter whereas the 95% confidence interval did. For Case 3, the opposite result occurred. The initial 95% confidence interval did not yield pH or peroxide level as significant parameters and the initial 90% confidence interval did. Therefore, it was concluded that it could be necessary to test the plausibility of certain independent variables being significant at more than one level of confidence when doing the analysis. Important effects may be considered statistically insignificant especially in the presence of correlated parameter values in which the value assigned to one parameter affects the value of another. In other words, the location of the initial estimates on the sum of squares surface could affect the final results.

Another interesting observation was that the mode of representation of the independent variables could affect their significance. In this case, the presence or absence of peroxide as an effect depended upon how it was represented.

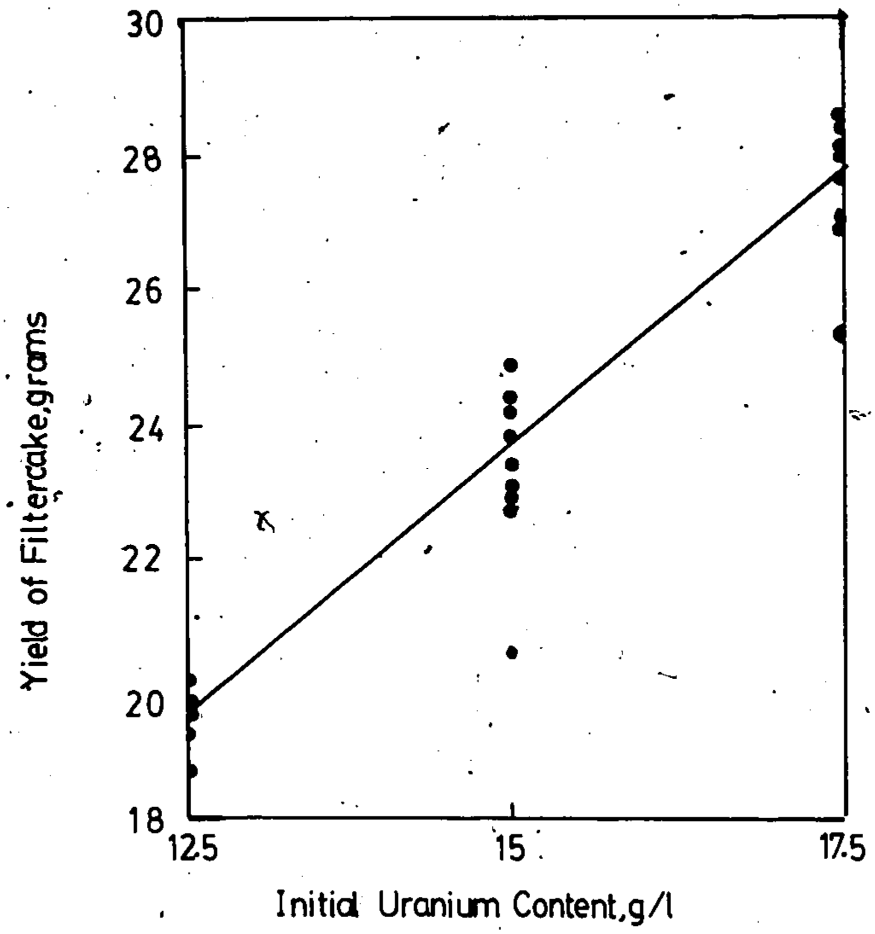

Figure 4.5: Effect of Initial Uranium Concentration upon the Filtercake Yield for Plan II - Model 1/1

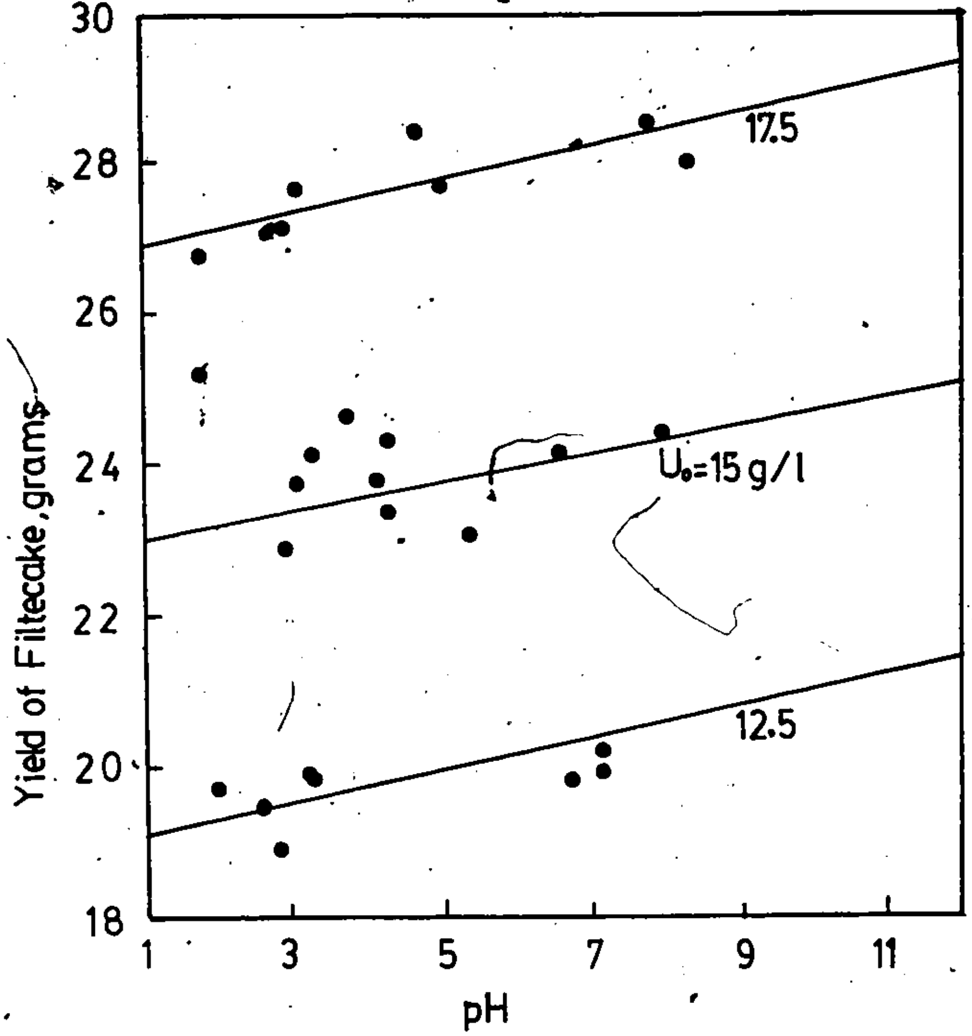

Figure 4.6: Resultant Model for Filtercake Yield for Plan II - Model 1/2

The initial peroxide concentration was not considered important when represented as a fraction of the amount of the initial uranium content. However, when represented directly as the initial peroxide concentration, it was a significant variable.

4.3 Uranium Precipitated

The amount of uranium precipitated for any given run was determined by multiplying the filtercake yield by the uranium content of the cake for that run. All of the models for the full experimental plan (Plan I) given in Table 4.4 demonstrated lack of fit. This was again due to the run at which the peroxide level was below the stoichiometric level. The model for Case 1 (Model 1/1) has been plotted and presented in Figure 4.7. The plot indicated that overall, the amount of uranium precipitated was proportional to the original uranium in solution except for the case in which insufficient peroxide was added to the solution. However, the residual value of this outlier was sufficiently large to cause the model to fail a quantitative lack of fit test because of the large proportion it contributed to the sum of squares of the residuals. Experimental run number 19 was dropped and the parameters for Case 1 were re-evaluated. The re-evaluated paramater values were not significantly different than those presented for Case 1 which in turn were not significantly different than those for Plan II given in Table 4.5.

Table 4.4

Plausible Models for the Uranium Precipitated for Experimental Plan I

Case/ Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	14.033± .420	52.216	1.536
		β_1	2.408± .515		
2/1	80	β_0	14.513± .432	35.601	1.079
		β_1	2.407± .432		
		β_{22}	- .721± .392		
2/2	90,95	β_0	14.033	179.820	5.138
3/1	80	β_0	14.441± .354	22.198	.716
		β_1	2.179± .400		
		β_2*	1.534± .716		
		β_{12}*	1.106± .868		
		β_{22}*	- 2.805±1.181		
3/2	90,95	β_0	14.445± .384	27.037	.845
		β_1	2.095± .428		
		β_2*	1.683± .767		
		β_{22}*	1.953±1.057		
4/1	80	β_0	14.374± .441	35.890	1.216
		β_1	2.559± .448		
		β_{12}*	1.408±1.071		
		β_{22}*	- 2.728±1.476		
4/2	90,95	β_0	14.371± .480	43.951	1.332
		β_1	2.496± .485		
		β_{22}*	- 1.604±1.311		

Table 4.4 (continued)

Q-test Results

Model A	Model B	Q	F
2/2	2/1	66.84	3.29
3/2	3/1	6.76	4.16
4/2	4/1	6.63	4.14

R-test Results

Case/Model	R	F
1/1	13.66	2.89
2/1	9.58	2.90
3/1	7.84	2.92
4/1	10.08	2.91

Table 4.5

Plausible Models for the Uranium Precipitated for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	$14.245 \pm .170$	4.703	.196
		β_1	$2.327 \pm .216$		
3/1	all	β_0	$14.319 \pm .192$	3.257	.148
		β_1	$2.327 \pm .218$		
		β_{14}*	$-.533 \pm .437$		
		β_{24}*	$.760 \pm .705$		

Q-test Results

Model A	Model B	Q	F
1/1	3/1	9.77	4.20

R-test Results

Case/Model	R	F
1/1	1.50	3.01
3/1	0.99	3.06

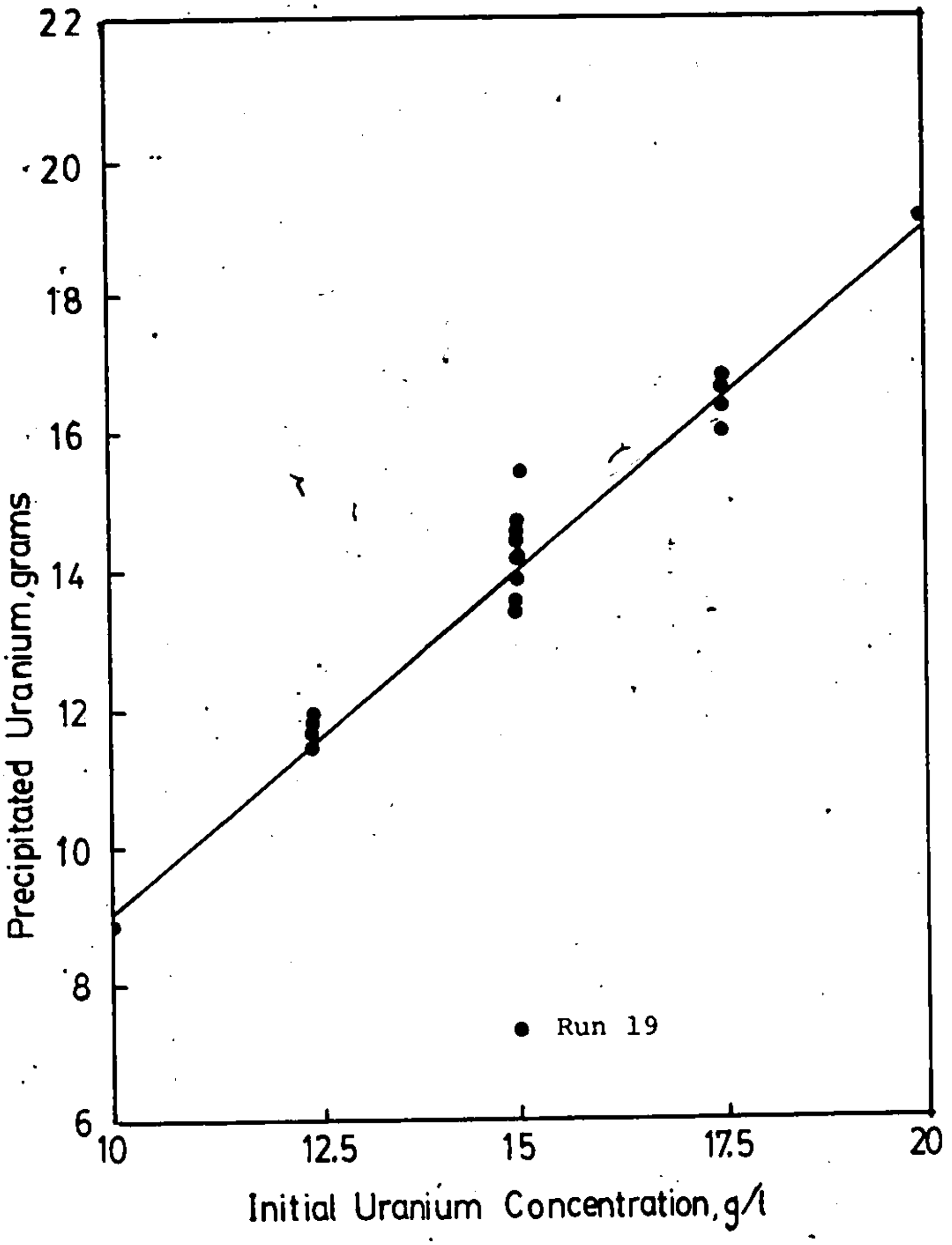

Figure 4.7: Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 1/1

The best models from the other central composite design cases have been plotted and presented in Figures 4.8 through 4.10. The plots confirmed the poor representation of the data by the models, especially because of the influence of run number 19.

The models for Plan II evaluated for Cases 1 and 3 have been given in Table 4.5. A plot of Case 1 has been presented in Figure 4.11. The plot indicated that the data was well represented by this model, however, Case 3 included possible interactive effects of peroxide and total sulphate upon the amount of uranium precipitated. The significance of β_{14}* could be explained by the presence of an equilibrium of the type

$$UO_2{}^{2+} + 2SO_4{}^{2-} \rightleftarrows UO_2(SO_4)_2{}^{2-} \qquad (4.4)$$

A large enough excess of sulphate would drive the equilibrium to the right causing the uranium to stay in solution. The possible cause of the interaction term between peroxide and sulphate being significant was the decomposition of the peroxide by H_2SO_4 meaning that as the sulphate level was increased, more peroxide was decomposed. Hence, more peroxide would need to be added to complete the reaction with the uranium. This was most evident at experimental point 10. The amount of precipitate at this point was significantly lower than at the other points with similar original uranium

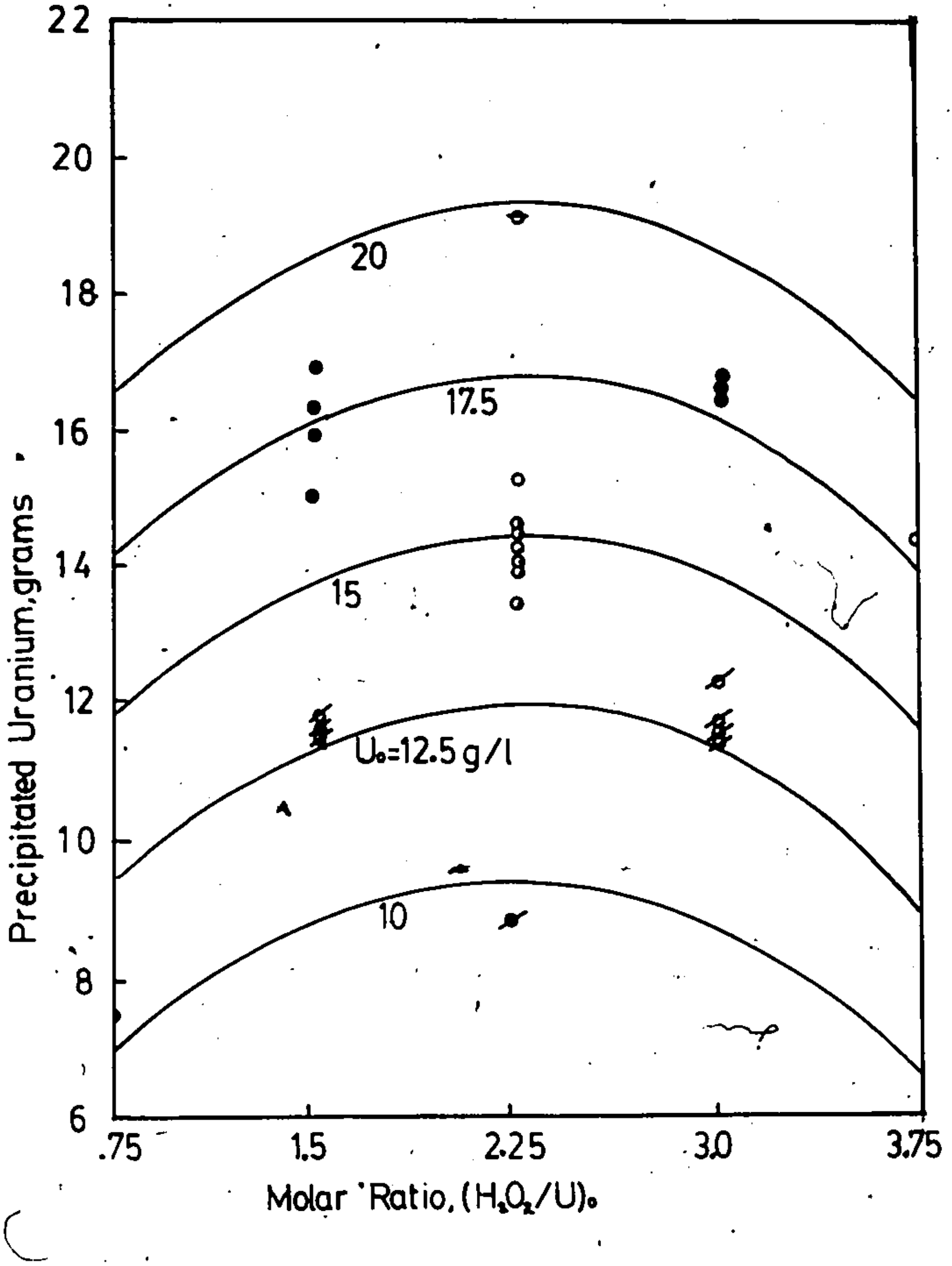

Figure 4.8: Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 2/1

(Refer to Figure 4.1 for the Legend)

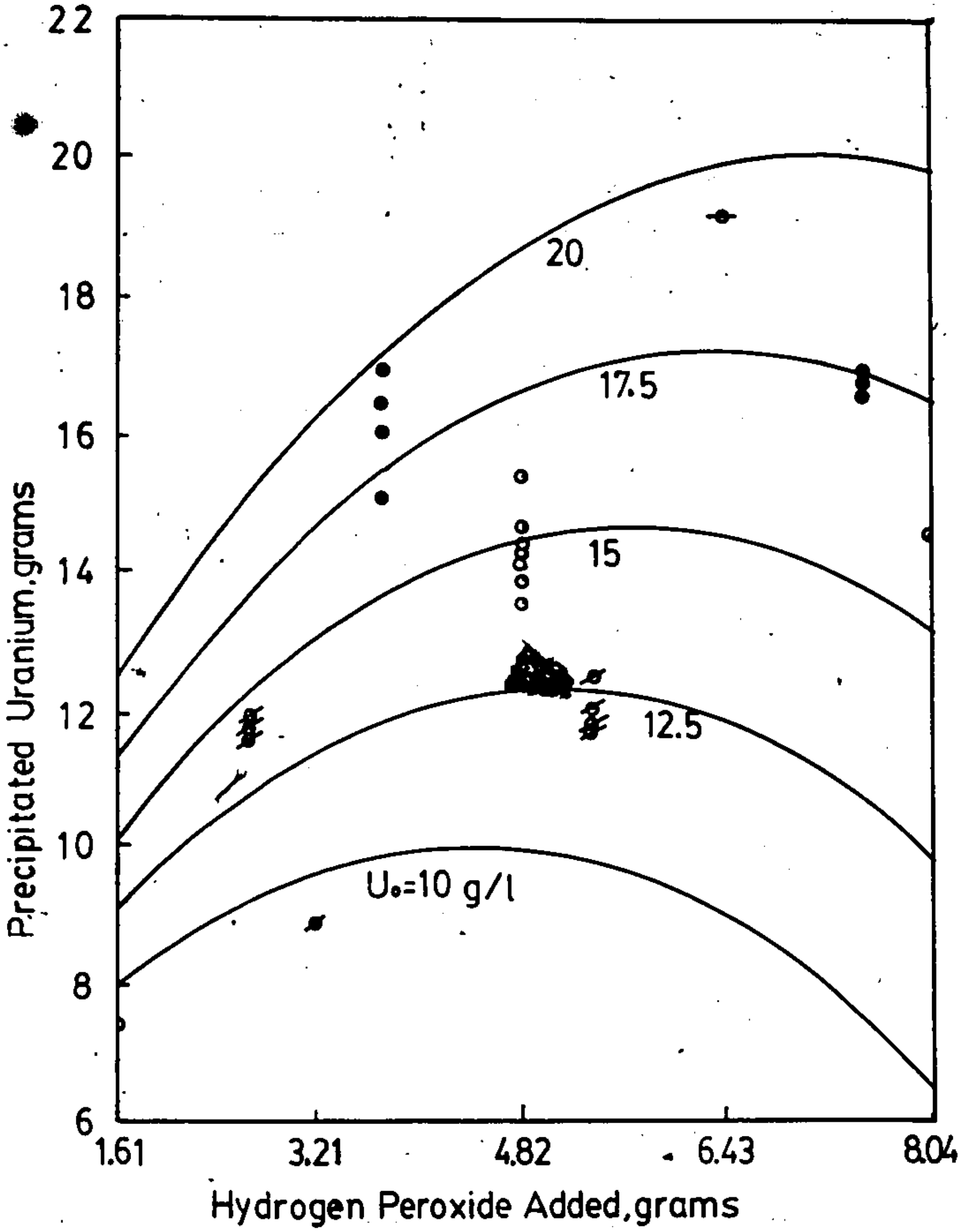

Figure 4.9: Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 3/1

(Refer to Figure 4.1 for the Legend)

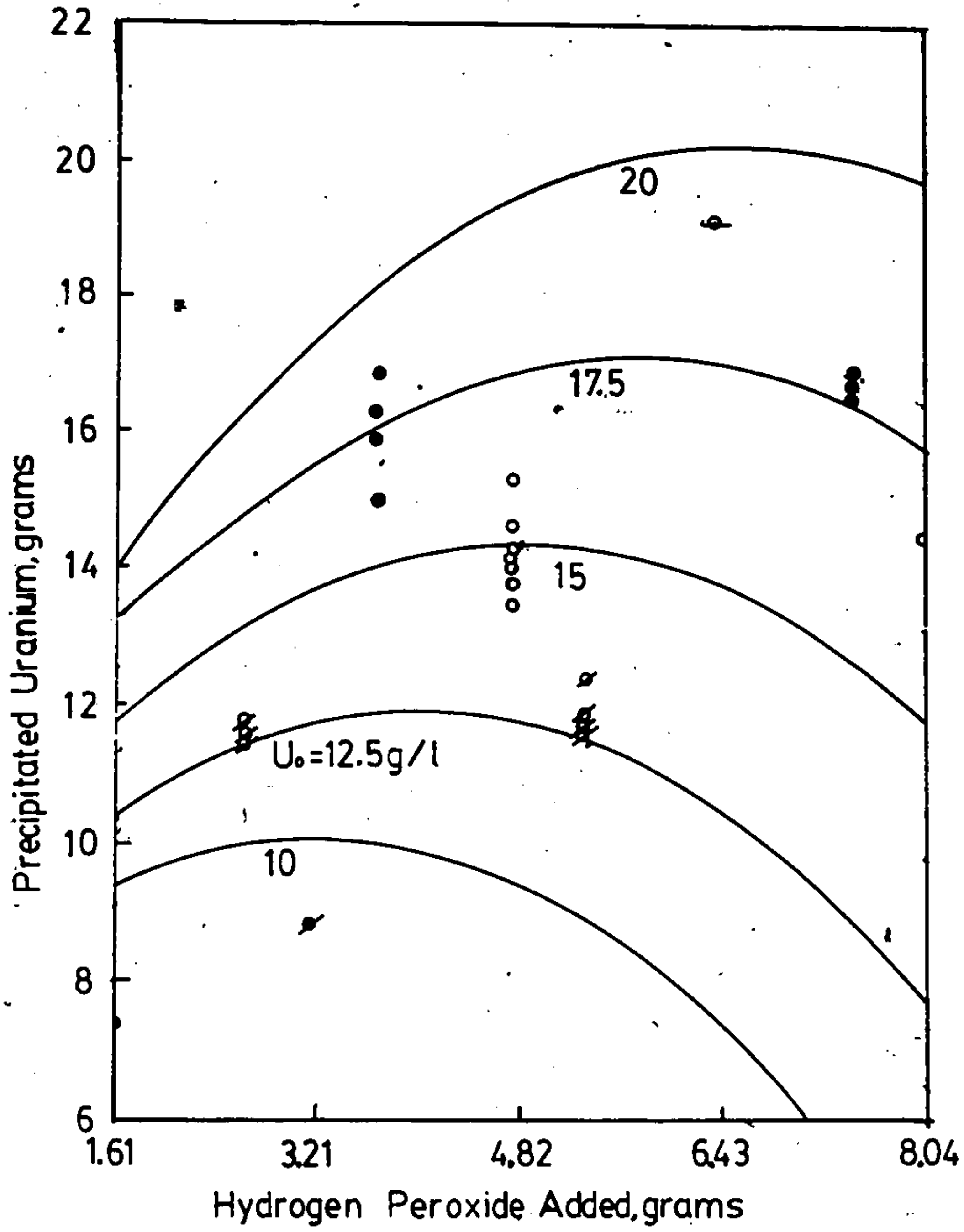

Figure 4.10: Resultant Model for the Amount of Uranium Precipitated for Plan I - Model 4/1

(Refer to Figure 4.1 for the Legend)

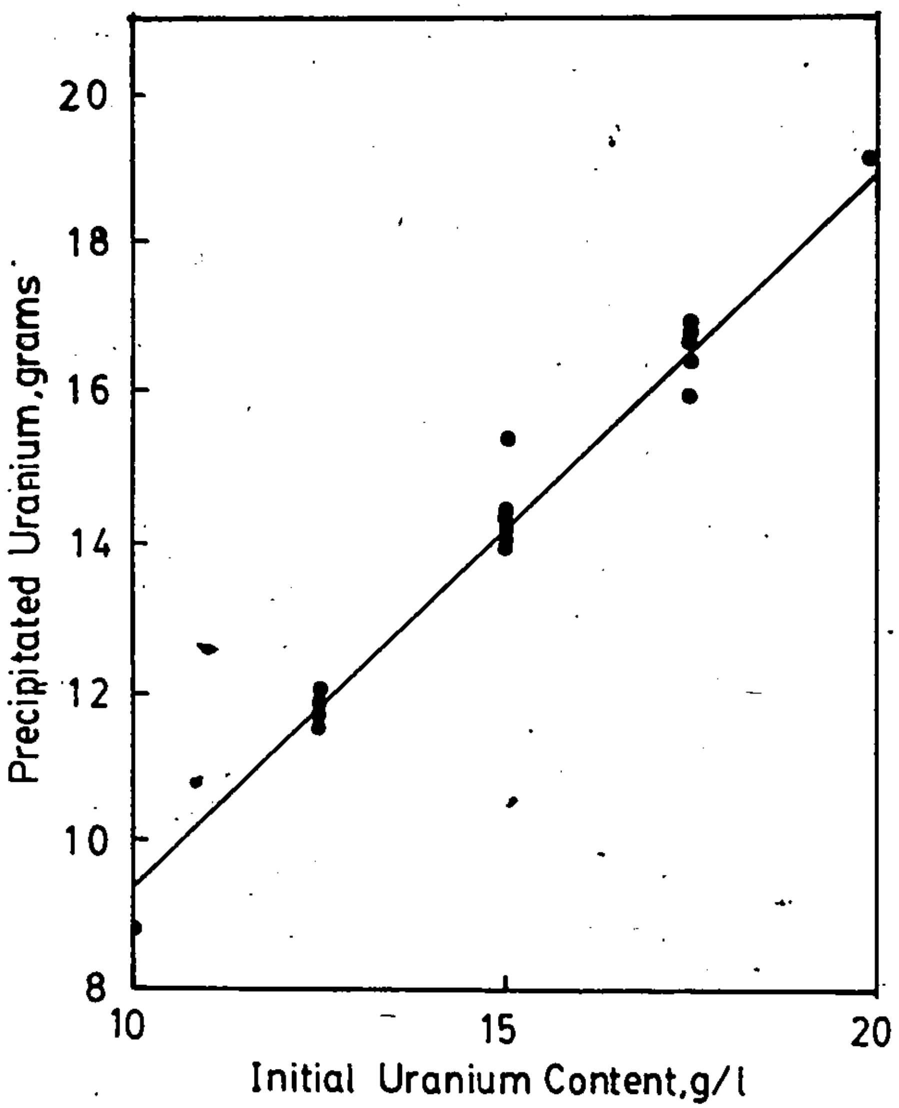

Figure 4.11: Resultant Model for the Amount of Uranium Precipitated for Plan II - Model I/1

content. The amount of precipitate was also slightly lower for point 14 (although not significantly). At this point, the peroxide and sulphate conditions were similar to point 10, however, the point was run at a higher pH indicating that an increase in pH could offset the effect. Over the entire experimental range, pH was deemed an insignificant factor.

4.4 Barrens Concentration

The plausible models for the barrens concentration for both the Plan I and Plan II given in Tables 4.6 and 4.7 failed the lack of fit test. The reason for this was that the barrens concentration data was spread over several orders of magnitude (e.g. for point 10, the concentration was 1.57 g/l while for point 31, the concentration was less than 0.0001 g/l). This large variation meant that the larger values for the barrens concentration determined the parameter estimates and the smaller values had negligible effect. The overall result was that the models only described the large values of barrens concentration and did not estimate the small values. Investigation of the residuals indicated that the residuals for a given experimental run were larger than the values at the experimental points.

The resultant model for Case 1 for Plan II for an initial 95% confidence interval contained all of the main effects in one form or another. Although the model failed a

Table 4.6

Plausible Models for the Barrens Concentration for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_{2} β_{22}	- .586± .301 - .764± .213	17.910	.527
2/1	all	β_{22}	.764± .270	29.582	.845
3/1	80,90	$\beta_{2}*$ $\beta_{12}*$ $\beta_{22}*$	- 1.004± .549 - 1.230± .738 2.505± .875	17.640	.535
3/2	95	$\beta_{2}*$ $\beta_{22}*$	- 1.906± .625 1.560± .780	23.802	.700
4/1	80	$\beta_{12}*$ $\beta_{22}*$	- 1.365± .861 - 2.405±1.038	25.036	.736
4/2	90,95	$\beta_{22}*$	1.337± .888	32.694	.934

Q-test Results

Model A	Model B	Q	F
3/2	3/1	11.53	4.14
4/2	4/1	10.40	4.13

R-test Results

Case/Model	R	F
1/1	311.12	2.90
2/1	494.34	2.91
3/1	319.19	2.90
4/1	435.05	2.91

Table 4.7

Plausible Models for the Barrens Concentration
For Experimental Plan II

Case/ Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	90	β_2	$-.175 \pm .132$	1.316	.060
		β_3	$-.306 \pm .301$		
		β_{24}	$-.153 \pm .132$		
		β_{34}	$-.292 \pm .215$		
1/2	95	β_0	$.109 \pm .100$	1.210	.058
		β_2	$-.131 \pm .126$		
		β_{12}	$-.179 \pm .132$		
		β_{24}	$-.135 \pm .129$		
		β_{35}	$.363 \pm .223$		

R-test Results

Case/Model	R	F
1/1	43.32	3.06
1/2	43.09	3.07

lack of fit test, the effects of the variables were consistent with what would be expected to happen. For example, it would be expected that an increase in peroxide would decrease the barrens (as was discussed with the amount or uranium precipitated). The interaction between peroxide and sulphate was opposite to that of the amount of uranium precipitated which would be expected (i.e. by a mass balance; Barrens (g/l) = Initial Uranium (g/l) Uranium Precipitated (g/l)). Residence time having to be increased with decreasing pH (increasing $[H^+]$) to decrease the barrens, as indicated by the β_{35} term could be expected. At lower pH's, the reaction would be retarded as shown by the rate equation given in equation 2.2.6 (i.e. k_{obs} would decrease with higher H^+ concentration). This was further illustrated when the log of barrens concentration against the pH was plotted for the centrepoints and the two runs for which only the pH was varied. As pH was increased, the barrens concentration decreased for a similar residence time. The effect of pH upon the barrens concentration has been presented in Figure 4.12.

4.5 Conversion

Conversion was calculated as follows:

$$\text{Conversion (\%)} = \frac{\text{Uranium Precipitated (g)}}{\text{Initial Uranium Added to the Solution (g)}} \times 100 \qquad (4.5)$$

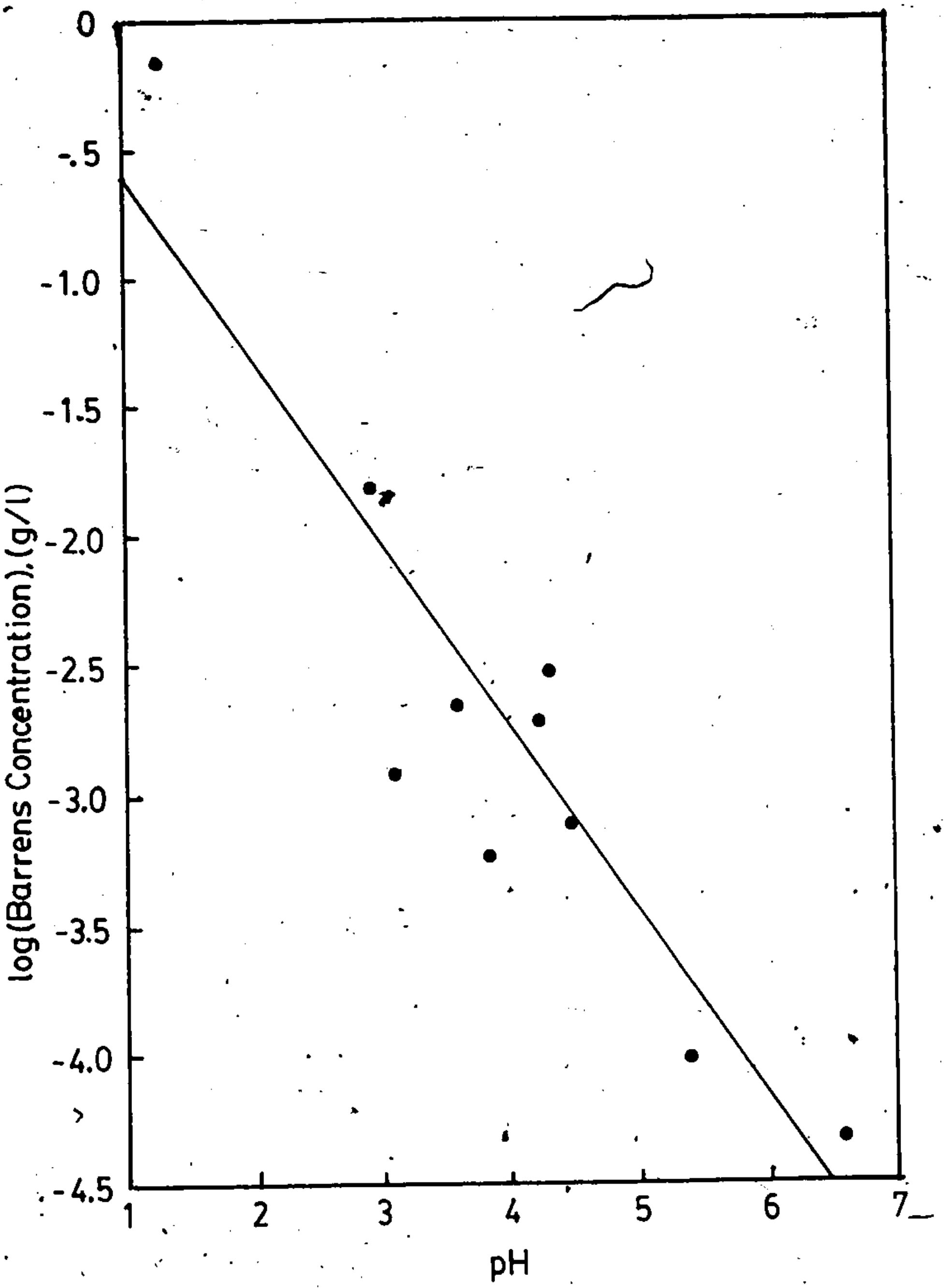

Figure [illegible].12: The Effect of pH upon the Barrens Concentration at the Centrepoint

All of the models in Tables 4.8 and 4.9 failed the lack of fit test. This was due both to run number 19 and run number 10 for Plan I and run number 10 for Plan II. The values of conversion at these points were greatly different than the others in both cases. Examination of the values plotted in Figures 4.13 through 4.16 for the central composite design models did not indicate any obvious effects of the original uranium content upon conversion. The wide variation at the centrepoint could possibly be due to a pH dependence. The conversion was plotted against pH with the resultant relationship presented in Figure 4.17. Analysis of the significance of the effect of pH at the centrepoint indicated that the effect was significant at a 90% confidence level, but not at a 95% confidence level.

The effect of H_2O_2 for the central composite design was primarily due to run number 19 since, at this point, there was insufficient peroxide to fully precipitate the uranium initially, hence, the conversion was low. Moreover, the conversion at this point was pro-rated (i.e. divided by .75 to determine the conversion in terms of the initial H_2O_2 content) and was found to be 71.61% which was also lower than the other values. The results observed for run numbers 10 and 19 did indicate that as sulphate level was increased, more H_2O_2 would need to be added to increase the conversion because of the decomposition of H_2O_2.

Table 4.8

Plausible Models for Conversion for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	99.267±2.086	831.306	25.191
		β_2	4.337±2.086		
		β_{22}	4.708±1.806		
2/1	all	β_0	99.267±2.550	1282.666	37.255
		β_{22}	4.708±2.208		
3/1	80	β_0	98.853±2.148	847.576	26.487
		β_2^*	8.134±3.900		
		β_{12}^*	7.526±5.200		
		β_{22}^*	-18.818±7.097		
3/2	90,95	β_0	98.902±2.383	1077.981	32.666
		β_2^*	8.703±4.304		
		β_{22}^*	-13.120±6.550		
4/1	80	β_0	98.328±2.625	1326.090	40.185
		β_{12}^*	8.620±6.366		
		β_{22}^*	-17.198±8.680		
4/2	90,95	β_0	98.343±2.866	1631.479	47.985
		β_{22}^*	-10.473±7.771		

Q-test Results

Model A	Model B	Q	F
3/2	3/1	8.70	4.15
4/2	4/1	7.60	4.14

R-test Results

Case/Model	R	F
1/1	23.40	2.90
2/1	34.84	2.89
3/1	24.90	2.91
4/1	37.55	2.90

Table 4.9

Plausible Models for Conversion for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	97.401	108.440	4.338
3/1	all	β_0 β_{14}* β_{24}*	97.857± .824 2.621±1.879 3.540±3.028	75.586	3.286

R-test Results

Case/Model	R	F
1/1	4.09	3.00
3/1	3.06	3.02

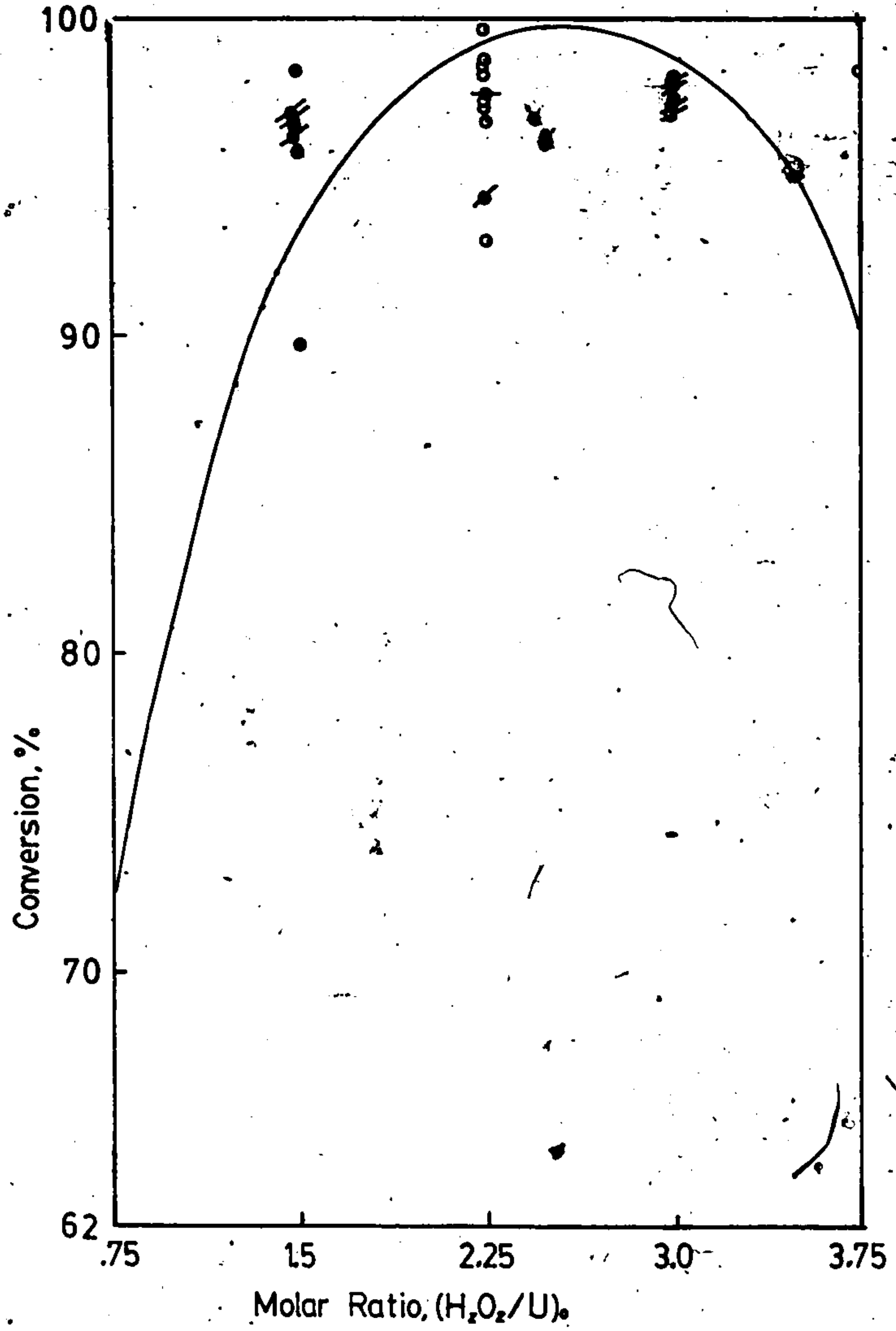

Figure 4.13: Resultant Model for Conversion for Plan I - Model 1/1 (⊸– U_0=20g/l, ● -U_0-17.5g/l, o -U_0=15g/l, ⌀-U_0=12.5g/l, ●-U_0=10g/l)

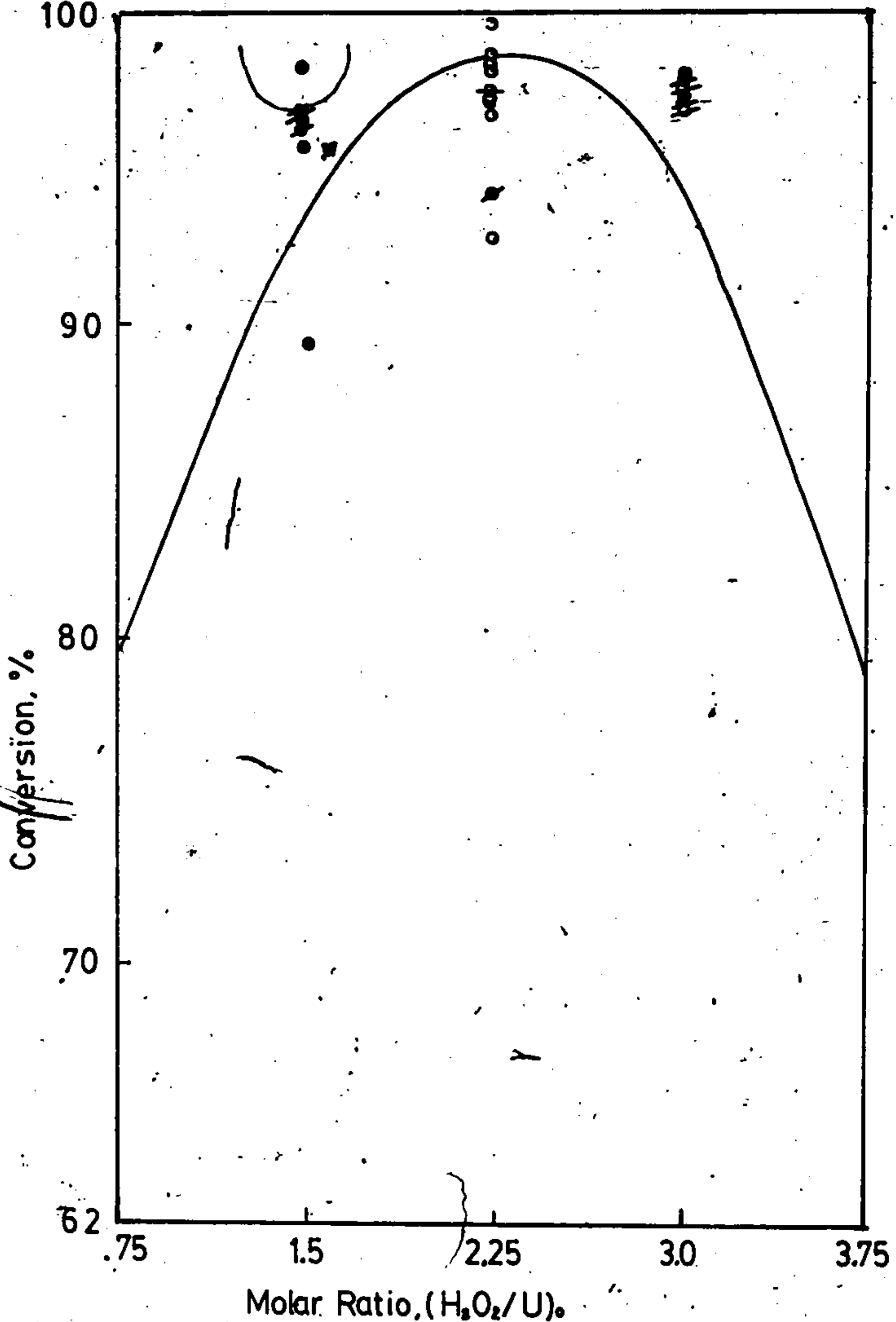

Figure 4.14: Resultant Model for Conversion for Plan I - Model 2/1 (Refer to Figure 4.13 for the Legend)

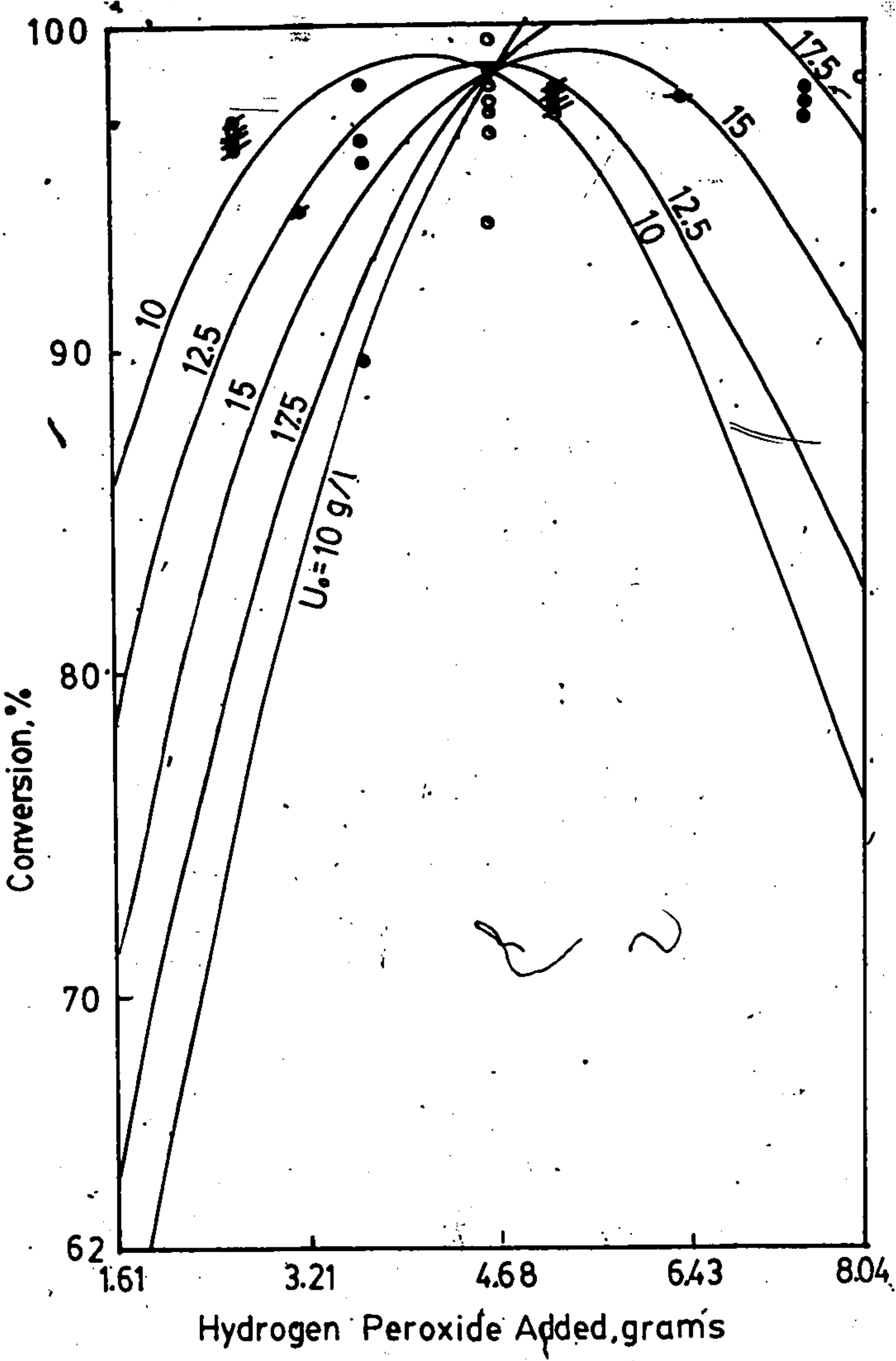

Figure 4.15: Resultant Model for Conversion for Plan I - Model 3/1 (Refer to Figure 4.13 for the Legend)

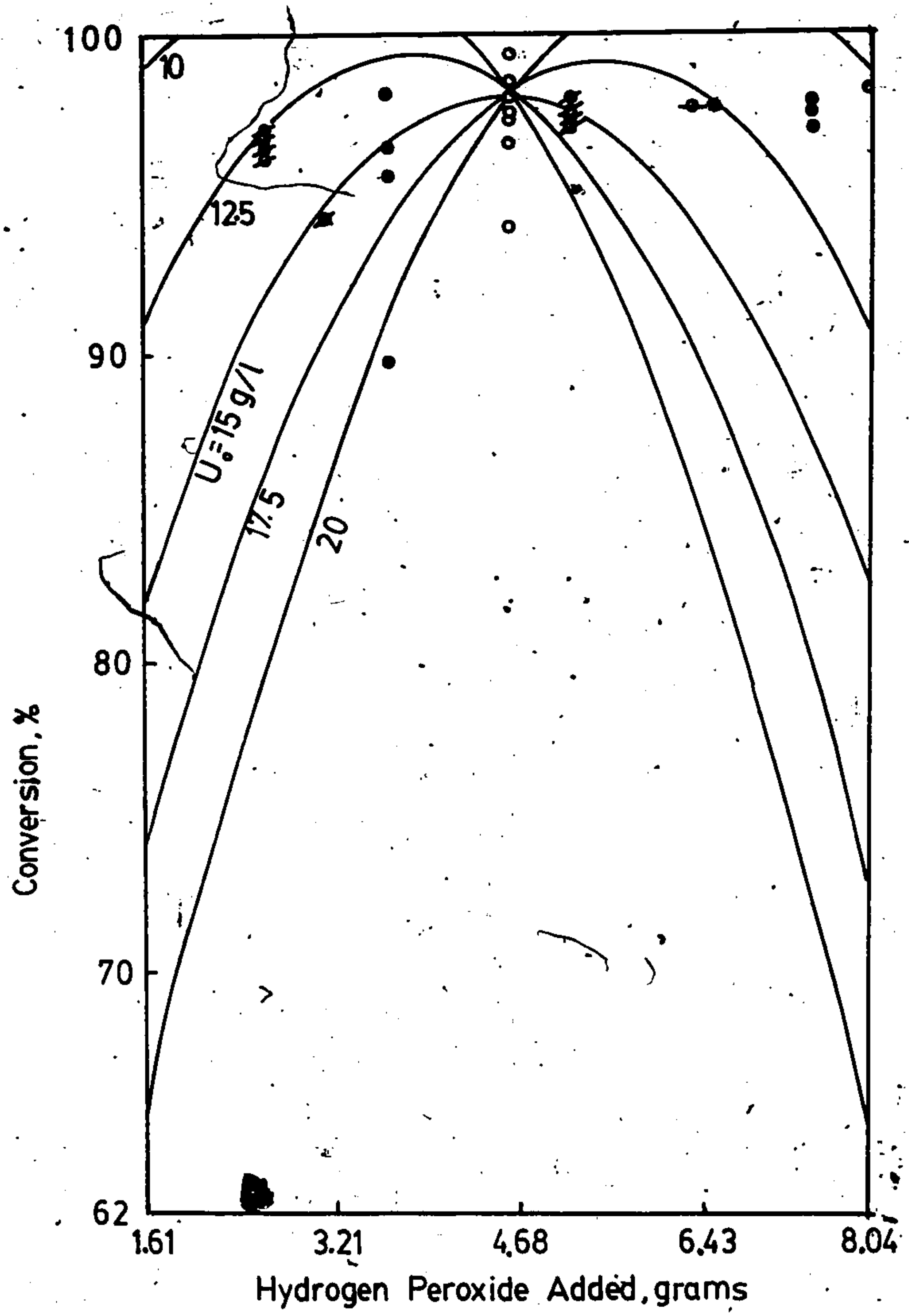

Figure 4.16: Resultant Model for Conversion for Plan I - Model 4/1 (Refer to Figure 4.13 for the Legend)

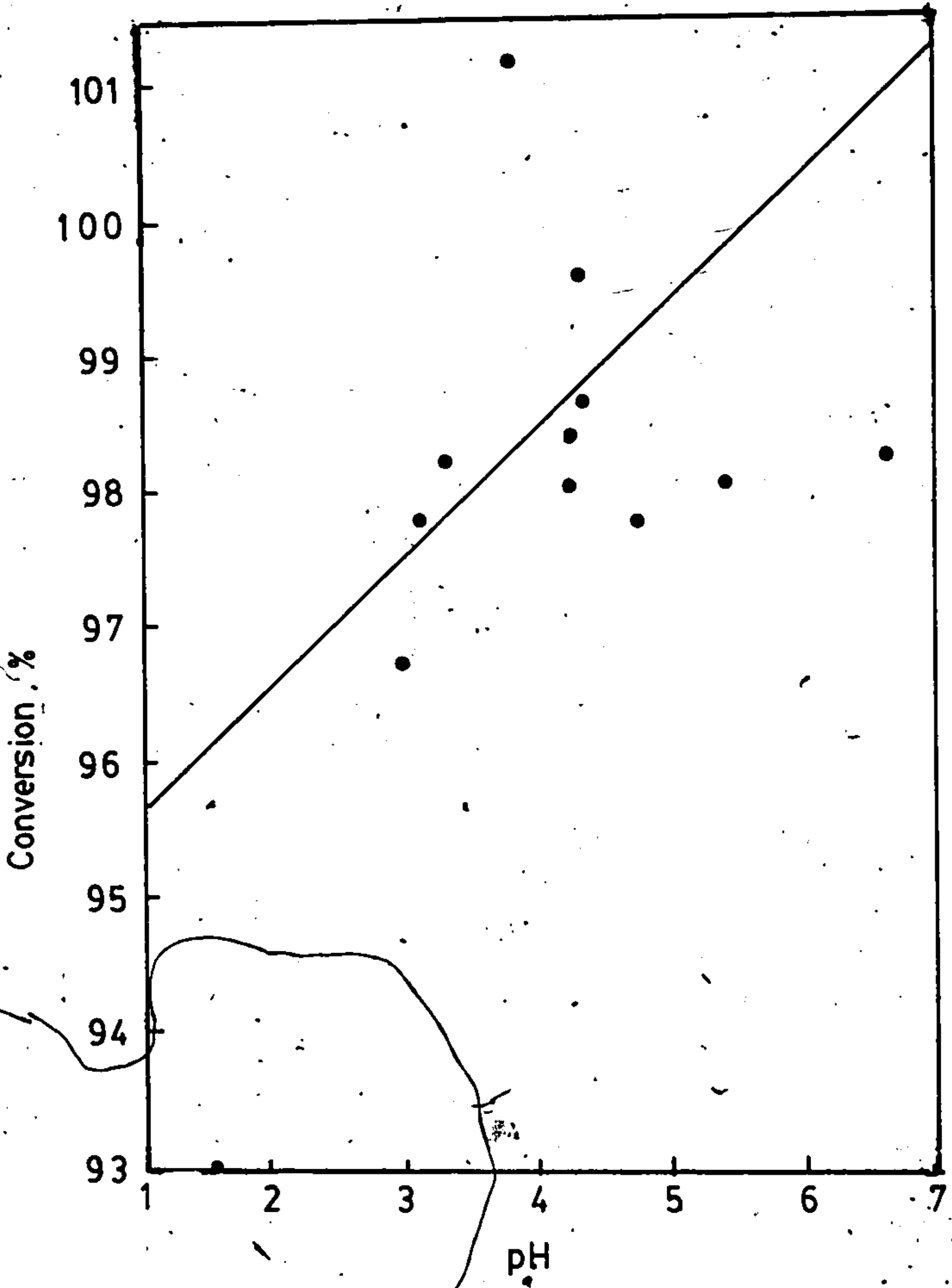

Figure 4.17: The Effect of pH upon Conversion at the Centrepoint

The possible effects of the original uranium, hydrogen peroxide and sulphate levels upon the conversion were tested for the factorial design region excluding run number 10. None of the terms were deemed to be significant indicating that the conversion at sufficient peroxide levels to account for the decomposition due to sulphate was not affected by these variables. The only possible effect was that of pH which was discussed earlier. The fact that the amount of uranium precipitated, (which was affected by the initial uranium content of the solution) was divided by the initial uranium content to calculate the conversion cancelled out any possible effect of this variable upon conversion.

4.6 Uranium Content

The models for the uranium content of the cake have been presented in Tables 4.10 and 4.11. All of the models which yielded pH as significantly affecting the uranium content of the cake passed the quantitative lack of fit test. The models for both Experimental Plan I and Plan II have been plotted and presented in Figure 4.18. Although the effect of pH was evident from this plot, the number of outliers indicated that other effects may have been present. One such effect could be the retained moisture in the cake after the air drying period. Since the cake was not properly dried, some residual moisture would be expected. Proper drying and calcining procedures would increase the uranium

Table 4.10

Plausible Models for the Uranium Content of the Filtercake for Experimental Plan I

Case/ Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0 β_3	59.954± .468 - 2.186± .833	64.972	1.911
2/1	all	β_0	59.950	114.603	3.274
3/1	all	β_0 β_3	59.954± .468 - 2.186± .833	64.972	1.911
4/1	80	β_0 β_3* β_{11}	60.322± .611 2.346±1.219 - .543± .529	71.295	2.160
4/2	90,95	β_0	59.950	114.603	3.274

Q-test Results

Model A	Model B	Q	F
4/2	4/1	10.02	3.29

R-test Results

Case/Model	R	F
1/1	2.38	3.01
2/1	4.37	3.00
3/1	2.38	3.01
4/1	2.86	3.02

Table 4.11

Plausible Models for the Uranium Content of the Filtercake for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0 β_3	60.096± .439 - 1.703± .833	27.705	1.154
3/1	90	β_0 β_3	60.096± .439 - 1.703± .833	27.705	1.154
3/2	95	β_0	60.096	48.130	4.203

Q-test Results

Model A	Model B	Q	F
3/2	3/1	17.70	4.26

R-test Results

Case/Model	R	F
1/1	0.672	3.01
3/1	0.672	3.01

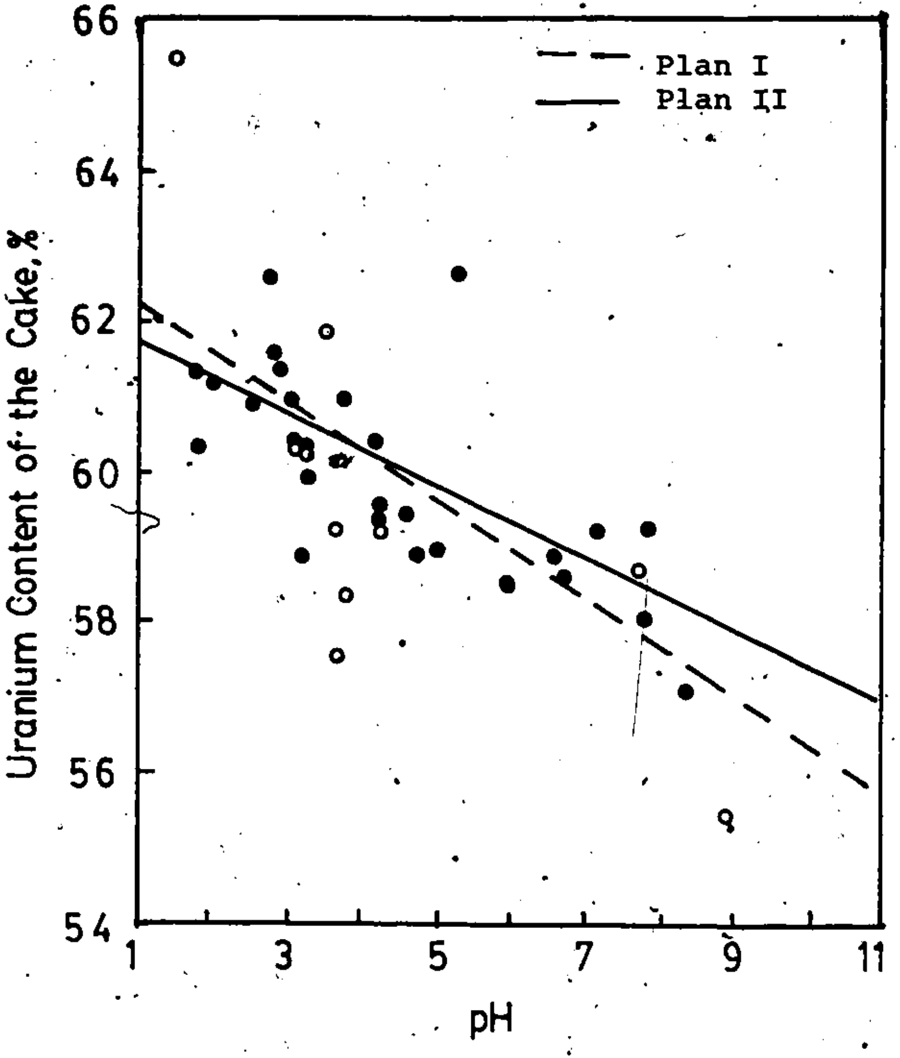

Figure 4.18: The Effect of pH upon the Uranium Content of the Cake
(●- Factorial Design and Centrepoints
○- Added Central Composite Design Points)

content of the cake. It was recognized that if the final precipitated product was $UO_2 \cdot 2H_2O$ as given by equation 2.1.11, then the maximum uranium content of the cake would be 70.41%. Therefore, in terms of the chemical formula, the purity was quite high, being in the range of 78.7% to 92.9%. Proper drying would also remove the hydrated water which would account for approximately 11% of the total filtercake weight. This indicated that proper drying could increase the purity in terms of the uranium content to a range of 88.43% to 100%. The reason for not drying the cakes properly, was to avoid affecting the particle size distribution.

The effect of pH upon the uranium content could be attributed to the presence of other impurities such as vanadium and molybdenum. The retained moisture in the cake was assumed to be random. Other researchers have indicated that a higher pH will increase the concentration of impurities in the final product. It should be noted that the assumption of retained moisture being a random variable would increase the experimental error which could have masked the importance of other variables upon the uranium content. Since the cake was considered pure enough to meet refiners' standards, however, the need to determine these effects by drying the cakes properly was considered unnecessary.

4.7 Sulphur Content

The primary reason for measuring the effect of sulphur content of the cake was to determine whether the formation of a uranium sulphate complex would occur at lower levels of peroxide concentration. A uranium sulphate complex has been observed for the NaOH and NH_3 precipitation methods (30). If this effect had occurred, the values of the sulphur content would have been abnormally high for some of the runs. Most probably run numbers 10 and 19 would have been affected considering the effect these runs had upon the other response variables. The sulphur content for the runs at these points were not abnormally high. None of the observed values were above the refiners' standards (31).

The models for the sulphur content of the cake have been presented in Tables 4.12 and 4.13. In all cases, any extra terms were deemed to be significant. For the central composite design (Plan I), the 11 parameter model for Case 3 and the 5 parameter model for Case 1 passed the lack of fit test. For Experimental Plan II, the models for both Cases 1 and 3 passed the lack of fit test.

All of the models which were deemed adequate indicated that decreasing the H_2O_2 concentration would increase the sulphur content of the cake, however, the increase was not of a large magnitude and would not be expected to cause sulphate levels to exceed refiners' standards.

Table 4.12

Plausible Models for the Sulphur Content of the Cake for Experimental Plan I

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	.240± .055	.365	.012
		β_2	- .065± .046		
		β_{24}	- .105± .056		
		β_{33}	- .134± .105		
		β_{55}	.059± .039		
2/1	all	β_0	.240± .046	.625	.018
		β_{24}	- .097± .069		
3/1	80	β_0	.231± .053	.204	.008
		β_2*	- .144± .076		
		β_4*	.094± .069		
		β_5	- .039± .036		
		β_{14}*	.145± .093		
		β_{24}*	- .420± .168		
		β_{34}*	- .110± .108		
		β_{45}*	- .090± .078		
		β_{22}	.120± .112		
		β_{33}	- .235± .111		
		β_{55}	.058± .033		
3/2	90	β_0	.250± .059	.388	.013
		β_2*	- .107± .091		
		β_{14}*	.157± .114		
		β_{24}*	- .345± .199		
		β_{33}	- .225± .135		
		β_{55}	.058± .041		
3/3	95	β_0	.212± .028	.578	.018
		β_{24}*	- .201± .189		
		β_{55}	.060± .047		
4/1	80	β_0	.200± .058	.659	.019
		β_{55}	.060± .050		
4/2	90,95	β_0	.212± .028	.578	.018
		β_{24}*	- .201± .189		
		β_{55}	.060± .047		

Table 4.12 (continued)

Q-test Results

Model A	Model B	Q	F
3/3	3/2	4.91	2.53
3/2	3/1	4.51	2.60
4/1	4/2	4.67	4.15

R-test Results

Case/Model	R	F
1/1	1.96	2.92
2/1	3.21	2.89
3/1	1.26	3.00
4/2	3.07	2.90

Table 4.13

Plausible Models for the Sulphur Content of the Cake for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	90	β_0	.236 ± .029	.098	.005
		β_2	- .049 ± .035		
		β_4	.053 ± .035		
		β_{24}	.097 ± .035		
		β_{45}	- .145 ± .035		
1/2	95	β_0	.236 ± .029	.195	.009
		β_2	- .049 ± .035		
		β_4	.053 ± .035		
		β_{24}	.097 ± .035		
3/1	all	β_0	.299 ± .046	.230	.011
		β_2*	- .118 ± .104		
		β_4*	.095 ± .093		
		β_{12}*	.149 ± .127		
		β_{24}*	- .294 ± .193		

Q-test Results

Model A	Model B	Q	F
1/2	1/1	19.4	4.32

R-test Results

Case/Model	R	F
1/1	0.42	3.07
3/1	1.99	3.07

The data presented in Tables 4.12 and 4.13 clearly indicated the importance of considering more than the 95% confidence interval when carrying out the analysis. The mode of representation of the independent variables was also important. This was evident for the number of different models which resulted for the central composite design which varied from a two parameter model for Case 2 to an eleven parameter model for Case 3.

4.8 Size and Size Distribution

The mean size and size distribution were calculated from the size analyses given in Appendix 1. Plots of the log of the size vs. the cumulative percentage yielded nearly straight lines over most of the probability range. This indicated that the size could be adequately represented as a log-normal distribution.

$$f(\log L) = \frac{1}{\sqrt{2\pi}\,\log \sigma'} \exp \frac{-\log^2(L/\bar{L}')}{2\log^2 \sigma'} \qquad (4.6)$$

$$\bar{L}' = L_{0.05} \qquad (4.7)$$

$$\sigma' = L_{.841}/L_{0.5} \qquad (4.8)$$

For the log-normal distribution, the population-weighted mean size was calculated by (32)

$$\bar{L} = L_{0.50} \exp(\tfrac{1}{2}\log^2\sigma') \qquad (4.9)$$

The measure of size distribution was the coefficient of variation which was a measure of the dispersity and was calculated by

$$\text{c.v.} = [\exp(\log^2\sigma')-1]^{\frac{1}{2}} \qquad (4.10)$$

The models for size and size distribution have been presented in Tables 4.14 to 4.16. For the central composite design, no effects were deemed important for the size distribution. Observation under the microscope indicated that a large amount of agglomeration had occurred. The image analysis technique could not distinguish between individual particles within the agglomerate and therefore measured the agglomerated particle as a single entity. The implication was that the measured particle sizes were much larger than the true particle size. Time was not a significant variable for determining the particle size as would be expected from crystal growth or agglomeration theory. Instead, the agglomeration was most likely due to the washing and drying of the filtercake before the sample was mounted on a slide. The samples of some of the runs were mounted directly upon the slides from the solution. The particles observed under the microscope for these cases were of a uniform size and below 1 micrometer in diameter. When these samples were washed and dried as before, the agglomeration occurred. The unwashed particles were too small to be analyzed by the image analysis technique. The effect of sulphate and peroxide levels upon the size and size distribution was more of an effect upon the caking properties than the true particle size. The results of the particle size analysis

Table 4.14

Plausible Models for the Mean Particle Size for Experimental Plan I

Case/ Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	95	β_0	11.100	778.288	25.943
1/2	80,90	β_0 β_4	11.090±1.769 2.094±2.011	673.077	23.210
3/1	all	β_0	11.100	778.288	25.943

Q-test Results

Model A	Model B	Q	F
1/1	1/2	4.53	4.18

R-test Results

Case/Model	R	F
1/2	3.64	5.79

Table 4.15

Plausible Models for Mean Particle Size for Experimental Plan II

Case/ Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0 β_4 β_{24}	10.177± .752 3.266± .987 - 2.203± .987	284.319	15.796
3/1	all	β_0 β_4*	10.177±1.999 5.316±3.748	363.861	19.150

R-test Results

Case/Model	R	F
1/1	2.58	5.87
3/1	3.17	5.86

Table 4.16

Plausible Models for the Size Distribution for Experimental Plan II

Case/Model	Initial Conf. Int. (%)	Significant Parameters	Parameter Values	SSR	$\hat{\sigma}^2$
1/1	all	β_0	.487± .083	.629	.033
		β_4	- .102± .095		
3/1	90	β_0	.427± .071	.408	.019
		β_4*	- .140± .116		
		β_{12}*	.186± .142		
		β_{35}	.204± .122		
3/2	95	β_0	.487	.791	.040

Q-test Results

Model A	Model B	Q	F
3/2	3/1	6.72	3.20

R-test Results

Case/Model	R	F
1/1	6.72	5.85
3/1	4.92	5.90

indicated that another method would have to be employed. Possible methods would include a light scattering technique or electron micrographs.

One variable that was not measured was the filtration rates of the slurries. For the most part, the slurries filtered quite easily; taking no more than two to three minutes. However, for run numbers 10 and 19, the filtration times were approximately 40 minutes. The filtration rate would be related to the particle size. This observation indicated that the true particle sizes for run numbers 10 and 19 were very different than those for the other runs. Examining the particle size and size analyses for the runs showed that the particle size and size distribution for run number 10 were significantly different than those for the other runs. This was possibly due to the actual particle size being much smaller than for the other cases and the particles agglomerated more readily since a smaller force would be needed to hold them together. The agglomerated particle size for run number 19 was also larger than those for the other runs.

4.9 Effectiveness of the Factorial Design

Primarily due to the deviation of run number 19 from the general behaviour of the system as a whole, the central composite design was unsuccessful in describing the system. As illustrated in Figures 4.4 and 4.7, exclusion of this point did indicate that the design method was capable of determining the significant parameters for the filtercake yield and the amount of uranium precipitated over the entire experimental range. Run number 19 was initially included in the design for two reasons:

1) The literature indicated that more than the stoichiometric amount of H_2O_2 would need to be added to the solution because of the potential decomposition of H_2O_2. It was therefore initially assumed that the decrease in the response variables (e.g. filtercake yield, amount of uranium precipitated, and conversion) with decreasing H_2O_2 concentration would follow a curve that could be described by a simple quadratic relationship rather than the sharp curve that resulted.

2) Even in light of the sharp decrease in the conversion, uranium precipitated, and filtercake yield at the lower level of H_2O_2, other variables were being measured. The effect of a low peroxide level upon variables such as size, size distribution, and sulphur content of the cake was considered worth studying.

The two level fractional factorial design with centrepoints used in the study was effective in describing the behaviour of the filtercake yield and the amount of uranium precipitated. It indicated that the filtercake yield was a function of both pH and the initial uranium concentration of the solution. The amount of uranium precipitated was a function of the initial uranium and hydrogen peroxide concentrations and the sulphate level. The effects of peroxide and sulphate levels were only significant, however, when they were represented in terms of their actual amounts rather than based upon the uranium in solution (i.e. in terms of x_2* and x_4* rather than x_2 and x_4). This indicated that the original representation of the independent variables was inadequate for screening out effects since two significant effects were deemed insignificant by the screening procedure. This was due to the fact that the hydrogen peroxide level and excess sulphate were both dependent upon the amount of uranium initially in solution. One was a fractional amount of the uranium in solution and the other was an excess added to the solution after a fixed amount had to be added to form $UO_2(SO_4)_3^{4-}$.

Barrens concentration of uranium and conversion were not adequately described by the linear models due to the behaviour of these properties. In the case of conversion, most of the points were of the same range but the value for run number 10 was significantly lower due to the different behaviour at this point (i.e. the decomposition of H_2O_2 by H_2SO_4 was sufficiently large to significantly reduce the conversion). In the case of the barrens concentration of uranium, the inadequacy pointed out the limitations of attempting to fit a linear equation to data which spans many orders of magnitude. However, the analysis did yield results that were consistent with the literature. The operating variables affected the barrens concentration in ways that could be expected.

The amount of uranium precipitated has most of the same effects as the barrens concentration with the added feature that an adequate model could be formed. The effects of the operating variables which were common to both were also in the opposite direction as would be expected by a mass balance. The one obvious variable which significantly affected the barrens, but did not affect the amount of uranium precipitated was the pH. The effect of pH at the centrepoint was evaluated for the amount of precipitate and was found to be insignificant although it was in the direction expected (i.e. as pH was increased, the barrens decreased and the amount of uranium precipitated increased). A possible explanation of the insignificance of the pH term for the amount of precipitate was that the experimental error, caused by small unavoidable losses of precipitate retained by the Buchner funnel, was large enough to render the effect of pH insignificant.

The experimental design methods would be useful in a uranium mill as long as the right response variables are measured. Rather than measuring the barrens concentration, the overall reaction could be estimated by a linear equation using the amount of uranium that is precipitated. The barrens concentration could then be estimated by doing a mass balance. Some of the operating variables that were changed in this study may not be adjustable in a uranium mill. These would include the uranium and sulphate content of the pregnant liquor since these variables would be dependent upon conditions in the stripping or elutriation circuit. However, the variables such as pH, precipitation reagent, and residence time could be adjusted to measure their effect upon the specific liquor for any given mill. The results indicated that adjustment of the parameters did not greatly affect the product purity so that an acceptable product would be formed despite any changes in the operating conditions.

5. CONCLUSIONS AND RECOMMENDATIONS

From the results, the following conclusions have been drawn:

1) The behaviour of run numbers 10 and 19 was different than the behaviour for the rest of the design region. For run number 10, the decomposition of H_2O_2 by H_2SO_4 caused the results to be different from the rest of the design. For run number 19, the fact that the peroxide level was initially below the stoichiometric amount and the decomposition of H_2O_2 that occurred affected the response giving a lower value than would be expected.

2) Comparison of the results obtained for run numbers 10 and 14 indicated that the decomposition of H_2O_2 would be offset by increasing the pH.

3) The precipitation pH had an effect upon the following variables. An increase in pH would:

- i) increase filtercake yield;
- ii) decrease the barrens concentration;
- iii) decrease the uranium content of the cake;
- iv) increase conversion;
- v) decrease the sulphur content of the cake.

In other words, an increase of pH was favourable to the results.

4) The filtercake yield and the amount of uranium precipitated were proportional to the initial uranium content.

5) Adjustment of the operating variables did not affect the purity of the cake to the degree of rendering the cake unacceptable to the refiner based upon the measured uranium and sulphur contents.

6) Some important effects may go unnoticed due to the nature in which they are represented (e.g. the effect of total sulphate as opposed to that of excess sulphate).

7) If correlated parameters are encountered, more than the 95% confidence interval should be examined when determining the significance of specific parameters since the value of one parameter affects the value of another.

8) Experimental design methods could be useful to the uranium mill operator if a changeover to peroxide precipitation is considered. By analyzing the amount of uranium precipitated rather than the barrens content, the process may be modelled by a simple linear equation.

The absence of time as an important variable indicated that the reaction was rapid. Studies have indicated that at higher sulphate levels, the reaction is slowed down to a level at which kinetic experiments could be carried out (18). If the crystallization kinetics were to be determined, it would have to be done at these higher sulphate levels.

At the higher sulphate levels, the particle sizes may also be large enough to use the image analysis technique.

Continuous precipitation should be considered as an alternative to a batch process in the experimental procedure. If a continuous process was run, the problem of pH control would be eliminated since the flow of the buffer could be adjusted until the proper pH was achieved. The system could then be allowed to reach steady-state and the responses measured at this time.

It may be interesting to perform an experimental design at hydrogen peroxide levels which are all below the required stoichiometric amount to determine system behaviour at these conditions in order to get an idea of the system response over the entire range. The responses of the ammonia precipitation method could also be evaluated by the experimental design methods.

Other factors should be considered in the experimental design. These factors include such things as the effects of mixing, the rate of addition of the precipitating agent, temperature and the levels of impurities such as molybdenum, vanadium and organic chemicals.

6. REFERENCES

1. Ritcey, G.M., Ashbrook, A.W., "Solvent Extraction, Principles and Application to Process Metallurgy, Part 2", pp 452-522, Elsevier Scientific Publishing Co., Amsterdam, (1979)

2. Boydell, D.W., "Production of Yellowcake and Uranium Fluorides", Proc. of an Advisory Group Meeting, Paris, 5-8 June 1979, p. 29, IAEA, Vienna (1980)

3. Litz, J.E., Coleman, R.B., ibid, Page 101

4. Alfredson, P.G., ibid, Page 149

5. Ritcey, G.M., Ashbrook, A.W., "Solvent Extraction, Principles and Application to Process Metallurgy, Part 2", Page 427, Elsevier Scientific Publishing Co., Amsterdam, (1979)

6. ibid, p. 486 (1979)

7. op.cit., p. 454 (1979)

8. Boydell, D.W., "Production of Yellowcake and Uranium Fluorides", p. 40 (1980)

9. ibid, p. 46 (1980)

10. Ritcey, G.M., Ashbrook, A.W., "Solvent Extraction, Principles and Application to Process Metallurgy, Part 2", p. 457 (1979)

11. ibid, p. 464 (1979)

12. Brown, R.A., "The Precipitation of Uranium with Hydrogen Peroxide", FMC Corp., Chemical Research and Development Centre, Princeton, N.J. (1980)

13. Tomazic, B., Samarzija, M. and Branica, M., J. Inorg. Nucl. Chem., <u>31</u>, 1771 (1969)

14. Stuart, W.L. and Whateley, T.L., J. Inorg, Nucl. Chem., <u>31</u>, 1639 (1969)

15. Merino, J.L., "Production of Yellowcake and Uranium Fluorides", Proc. of an Advisory Group Meeting, Paris, 5-8 June 1979, p. 63, IAEA, Vienna, (1980)

16. Rodriguez, B., ibid, p. 83

17. Bryson, A.W., J. S. Afr. Inst. Min and Met., Sept. 1975, p. 13

18. Shabbir, M. and Tame, J.E., U.S. Bureau of Mines Report of Investigation 1974, Rl-7931

19. Bhattacharyya, P.K., Saini, R.D., Ruikar, P.B., Intl. J. Chem. Kin., 14, 1219 (1982)

20. Bhattacharyya, P.K., Saini, R.D., Ruikar, P.B., Intl. J. Chem. Kin., 13, 385 (1981)

21. Caropreso, F.E. and Badger, W.P., Trans. Soc. Min. Eng., AIME, Dec 1973, p. 281 (1973)

22. Kresin, P., "Hydrogen Peroxide Precipitation of Uranium, A Laboratory Study", Madawaska Mines (1981)

23. Mullin, J.W., "Crystallization", 2nd Ed., CRC Press (1972)

24. Randolph, A.D. and Larson, M.A., "Theory of Particulate Processes, Analysis and Techniques of Continuous Crystallization", Academic Press (1971)

25. Misra, C. and White, E.T., Chem. Eng. Prog. Symp. Ser., 67, 110, p. 43, AIChE (1971)

26. Bacon, D.W., "Collection and Interpretation of Industrial Data", p. 174, Queen's University, Kingston, Canada

27. Donaldson, E.M., "Methods for the Analysis of Ores Rocks, and Related Minerals", 2nd Ed., pp. 251-262, EMR Monograph 881, Energy Mines and Resources, Canada (1982)

28. Bacon, D.W., "Collection and Interpretation of Industrial Data", p. 101

29. ibid, p. 96

30. Litz, J.E. and Coleman, R.B., E. and M.J. Dec 1979, p. 78

31. Stinson, W.J., "Possible Changes in Concentrate Specifications for UF_6 Conversion", CUPMC Meeting, Ottawa, May 19 (1977)

32. Randolph, A.D. and Larson, M.A., "Theory of Particulate Processes, Analysis and Techniques of Continuous Crystallization", p. 32, Academic Press (1971)

33. Hornbeck, R.W., "Numerical Methods", p. 294, Quantum Publishers Inc., New York (1975)

APPENDIX I

Experimental Results

Table A1.1

Experimental Results 1

Run Number	Filtercake Yield (g)	Uranium Precipated (g)	Barrens Concentration (g U/l)	Conversion (%)
1	18.86	11.799	.061	96.952
2	26.81	16.445	.160	96.526
3	19.71	12.039	.045	97.976
4	27.67	16.879	.0022	98.217
5	19.93	11.787	<.0001	97.144
6	28.57	16.931	.0002	98.371
7	20.17	11.697	.0002	96.784
8	28.25	16.636	.0001	97.531
9	19.87	11.688	.0065	96.728
10	25.08	15.121	1.57	88.714
11	19.44	11.831	.029	97.208
12	27.11	16.689	.010	97.651
13	19.81	11.605	.0003	96.416
14	28.11	16.031	.0005	95.800
15	19.81	11.951	.0074	97.776
16	28.45	16.882	.0005	98.234
17	16.06	8.899	.026	94.360
18	31.83	19.178	.023	97.885
19	12.62	7.352	6.24	53.710
20	24.63	14.576	.060	98.387
21	20.70	13.546	.640	93.020
22	24.63	14.603	.0032	98.667
23	24.06	14.501	.0049	98.320
24	24.43	14.331	.0004	97.767
25	24.78	14.231	.0033	97.427
26	21.98	13.597	.0008	98.653
27	22.88	14.035	.013	96.727
28	24.41	14.348	.0004	97.827
29	23.87	14.42	.002	98.060
30	23.42	13.895	.0019	99.647
31	24.19	14.490	<.0001	98.300
32	23.00	14.433	.0001	98.107
33	24.19	14.485	.0023	98.273
34	24.81	15.362	.0006	101.207
35	23.74	14.348	.0015	97.820
36	24.42	14.53	.0008	98.433

Table A1.2

Experimental Results 2

Run Number	Uranium Content of Cake (%)	Sulphur Content of Cake (%)	Mean Particle Size (µ)	Particle Size Distribution
1	62.56	.25	5.59	.43
2	61.34	.14	7.03	.74
3	61.08	.13	8.82	.58
4	61.00	.29	5.88	.91
5	59.14	.10	4.86	.52
6	59.26	.10	7.36	.33
7	58.00	.35	6.90	.80
8	58.89	.20	12.05	.65
9	58.82	.63	14.29	.45
10	60.29	.53	28.59	.02
11	60.86	.15	8.22	.35
12	61.56	.18	8.70	.51
13	58.58	.26	14.31	.62
14	57.03	.37	11.42	.66
15	60.33	.15	13.63	.35
16	59.34	.14	11.61	.37
17	55.41	.07	18.37	.35
18	60.25	.29	9.07	.42
19	58.26	.44	20.46	.23
20	59.18	.22	10.82	.34
21	65.44	.10	8.36	.42
22	59.29	.18	19.23	.28
23	60.27	.17	11.21	.39
24	58.66	.12	10.21	.47
25	57.43	.72	9.11	.45
26	61.86	.21	13.24	.29
27	61.34	.16	10.85	.43
28	58.78	.22	---	---
29	60.41	.40	12.01	.27
30	59.33	.22	---	---
31	59.90	.08	6.09	.45
32	62.59	.20	---	---
33	59.88	.24	6.27	.36
34	61.92	.26	---	---
35	60.44	.15	9.20	.43
36	59.50	.23	---	---

Table A1.3

Particle Size Distribution for Run Number 1

Size, D_p (μ)	Difference %	Cumulative %
1.67	9.02	9.02
2.35	9.68	18.70
3.30	21.52	40.22
4.70	16.34	56.56
6.60	18.80	75.36
9.40	12.37	87.73
13.20	8.56	96.29
18.60	1.61	97.90
26.30	2.10	100.00

Table A1.4

Particle Size Distribution for Run Number 2

Size, D_p (μ)	Difference %	Cumulative %
1.67	3.65	3.65
2.35	18.00	21.65
3.30	17.53	39.18
4.70	16.84	56.02
6.60	9.05	65.07
9.40	7.43	72.50
13.20	7.26	79.76
18.60	5.33	85.09
26.30	6.85	91.94
37.10	8.06	100.00

Table A1.5

Particle Size Distribution for
Run Number 3

Size, D_p (μ)	Difference %	Cumulative %
1.67	6.78	6.78
2.35	10.41	17.20
3.30	9.47	26.67
4.70	17.92	44.59
6.60	15.01	59.60
9.40	12.50	72.10
13.20	7.07	79.18
18.60	5.28	84.46
26.30	2.01	86.47
37.10	13.53	100.00

Table A1.6

Particle Size Distribution for Run Number 4

Size, D_p (μ)	Difference %	Cumulative %
1.67	1.25	1.25
2.35	21.66	22.91
3.30	25.40	48.31
4.70	18.71	67.02
6.60	9.66	76.68
9.40	4.46	81.14
13.20	1.55	82.69
18.60	6.52	89.22
26.30	2.71	91.93
37.10	8.07	100.00

Table A1.7

Particle Size Distribution for Run Number 5

Size, D_p (μ)	Difference %	Cumulative %
1.67	5.86	5.86
2.35	20.27	26.13
3.30	25.59	51.72
4.70	18.01	69.73
6.60	11.51	81.24
9.40	5.97	87.21
13.20	3.91	91.12
18.60	5.27	96.39
26.30	3.61	100.00

Table Al.8

Particle Size Distribution for Run Number 6

Size, D_p (μ)	Difference %	Cumulative %
1.67	2.51	2.51
2.35	7.48	9.99
3.30	12.01	22.00
4.70	16.66	38.66
6.60	22.69	61.35
9.40	16.91	78.26
13.20	10.98	89.24
18.60	5.43	94.67
26.30	1.77	96.44
37.10	3.56	100.00

Table A1.9

Particle Size Distribution for Run Number 7

Size, D_p (μ)	Difference %	Cumulative %
1.67	4.61	4.61
2.35	13.33	17.94
3.30	24.60	42.54
4.70	13.73	56.27
6.60	15.48	71.75
9.40	3.05	74.81
13.20	8.25	83.05
18.60	3.81	86.86
26.30	5.45	92.31
37.10	7.69	100.00

Table A1.10

Particle Size Distribution for Run Number 8

Size, D_p (μ)	Difference %	Cumulative %
1.67	-4.34	-4.34
2.35	10.94	6.61
3.30	20.34	26.95
4.70	4.26	31.20
6.60	20.61	51.81
9.40	6.63	58.44
13.20	6.44	64.88
18.60	4.05	68.93
26.30	0.06	68.99
37.10	31.01	100.00

Table A1.11

Particle Size Distribution for Run Number 9

Size, D_p (μ)	Difference %	Cumulative %
1.67	-6.64	-6.64
2.35	5.30	-1.34
3.30	13.29	11.94
4.70	15.33	27.27
6.60	12.13	39.39
9.40	13.70	53.09
13.20	10.88	63.97
18.60	3.40	67.37
26.30	9.90	77.27
37.10	22.73	100.00

Table A1.12

Particle Size Distribution for Run Number 10

Size, D_p (μ)	Difference %	Cumulative %
1.67	5.65	5.65
2.35	0.05	5.70
3.30	2.00	7.70
4.70	-0.80	6.90
6.60	-1.90	5.00
9.40	3.39	8.39
13.20	2.51	10.90
18.60	0.30	11.20
26.30	18.15	29.35
37.10	70.65	100.00

Table A1.13

Particle Size Distribution for Run Number 11

Size, D_p (μ)	Difference %	Cumulative %
1.18	1.21	1.21
1.67	1.30	2.52
2.35	2.06	4.58
3.30	9.48	14.07
4.70	21.04	35.10
6.60	22.71	57.81
9.40	18.42	76.23
13.20	9.83	86.07
18.60	5.77	91.84
26.30	3.87	95.70
37.10	2.40	98.10
52.40	.52	98.62
74.00	1.38	100.00

Table A1.14

Particle Size Distribution for Run Number 12

Size, D_p (μ)	Difference %	Cumulative %
1.67	9.13	9.13
2.35	8.51	17.64
3.30	12.83	30.47
4.70	14.56	45.03
6.60	11.71	56.74
9.40	12.33	69.07
13.20	9.93	79.00
18.60	7.49	86.49
26.30	13.51	100.00

Table A1.15

Particle Size Distribution for Run Number 13

Size, D_p (μ)	Difference %	Cumulative %
1.18	3.83	3.83
1.67	1.50	5.33
2.35	1.18	6.51
3.30	4.55	11.06
4.70	15.49	26.55
6.60	19.92	46.46
9.40	14.85	61.32
13.20	8.32	69.64
18.60	5.42	75.06
26.30	5.45	80.51
37.10	3.96	84.47
52.40	3.66	88.13
74.00	2.18	90.31
104.00	6.28	96.60
147.00	3.40	100.00

Table A1.16

Particle Size Distribution for Run Number 14

Size, D_p (μ)	Difference %	Cumulative %
1.18	2.80	2.80
1.67	[illegible].67	4.47
2.35	3.06	7.53
3.30	12.11	19.64
4.70	17.34	36.98
6.60	16.85	53.84
9.40	12.00	65.84
13.20	3.95	69.79
18.60	5.58	75.38
26.30	7.71	83.09
37.10	5.97	89.06
52.40	4.08	93.14
74.00	2.99	96.13
104.00	3.87	100.00

Table A1.17

Particle Size Distribution for Run Number 15

Size, D_p (μ)	Difference %	Cumulative %
1.18	2.91	2.91
1.67	3.33	6.25
2.35	-2.02	4.23
3.30	1.94	6.17
4.70	8.97	15.14
6.60	16.92	32.06
9.40	19.53	51.59
13.20	16.08	67.67
18.60	12.35	80.01
26.30	7.63	87.65
37.10	5.33	92.97
52.40	2.06	95.03
74.00	3.01	98.04
104.00	1.96	100.00

Table A1.18

Particle Size Distribution for Run Number 16

Size, D_p (μ)	Difference %	Cumulative %
1.18	2.58	2.58
1.67	1.16	3.75
2.35	-0.39	3.36
3.30	5.52	8.88
4.70	10.88	19.76
6.60	20.93	40.69
9.40	19.30	59.99
13.20	15.15	75.14
18.60	9.37	84.52
26.30	5.74	90.26
37.10	3.90	94.16
52.40	3.66	97.81
74.00	2.19	100.00

Table A1.19

Particle Size Distribution for Run Number 17

Size, D_p (μ)	Difference %	Cumulative %
1.18	3.81	3.81
1.67	-2.14	1.67
2.35	2.26	3.93
3.30	6.85	10.78
4.70	9.38	20.16
6.60	13.59	33.75
9.40	9.37	43.12
13.20	9.31	52.43
18.60	9.53	61.96
26.30	12.94	74.90
37.10	16.10	91.00
52.40	6.35	97.35
74.00	2.65	100.00

Table A1.20

Particle Size Distribution for Run Number 18

Size, D_p (μ)	Difference %	Cumulative %
1.18	7.91	7.91
1.67	3.81	11.72
2.35	3.08	14.81
3.30	4.56	19.37
4.70	16.40	35.76
6.60	20.16	55.93
9.40	16.69	72.62
13.20	9.18	81.80
18.60	4.63	86.43
26.30	5.58	92.00
37.10	3.50	95.51
52.40	3.39	98.89
74.00	1.11	100.00

Table A1.21

Particle Size Distribution for Run Number 19

Size, D_p (μ)	Difference %	Cumulative %
1.18	1.43	1.43
1.67	1.61	3.04
2.35	0.65	3.70
3.30	2.97	6.67
4.70	5.60	12.27
6.60	9.15	21.42
9.40	11.22	32.64
13.20	12.42	45.05
18.60	16.62	61.68
26.30	16.00	77.67
37.10	12.81	90.48
52.40	6.67	97.15
74.00	2.85	100.00

Table A1.22

Particle Size Distribution for Run Number 20

Size, D_p (μ)	Difference %	Cumulative %
1.18	3.44	3.44
1.67	1.05	4.49
2.35	2.05	6.54
3.30	4.78	11.32
4.70	13.53	24.85
[illegible].60	19.03	43.88
9.40	17.68	61.56
13.20	16.78	78.04
18.60	10.96	89.00
26.30	3.23	92.23
37.10	3.06	95.29
52.40	2.11	97.40
74.00	1.34	98.74
104.00	1.26	100.00

Table A1.23

Particle Size Distribution for Run Number 21

Size, D_p (μ)	Difference %	Cumulative %
1.18	9.91	9.91
1.67	3.55	13.46
2.35	5.16	18.62
3.30	8.03	26.65
4.70	12.78	39.43
6.60	18.77	58.20
9.40	13.63	71.83
13.20	11.61	83.43
18.60	7.45	90.88
26.30	4.41	95.29
37.10	4.07	99.36
52.00	0.64	100.00

Table A1.24

Particle Size Distribution for Run Number 22

Size, D_p (μ)	Difference %	Cumulative %
1.18	2.70	2.70
1.67	2.30	5.00
2.35	2.87	7.87
3.30	4.64	12.51
4.70	12.46	24.97
6.60	14.44	39.41
9.40	20.21	59.62
13.20	18.60	78.22
18.60	11.80	90.02
26.30	7.18	97.21
37.10	2.38	99.58
52.40	0.42	100.00

Table Al.25

Particle Size Distribution for Run Number 23

Size, D_p (μ)	Difference %	Cumulative %
1.18	5.84	5.84
1.67	0.23	6.08
2.35	2.59	8.66
3.30	4.00	12.66
4.70	14.33	26.99
6.60	17.64	44.63
9.40	18.56	63.19
13.20	15.23	78.43
18.60	9.22	87.64
26.30	6.37	94.02
37.10	3.53	97.55
74.00	2.45	100.00

Table A1.26

Particle Size Distribution for
Run Number 24

Size, D_p (μ)	Difference %	Cumulative %
1.18	2.91	2.91
1.67	1.29	4.19
2.35	1.62	5.81
3.30	8.69	14.50
4.70	16.79	31.29
6.60	19.91	51.21
9.40	16.60	67.81
13.20	10.15	77.96
18.60	6.88	84.84
26.30	5.20	90.04
37.10	7.67	97.71
52.40	2.29	100.00

Table A1.27

Particle Size Distribution for Run Number 25

Size, D_p (μ)	Difference %	Cumulative %
1.18	3.55	3.55
1.67	2.27	5.83
2.35	2.57	8.39
3.30	7.65	16.05
4.70	18.76	34.81
6.60	22.08	56.89
9.40	15.35	72.24
13.20	8.70	80.94
18.60	4.29	85.22
26.30	4.48	89.70
37.10	2.84	92.54
52.40	5.25	97.79
74.00	0.80	98.59
104.00	1.41	100.00

Table A1.28

Particle Size Distribution for Run Number 26

Size, D_p (μ)	Difference %	Cumulative %
1.18	2.64	2.64
1.67	2.34	4.97
2.35	0.02	4.99
3.30	4.73	9.72
4.70	11.04	20.76
6.60	14.11	34.87
9.40	15.42	50.29
13.20	19.12	69.41
18.60	13.67	83.08
26.30	6.15	89.23
37.10	6.71	95.94
52.40	3.01	98.94
74.00	1.06	100.00

Table A1.29

Particle Size Distribution for
Run Number 27

Size, D_p (μ)	Difference %	Cumulative %
1.18	2.64	2.64
1.67	2.95	5.58
2.35	2.72	8.30
3.30	5.34	13.64
4.70	14.57	28.22
6.60	19.31	47.52
9.40	17.06	64.58
13.20	12.93	77.51
18.60	6.19	83.70
26.30	3.55	87.25
37.10	4.30	91.55
52.40	3.02	94.57
74.00	2.77	97.34
104.00	2.66	100.00

Table A1.30

Particle Size Distribution for Run Number 29

Size, D_p (μ)	Difference %	Cumulative %
1.18	-0.15	-0.15
1.67	1.82	1.67
2.35	-0.77	0.90
3.30	4.33	5.22
4.70	12.44	17.67
6.60	15.92	33.58
9.40	20.93	54.52
13.20	19.79	74.30
18.60	12.70	87.00
26.30	6.45	93.45
37.10	3.73	97.18
52.40	2.12	99.30
74.00	0.70	100.00

Table A1.31

Particle Size Distribution for Run Number 31

Size, D_p (μ)	Difference %	Cumulative %
1.18	6.13	6.13
1.67	6.21	12.34
2.35	2.43	14.77
3.30	16.88	31.65
4.70	24.42	56.07
6.60	18.01	74.07
9.40	9.97	84.04
13.20	4.57	88.61
18.60	2.79	91.40
26.30	2.67	94.08
37.10	2.13	96.21
52.40	-0.05	96.16
74.00	3.84	100.00

Table A1.32

Particle Size Distribution for Run Number 33

Size, D_p (μ)	Difference %	Cumulative %
1.18	4.97	4.97
1.67	5.40	10.38
2.35	4.12	14.50
3.30	11.57	26.07
4.70	25.26	51.33
6.60	22.10	73.43
9.40	14.10	87.53
13.20	5.69	93.22
18.60	2.75	95.96
26.30	2.46	98.43
37.10	1.02	99.45
52.40	0.55	100.00

Table A1.33

Particle Size Distribution for
Run Number 35

Size, D_p (μ)	Difference %	Cumulative %
1.18	8.33	8.33
1.67	-1.58	6.75
2.35	4.94	11.70
3.30	8.74	20.44
4.70	15.58	36.02
6.60	19.27	55.29
9.40	13.94	69.23
13.20	11.08	80.31
18.60	7.56	87.87
26.30	6.86	94.74
37.10	4.42	99.15
52.40	0.85	100.00

APPENDIX II

Least Squares Equations and Computer Program

Appendix II

Least Squares Equations and the Computer Program

When using linear least squares, the objective is to fit data to an equation such as

$$Y = \beta_0+\beta_1x_1+\beta_2x_2+\beta_{12}x_1x_2+\beta_{11}x_1^2+\beta_{22}x_2^2+\varepsilon \qquad (A2.1)$$

This is accomplished by minimizing the sum of squares of the residuals, i.e.

$$\sum_{u=1}^{n} e_u^2=\sum_{u=1}^{n} (y_u-(\beta_0+\beta_1x_1+\beta_2x_2+\beta_{12}x_1x_2+\beta_{11}x_1^2+\beta_{22}x_2^2)) \qquad (A2.2)$$

This expression is minimized when the partial derivatives with respect to the parameters are set equal to zero, e.g.

$$\frac{\partial}{\partial\beta_0}(\sum_{u=1}^{n} e_u^2) = 0$$

$$\frac{\partial}{\partial\beta_1}(\sum_{u=1}^{n} e_u^2) = 0$$

$$\vdots$$

$$\frac{\partial}{\partial\beta_{22}}(\sum_{u=1}^{n} e_u^2) = 0$$

In matrix form, the equations may be written as:

$$\underline{X}^T\underline{X}\ \hat{\underline{\beta}} = \underline{X}^T\underline{Y} \qquad (A2.3)$$

To solve for $\hat{\underline{\beta}}$:

$$\hat{\underline{\beta}} = (\underline{X}^T\underline{X})^{-1}(\underline{X}^T\underline{Y}) \qquad (A2.4)$$

$\underline{X}^T\underline{X}$ is a p x p matrix and $\underline{X}^T\underline{Y}$ is a p x 1 vector where p is the number of parameters in the equation.

If there are non-zero values for the off-diagonal terms in the matrix, $\underline{X}^T\underline{X}$, then, correlation among the parameter estimates will occur. This correlation may be reduced if the independent variables are redefined as

$$x_i = \frac{X_i - \overline{X}_i}{\frac{1}{2}\text{ Range of }X} \qquad \text{(A2.5)}$$

where x_i = coded form of X_i
X_i = actual value of X_i

If a series of experimental runs is predetermined at a specific set of points, then all parameter correlation can be eliminated because the experimental runs in coded form will result in all off-diagonal terms of the $\underline{X}^T\underline{X}$ matrix being zero, hence the parameter value, β_i, will depend only upon the value of $\sum_{u=1}^{n} (x_{iu}y_u)$ for any given run.

The procedure for determining where experiments should be performed is as follows:

1) determine the range of the operating variables
2) set up a grid of the $\underline{X}$ matrix in coded form in the following manner.
   a) all values of $x_0 = 1$

b) the values of $x_1 = -1$ for odd numbered runs
$= 1$ for even numbered runs

c) the values of $x_2 = -1$ for $u = 1,2,5,6,...$
$= 1$ for $u = 3,4,7,8,...$

d) the values of $x_i = -1$ for 2^{i-1} runs
$= 1$ for 2^{i-1} runs

The significance of the parameters may be evaluated for screening purposes by determining the 95% confidence intervals of the parameters using a t-distribution.

$$\beta_i = \hat{\beta}_i \pm t_\nu \sqrt{\mathrm{Var}(\beta_i)} \qquad \text{(A2.6)}$$

where Var $(\beta_i) = c_{ii}$ where c_{ii} is the term in the matrix

$$\underline{C} = (\underline{X}^T \underline{X}) \hat{\sigma}^2 \qquad \text{(A2.7)}$$

$\hat{\sigma}^2$ = estimated pure error variance = SSR/(n-p)

ν = the degrees of freedom associated with $\hat{\sigma}^2$

= n-p

If 0 falls within the confidence interval, then the parameter may be dropped. If the parameter estimates are uncorrelated, then dropping of any insignificant terms will not change the values of the significant parameters.

In this study, the experiments were not run at the design points due to the problems with pH control. Because of these problems, a matrix inversion routine had to be employed. The subroutine used a Gauss-Jordan elimination (33). The entire program using the above equations follows:

```
$JOB   SF082161,'HOPKINS',TIME=120,PAGES=50
C *****************************************
C LINEAR REGRESSION PROGRAM
C PROGRAM READS IN  X,Y ,CALCULATES X-TRANSPOSE
C XTX, XTX-INVERSE,XTY AND THE PARAMETER VALUES
C THE RESIDUALS AND SUM OF SQUARES OF THE RESIDUALS
C ARE ALSO CALCULATED
C
C ********************************************
      DIMENSION YC(70),R(70)
       DIMENSION B(70)
      DIMENSION X(70,70)
      DIMENSION XT(70,70)
      DIMENSION Y(70)
      DIMENSION C(70,70)
      DIMENSION D(70)
      READ,N,M
      DETM=0.
      DTNRM=0.
      DO 10 K=1,M
      DO 9 J=1,N
      READ,X(J,K)
    9 CONTINUE
   10 CONTINUE
C ********************************************
C
C         FIND XT
C
C **********************************************
      DO 20 K=1,M
      DO 19 J=1,N
      XT(K,J)=X(J,K)
   19 CONTINUE
   20 CONTINUE
C *********************************************
C FIND THE MATRIX C=XTX
C *********************************************
C
      DO 30 I=1,M
      DO 29 J=1,M
      C(I,J)=0.
      DO 28 K=1,N
      C(I,J)=C(I,J)+XT(I,K)*X(K,J)
   28 CONTINUE
   29 CONTINUE
   30 CONTINUE
C
C ********************************************
C FIND THE INVERSE OF C
C
C THIS IS DONE USING THE SUBROUTINE 'INVDET FOUND IN
C THE BOOK 'NUMERICAL METHODS' BY ROBERT W. HORNBECK
C *********************************************
      CALL INVDET(C,M,DTNRM,DETM)
C ****************************************
C FINDTHE MATRIX D=XTY
C ******************************************
       DO 50 I=1,N
      READ,Y(I)
   50 CONTINUE
      DO 60 I=1,M
      D(I)=0.
      DO 59 J=1,N
      D(I)=D(I)+XT(I,J)*Y(J) /
```

```
   59 CONTINUE
   60 CONTINUE
C ********************************************
C FIND THE VALUES OF THE PARAMETERS,BETA
C I.E. THE PARAMETERS IN THE LINEAR EQUATION
C ********************************************
      DO 70 I=1,M
      B(I)=0.
      DO 69 J=1,M
      B(I)=B(I)+C(I,J)*D(J)
   69 CONTINUE
   70 CONTINUE
C ********************************************
C CALCULATION OF THE RESIDUALS AND RESIDUAL SUM
C OF SQUARES
C ********************************************
      SSR=0.
      DO 80 I=1,N
      YC(I)=0.
      DO 79 J=1,M
      YC(I)=YC(I)+X(I,J)*B(J)
   79 CONTINUE
      R(I)=Y(I)-YC(I)
      SSR=SSR+R(I)*R(I)
   80 CONTINUE
      VAR=SSR/(N-M)
C ******************************************
C CALCULATE AND PRINT THE VALUES OF
C THE VARIANCE-COVARIANCE MATRIX
C ********************************************
      PRINT,'THE VARIANCE-COVARIANCE MATRIX'
      DO 82 I=1,M
      DO 81 J=1,M
      C(I,J)=C(I,J)*VAR
      PRINT,I,J,C(I,J)
   81 CONTINUE
   82 CONTINUE
C ********************************************
C PRINT ALL OTHER VALUES
C ********************************************
      PRINT,'THE PARAMETER VALUES'
      DO 83 I=1,M
      PRINT,I,B(I)
   83 CONTINUE
      PRINT 84
   84 FORMAT (T6,'Y',T15,'YC',T25,'RESIDUAL')
      DO 85 I=1,N
      PRINT,Y(I),YC(I),R(I)
   85 CONTINUE
      PRINT,'THE SUM OF SQUARES OF THE RESIDUALS=',SSR
      PRINT,'THE VARIANCE=',VAR
      STOP
      END

      SUBROUTINE INVDET(C,N,DTNRM,DETM)
      DIMENSION C(70,70),J(120)
      PD=1.
      DO 124 L=1,N
      DD=0.
      DO 123 K=1,N
  123 DD=DD+C(L,K)*C(L,K)
      DD=SQRT(DD)
  124 PD=PD*DD
      DETM=1.
```

```
      DO 125 L=1,N
  125 J(L+20)=L
      DO 144 L=1,N
      CC=0.
      M=L
      DO 135 K=L,N
      IF ((ABS(CC)-ABS(C(L,K))) .GE. 0.) GO TO 135
  126 M=K
      CC=C(L,K)
  135 CONTINUE
  127 IF (L .EQ. M) GO TO 138
  128 K=J(M+20)
      J(M+20)=J(L+20)
      J(L+20)=K
      DO 137 K=1,N
      S=C(K,L)
      C(K,L)=C(K,M)
  137 C(K,M)=S
  138 C(L,L)=1.
      DETM=DETM*CC
      DO 139 M=1,N
  139 C(L,M)=C(L,M)/CC
      DO 142 M=1,N
      IF (L .EQ. M) GO TO 142
  129 CC=C(M,L)
      IF (CC .EQ. 0.) GO TO 142
  130 C(M,L)=0.
      DO 141 K=1,N
  141 C(M,K)=C(M,K)-CC*C(L,K)
  142 CONTINUE
  144 CONTINUE
      DO 143 L=1,N
      IF (J(L+20) .EQ. L) GO TO 143
  131 M=L
  132 M=M+1
      IF (J(M+20) .EQ. L) GO TO 133
  136 IF (N .GT. M) GO TO 132
  133 J(M+20)=J(L+20)
      DO 163 K=1,N
      CC=C(L,K)
      C(L,K)=C(M,K)
  163 C(M,K)=CC
      J(L+20)=L
  143 CONTINUE
      DETM=ABS(DETM)
      DTNRM=DETM/PD
      RETURN
      END
```

APPENDIX III

Determination of Uranium By Fluorimetry

Appendix III

Analysis for Uranium Using Fluorimetry

Uranium, is determined by measuring the fluorescence produced when a sodium fluoride-lithium fluoride bead containing the uranium is illuminated by ultra-violet light. The fluorescence is measured using a Jarrell-Ash Fluorimeter by taking a galvanometer reading and comparing this reading to that of a uranium standard. Minimum error occurs if the uranium in the sample bead is 50-200 ng. It is therefore necessary to have a good estimate of the sample's uranium content beforehand. The standard bead should contain 100 ng of uranium.

The uranium sample (1-5g) is dissolved in 10 ml concentrated in a 250 ml beaker. The solution is heated gently. Ten millilitres each of H_2SO_4 and HNO_3 are added and the solution is heated. Then 5 ml of HF are added and the solution is boiled to dryness, add 5 ml of HNO_3 and 50 ml of water and heat to dissolve the soluble salts. The solution is then diluted to an estimated uranium concentration that will yield 50 to 200 ng in a 0.1 ml aliquot.

Place a 0.1 ml aliquot in each of two platinum dishes. Up to nine different samples may be analyzed at once. Use 4 standards and 2 blanks for comparison purposes.

The platinum dishes are placed in an infra-red oven and slowly dried. A NaFl-LiFl pellet is placed in each dish then the samples are placed in the ring supports of a rotary burner and subjected to the flame for 5 minutes to induce fusion of the uranium into the pellets.

The fluorescence is measured for all the samples, the standards, and the blanks. From the galvanometer readings, the uranium in 0.1 ml aliquot of the sample may be calculated as follows.

$$\text{U in 0.1 ml aliquot (ng)} = \frac{GR_S - GR_B}{GR_U - GR_B} \qquad \text{(A3.1)}$$

GR_S = mean galvanometer reading for the sample
GR_B = mean galvanometer reading obtained for the blank
GR_U = mean galvanometer reading for 100 ng of uranium

The uranium content of the sample in percent may be calculated by

$$\%U = \frac{U(ng) \times 10^{-9}}{\text{sample mass}(g)} \times \frac{V_{1D}}{0.1} \times \frac{V_{2D}}{v} \times 100$$

V_{1D} = volume (ml) of the initial sample solution

V_{2D} = volume (ml) of the solution after the second dilution (if necessary)

v = volume (ml) of the solution taken for the second dilution step.