

THE RECOVERY OF POTASSIUM FROM

SEAWATER AND BRINES

USING

DIPICRYLAMINE

by

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## A B S T R A C T

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This thesis gives a literature survey of the physical and chemical properties of dipicrylamine (2,4,6,2',4',6' - hexanitrodiphenylamine), its synthesis and analysis, and its use in a process for the recovery of potassium from seawater and brines. Where data is not available in the literature it is obtained by experiment. The published and experimental data are used for the design of a process using dipicrylamine for the recovery of potassium and an analysis of its economic viability. Four process steps are identified and examined. These are (i) the precipitation of the potassium salt of dipicrylamine (KDPA) from seawater or brines, (ii) the recovery of dipicrylamine from the spent seawater or brine, (iii) the conversion of KDPA to produce a potassium salt and the insoluble hydrogen form of dipicrylamine (HDPa) by reaction with an acid and (iv) the conversion of HDPa to a soluble form for recycling and reuse. It is concluded that the recovery of potassium from seawater and brines is technically viable. While the brine process is economically viable at present, the large flowrates found in process step (ii) limit the viability of the seawater process.

SUMMARY

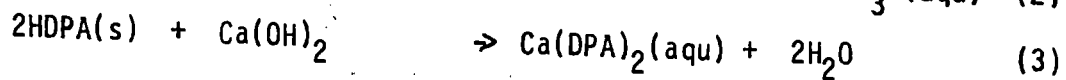
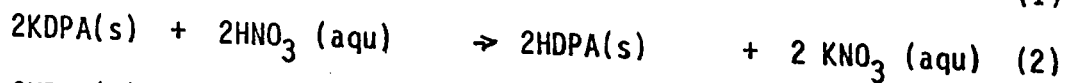
This thesis studies the use of dipicrylamine for the recovery of potassium from seawater and brines. The purpose of this study is to see whether this reagent can be used in an industrial process for the production of potassium from the sea. To this end a literature survey of the properties of dipicrylamine and on its use for the recovery of potassium was conducted. Where gaps existed in the literature, experimental work was conducted to collect data. This data, together with that obtained from the literature survey, was used to design and cost a process for the recovery of potassium from seawater and a bittern (which is the brine which remains after the evaporation of seawater in the production of salt).

South Africa imports all its requirements for potassium and it would be useful to develop a local source of this material. Seawater or bitterns are the only potential local sources.

Several processes have been suggested for the recovery of potassium from seawater and brines. Potassium is produced on a large scale in Israel by the evaporation of brines. In addition, a number of reagents can be used to selectively precipitate potassium from solution. One of these is dipicrylamine. Other methods suggested in the literature include liquid extraction and ionexchange techniques.

In the dipicrylamine process, potassium is recovered from solution by selective precipitation of the potassium salt of dipicrylamine (KDPA). A soluble salt of dipicrylamine (such as  $\text{Ca}(\text{DPA})_2$ ) is added to the seawater or brine whereupon the sparingly soluble KDPA precipitates from solution. This KDPA is then reacted with an acid (for instance  $\text{HNO}_3$ ) to produce the hydrogen form of dipicrylamine (HDPA) and the potassium salt of the acid ( $\text{KNO}_3$ ). The HDPA is then reacted with lime to form the soluble calcium salt  $\text{Ca}(\text{DPA})_2$ . This reagent is then recycled.

(X1)  
The reactions are as follows :



The first step of the process, the precipitation of KDPA, has been quite well studied in the literature. The fractional recovery (or yield) of potassium from seawater and bitterns varies with the amount of dipicrylamine added but yields of 80 and 90%, respectively, are practicably attainable. The settling characteristics and washing of this solid are not discussed in the literature but are examined in the experimental work. KDPA precipitated from seawater settles in the discrete settling regime with an upflow velocity of 0,5mm/s for 99% recovery. KDPA precipitated from a bittern undergoes zone settling with a minimum flux at 0,04 kg/m<sup>3</sup> for an underflow concentration of 440 kg/m<sup>3</sup>. To reduce the sodium contamination of the final potassium product the KDPA must be washed before reaction with acid. KDPA precipitated from seawater should be washed with twice its mass in freshwater and bittern KDPA with six times its mass in seawater and then with twice its mass of freshwater. This reduces the sodium contamination to less than 5% m/m.

KDPA is not completely insoluble. Thus the seawater or bittern from which potassium has been precipitated (the 'spent' seawater or bittern) contains about 600 or 25mg KDPA in solution respectively. This must be recovered for environmental and economic reasons as dipicrylamine is toxic and expensive. The method commonly suggested in the literature is to acidify the solution to precipitate insoluble HDPA. Alternatively, polyurethane foam can be used as a solid sorbent for the recovery of this dipicrylamine. The use of foam is studied in detail in the experimental work. The foam absorbs about half of its own mass of dipicrylamine when in equilibrium with spent seawater or bittern of the abovementioned concentration. The foam is regenerated for reuse by elution of the dipicrylamine with hot water. The experimental work also examines the use of liquid extraction for the recovery of the dipicrylamine. Tributylphosphate (with a suitable diluent) can be used to recover dipicrylamine from the spent seawater and a process scheme is presented for the industrial use of this solvent.

The KDPA is reacted with an acid to give the potassium salt of the acid and HDPA. This step is well studied in the literature. The reaction occurs in the solid phase and is a slow one. For instance, the reaction of KDPA with a five fold stoichiometric excess of  $2N^{\circ}HNO_3$  takes about two hours to reach 95% of the equilibrium conversion value. A number of alternative methods for the production of the potassium salt are given in the literature. KDPA can be converted to HDPA by reaction with acid in a acetone/ aqueous solution. The KDPA dissolves in the solution and is instantaneously converted to HDPA on addition of acid. However, the acetone has to be recovered by distillation and this may be expensive. Similarly, KDPA can be reacted with certain inorganic salts in an acetone/aqueous medium.

A fourth method, where KDPA is reacted with acid in aqueous solution in the presence of an immiscible organic solvent, is briefly suggested in the literature and is studied in detail in the experimental work. The KDPA is converted to HDPA much more rapidly (about four times as fast) when this method is used. This is probably because the KDPA dissolves to some extent in the organic solvent where it then reacts with the acid. The most suitable solvent is tributylphosphate (with a suitable diluent). The advantages and problems that the use of this solvent would incur are discussed and a process scheme is suggested.

The most commonly suggested method of converting HDPA to a soluble form and recycling it is to react the HDPA with lime. This can be done in a seawater medium which reduces the freshwater requirements of the process. In the experimental work the kinetics of this reaction are briefly studied. The HDPA is converted to  $Ca(DPA)_2$  by reaction with a 10% excess of lime in seawater at  $35^{\circ}C$  in about 30 minutes. The maximum attainable concentration of reagent is about 10% m/v  $Ca(DPA)_2$ .

Using data collected from the literature and experimental work designs are given for processes which recover potassium from seawater and from a bittern. The major items of equipment are costed and an order of magnitude estimate for the total fixed capital cost is given. For the seawater process a plant which produces 100 tons/day potassium nitrate is estimated to cost  $R7,0 \times 10^6$  whereas the bittern process is estimated to cost  $R3,6 \times 10^6$ . Using assumed values for variable costs and operating capital, a net present value analysis of the process is given. This analysis shows that the bittern process has a far better chance of being economical than the seawater process. The profitability of the process depends almost entirely on the differential between the price of potassium nitrate and nitric acid. The bittern process appears to be profitable using the current potassium nitrate and nitric acid prices. Estimates of the economic viability of the seawater process cannot be made until certain aspects, such as the equipment for the recovery of dipicrylamine from the spent seawater, are examined in further detail.

## G L O S S A R Y

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- Absorption : Retention of molecules within a solid phase
- Adsorption : Retention of molecules on the surface of a solid phase
- Bittern : Brine remaining after the evaporation of seawater to produce salt
- Spent Bittern : Bittern from which potassium has been extracted by precipitation with dipicrylamine
- Waste Bittern : Spent bittern from which traces of dipicrylamine have been removed and is discharged to waste
- Brine : Concentrated solution of inorganic salts
- Sorption : Retention of molecules on the surface of or within a solid phase

L I S T O F S Y M B O L S

HDPA	-	dipicrylamine ( $C_{12}H_5N_7O_{12}$ )
KDPA	-	potassium salt of dipicrylamine ( $KC_{12}H_4N_7O_{12}$ )
NaDPA	-	sodium salt of dipicrylamine ( $NaC_{12}H_4N_7O_{12}$ )
$Ca(DPA)_2$	-	calcium salt of dipicrylamine ( $CaC_{24}H_8N_{14}O_{24}$ )
$Mg(DPA)_2$	-	magnesium salt of dipicrylamine ( $MgC_{24}H_8N_{14}O_{24}$ )
TBP	-	tributylphosphate
per	-	perchloroethylene
(aqu)	-	aqueous phase
(foam)	-	polyurethane foam phase
(org)	-	organic phase
(s)	-	solid phase
m/m	-	mass/mass
v/v	-	volume/volume
N	-	normal. 1N $HNO_3$ solution contains 1 equivalent $HNO_3$ per litre
R.O.	-	reverse osmosis

Potassium is an essential constituent of fertilisers in South Africa. In fact, South Africa annually imports some 250 000 tons of potassium compounds, principally potassium chloride, at a cost of about R20 million. In view of this dependence on imports, it would be useful if a local supply of potassium could be developed. The only local source which could potentially supply South Africa's needs is the sea. Seawater contains 0,38 kg K/m<sup>3</sup>. In addition bitterns, which are the brines which remain after the evaporation of seawater in the production of sodium chloride, contain between 5 and 20 kg K/m<sup>3</sup>.

Many processes have been suggested for recovering potassium from seawater and brines. One process uses dipicrylamine to selectively precipitate potassium from solution. This process offers a number of important advantages. For instance, it is possible to obtain a variety of potassium products (for example, KNO<sub>3</sub>, K<sub>2</sub>SO<sub>4</sub>, KCl) and the products are obtained in high purity and high yield. Also the process is very flexible - it can recover potassium from dilute sources such as seawater and also from concentrated sources such as bitterns.

There are several problems which prevent the commercial exploitation of this process. Firstly, the spent seawater or bittern (seawater or bittern from which potassium has been extracted) will contain some dipicrylamine which must be recovered for economic and environmental reasons. This is a difficult technical problem in the seawater process because very large flowrates are encountered in this process. Secondly, the reagent dipicrylamine is hazardous and the process must be designed to reduce the risk of handling this compound. Thirdly, some of the reaction steps described in the literature are reported to be very slow. This will require large residence times and therefore large equipment.

The aim of this thesis is to investigate the possible commercial use of this process. To this end a literature survey was undertaken of the properties of dipicrylamine and of the published work on the process using this reagent for the recovery of potassium from seawater and brines. Where gaps existed in the information available in the literature, experimental work was undertaken in an attempt to obtain this information. The published information and experimental results were then used in a preliminary design and economic evaluation of the process.

## 2. THE EXTRACTION OF POTASSIUM FROM SEAWATER AND BRINES

### 2.1 Introduction

This section gives a literature survey of the methods that have been suggested and employed for the recovery of potassium from seawater and bitterns. An excellent review of these methods is given by Hanson and Murthy (1). The suggested processes will be discussed under three headings. Firstly, the methods based on evaporation and crystallisation are given, followed by those which use reagents for the selective precipitation of potassium and, finally, the miscellaneous methods are described.

The composition of seawater (1) is given in Table 2.1. The composition of several bitterns is given in Section 4.2.

TABLE 2.1 : THE CONCENTRATION OF SOME ELEMENTS IN SEAWATER (1)

<u>ELEMENT</u>	<u>CONCENTRATION</u> (parts per million)
Cl	19 000
Na	10 500
Mg	1 350
S	885
Ca	400
K	380
B	65

### 2.2 Evaporation

These methods are well summarised by Hanson and Murthy (1) and Epstein (2) who describes the recovery of potassium from the Dead Sea.

During the evaporation of seawater to produce sodium chloride the potassium remains in solution until a density of about  $30^{\circ}\text{Be}$  (s.g. 1.26) is attained. Further evaporation results in the precipitation of salt mixtures containing chlorides and sulphates of sodium, magnesium and potassium. The most common method of processing is to produce carnallite ( $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ ). This is done, in one method, by mixing the bittern with a magnesium rich brine from a later stage in the evaporation to obtain a high magnesium to potassium ratio which, with further evaporation, results in the crystallisation of carnallite. Alternatively, the mixed salts obtained by continuing the evaporation past  $30^{\circ}\text{Be}$  can be treated by a leaching process to obtain carnallite. Both these methods give yields of the order of 80% based on KCl.

The recovery of potassium from carnallite follows the same methods used in carnallite ore processing and is achieved by treating the solid with a calculated quantity of water to obtain a solution of magnesium chloride and solid potassium chloride. The solid usually has to undergo further treatment to remove any sodium chloride impurity.

This method is used on a large scale for the production of potassium from the Dead Sea (2). The principle advantage of evaporation and crystallisation as a production method is its apparent simplicity. However, there are several disadvantages (1). Firstly, the complex nature of the equilibrium relationships in the crystallisation stage demand a high degree of control during evaporation. Even so, the product may contain hygroscopic compounds which will seriously affect its keeping qualities. Secondly, the brines are difficult to handle both because they are very corrosive and also because they are at saturation and are likely to crystallise in the equipment. Thirdly, the product is potassium chloride which is the least valuable of the salts (147).

### 2.3

#### Selective Precipitation of Potassium

There are several methods which are based on the difference in solubility between certain potassium salts, on the one hand, and sodium, calcium and magnesium salts on the other. Table 2.2 compares the solubility of some of these salts (3 - 7, 45).

The use of perchlorate has been studied by George, Riley and Ross (9) and by Epstein et al (10). In this method calcium perchlorate solution is added to the brine at 0°C. The potassium is recovered from the resulting solid and the perchlorate recycled by an ionexchange procedure. The problem areas are the cost of cooling (both capital and running costs) and the cost of lost reagents. This procedure has the advantage that it can produce a variety of potassium salts. It cannot be used with seawater however, as the potassium concentration is too low.

TABLE 2.2 : COMPARISON OF THE SOLUBILITIES OF SEVERAL COMPOUNDS  
(Solubilities in g/l at 20°C)

<u>ANION</u>	<u>CATION</u>			
	<u>K</u>	<u>Na</u>	<u>Mg</u>	<u>Ca</u>
$\text{ClO}_3^-$	74	1010	1380	vs
$\text{ClO}_4^-$	18	2090	1000	1890
$\text{BF}_4^-$	7	1080	vs	vs
$\text{SiF}_6^{2-}$	1,5	9,5	307	106
$\text{TiF}_6^{2-}$	12,8	65		
$\text{DPA}^-$	1	115	vs	vs
$\text{BPh}_4^-$	0,05	s	s	s

s = soluble

vs = very soluble

The use of  $\text{BF}_4^-$  resembles the use of  $\text{ClO}_4^-$ , however, the reagent is difficult to regenerate (2).

$\text{SiF}_6^{2-}$  and  $\text{TiF}_6^{2-}$  cannot be used because the selectivity for potassium over sodium and magnesium is not high enough (2, 11).

Tetraphenylboron ( $\text{BPh}_4^-$ ), or its derivatives (12), is the most selective of all the reagents. However, it is a very expensive reagent and it could not be used in industry (2).

Dipicrylamine is selective for potassium in that the potassium salt is much less soluble than either the sodium, magnesium or calcium salt. On addition of, for instance, calcium dipicrylamine to a brine, potassium dipicrylamine precipitates from solution. The potassium dipicrylamine can be converted by reaction with an acid to produce the potassium salt of the acid and regenerate the reagent. The dipicrylamine method has several advantages (1). Firstly, it produces potassium in high yield and purity. Secondly, a variety of potassium salts can be made depending on the acid used. Finally, the process can be used with potassium solutions as dilute as seawater.

There are several problems which prevent the commercial exploitation of this process (1, 107). Firstly, the spent seawater or bittern (seawater or bittern from which potassium has been extracted) will contain some dipicrylamine which must be recovered for economic and environmental reasons. This is a difficult technical problem in the seawater process because very large flowrates are encountered in this process. Secondly, the reagent dipicrylamine is hazardous and the process must be designed to reduce the risk of handling this compound. Thirdly, some of the reaction steps described in the literature are reported to be very slow (109). This will require large residence times and therefore large equipment.

## 2.4 Miscellaneous Methods

### 2.4.1 Liquid Extraction

Several authors have studied the selective recovery of potassium from solution by crown ethers in a liquid extraction process. Pedersen (13) discusses the properties of crown ethers and their complexes with metal salts. The selectivity of a crown ether in nitrobenzene solution for potassium is given by Danesi et al (14) while Marcus and Asher (15), in an Israeli patent, present a process for the recovery of potassium from brines using crown ether extraction. This process is further described in a paper by Marcus et al (16).

The advantage of using crown ethers is that they extract the potassium salt as a whole (such as KCl) rather than just the potassium cation. This eliminates the use of acid to supply the anion. Disadvantages are that the crown ethers are very expensive and there will be a loss of this reagent in the process. Also the product is contaminated by sodium and is a dilute solution of potassium chloride (16). The process cannot be used to recover potassium from seawater.

Many other liquid extraction processes have been studied but none have a very high selectivity for potassium over sodium. These include organic nitrosolvents (17), polymerised octyl phenols (18), C<sub>7</sub>-C<sub>9</sub> acids in kerosene (19), isoamyl alcohol and alkylphenols (20).

#### 2.4.2 Ionexchange

Ionexchange has been studied as a possible route to potassium recovery. Certain forms of the inorganic ionexchanger zirconium phosphate have a very high selectivity for potassium over sodium. Alberti, Contantino and Gupta (21) report that the exchanger is completely converted to the potassium form when contacted with dilute (0,1 molar) potassium/sodium solutions with a potassium mol fraction of 0,10 or higher. However, the selectivity of the exchanger is not high when the mol fraction is less than this figure. The properties of zirconium phosphate ionexchangers have been well studied (22 - 25) but so far only one process has been patented which uses them to recover potassium from seawater (26). The selectivity for potassium of conventional organic ionexchange resins can be increased by impregnating them with aminophenols or nitrophenols (27, 28).

#### 2.4.3 Solvent Addition

The addition of certain solvents to concentrated brines results in the precipitation of potassium and magnesium salts. Fernandez Lozano (8) has developed a process where methanol is added to a bittern to precipitate a mixed salt of potassium and magnesium sulphate. However, the methanol must be recovered from the bittern by distillation and the energy cost of this is likely to be high.

#### 2.4.4 Coprecipitation

Potassium sulphate and gypsum form an insoluble double salt ( $K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$ ) under suitable conditions. A process using their precipitation, known as the Salutsky method, is described by Al-Awadi and Al-Mahdi (29). The advantage of this process is that a waste material ( $CaSO_4$ ) is used to recover potassium in a useful form without any additional reagent. Disadvantages are that the product may be contaminated with sodium and magnesium. Also the yields reported by Al-Awadi and Al-Mahdi are very low.

Precipitation of potassium from seawater and brines as a complex potassium magnesium phosphate has been suggested in US patents (30, 31, 32). However, the losses of phosphate make this method of doubtful value (1).

#### 2.4.5 Miscellaneous

Numerous possible methods have been mentioned in the literature. Most of them are in the early stages of development.

For example, the use of nitridotrisulfate has been suggested in a Japanese patent as a precipitant of potassium (33). Liquid membranes have been proposed for the selective transport of potassium (34). In reverse osmosis, some membranes pass 4 - 5 moles of sodium per mol of potassium leading to separation of these cations (35). Froth flotation has been suggested to concentrate potassium salts from brines containing 6% m/m  $K_2O$  (36). KOH can be separated from NaOH produced in the electrolysis of brines in chlorine manufacture (37). Davis (38) reports the solvent extraction of potassium from brines with iso-octylchlorosaligenin.

#### 2.5 Conclusion

A large number of processes have been suggested in the literature for the recovery of potassium from seawater or brines. Only one of them, the recovery of potassium from brines by evaporation and crystallisation, is used commercially.

Of all the methods suggested only two are, at present, selective enough to be used for the direct recovery of potassium from seawater (as opposed to recovery after evaporation of the seawater to concentrate the potassium).

The first uses tetraphenylboron for the extraction of potassium. However, the reagent is too expensive for commercial use (2).

The second method, which uses dipicrylamine for the selective precipitation of potassium from seawater and brines, offers a number of advantages (1). It can be used to produce a variety of potassium salts in high yield and purity. A number of problems will have to be solved before this process can be used commercially. Principle amongst these is the problem of the loss of reagent in the waste seawater leaving the process (1, 107).

The supply of brines and bitterns is limited and seasonal. If potassium is to be recovered on a large scale from the sea it will probably have to be extracted directly from seawater.

Accordingly, it was decided to investigate the dipicrylamine process as it offers a number of advantages and can be used to recover potassium both from seawater and brines.

### 3. REVIEW OF THE DIPICRYLAMINE PROCESS

#### 3.1 Introduction

This chapter reviews the properties and use of dipicrylamine as a reagent for the selective recovery of potassium from seawater and brines. The chapter is divided into three sections.

The first section (Section 3.2) is a review of the published data on the chemical and physical properties of dipicrylamine, its synthesis and analysis.

The second section (Section 3.3) gives an overall review of the process where potassium is recovered by precipitation as KDPA. The objective of this review is twofold; firstly to define the process steps and describe briefly the published work on each of these and, secondly, to identify those areas which need further investigation in the experimental work.

The literature contains a number of suggestions for alternative processes which use dipicrylamine to recover potassium from seawater and brines. These processes differ from that described in Section 3.3 in that they do not involve the precipitation of KDPA. They are discussed in Section 3.4.

#### 3.2 The Properties of Dipicrylamine

##### 3.2.1 General

##### 3.2.1.1 Structure

The structure of dipicrylamine is shown in Fig. 3.1

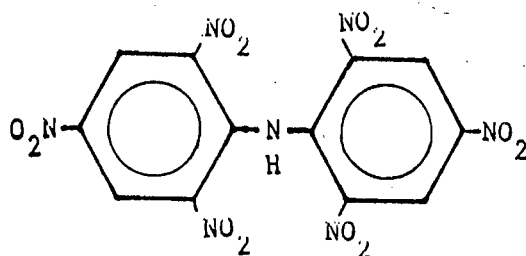


FIG. 3.1 : STRUCTURE OF DIPICRYLAMINE

Dipicrylamine is also called Hexyl(4). Other names for this compound are 2,4,6,2',4',6' - hexanitrodiphenylamine (3) and, in Chemical Abstracts, 2,4,6 trinitrophenyl-2',4',6' trinitrobenzeneamine. In this work the compound is abbreviated as HDPA and the sodium, potassium and calcium salts as NaDPA, KDPA, Ca(DPA)<sub>2</sub> respectively.

The crystal structure of HDPA and NaDPA is orthorhombic whereas KDPA is monoclinic. Further crystallographic data is given in the literature (39 - 42).

### 3.2.1.2 Solubility Data

The solubility of dipicrylamine (HDPA) in various solvents is given by Desvergues (43). This data is given in Table 3.1. Kielland (44) describes the properties of dipicrylamine in solution. The solubility of alkali salts of dipicrylamine in water is given, inter alia, by Treadwell and Hepenstrick (45), Toei (46), Shui Feng Lin (47) and Matsuda, Masuda and Ishizaka (110). Some of this data is shown in Figs. 3.2,3.3,3.4. Maestre et al (48) discuss the solubility of KDPA in aqueous solution in the presence of different electrolytes. The data of Treadwell and Hepenstick, who summarised the data available in the literature, is given in Table 3.2. Note that they give two figures for the solubility of KDPA at 25<sup>0</sup>C. No reference was found in the literature to the solubility of alkali salts of dipicrylamine in organic solvents. The ion pairing of the dipicrylamine anion and alkali metal cations has been studied in the literature (49, 50).

TABLE 3.1 : THE SOLUBILITY OF HDPA IN VARIOUS SOLVENTS (43)  
Temp. = 17<sup>0</sup>C

<u>SOLVENT</u>	<u>SOLUBILITY</u> (g HDPA/g solvent)
Acetone	0,573
Ethanol (96%)	0,073
Ethanol (abs)	0,030
Methanol	0,092
Benzene	NIL
Trichloromethane	NIL
Diethylether	TRACE
Toluene	0,131

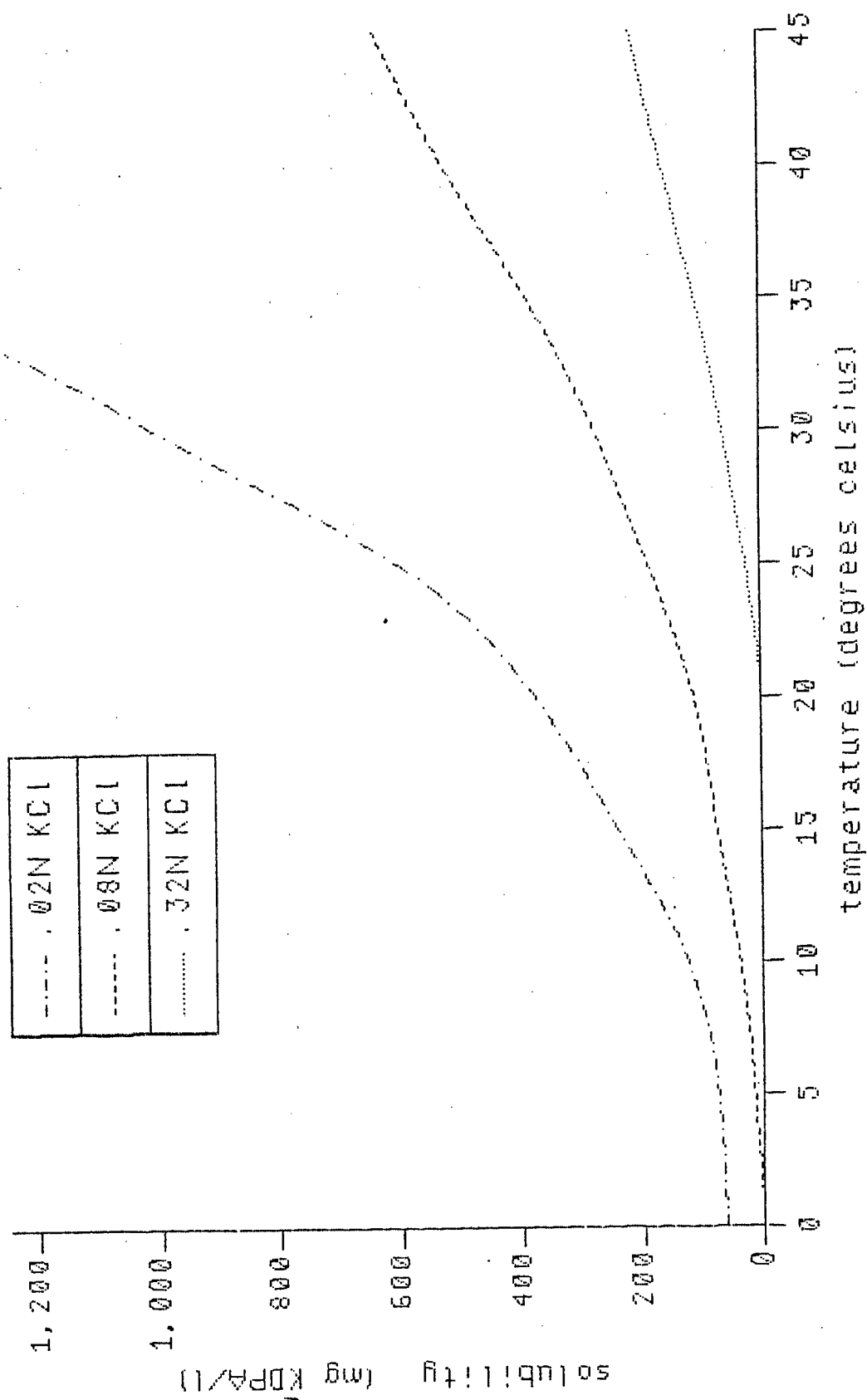


Fig. 3.2 THE SOLUBILITY OF KDPA IN THE PRESENCE OF KCl (410)

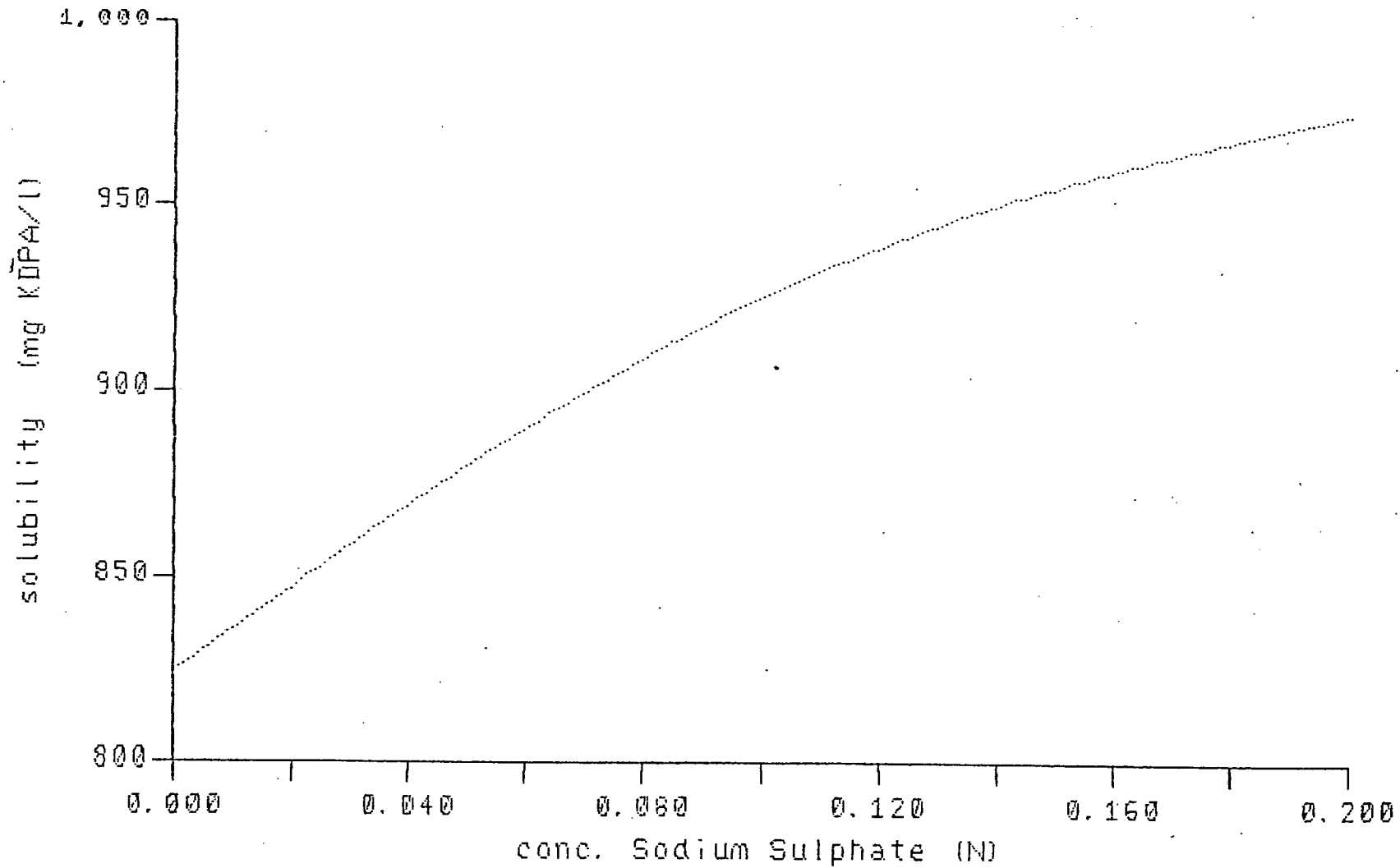


Fig. 3.3 THE SOLUBILITY OF KDPa - THE EFFECT OF A DISSOLVED SALT (48)

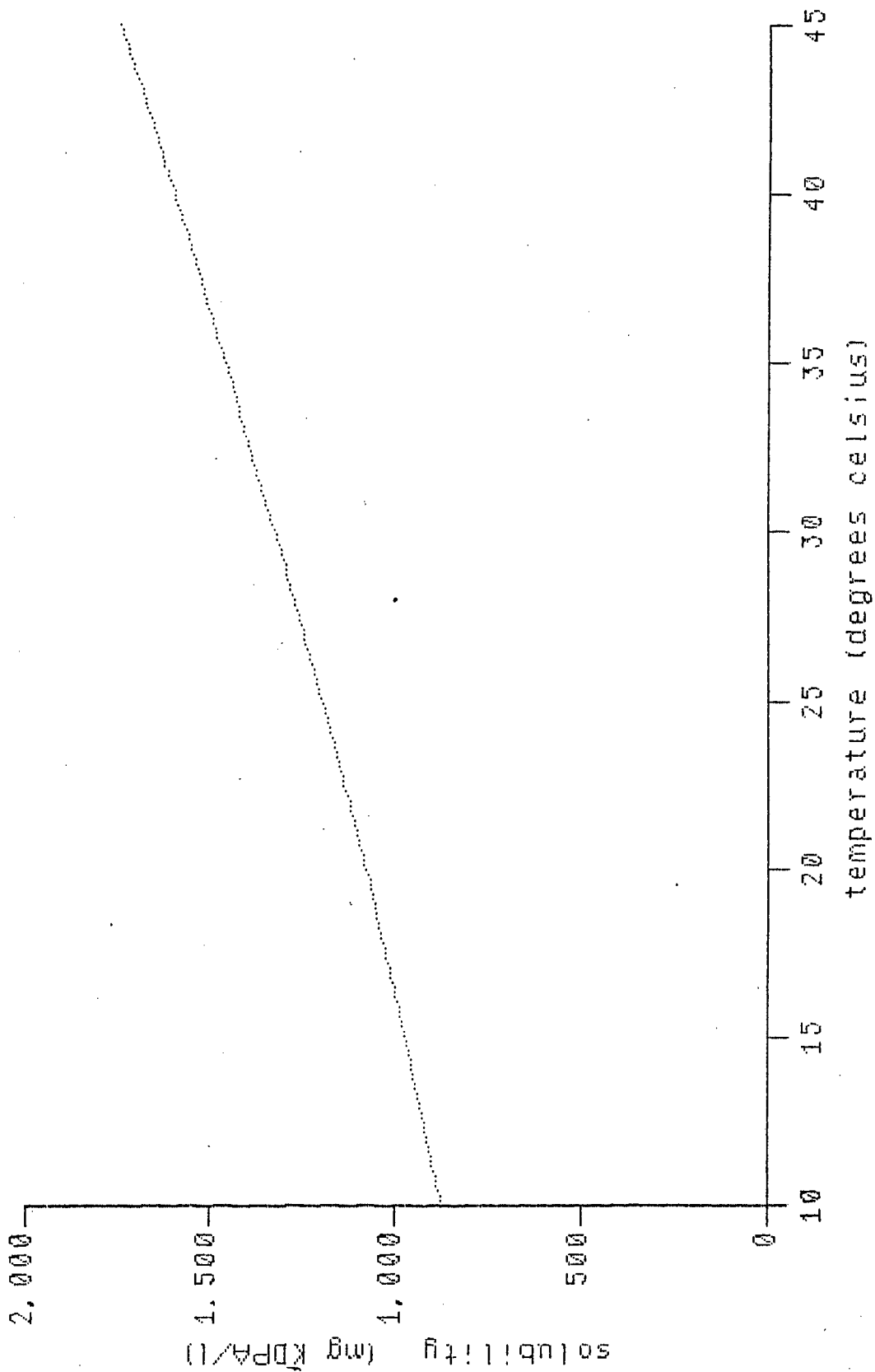


Fig. 3.4 THE SOLUBILITY OF KDP - THE EFFECT OF TEMPERATURE (45)

TABLE 3.2 : THE SOLUBILITY OF SALTS OF DIPICRYLAMINE IN WATER (45)

<u>COMPOUND</u>	<u>SOLUBILITY (mol/l)</u>					
	0°	15°	25°	30°	35°	45°C
HDPA		.8x10 <sup>-5</sup>	1.2x10 <sup>-5</sup>		1.7x10 <sup>-5</sup>	
KDPA	1.5x10 <sup>-4</sup>	2.0x10 <sup>-3</sup>	2.5x10 <sup>-3</sup>	3.06x10 <sup>-3</sup>	3.1x10 <sup>-3</sup>	3.7x10 <sup>-3</sup>
NaDPA			1.9x10 <sup>-3*</sup>			
			2.5x10 <sup>-1</sup>			

\*See text (Sec. 3.2.1.2)

### 3.2.1.3 Thermal Stability of Dipicrylamine

Dipicrylamine (HDPA) decomposes on heating close to its melting point (3). The thermal stability of HDPA and KDPA, relative to other polynitroaromatic compounds, was studied by Zeman (74). He found that the crystal lattice stabilises dipicrylamine, but this influence can be removed by dissolving it in a solvent.

According to Duval (54) KDPA can be heated to 220°C without loss of weight. Similarly, Sato and Ujino (52) report that NaDPA is stable up to 250°C and can be heated at 110°C for three hours without loss of weight.

### 3.2.2 Dipicrylamine as an Analytical Reagent

Koltoff and Bendix (53) and Duval (54) suggest the use of dipicrylamine for the selective analysis of potassium in aqueous solutions. A colorimetric method was proposed by Kühn (55). A very thorough study of the analytical use of dipicrylamine is given by Sato (56 - 60) and Sato and Ujino (52). The analytical techniques use the precipitation of potassium as KDPA. This gravimetric method is selective to potassium with interferences given by Sato (56 - 60).

### 3.2.3 Toxicity of Dipicrylamine

#### 3.2.3.1 Toxicity to Humans

Dipicrylamine is a toxic substance (61) which causes neoplasms in rats but it is not carcinogenic (62). It can cause dermatitis and the literature contains several references to its effects on the human skin (63 - 66).

Kielland (107) discusses the problems encountered with the toxicity of dipicrylamine in a pilot plant. He reports that 20% of workers showed sensitivity to the compound. No clear cases of chronic repetition of eczema after contact-dermatitis were observed. However this may have been a lucky escape, he suggests. He concludes that no serious difficulties should arise in a commercial plant for the recovery of potassium so long as :

- (i) Persons showing sensitivity to dipicrylamine are not employed on the plant.
- (ii) Very consistent and controlled personal and operational prophylactic means are taken to avoid contamination of human skin by dipicrylamine.
- (iii) More attention is given to designing the plant so that the chance of contamination is minimised.

#### 3.2.3.2 Toxicity to Sea Life

The toxicity of dipicrylamine to crabs, shrimps and various species of fish is described in detail by Tammes (67). According to Lipshitz (68) dipicrylamine itself is not toxic but may become toxic by chemical reduction in the cells of the organism. Tammes found that there is a dipicrylamine concentration threshold below which no deaths occurred amongst the organisms he studied. This threshold varies with temperature. For instance, with one species of fish the threshold was 0,12-0,15 mg/l at 3<sup>0</sup>C and 0,50-0,60 mg/l at 20<sup>0</sup>C. Seifert (69) gives the toxic level as 0,15 mg/l.

Kielland (107) also reports that dipicrylamine is very toxic to sea life but he notes that the compound breaks down under aerobic conditions, for example in living algae. So long as the effluent from a plant contains a low concentration of dipicrylamine which is further diluted in a large body of seawater no problems should be encountered.

### 3.2.3.3 Toxicity to Plants

Dipicrylamine is toxic to plants. Some could appear in the final product (for instance  $\text{KNO}_3$ ) which could be used as a fertiliser. The toxicity of dipicrylamine to plants has been studied in the literature (70 - 73). According to Oetmeier and Renger (73), diphenylamines with highly electronegative substituents (as is the case with dipicrylamine) are effective inhibitors of photosynthesis. However, in a test they describe, dipicrylamine was found to have only weak herbicidal activity. Furthermore, Kielland (107) reports that this problem was investigated in detail and no effect is expected with the small amounts of contamination that would be found in the product.

### 3.2.4 Dipicrylamine as an Explosive

Dipicrylamine and its salts are powerful explosives (107). However, it is extremely stable (61). Médard (63) gives, inter alia, drop sensitivity and detonation velocity for dipicrylamine. The properties of this compound are compared to other polynitroaromatic compounds by Zeman (74).

Kielland (107) summarises the explosive properties of dipicrylamine. He reports that, firstly, when the water content is more than 28% a very powerful inductor was needed to start an explosion. Secondly, when the water content was higher than 53% (for KDPA), 36% (for HDPA) or 46% (for  $\text{Ca}(\text{DPA})_2$ ), the material is no longer an explosive. Thus the sensitivity of this compound declines with increasing water content.

He suggests that the plant should be designed with the explosive properties of dipicrylamine in mind and the build-up of solid at any point, and particularly in confined spaces, should be avoided.

### 3.2.5 Analysis of Dipicrylamine

A very detailed study of the analysis of dipicrylamine in aqueous solutions using spectrophotometric methods has been carried out by Shui-Feng Lin (75 - 78).

Savage, Butt and Tallmadge (79) describe the use of UV/Visible spectrophotometry for the determination of the concentration of salts of dipicrylamine in aqueous solution.

A potentiometric method for analysis of dipicrylamine is given by Hassan (80).

### 3.2.6 Synthesis of Dipicrylamine

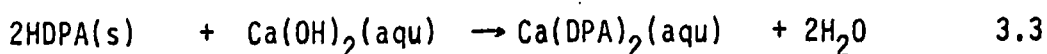
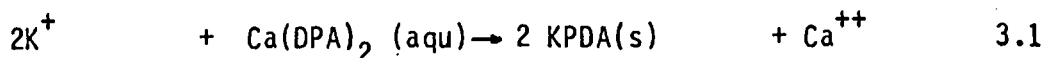
Hoffman and Dame (81) and Kapoor and Sarkar (82) give a method for the synthesis of dipicrylamine. This method is described in detail in Appendix A1. The first step is the nitration of chlorobenzene to 2,4-dinitrochlorobenzene. The second step is the reaction of this compound with aniline to produce 2,4-dinitrodiphenylamine. This product is further nitrated in two steps to 2,4,6,2',4',6'-hexanitrodiphenylamine (dipicrylamine). Except for the first step, the yields for each step are very good.

Kuboszek et al (83) give an improved version of the method described above. This method is also described in Appendix A1.

## 3.3 The Dipicrylamine Process

### 3.3.1 Early Work

The first references in the literature to the use of dipicrylamine for the selective precipitation of potassium from brines and seawater are the patents of Kielland and Fleischer (84 - 88). The reactions they use are :



The dipicrylamine is added in a soluble form such as  $\text{Ca}(\text{DPA})_2$  shown above in Reaction 3.1. The solid KDPA is filtered off and reacted with a strong acid. Kielland (84) suggests that any strong acid such as  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and acetic acid can be used in this reaction. Kielland and Fleischer (85) describe the conditions under which Reaction 3.2 should be carried out. The filtrate obtained after the KDPA is filtered off (called the spent brine or seawater) contains some dissolved dipicrylamine. This is recovered (84, 87) by the addition of an acid to precipitate HDPA according to Reaction 3.4.



Other early patents (89 - 94) describe the basic features of this process.

The operation of two pilot plants in the 1930's and 1950's for the extraction of potassium from seawater is described by Kielland (107).

### 3.3.2 Process Flowsheet

Using the information given in patents described in the previous section (84 - 94) and from flowsheets given by Butt, Tallmadge and Savage (103) and Kielland (107), one can draw up a simple flowsheet for the dipicrylamine process. This is shown in Fig 3.5. This flowsheet shows only the major process streams and is based on the use of Reactions 3.1, to 3.4.

There are four basic process steps (107); the precipitation of KDPA in a reactor/settler (Reaction 3.1), the conversion of KDPA to HDPA by reaction with an acid (Reaction 3.2), the conversion of HDPA to a soluble salt of dipicrylamine by reaction with a base (Reaction 3.3), and the recovery of traces of dipicrylamine from the spent brine or seawater. An additional step may be required to remove traces of dipicrylamine from the product  $\text{KNO}_3$  steam (a KDPA scavenge step).

### 3.3.3 The Precipitation of Potassium Dipicrylamine

A detailed survey of the published data on this process step is given in Section 4.2.

Instead of using  $\text{Ca}(\text{DPA})_2$  as shown in Reaction 3.1 one can use  $\text{NaDPA}$  (110) or  $\text{Mg}(\text{DPA})_2$  (101, 102, 108, 109), in which case the base used in Reaction 3.3 is  $\text{NaOH}$  or  $\text{Mg}(\text{OH})_2$  respectively.

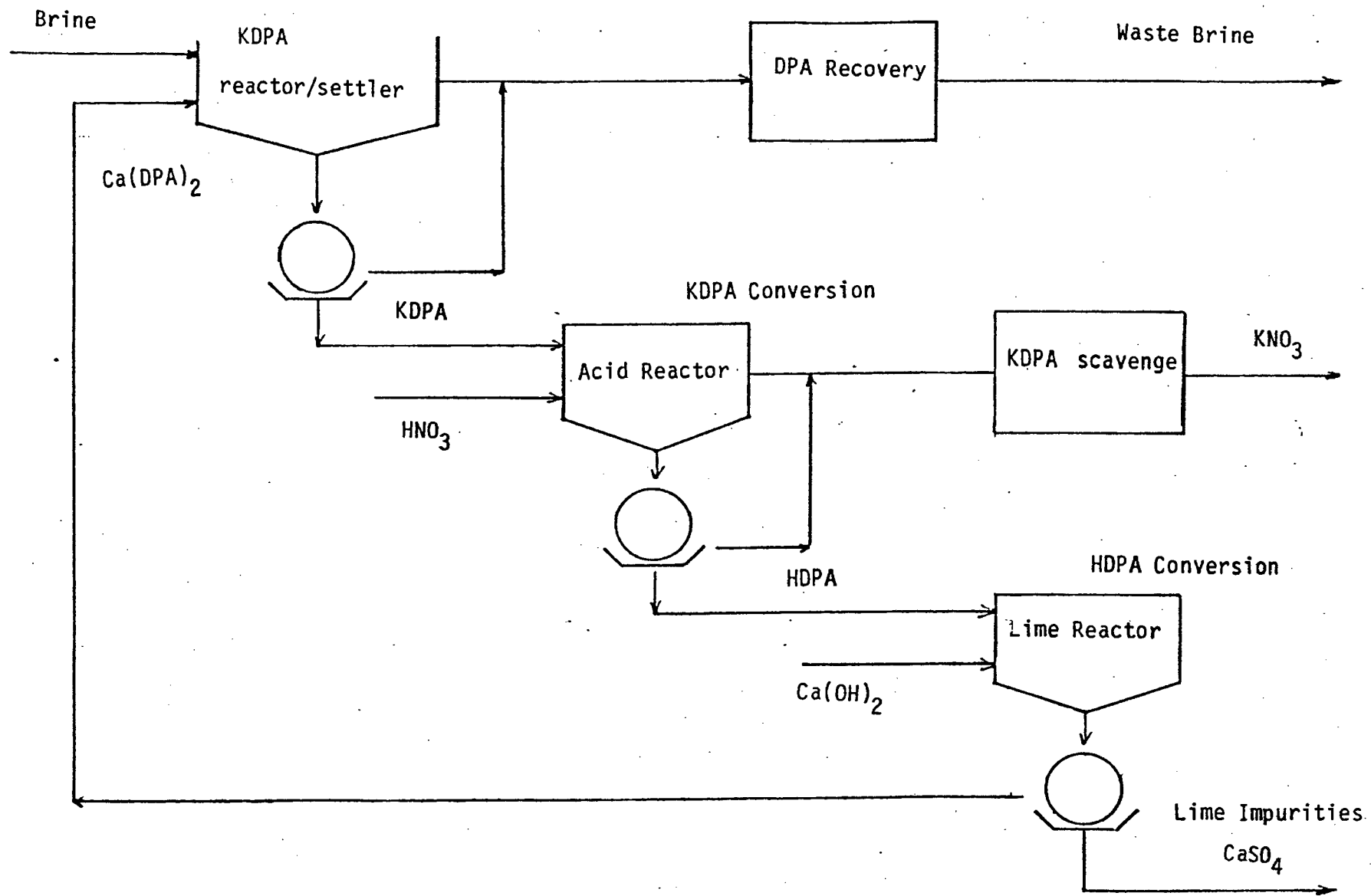


Fig. 3.5 Process Flowsheet

The fractional recovery (or yield) of potassium from seawater by precipitation with dipicrylamine can be calculated from solubility data given in the literature. The yield was measured by Butt, Tallmadge and Savage (103). The yield of potassium from a bittern has been studied in detail by Massazza and Riva (101, 102), Bakr and Zatout (109) and Matsuda, Masuda and Ishizaka (110)

Reaction 3.1 should take place in a reactor designed to promote the formation of large crystals. These crystals can then be separated by settling. The design of such a reactor/settler has been studied by Plum, Sipkes and Van Steeden (95) and the problems encountered in the operation of this reactor are discussed by Kielland (107).

Finally, the kinetics of the formation of crystals of KDPA from aqueous solution by the addition of NaDPA have been studied by Savage, Butt and Tallmadge (105).

#### 3.3.4 The Recovery of Dipicrylamine from Spent Brine and Seawater

The spent seawater or brine leaving the KDPA reactor/settler will contain some dissolved KDPA. Since the reagent is toxic and expensive it must be recovered for environmental and economic reasons (1, 103).

Two methods are suggested in the literature to solve this problem. They are reviewed in detail in Section 5.2. The first uses a cheap acid to reduce the pH of the spent seawater or brine to below 4 where upon insoluble HDPa precipitates from solution. The conditions under which the precipitation should take place have been examined by Kielland and Fleischer (85, 88). The second method, suggested by Matsuda, Masuda and Ishizaka (110), is the use of a solid sorbent, polyurethane foam, for the recovery of the dipicrylamine.

#### 3.3.5 The Conversion of KDPA

The KDPA precipitated in the reactor/settler must be treated to recover the potassium and recycle the reagent. Several methods are suggested in the literature for this conversion. These are reviewed in depth in Section 6.2.

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The most commonly suggested method is to react KDPA with an acid as in Reaction 3.2 (84 - 86, 88 - 90, 94, 97, 101 - 104, 106 - 110). An alternative method, where the KDPA is first dissolved in acetone and then reacted with an acid, was developed by Dijkema and Pluim (91, 93).

Klennert (96) and Henne and Klenert (99) dissolved the KDPA in acetone and then added an inorganic salt (such as  $MgSO_4$ ) to the organic solution to precipitate  $K_2SO_4$  and generate  $Mg(DPA)_2$  in solution. In another patent (98) Henne and Klennert present a similar process where ammonia was used as solvent in place of acetone.

Finally, Ishibashi (100) converted KDPA to HDPA by reaction with HCl in the presence of an immiscible organic solvent.

### 3.3.6 The Conversion of HDPA to a Soluble Form of Dipicrylamine

The published data on this step is reviewed in detail in Section 7.2.

As was mentioned in Section 3.3.3 one can use either NaOH or  $Mg(OH)_2$  in place of  $Ca(OH)_2$  in Reaction 3.3. The reaction of HDPA with  $Mg(OH)_2$  was studied by Bakr and Zatout (109).

Kielland (107) describes the conversion of HDPA to  $Ca(DPA)_2$  by reaction with lime in pilot plants operated in the 1930's and 1950's. He gives a flowsheet for this reaction.

## 3.4 Alternative Process for the Recovery of Potassium Using Dipicrylamine

### 3.4.1 Liquid Extraction

The extraction of potassium from aqueous solution by dipicrylamine dissolved in an organic solvent was first suggested by Iwachido and Toei (114, 115). The solvent used was nitrobenzene. Their work follows development of the technique for liquid extraction of caesium from aqueous solution by dipicrylamine in nitrobenzene by Kyrs and his co-workers (111 - 113).

In this method a 0,05N solution of NaDPA in nitrobenzene is contacted with an aqueous solution containing potassium. The sodium in the organic phase exchanges for the potassium in solution. The potassium in the organic phase (as KDPA) is stripped by contacting the nitrobenzene with an acid, say HCl, to convert the KDPA to HDPa. This results in an aqueous solution of KCl and an organic solution of HDPa. The organic phase is contacted with NaOH to reconvert the dipicrylamine to NaDPA and the solvent is thus recycled.

The mechanism of the extraction of alkali metals by dipicrylamine in nitrobenzene has been studied quite extensively (49, 50, 116 - 119). The extraction of potassium into nitrobenzene in the presence of both crown ethers and dipicrylamine has been studied as well (120, 121). Finally, the extraction in the presence of linear polyethers has also been examined (122).

There are two problems which prevent the industrial use of these methods. Firstly, nitrobenzene is extremely hazardous being both toxic and explosive (61). It is quite volatile and the vapour is very toxic. Secondly, the selectivity for potassium over sodium is not very high so the final product may be contaminated with sodium (114, 115).

### 3.4.2 Ion Exchange

Another alternative process is to use dipicrylamine immobilised in a solid matrix as a selective ion exchange material for potassium.

Isobe and Shimamoto, in a Japanese patent (123) suggest a process where dipicrylamine, as  $\text{Ca}(\text{DPA})_2$ , is absorbed into activated carbon. The carbon is then contacted with seawater. The calcium exchanges for sodium and potassium. The dipicrylamine on the carbon,  $\text{NaDPA}$  and  $\text{KDPA}$ , is converted to  $\text{HDPA}$  by elution with nitric acid to give a solution of  $\text{NaNO}_3$  and  $\text{KNO}_3$ .

A similar process using styrene-divinylbenzene copolymer beads instead of activated carbon, was suggested by Keihel (124). Again the product was a mixture of Na and K salts.

The extraction of potassium by polyurethane foam in the presence of the picric anion and crown ethers was studied by Khan, Baldwin and Chow (126). The extraction of caesium with dipicrylamine immobilised in several solids is described by Iten, Keil and Loewenschuss (125).

Kielland (107) mentions that as an alternative to dipicrylamine an analogous compound was synthesised as an organic base exchanger. This was polystyrene(4)-2,6,2<sup>X</sup>,4<sup>X</sup>,6<sup>X</sup>- pentanitro-diphenylamine. The selectivity for potassium was however found to be too low to be useful.

### 3.5

#### Conclusion

From the overall review of the published work on the dipicrylamine process given in Section 3.3 one can identify areas which need further investigation.

The settling characteristics of  $\text{KDPA}$  are not described in the literature. Also, no details are given of the washing of  $\text{KDPA}$  before it is reacted with acid. This washing is surely necessary to avoid contamination of the final  $\text{KNO}_3$  product with  $\text{NaCl}$ , from the bittern or seawater. Also, there is little information on how the reactants ( $\text{Ca}(\text{DPA})_2$  and bittern or seawater) should be added to the reaction vessel. These aspects were studied in the experimental work described in Chapter 4

The literature does not mention the use of activated carbon, synthetic polymeric resins or ionexchange resins for the recovery of dipicrylamine from spent seawater or brine. The use of polyurethane foam warrants further investigation. The use of liquid extraction for the recovery of the dipicrylamine is not suggested. The experimental work given in Chapter 5 examined these methods.

The method of Ishibashi (100) for the conversion of KDPA to HDPA could offer advantages. This method was further developed in the experimental work discussed in Chapter 6.

Information on the kinetics of reaction of  $\text{Ca(OH)}_2$  with HDPA is necessary for the design of a plant for the industrial application of the dipicrylamine process. This information is not given in the literature. The reaction was studied in the experimental work given in Chapter 7.

The alternative processes discussed in Section 3.4 have the disadvantage of low selectivity for potassium over sodium. They were not further examined in the experimental work.

## 4. THE PRECIPITATION OF POTASSIUM DIPICRYLAMINE

### 4.1 Introduction

This chapter is divided into two sections. In the first section a detailed survey is given of the published work on aspects of the precipitation of potassium dipicrylamine. These aspects include the fractional recovery (or yield) of potassium from seawater and bitterns, the geometry of the KDPA reactor/settler and the kinetics of the formation of crystals of KDPA from solution. In the second section the experimental work is discussed. The reaction of  $\text{Ca(DPA)}_2$  with potassium, in both seawater and a bittern, is studied. The washing of KDPA and the settling characteristics of KDPA crystals are examined.

### 4.2 Literature Survey

#### 4.2.1 The Solubility of KDPA in Aqueous Solution.

The yield of potassium obtained on the addition of a soluble form of dipicrylamine to a bittern or seawater is dependent on the temperature, the amount of dipicrylamine added, the potassium concentration in solution and the level of total dissolved solids in the liquor. In brief, the yield from a particular solution is dependent on the solubility of KDPA in that solution. Potassium dipicrylamine is a slightly soluble compound whose solubility in aqueous solution depends on the temperature, the potassium concentration in solution and the total dissolved solids concentration. The dependence of KDPA solubility on these factors has been studied by, inter alia, Matsuda, Masuda and Ishizaka (110), Maestre et al (48) and Treadwell and Hepenstrick (45). The dependence on KDPA solubility on these factors is shown in Fig. 3.2, Fig. 3.3 and Fig. 3.4.

## 4.2.2 The Yield of Potassium

### 4.2.2.1 The Yield of Potassium from Seawater

The yield of potassium from seawater can be calculated from the solubility data described above. It has been measured by Butt, Tallmadge and Savage (103).

The yield is dependent on two factors; temperature and the amount of dipicrylamine added to the solution. The data of Butt, Tallmadge and Savage is given in Fig. 4.1. This graph shows the percentage recovery of potassium from seawater as a function of the mol ratio of NaDPA to K for three temperatures ( $-1^{\circ}\text{C}$ ,  $9^{\circ}\text{C}$  and  $21^{\circ}\text{C}$ ).

### 4.2.2.2 The Yield of Potassium from a Bittern

The yield of potassium from a bittern has been studied by Massazza and Riva (101, 102), Matsuda, Masuda and Ishizaka (110) and Bakr and Zatout (109).

This yield depends on three factors; the temperature, the amount of dipicrylamine added to the bittern and the composition of the bittern. The potassium content of a bittern increases with increasing density. However, the composition of bitterns of a particular density can vary from one bittern to another depending on how they were produced.

The potassium content of bitterns as a function of density is shown in Table 4.1. This table shows data given by Fernandez Lozano (8) and Massazza and Riva (101).

TABLE 4.1 : THE POTASSIUM CONTENT OF BITTERNS AS A FUNCTION OF DENSITY

<u>Data of Fernandez Lozano (8)</u>		<u>Data of Massazza and Riva (101)</u>	
<u>Density</u>	<u>K Content</u>	<u>Density</u>	<u>K Content</u>
(s.g.)	(g/l)	(s.g.)	(g/l)
1,107	1,8	1,03	0,48
1,208	4,4	1,07	1,25
1,262	14,8	1,16	3,59
1,282	18,1	1,21	7,11
1,310	27,2	1,30	20,45
1,320	29,3	1,32	22,06

The results obtained by Massazza and Riva (101) are shown in Table

TABLE 4.2 : THE YIELD OF POTASSIUM - DATA OF MASSAZZA AND RIVA (101)

Temp. °C	%					
	Bittern 1	Bittern 2	Bittern 3	Bittern 4	Bittern 5	Bittern 6
s.g. =	1.03	1.07	1.16	1.21	1.30	1.32
20	83,4	85,6	90,5	94,8	98,0	99,3
25	79,2	84,0	89,7	94,2	96,6	97,8
30	75,0	81,0	88,6	93,3	94,1	95,9
35	70,9	77,6	86,4	91,3	92,0	92,9
40	60,4	74,4	80,0	85,8	86,2	86,7

From Table 4.2 it is clear that the yield increases with increasing density and thus with increasing K content (see Table 4.1 for composition of bittern as a function of density). Also the higher the temperature the lower the yield. The mol ratio of dipicrylamine to potassium used by Massazza and Riva was 3 to 2.

Matsuda, Masuda and Ishizaka (110) studied the variation of the yield with changing mol ratio of dipicrylamine added to potassium in the bittern. Their results are shown in Table 4.3 and the analysis of their bittern is shown in Table 4.4.

TABLE 4.3 : THE YIELD OF POTASSIUM - DATA OF MATSUDA, MASUDA AND ISHIZAKA (110)

<u>MOL RATIO</u> DPA <sup>-</sup> /K <sup>+</sup>	<u>YIELD OF KDPA</u> %
0,80	76,4
0,85	80,5
0,90	85,2
0,95	89,8
1,0	92,5
1,05	93,7

TABLE 4.4 : COMPOSITION OF BITTERN USED  
BY MATSUDA, MASUDA AND ISHIZAKA (110)

<u>ION</u>	<u>CONCENTRATION</u> (mol/l)
Cl <sup>-</sup>	4,02
SO <sub>4</sub> <sup>=</sup>	0,005
Na <sup>+</sup>	3,71
K <sup>+</sup>	0,14
Mg <sup>++</sup>	0,05
Ca <sup>++</sup>	0,04

Bakr and Zatout (108, 109) also studied the change in the recovery of potassium with changing mol ratio of dipicrylamine to potassium. Their results are shown in Table 4.5 and the composition of their bitterns is given in Table 4.6. Two of their bitterns were synthesised in the laboratory using chemical reagents.

TABLE 4.5 : THE YIELD OF KDPA - DATA OF BAKR AND ZATOUT (109)

Mol Ratio DPA/K <sup>+</sup>	% K recovered			
	Bittern 1	Bittern 2	Bittern 3	Bittern 4
1,0	92,8	94,0	93,9	93,7
0,833	82,9	82,9	82,8	83,1
0,714	71,8	71,3	71,2	71,2
0,625	62,8	62,8	62,4	62,2
0,556	54,1	54,6	54,1	54,5

TABLE 4.6 : COMPOSITION OF BITTERNS USED BY BAKR AND ZATOUT (109)

<u>Kind of Bittern</u>	<u>Concentration of Salt (g/l)</u>			
	KCl	MgCl <sub>2</sub>	MgSO <sub>4</sub>	NaCl
Bittern 1 (natural)	13,35	80,0	49,92	197,14
Bittern 2 (natural)	24,00	168,87	90,80	95,34
Bittern 3 (synthetic)	32,32	160,83	78,92	66,89
Bittern 4 (synthetic)	47,49	203,34	59,67	28,94

The work of Bakr and Zatout shows that the yield of KDPA is almost identical to the ratio of dipicrylamine when the ratio is below 0,80. The yield begins to level off above this figure. This can be explained by the fact that as more dipicrylamine is added KDPA precipitates and the concentration of potassium in solution declines. Accordingly the solubility of KDPA increases and the marginal yield of KDPA decreases.

#### 4.2.3 Reactor Geometry

The literature suggests a geometry for a reactor in which the crystallisation takes place. Plum, Sipkes and van Steeden, in an American patent (95), describe apparatus for crystallising and separating slightly soluble substances, such as KDPA, from liquids. The apparatus is essentially a large circular settler designed in such a way that crystal growth occurs in a sump set concentrically into the base of the settler. The apparatus produces large crystals which settle rapidly, are easy to filter and easy to wash.

Kielland (107) describes a pilot plant which was built in 1953 to recover potassium from seawater. Here a problem was found in that the KDPA grew in a thick layer on the walls of their settler and impeller. This was considered unsafe because of the explosivity of KDPA. The problem was reduced by scraping the walls with chains which travelled around the tank.

#### 4.2.4 The Kinetics of the Formation of Crystals of KDPA

The kinetics of crystallisation of KDPA from solutions containing 100 - 300 mgK/l have been studied in detail by Savage, Butt and Tallmadge (105) who present a mathematical model for the crystallisation. The rate of crystallisation of KDPA in a bittern has not been studied in detail in the literature.

Savage, Butt and Tallmadge precipitated KDPA from solution by the addition of NaDPA. They found that the overall kinetics of crystallisation increased with increasing temperature. Also, the higher the initial potassium concentration or the higher the NaDPA concentration the faster the rate of crystallisation. Finally, the rate of crystallisation increases with increasing speed of agitation and initial seed crystal mass.

They demonstrated that the system could be modelled by the application of the Burton-Cabrera-Frank theory of crystal growth.

Their batch experiments were conducted under a wide range of conditions. In most of the experiments the crystallisation was complete in less than five minutes.

#### 4.2.5 Conclusion of the Literature Survey

The yield or fractional recovery of potassium has been well studied in the literature. This is particularly true in the case of the recovery of potassium from a bittern.

The method of reacting or mixing the dipicrylamine reagent and a bittern has not been described and the settling characteristics of KDPA suspensions have not been studied. The problem of washing the KDPA has not been discussed in the literature.

It was decided to examine these and other aspects in the experimental work.

## 4.3 Experimental

### 4.3.1 Overall Objective

The overall objective of the experimental work was to study aspects of dipicrylamine with potassium with a view to the preliminary design of a KDPA reactor/settler for an industrial process for the recovery of potassium from seawater or bitterns.

### 4.3.2 The Reaction of Dipicrylamine with Potassium in Seawater

#### AIM :

The aim of the work described below was to investigate the reaction of calcium dipicrylamine with potassium in seawater. Of particular interest was the change in the concentration of dipicrylamine in the spent seawater with a change in the mol ratio of the reactants dipicrylamine and potassium.

#### METHOD :

One litre of seawater was filtered to remove coarse solids such as silt and organic solids. The seawater was then placed in a beaker. A known mass (about 0,5g) of KDPA crystals was added as seed crystal. Then a known volume (for instance 40 ml) of 0,25N  $\text{Ca(DPA)}_2$  (110g  $\text{Ca(DPA)}_2$ /l in seawater) was added using a burette. The dipicrylamine solution was added in less than 15 seconds. The contents of the flask were thoroughly stirred for an hour and the experiment was carried out at 20°C. After the hour of stirring the solid was filtered off, washed, dried and weighed. The washing formed a separate experiment and is described in Sec. 4.3.5. The concentrations of potassium and dipicrylamine in the spent seawater were determined by Atomic Absorption and UV/Visible spectroscopy respectively (see Appendix A2).

#### RESULTS :

Immediately on the addition of the calcium dipicrylamine reagent solution the seawater turned to a dark red colour. Small crystals of KDPA were seen in the seawater after about a minute. The crystallisation appeared to be complete in about five minutes. The crystals settled rapidly to the floor of the beaker if the stirring was interrupted.

## DISCUSSION :

The above experiment was repeated several times using different volumes of calcium dipicrylamine solution. Thus the mol ratio of dipicrylamine to potassium was varied by varying the amount of  $\text{Ca(DPA)}_2$  solution added. In this way the change in the concentration of dipicrylamine in the spent seawater with a change in the mol ratio of reagents was investigated. The concentration of dipicrylamine in the spent seawater vs the mol ratio of dipicrylamine to potassium is shown in Fig. 4.2.

If the dipicrylamine process was used industrially there would be two conflicting aims. Firstly, a high yield of potassium would be sought. Secondly, a low dipicrylamine concentration in the spent seawater would be desired since this dipicrylamine must be recovered using one of the methods described in Chapter 5. These two aims are in conflict because a high yield of potassium is obtained by adding a larger amount of dipicrylamine. However, the more dipicrylamine added the higher the concentration of this reagent will be in the spent seawater. A compromise has to be found between these aims.

Inspection of Fig. 4.1 and 4.2 shows that, at a temperature of 20 - 25°C, there is little benefit from adding more than 0,85 moles of dipicrylamine per mol of potassium in the seawater since, firstly, the yield drops off rapidly above this ratio (Fig. 4.1) and the dipicrylamine concentration in the spent bittern begins to rise rapidly (Fig. 4.2).

Thus, for seawater at 20 - 25°C, the reactant ratio ( $\text{DPA}^-/\text{K}^+$ ) should be chosen at 0,85 giving a yield of about 75% recovery of the potassium from solution and about 500mg NaDPA/l in the spent seawater. If the seawater temperature is lower (about 12°C) the reactant ratio can be increased to about 0,90 to give a yield of about 80% and the same concentration of NaDPA in the spent seawater as before.

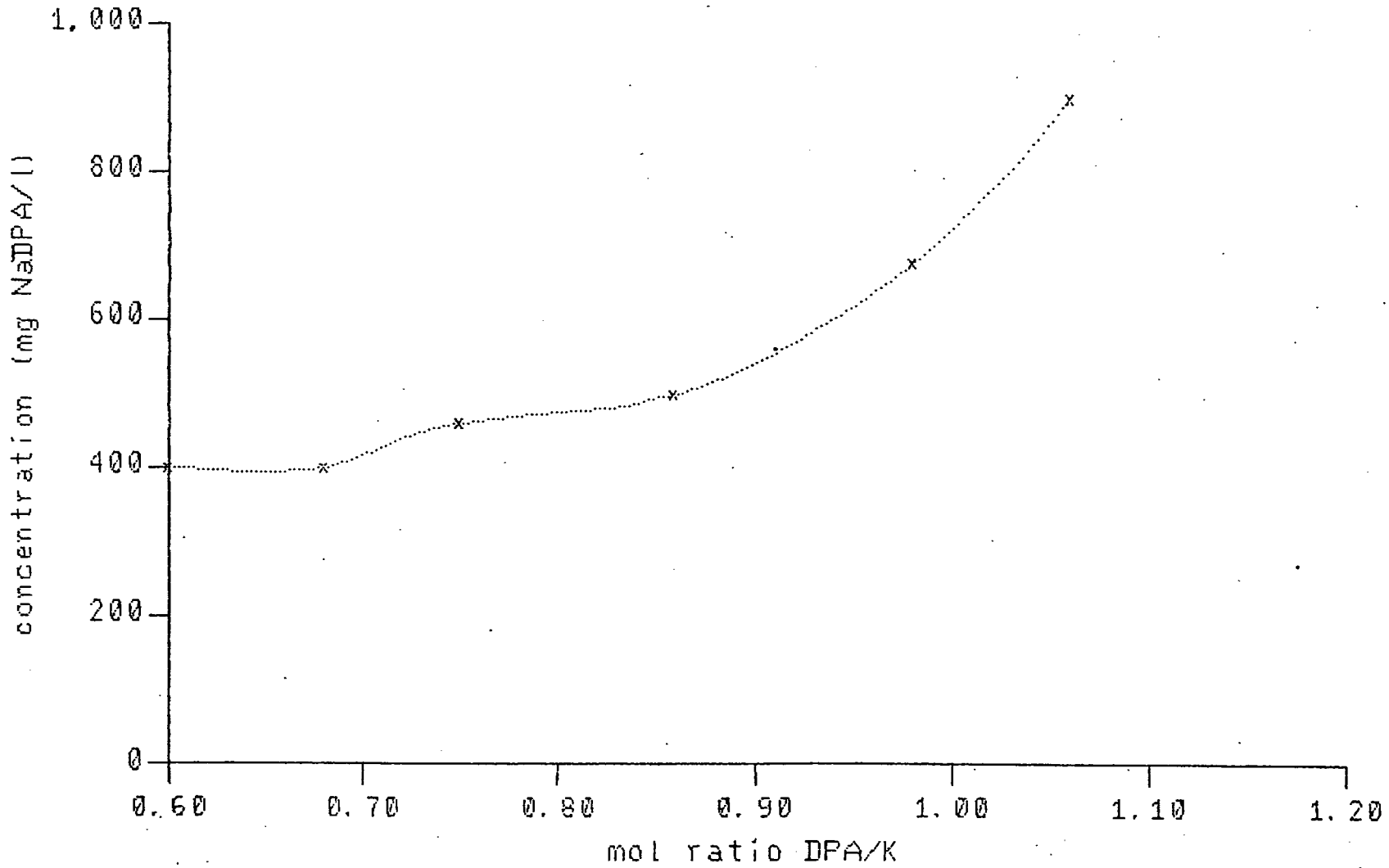


Fig. 4.2 CONCENTRATION OF NaDPA IN SPENT SEAWATER

#### 4.3.3 The Reaction of Dipicrylamine with Potassium in a Bittern - First Method

##### AIM :

There are two ways of reacting dipicrylamine with potassium in a bittern - either the calcium dipicrylamine solution is placed in a beaker and the bittern added slowly to the beaker with stirring (this shall be referred to as the 'first method') or the reagent is added gradually to a beaker containing bittern (the 'second method'). It will be seen that these two methods have very different consequences. The first method was apparently used by Bakr and Zatout (109) except that their reagent was a solution of  $Mg(DPA)_2$ .

The aim of the experimental work described below was to investigate the first method.

##### METHOD :

A volume of 200 ml of 0,25N  $Ca(DPA)_2$  solution (110g  $Ca(DPA)_2$ /l in seawater) was placed in a 1 litre beaker. The contents of the beaker were very vigorously stirred with an electric stirrer. Bittern (with a specific gravity of 1,25 and a potassium content of 10g K/l) was added in small amounts (5 ml) using a burette. The temperature was held at 25°C.

##### RESULTS :

On addition of the first 5ml of bittern the aqueous phase separated into two layers. The lower layer was a dark inky red (indicating a high  $Ca(DPA)_2$  concentration) while the upper layer had a  $Ca(DPA)_2$  concentration of only about 50mg/l. On addition of further bittern (total addition 50ml) the lower layer turned into a slurry of  $Ca(DPA)_2$  solution and a solid, presumably KDPA. Further addition (total 100ml) resulted in the formation of large clumps of solid (the size and shape of rice grains). The liquid contained about 50mg dipicrylamine/l. Bittern was added until a total of 200ml had been added (this being approximately the same stoichiometric amount of potassium as the dipicrylamine originally added). No further change was seen in the appearance of the contents of the beaker.

The contents of the beaker were stirred for more than twelve hours. At the end of this time the K concentration was still 3,5 g/l. This represents a yield of about 30% (30% of the K was converted to KDPA). The solid was washed, dried and analysed and was found to consist of approximately one third KDPA and two thirds NaDPA (the solid was analysed using the method given in Sec. 4.3.5). This confirms the low yield that was obtained.

#### DISCUSSION :

It is not clear why this two phase behaviour is found. This behaviour is also found when reacting  $\text{Ca}(\text{OH})_2$  with HDPA to make a concentrated solution of  $\text{Ca}(\text{DPA})_2$  in seawater (see Sec. 7.3.3). This phase phenomenon was first noted by Kielland (44). The result of this experiment cannot be compared with those of Bakr and Zatout because they used  $\text{Mg}(\text{DPA})_2$ . Also they do not say how concentrated their reagent solution was. The method of adding bittern to the reagent was abandoned in favour of the alternative process, of adding reagent to the bittern, which worked well.

#### 4.3.4 The Reaction of Dipicrylamine with Potassium in a Bittern - Second Method

##### AIM :

The aim of the experimental work was to investigate the second method of reacting dipicrylamine and potassium in a bittern. The second method is where the calcium dipicrylamine reagent solution is added to a beaker containing bittern.

##### METHOD :

One of the experiments will be described. A sample of 250 ml of bittern (containing 10g K/l) was placed in a beaker. About 0,2g of KDPA (from a previous experiment) was added as seed crystal. The contents of the beaker were very vigorously stirred and the temperature was held at 25°C by standing in a water bath at this temperature. Then 150 ml of 0,20N  $\text{Ca}(\text{DPA})_2$  solution in seawater (92g  $\text{Ca}(\text{DPA})_2$ /l) was added dropwise using a burette over 15 minutes. A further 75 ml of  $\text{Ca}(\text{DPA})_2$  solution was added in 6 minutes. Finally, 12,5 ml of solution was added in 1 minute. The contents of the beaker were stirred for a further half an hour and then allowed to settle. The concentration of potassium and dipicrylamine in the supernatant spent bittern was measured by Atomic Absorption and UV/Visible spectrophotometry (see Appendix A2), respectively. The solid was filtered off, washed (the washing is described in Section 4.3.5), dried, weighed and analysed.

## RESULTS :

On the addition of the first few ml of dipicrylamine solution a very fine precipitate of orange solid was immediately formed. The colour of the bittern turned to a pale yellow. Further addition of reagent solution resulted in the formation of more precipitate. The colour of the bittern gradually changed to orange/red. The concentration of dipicrylamine in the spent bittern was about 25 mg NaDPA/l. The solid was found on analysis to contain 95% KDPA, 3,5% NaDPA and 1,5% Mg(DPA)<sub>2</sub>. The method of analysis is described in Sec. 4.3.5.

## DISCUSSION :

The above experiment was repeated several times with varying additions of calcium dipicrylamine reagent. In this way the change in yield with a change in mol ratio of reactants was determined. The results are shown in Table 4.7.

TABLE 4.7 : THE YIELD OF KDPA - EXPERIMENTAL RESULTS

Temp = 25 <sup>0</sup> C	s.g. = 1,25
<u>DPA/K Ratio</u>	<u>Percentage Recovery of K</u>
<u>(mol/mol)</u>	<u>(%)</u>
0,66	63
0,69	70
0,75	73
0,95	93

4.3.5 The Washing of KDPA

## AIM :

The KDPA from the filter after the KDPA Reactor/Settler will have either seawater or bittern adhering to it. This adhering liquid, which contains salts of, inter alia, sodium and magnesium, must be removed to prevent contamination of the final potassium product. The aim of the experimental work was to investigate the washing of both the KDPA precipitate from bittern and from seawater.

**METHOD :**

The washing method for KDPA precipitated from seawater and bittern will be described separately.

100g moist KDPA (80g dry KDPA 20g seawater), obtained by precipitation from seawater, was placed in a Buchner funnel on a vacuum flask and 200ml of tap water was poured over the solid in aliquots of 50ml each. A vacuum was applied and the solid sucked dry for three minutes after the addition of each aliquot. A measured amount of this KDPA (ca.1g) was dissolved in about 10 ml A.R. acetone and acidified with  $\text{HNO}_3$ . Distilled water was added and the resulting HDPA solid filtered off. The filtrate and washings were collected and diluted to 100 ml. This solution was then analysed for K and Na on an Atomic Absorption Spectrophotometer.

100g Moist KDPA (67g KDPA, 33g bittern), obtained by precipitation from a bittern, was placed in a Buchner funnel on a vacuum flask and washed successively with six aliquots of 100ml seawater each. A vacuum was applied between each wash to suck the solid dry for three minutes. The solid was then washed with two aliquots of tapwater of 100 ml each with vacuum being applied after each wash. The KDPA was dissolved in acetone and the K, Mg and Na content analysed in the same way as above.

**RESULTS :**

The KDPA precipitated from seawater was found to be contaminated by less than 5% Na (mass percent) after washing.

The KDPA precipitated from a bittern was found to be contaminated by less than 2% Mg and 5% Na (mass percent) after washing.

**DISCUSSION :**

The KDPA precipitated from seawater is very easy to wash. This is because it consists of large crystals which filter easily. The solid obtained after filtration of the underflow of the reactor/settler contains about 20% w/w moisture (96, 98). In the experiment described above it was found that if this solid was washed with twice its own mass of fresh water the sodium contamination was reduced to less than 5% (m/m) of the potassium content of the solid.

The KDPA precipitated from a bittern is somewhat more difficult to wash than the seawater KDPA because, firstly, the solid consists of fine crystals which pack closely together and, secondly, the adhering bittern has a very high salinity which must all be removed to reduce the contamination. Moreover, the solid contains about 33% w/w moisture. In the experimental work described above it was found that the sodium and magnesium contamination was reduced to less than 5% (m/m) and 2% (m/m) respectively of the potassium content if the solid was first washed with six times its mass of seawater and then twice its mass of fresh water. If the solid is only washed with seawater the sodium contamination is more than 10% m/m of the potassium content.

The fresh water used for washing both the seawater and bittern KDPA took up only about 3 to 4,5g/l dissolved salt respectively. The salinity of the resulting wash liquor is thus between about one tenth and one seventh that of seawater. For instance, the washing of 100 kg of seawater KDPA (which contains 20 kg of seawater) with 200 kg of freshwater results in a wash liquor of concentration about one tenth that of seawater.

It should be cheaper to use Reverse Osmosis (R.O.) to treat this dilute saline solution to recover the water than to throw it away and replace it with purchased freshwater. The freshwater produced by R.O. can be recycled for the washing of solid. An important point is that the salinity of the recycled freshwater can be much higher than would be acceptable for potability. This makes recovery much cheaper than the production of potable freshwater by reverse osmosis of seawater. The estimated cost of recycling the wash liquor is about 8c/m<sup>3</sup> (see Appendix A2).

The wash liquor contains dipicrylamine and this may have to be removed by one of the methods outlined in Chapter 5 before the water is recovered by Reverse Osmosis.

#### 4.3.6 The Settling Characteristics of KDPA

##### AIM :

The settling characteristics of KDPA were investigated in a student project supervised by the author. The aim of the work was to collect data for the preliminary design of a settler.

The work will be briefly outlined. A full description can be found in the student report (127).

##### METHOD :

The settling characteristics of KDPA in seawater and bitterns were investigated separately. A novel technique was developed in the Department to study the settling properties of a dilute suspension of KDPA in seawater (127). This technique measured the change in optical density of a solution with time. The optical density can be correlated with the concentration of the suspension. Thus a plot of the change of suspension concentration at a given depth in the settler vs time can be obtained. This technique was applied to the settling of KDPA in seawater.

The settling characteristics of KDPA precipitated from a bittern were investigated in equipment of the Department of Civil Engineering at the University of Cape Town. The equipment, which was designed to eliminate the influence of wall effects on the settling rate, is described by Broderick (127).

##### RESULTS :

The results of the seawater KDPA settling Tests were analysed by Camp's Method (128). The regime is discrete settling. The results of the analysis are shown in Fig. 4.3.

The results of the bittern KDPA settling tests were analysed using the method of flux plot analysis of Yoshioka (128). The analysis applies to the Zone Settling regime.

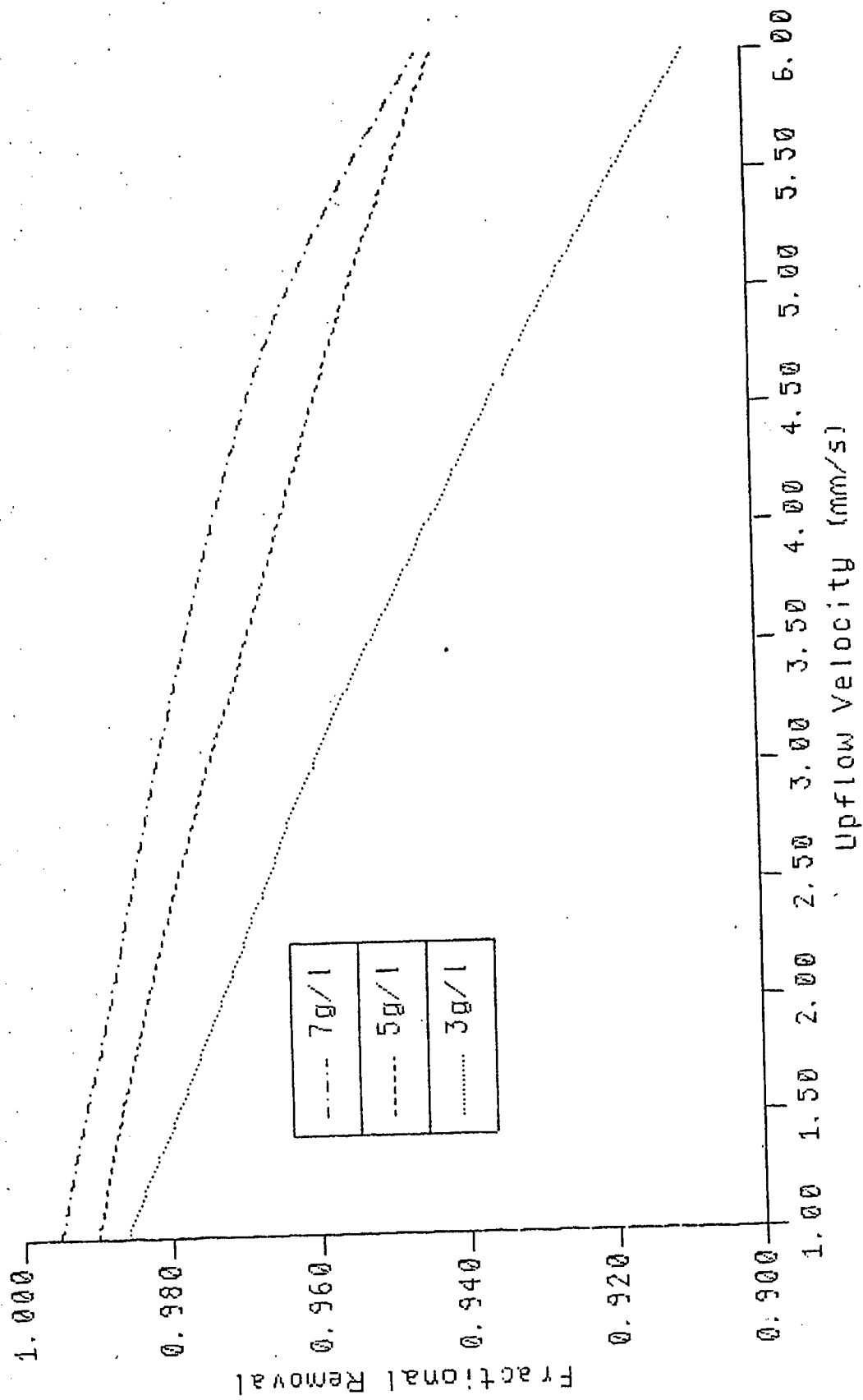


Fig. 4.3 SETTLING CHARACTERISTICS OF KDPa

## DISCUSSION :

In the case of seawater settling, Fig. 4.3 can be used to obtain the upflow velocity required to obtain the required fractional removal of solids for suspensions of varying initial concentration. Thus, for instance, a suspension of  $5\text{kg KDPA/m}^3$  requires an upflow velocity of  $0,5\text{mm/s}$  for 99% recovery of the solids by settling. A flow rate of  $1\text{m}^3$  per second of this suspension would require a circular reactor/settler with a diameter of 50m to achieve a 99% recovery. The underflow would be  $4,95\text{kg KDPA/s}$  while the overflow would contain  $.05\text{ kg KDPA/s}$ .

The bittern suspensions studied had a concentration of about  $70\text{kg KDPA/m}^3$ . The KDPA undergoes zone settling and the method of flux plot analysis of Yoshioka (128) was used to determine the minimum flux. This was  $.04\text{ kg/m}^2$  for an underflow concentration of  $440\text{ kg/m}^3$ . Thus a circular reactor/settler which treats  $0,1\text{m}^3/\text{s}$  of KDPA suspension of concentration  $70\text{kg KDPA/m}^3$  will require an area of  $175\text{m}^2$  or a diameter of 15m.

### 4.3.7 Conclusion of the Experimental Work

The experimental work investigated the precipitation of KDPA from seawater and a bittern, the washing of this KDPA and its settling characteristics.

For the precipitation of KDPA from seawater a compromise will have to be found between two aims; a high yield of potassium and a low concentration of dipicrylamine in the spent seawater. Figs 4.1 and 4.2 show how the reactant mol ratio affects these variables. Thus, for seawater at about  $20^\circ\text{C}$ , the reactant ratio ( $\text{DPA}^-/\text{K}^+$ ) should be chosen at 0,85 giving a yield of about 75% recovery of the potassium from solution and about  $500\text{mg NaDPA/l}$  in the spent seawater. The experimental work investigated two procedures for the reaction of  $\text{Ca(DPA)}_2$  with potassium in a bittern. The first procedure (where the bittern is added to a vessel containing the reagent) results in very low yields of KDPA. The second procedure (where the reagent was added to the bittern) works well and yields comparable to those in the literature are obtained.

The KDPA which is precipitated from seawater should be washed with twice its own mass of fresh water. This reduces the sodium contamination of the final product to less than 5% (mass Na/mass K). The KDPA which is precipitated from a bittern should be washed with six times its own mass in seawater and twice its mass in freshwater. This reduces the sodium and magnesium contamination to less than 5% and 2% (mass Na or Mg/mass K) respectively.

The settling characteristics of KDPA precipitated from seawater and bitterns can be classified as discrete and zone settling respectively. The results of the experimental work can be used to estimate the size of the KDPA reactor/settler.

## 5. THE RECOVERY OF DIPICRYLAMINE FROM SPENT BRINE AND SEAWATER

### 5.1 Introduction

The bittern or seawater leaving the reactor/settler (refer to Fig. 3.5) will contain some dipicrylamine in solution. This dipicrylamine must be recovered for environmental and economic reasons (1, 107). This chapter gives a survey of the methods suggested in the literature for the recovery of dipicrylamine from the spent bittern or seawater (Section 5.2) and discusses the experimental work on this aspect of the dipicrylamine process (Section 5.3).

Two methods are given in the literature for the recovery of the dipicrylamine. The first uses a cheap acid to precipitate the dipicrylamine as HDPA. The second uses a solid sorbent, polyurethane foam, for the recovery. These methods are discussed in Section 5.2.1 and 5.2.2 respectively.

The experimental work is divided into three sections. In the first section (Section 5.3.1) the experimental work on the use of polyurethane foam for the recovery of dipicrylamine is described. Two types of polyurethane foam are available; polyether and polyester foams. It was found in the experiments that polyether foam is more effective for recovering dipicrylamine. In all the subsequent work this type of foam was used. The isotherms for the loading of dipicrylamine from seawater and a bittern were obtained as were the isotherms for the regeneration of the foam. The kinetics of loading were studied and the effect of varying foam hardness or density on the effectiveness of the foam was investigated. Finally, treated and plasticized foams were studied. An overall discussion of the experimental results and the possible industrial use of polyurethane foam is given in Section 5.3.1.9.

The use of various solid sorbents for the recovery of dipicrylamine is investigated in the second section of the experimental work (Sec. 5.3.2). The solid sorbents were activated carbon, synthetic polymer resins and ionexchange resins.

The third section (Section 5.3.3) describes the experimental work on the use of liquid extraction for the recovery of dipicrylamine. The first task of the experimental work was to find solvents in which dipicrylamine is soluble but which are themselves immiscible in water. The selectivity of the solvents and their regeneration were also examined. Only one solvent, tributylphosphate (TBP), showed a high selectivity for dipicrylamine and a low solubility in water. The possible industrial use of this solvent is discussed in Section 5.3.3.7.

## 5.2 Literature Survey

### 5.2.1 The Use of Acid to Precipitate HDPA

This is the standard method suggested in the literature for the recovery of dipicrylamine foam from spent seawater and brine (1).

The hydrogen form of dipicrylamine (HDPA) is only slightly soluble in water (about 4 mg/l) (45). Thus if a solution of a dipicrylamine salt is acidified the dipicrylamine is converted to HDPA and precipitates from solution. The reaction is :



The HDPA is filtered from solution and the liquor, after neutralisation with lime, is discarded. This method has two disadvantages. Firstly it cannot reduce the dipicrylamine level below about 4 mg/l - the solubility of HDPA. This is too high for environmental reasons (the toxicity level to fish is about 0,1 mg/l (67 - 69)) and would necessitate the pumping of large quantities of seawater to dilute the waste before discharge. This might be acceptable in a bittern process (because of the low volume of bittern to be diluted) but may be impractical for the seawater process. According to Kielland (107), the spent seawater should be diluted with 500 times as much uncontaminated seawater even after the removal of most of the dipicrylamine by precipitation with acid.

The second disadvantage is that the very fine floc of HDPA produced during the precipitation is difficult to filter from solution. This problem is described by Kielland and Fleischer (85, 88). The solution they propose to this problem is that the pH of the seawater should be reduced gradually in several stages in series. This results in a larger floc which is easier to filter.

The process for producing an easily filterable HDPA precipitate is given in a German patent 704546 (1941) of Kielland (88) and in an Australian patent 112 196 (1939) of Kielland and Fleischer (85). The process is a stepwise precipitation of HDPA.

They proposed a flowsheet for this process. It is reproduced in Fig 5.1. The example they give is as follows : 1 750m<sup>3</sup> of seawater containing 0,36 kg K per m<sup>3</sup>, is pumped per hour into a tank (see Fig. 5.1), to which is added 50m<sup>3</sup> per hour a solution of calcium dipicrylamine containing 5.6 tons of dipicrylamine. Approximately 75% of the potassium content of the seawater is precipitated. This precipitate is separated on a filter (refer to Fig. 5.1) and is removed for the production of potassium salt. Then 300kg of nitric acid, diluted in about 150m<sup>3</sup> per hour of recycled filtrate or recycled suspension, is added in three stages to the filtrate. In the first stage (I) 100m<sup>3</sup> of dilute acid is added to obtain a pH of approximately 5.5. The residence time at this stage is approximately 10 minutes.

The liquid is conveyed to the second stage (II) to which a further 20m<sup>3</sup> of the dilute acid is added, reducing the pH to between 4.0 and 5.0. Again the residence time is about 10 minutes. The rest of the acid, 30m<sup>3</sup>, is added in the third stage giving a pH of approximately 3.5. After a residence time of 10 minutes the liquid is conveyed to the filtering plant from which 300kg of dipicrylamine is recovered per hour.

They report that this process improved the filterability of the HDPA precipitate considerably. For example, they found that a 30 litre suspension, precipitated in the three stage process described above, passed through a 1 dm<sup>2</sup> filtering surface in half an hour when a vacuum of 500 mmHg was applied. A corresponding amount of the suspension which was treated in one stage took two and a half hours to filter under the same conditions.

An even greater improvement was seen in the use of a pressure filter operating at 8 kg/cm<sup>2</sup> where the time required was 90 and 45 minutes respectively.

### 5.2.2 Recovery by Sorption with Polyurethane Foam

Dressler (129) reviews the use of solid sorbents for the recovery of organic species from solution. One of the sorbents he discusses is polyurethane foam. Excellent reviews of the use of polyurethane foam are given by Bowen (130) and Moody and Thomas (131). Flexible, open cell polyurethane foam has been used by a number of workers as a sorbent for organic species mainly in analytical chemistry (132, 133). Matsuda, Masuda and Ishizaka (110) suggest polyurethane foam as a sorbent for dipicrylamine.

They found that the foam took up as much as 0,5g dipicrylamine/g foam when in equilibrium with a solution containing 500 mg NaDPA/l. When equilibrated with a solution containing 5 mg NaDPA/l the foam took up about 0,05g dipicrylamine/g foam. The loading varied greatly with temperature. The higher the temperature, the lower the degree of loading when in equilibrium with a dipicrylamine solution of the same concentration. In addition they found that the amount of dipicrylamine taken up increased with an increase in the salinity of the brine from which it was removed.

They regenerated the foam, and recovered the dipicrylamine, by eluting it with hot water. They note that by this simple method of regeneration the foam can be easily loaded, stripped and re-used.

### 5.2.3 Conclusion of the Literature Survey

The recovery of dipicrylamine from the spent bittern of seawater from the KDPA precipitation step is necessary for economic and environmental reasons. It is a difficult technical problem particularly for the seawater process where very large volumes of spent seawater must be treated to reduce the dipicrylamine content to a sufficiently low level.

The simplest answer might appear to be the acidification of the spent liquor to precipitate HDP. In practice, the problems associated with the filterability of the resulting HDP flocc may be overwhelming. Even with the improvement of Kielland and Fleischer, the capital cost of the filtering plant will be high. For instance, using their figures for the filtration rate, and assuming that the filter cloth they used was one that would be used in industry, the area required for a vacuum filter would be  $500\text{m}^2$  for a plant which produces 100 tons/day potassium nitrate per day. The cost of this equipment would be approximately R1 million for 5 drum filters of area  $100\text{m}^2$  each (139). Also this method cannot reduce the dipicrylamine level below about 4 mg/l which may be unacceptable for environmental reasons as the toxic level of dipicrylamine to fish is about 0,1 mg/l (67). It would be useful to find an alternative solution to the problem of recovering the dipicrylamine.

The absorption of dipicrylamine into polyurethane foam, as suggested by Matsuda, Matsuda, Masuda and Ishizaka (110), is an elegant solution to this problem. This method needs to be looked at in more detail.

The use of liquid extraction for the recovery of dipicrylamine from the spent brine or seawater has not been studied in the literature. This method could offer advantages and needs to be investigated.

### 5.3 Experimental

#### 5.3.1 The Use of Polyurethane Foam

##### 5.3.1.1 Overall objective

The overall objective of the experimental work described in this section was to investigate the use of polyurethane foam for the recovery of dipicrylamine from spent seawater and brines.

##### 5.3.1.2 Types of Polyurethane foam

###### AIM :

Polyurethane foam is manufactured in two basic types - polyester and polyether polyurethane. The aim was to see whether there was any difference in their properties for the sorption of dipicrylamine.

###### METHOD :

The equilibrium uptake of a foam was determined by the following method. A sample of the foam to be tested (approx 1 g) was dried in an oven at 60°C for several hours. A small piece of the foam was cut from the sample and accurately weighed. This piece of foam was placed in a 250 ml conical flask. Then 100 ml of seawater containing 118 mg NaDPA/l was added to the bottle. The foam was squeezed repeatedly with a spatula to remove any air bubbles trapped within the foam. The flask was stoppered and placed on a shaker and shaken for at least 48 hours at room temperature. The concentration of dipicrylamine in solution was then determined by UV/Visible spectroscopy (Appendix A2). The mass of dipicrylamine loaded onto the foam was calculated by difference. The dipicrylamine was then stripped from the foam using acetone and it was found (by analysis for Na and K by Atomic Absorption spectroscopy) that the dipicrylamine was taken up as NaDPA (rather than KDPA). Accordingly the loading was calculated as g NaDPA/g foam.

###### RESULTS :

The results are summarised in Table 5.1

TABLE 5.1 : A COMPARISON OF POLYESTER  
(EX22, EX34) AND POLYETHER (V7) FOAMS

Initial solution concentration = 118 mg NaDPA/l

Sample	Sample Mass (g)	Final Conc. (mg NaDPA/l)	Equilibrium Loading (g NaDPA/g foam)
EX 22	0,0258	38,6	0,308
EX 34	0,0267	38,8	0,297
V7	0,0160	40,1	0,487

DISCUSSION :

The polyether sample was considerably more effective in taking up dipicrylamine. This is probably due to the different chemical nature of the foam matrix.

5.3.1.3 Determination of Loading Isotherms

AIM :

The aim of the experimental work given below was to determine the equilibrium isotherms for the loading of dipicrylamine onto flexible polyether polyurethane foam from either spent seawater or bittern.

METHOD :

The equilibrium loading of the foam was measured for a variety of final solution concentrations. The method used for determining the equilibrium loading was the same as that given in Section 5.3.1.2. The isotherms were determined at room temperature (25°C).

The spent seawater used had an initial dipicrylamine concentration of either 250 mg NaDPA/l or 500 mg NaDPA/l. The concentration of K in the spent seawater was less than 50 mg/l.

The spent bittern had an initial concentration of 112 mg NaDPA/l and was a 50/50 v/v mixture of bittern and seawater. The spent bittern contained about 1g K/l. This was assumed to correspond with the composition of the spent bittern that would be produced in an industrial process.

## RESULTS :

The results are tabulated in Appendix A3. The isotherms for seawater and bittern are shown in Figs 5.2 and 5.3 respectively.

## DISCUSSION :

Polyurethane foam loads up to about 0,5g NaDPA/g foam when in equilibrium with spent seawater containing more than 100 mg NaDPA/l or spent bittern containing more than about 10 mg NaDPA/l. In addition the foam loads to a significant degree (about 0,05g NaDPA/g foam) when in equilibrium with solution containing low levels of dipicrylamine. It should be possible to use this foam for the reduction of the concentration of dipicrylamine in the waste seawater or bittern to below the toxic level to fish (0,1 mg NaDPA/l (67 - 69)).

The mechanism of sorption of dipicrylamine appears to be absorption into the solid phase rather than adsorption onto the surface of the solid phase. There are two reasons for this. Firstly, the surface area of polyurethane foams is very low, about 10 - 30m<sup>2</sup>/kg (134). This surface area is too small to account for the high capacity of the foam. Secondly, by examination under a microscope, it was evident that the whole of the solid phase is discoloured by the dipicrylamine, indicating absorption throughout the solid phase.

### 5.3.1.4 Regeneration of Polyurethane Foam

#### AIM :

Polyurethane foam which is loaded with dipicrylamine can be regenerated and the dipicrylamine recovered by elution with hot freshwater (110). The aim of the experimental work described below was to obtain the absorption/desorption isotherms for polyether polyurethane foams at various temperatures.

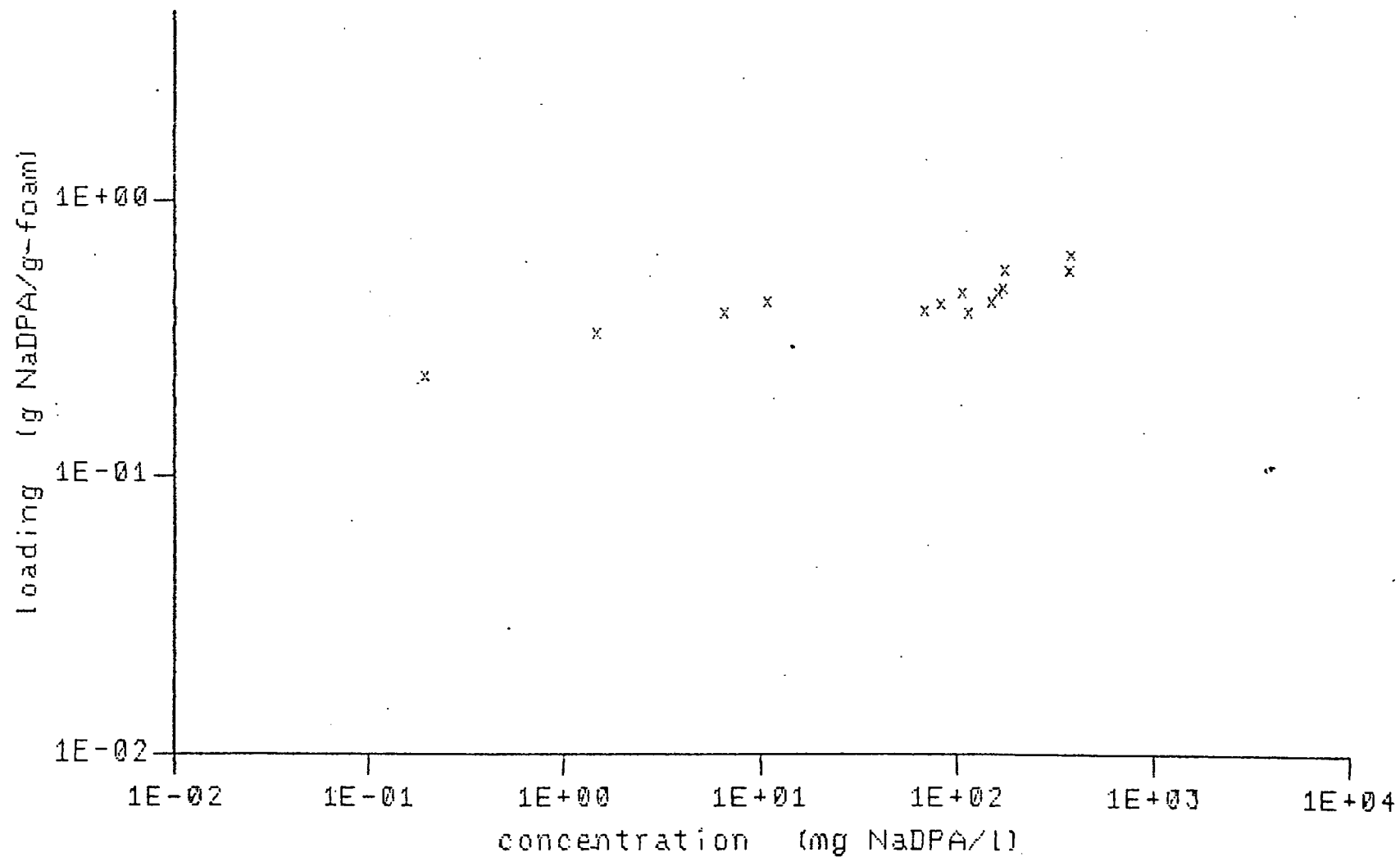


Fig. 5.2 ABSORPTION ISOTHERM FOR POLYURETHANE FOAM (SEAWATER)

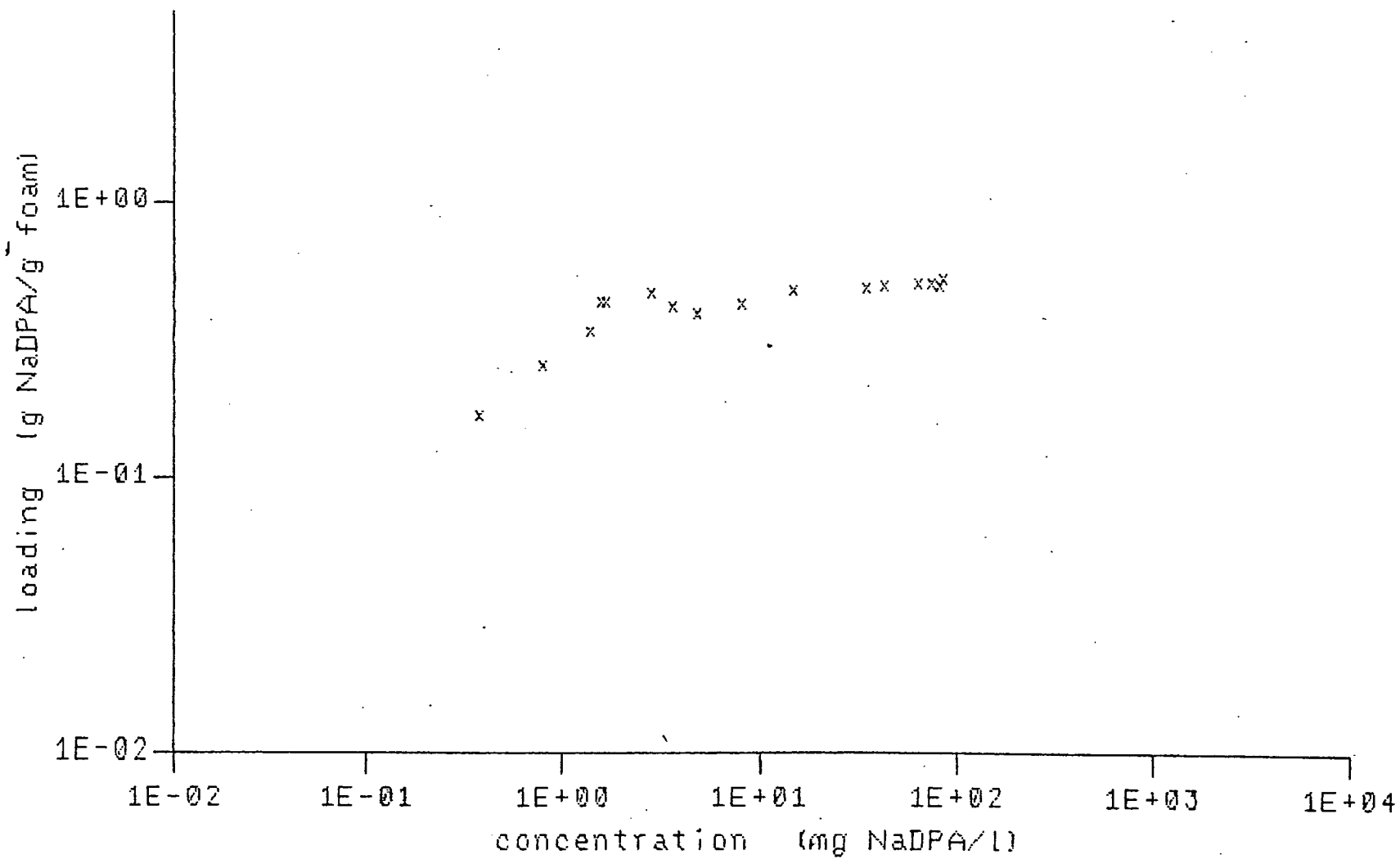


Fig. 5.3 ABSORPTION ISOTHERM FOR POLYURETHANE FOAM (BITTERN)

#### METHOD :

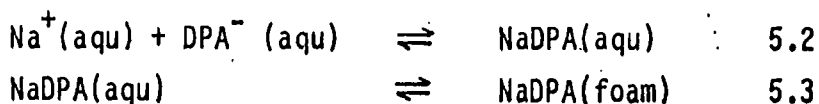
The method used for obtaining the isotherms is similar to that given in Sec. 5.3.1.2. An accurately measured mass of foam (Sample V7) was placed in a flask. To this was added 100ml of dipicrylamine solution (NaDPA in distilled water) at known initial concentration. The flask was placed in a constant temperature water bath fitted with a shaker and allowed to equilibrate over 48 hrs. The temperature was fixed at 70°C. A small amount of solution (less than 1 ml) was withdrawn and diluted for analysis on a UV/Visible spectrophotometer (see Appendix A2). The temperature was then reduced to 50°C, the system equilibrated and the equilibrium solution concentration determined in the same way. This was repeated at a temperature of 30°C. This experiment was repeated for a number of initial solution concentrations and foam sample sizes to give a range of equilibrium solution concentrations and loadings (see Appendix A3).

#### RESULTS :

The results are tabulated in Appendix A3 and the isotherms are shown in Fig. 5.4.

#### DISCUSSION :

The ability to regenerate polyurethane foam with hot water is a very useful property. One can speculate as to why this is possible. The absorption reaction can be visualised as :



Obviously this is a simplification, but it does serve to illustrate how a high concentration of  $\text{Na}^+$  can drive the equilibrium to the right. In other words, the high level of sodium ion 'drives' the dipicrylamine onto the foam. Similarly, if the sodium ion level is low, the equilibrium lies to the left.

If a sample of loaded polyurethane foam is placed in cold distilled water, dipicrylamine immediately starts to desorb from the foam. If the water is hot the process is more rapid and, since the degree of absorption decreases with increasing temperature, the final concentration of desorbed dipicrylamine is higher. A method for the industrial application of the regeneration of polyurethane foam by hot water is proposed in the overall discussion of the experimental work (Sec 5.3.1.9)

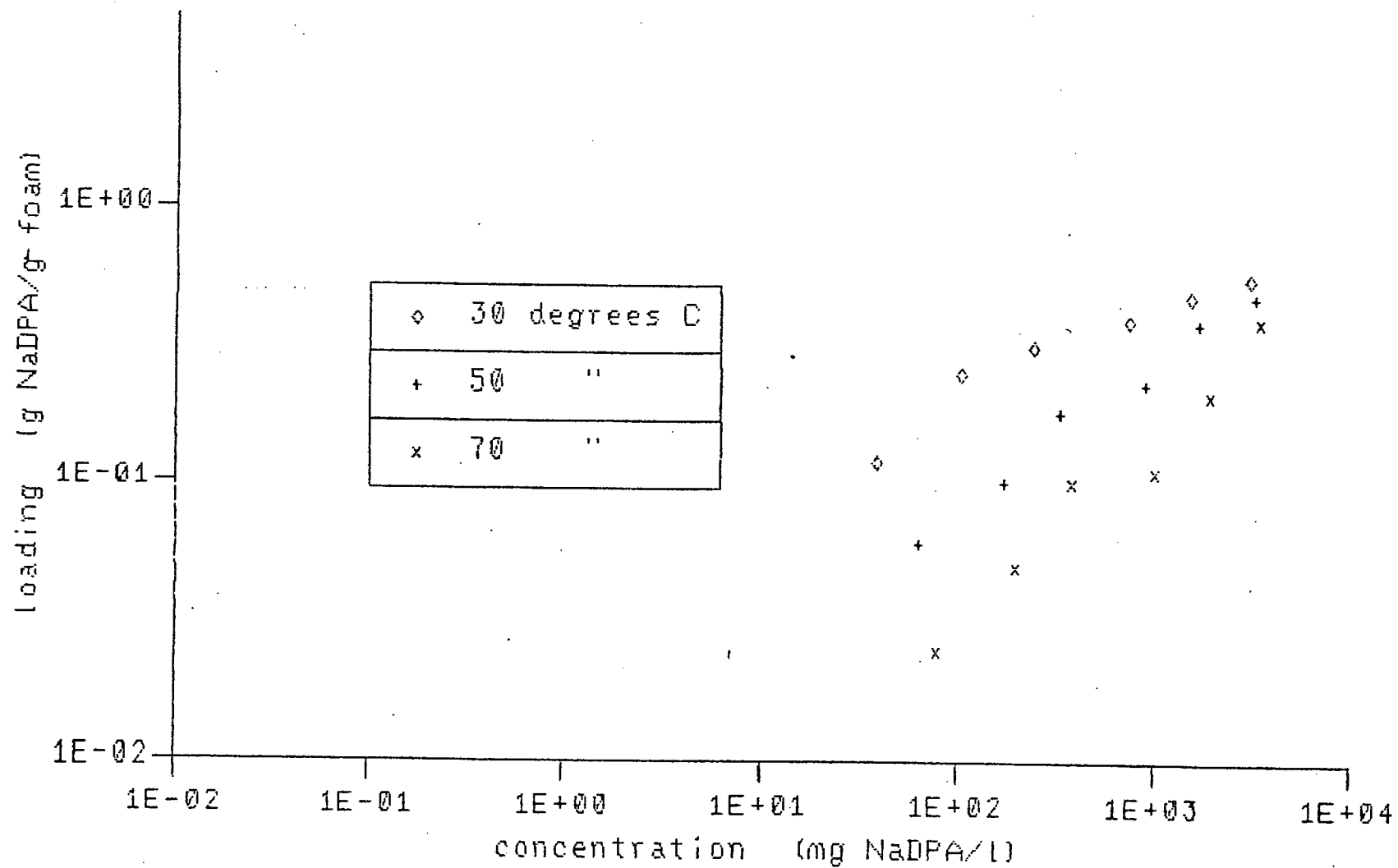


Fig. 5.4 ABSORPTION ISOTHERM FOR POLYURETHANE FOAM (HIGH TEMPERATURE)

### 5.3.1.5 Kinetics of Loading

#### AIM :

Matsuda, Masuda and Ishizaka (110) give very little information on the kinetics of loading of dipicrylamine onto polyurethane foam. This information is essential for the design of an industrial process. The aim of the experimental work was to study the kinetics of absorption of dipicrylamine into polyurethane foam from both spent bittern and seawater.

#### METHOD :

The kinetics of loading dipicrylamine into polyurethane foam from a bittern were measured in the following way. A measured amount of foam (0,25g) was placed in a 1 litre beaker which contained 100 ml of spent bittern with a very low dipicrylamine concentration (less than 0,1mg NaDPA/l). The foam was squeezed to remove trapped air and to wet it completely. The contents of the beaker were continuously stirred and the beaker was placed in a water bath at 25°C. Then 400 ml of spent bittern containing 26,6 mg NaDPA/l was added. The change in dipicrylamine concentration with time was then monitored by using a flow through cell in a Varian Superscan 3 UV/Visible Spectrophotometer. The bittern was pumped by peristaltic pump from the beaker through the cell and back to the beaker. The volume of the tubing was about 7ml and it took about 5 seconds for this to pass through the tubing. Thus this method of measurement should have had negligible interference with the results of the experiment.

On reaching equilibrium, 400 ml of the spent bittern (now with a low dipicrylamine concentration) was decanted. A further 400 ml of spent bittern containing 26,6 mg NaDPA/l was added at the beginning of the next run.

In this way the same sample of foam was loaded in a stepwise fashion with the loading increasing with each run. The spectrophotometer was equipped with a chart recorder so the concentration vs time curve was obtained directly.

A similar method to that described above was used for the measurement of the kinetics of loading polyurethane foam from spent seawater. An accurately measured amount of foam (2g) was placed in a litre beaker containing 100 ml of seawater. At time zero 400 ml of seawater containing 375 mg NaDPA/l was added. The contents of the beaker were well stirred and maintained at 25°C. From time to time a small amount (0,2ml) of the seawater was removed and diluted for analysis of the NaDPA concentration by UV/Visible spectroscopy. The total amount of seawater removed was less than 4 ml so the conditions in the experiment were not greatly affected by the sampling.

Once equilibrium was achieved, 400ml of seawater was decanted. A further 400ml of seawater (375 mg NaDPA/l) was added at the beginning of the next run. In this way the foam was successively loaded in a stepwise manner.

#### RESULTS :

The concentration vs time curves for the bittern kinetic experiments were obtained directly from the chart recorder of the UV/Visible spectrophotometer. Fig 5.5 shows three of these curves. The first curve is for the first loading run. The second curve shows the change in concentration with time for the fifth successive loading while the third curve shows the results for the eighth loading run.

Fig 5.6 and 5.7 show the successive loading curves for the recovery of dipicrylamine from seawater. These curves were obtained by manually plotting the concentrations vs time data.

#### DISCUSSION :

The kinetics of loading decrease rapidly as the foam takes up dipicrylamine. The foam samples used in the kinetic experiments were cut into small chips. It was noticed that the size of the chips of foam used in the experiment had no effect on the kinetics. In other words, if the sample of foam used in the experiment was cut up into many small pieces (say 50) or left in one large piece, no significant change was seen in the results. From this it was concluded that the kinetics are not limited by bulk diffusion or transport in the macropores or cells of the foam.

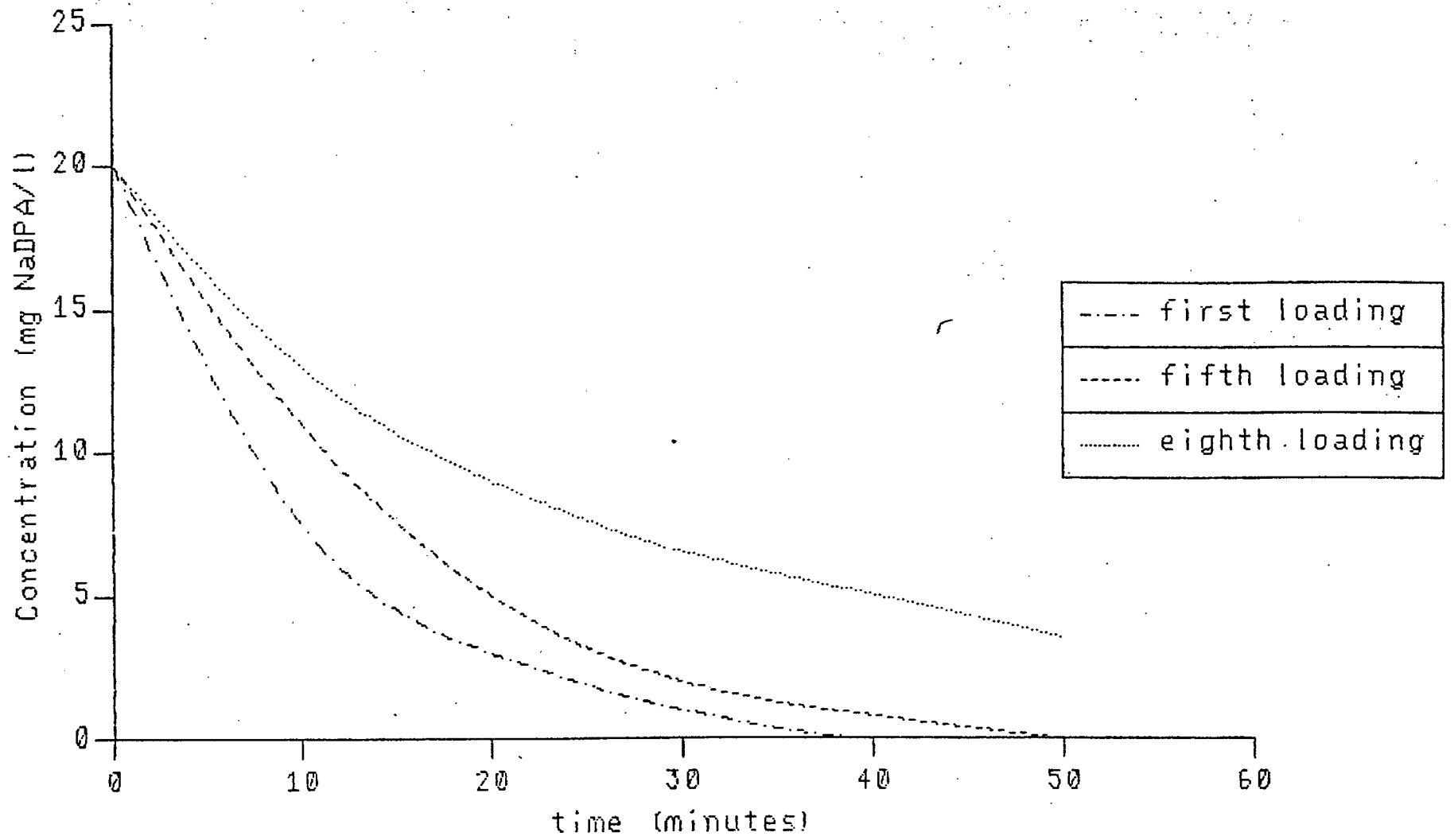


Fig. 5.5 Kinetics of Absorption of Dipicrylamine from a Bittern

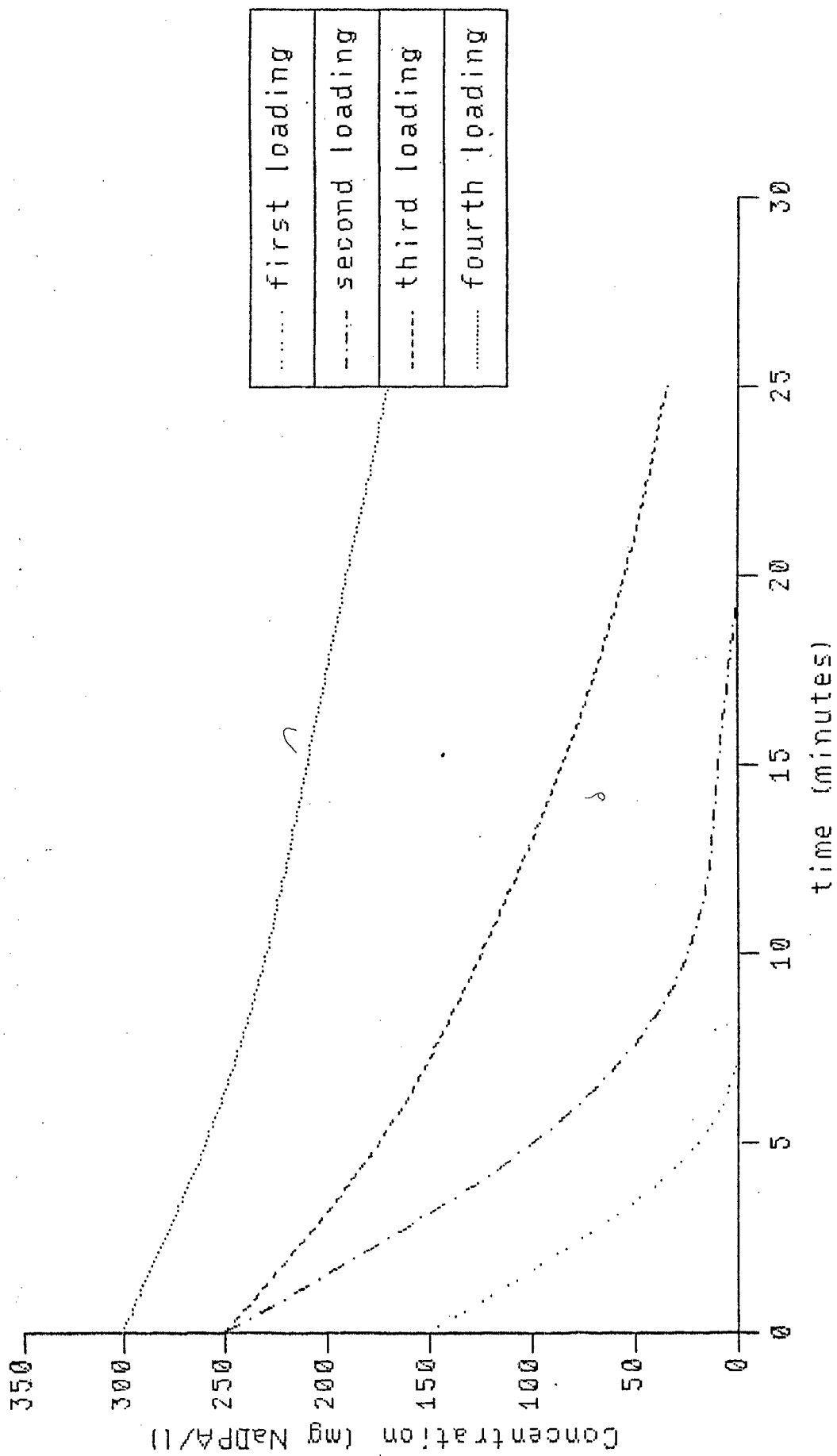


Fig. 5.6 Kinetics of Absorption of Dipicrylamine from Seawater

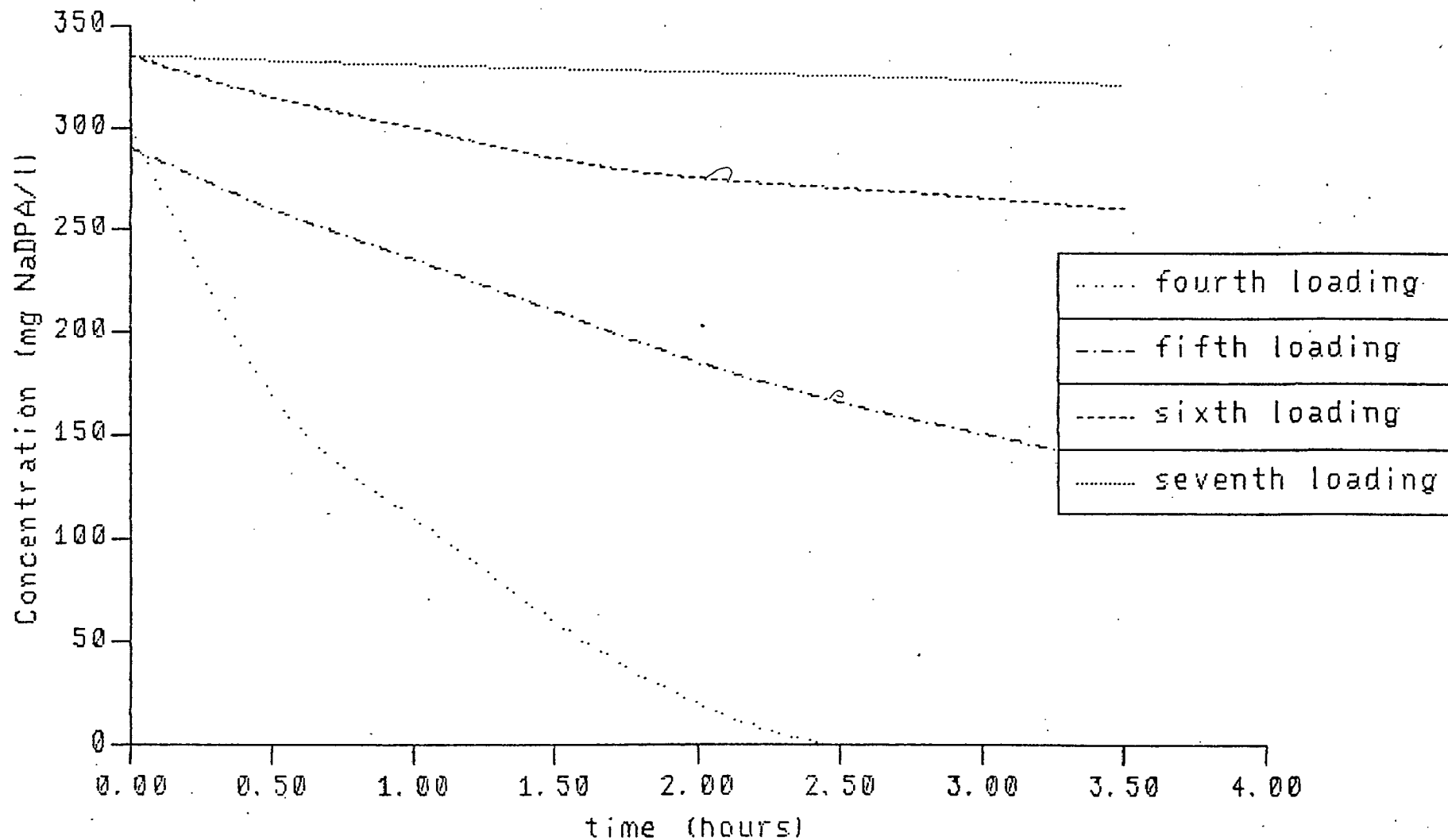


Fig. 5.7 Kinetics of Absorption of Dipicrylamine from Seawater

It was also found that the degree of agitation did not affect the kinetics either. Thus the kinetics are not limited by diffusion in the surface film of the solid matrix. This suggests that the kinetics of absorption are limited by diffusion in the solid phase.

#### 5.3.1.6 The Effect of Foam Density and Hardness

##### AIM :

Polyurethane foam is made in a variety of densities and degrees of hardness. This variation in properties is obtained by varying the amount of reagent used in the manufacture of the foam. The aim of the experimental work was to study the effect of these variables on the loading capacity of the foams.

##### METHOD :

Sixteen samples of polyether polyurethane foams of varying hardness and density were tested. These samples were supplied by Vitafoam (Pty) Limited. An equilibrium experiment was carried out for each sample where a known mass of foam (either about 0,025g or 0,10g) was placed in 100 ml of seawater with a dipicrylamine concentration of 110 mg NaDPA/l and allowed to reach equilibrium loading at room temperature. The method was identical to that described in Sec. 5.3.1.2.

##### RESULTS :

The results of this experiment are shown in Table 5.2. The final (equilibrium) concentration of dipicrylamine varies from about 1,7 mg NaDPA/l to about 6,4 mg NaDPA/l when about 0,025g of foam was used.

TABLE 5.2 : EQUILIBRIUM LOADING OF VARIOUS FOAM SAMPLES

SAMPLE	FOAM MASS (g)	FINAL DPA CONC. (mg/l)	HARDNESS OR HARDNESS RANGE ( - ) *	DENSITY (kg/m <sup>3</sup> )
V1	0,025	2,3	14	30
V2	0,026	1,7	11	30
V3	0,025	2,9	18	29
V4	0,025	6,4	22	26
V5	0,026	2,1	15	26
V6	0,026	5,1	18	25
V7	0,027	2,9	14	23
V8	0,025	2,5	12	23
V9	0,026	2,1	9	19
V10	0,025	5,2	12	18
V11	0,024	2,6	7	18
V12	0,026	1,8	6	16
FX40FG	0,027	2,3	15 - 19	23
FX64	0,026	1,7	17 - 19	50
FX80	0,026	2,1	19 - 23	29
LT100	0,026	1,7	17 - 21	34
V2	0,11	0,59	11	30
V6	0,10	0,71	18	25
V10	0,10	0,82	12	18
V12	0,10	0,68	6	16

\* These empirical figures were supplied by the manufacturers.

#### DISCUSSION :

The results are inconclusive. They indicate that there is some variation in the properties of the foam but this is not easily correlated to hardness or density variation.

#### 5.3.1.7 Treated Foams

##### AIM :

Several workers have used polyurethane foam, treated with a suitable reagent, as a sorbent (131, 137). The properties of the foam can be altered by treating it with a reagent such as an organic solvent. The foam absorbs some of the reagent and as a result its properties change. Alternatively the foam acts as a support for a liquid extraction solvent which itself extracts the dipicrylamine. The aim of the experimental work was to see if treated foams were more effective in the recovery of dipicrylamine from spent seawater or bittern than untreated foam.

## METHOD :

The method for treating foams is given by Braun and Farag (135). The foam is allowed to stand overnight in the solvent (or, if the reagent is a solid, in a solution of the reagent in diethylether). The foam then takes up the reagent. In the present work sixteen reagents were tested to see if pretreating polyurethane foam with them resulted in a better absorbent for dipicrylamine. The reagents may be divided into three groups. The first group (acetone, methyl ethyl ketone, ethyl acetate, methanol, ethanol, diethylether, diisopropylether) are solvents which have a high solvent power for dipicrylamine. This is particularly true for acetone and methyl ethyl ketone (see Section 5.3.3.2). The second group included benzene, toluene, chlorobenzene, kerosene and acetic acid. The third group (aniline, nitrobenzene and 2,4 dinitrochlorobenzene) are compounds whose structures contain groups found in dipicrylamine.

The experimental method was as follows : a mass of 0,020g of foam was allowed to stand overnight in the appropriate reagent (or, in the case of 2,4 dinitrochlorobenzene, a solution of the reagent in diethylether). The foam sample was then removed and squeezed dry between filter paper. The sample was accurately weighed. It was then placed in a flask and allowed to reach equilibrium at room temperature with 100 ml of a solution of dipicrylamine in seawater with an initial concentration of 110mg NaDPA/l. The equilibrium concentration was then measured. The equilibration method was identical to that described in Section 5.3.1.2.

## RESULTS :

Pretreatment by the reagents in the first and second group had no effect on the loading of the polyurethane foam.

Pretreatment by reagents in the third group showed a marginal improvement in the absorption properties. This can be seen from the results given in Table 5.3.

TABLE 5.3 : PROPERTIES OF TREATED FOAMS

REAGENT	MASS OF TREATED FOAM (g)	FINAL DPA CONCENTRATION (mg NaDPA/l)
Nitrobenzene	0,040	8,3
2,4 dinitrochlorobenzene	0,020	9,9
Aniline	0,034	11,6
Untreated Foam	0,020	13,6

DISCUSSION :

The slight improvement in the absorption ability of polyurethane foam for dipicrylamine when it is pretreated with nitrobenzene, 2,4 dinitrochlorobenzene or aniline is probably because these reagents are structually somewhat similar to dipicrylamine.

It was decided to abandon the technique of pretreating the foams for three reasons. Firstly, the improvement found was only marginal. Secondly, the reagents which did work are all toxic and dangerous (61). Finally, the cost of the reagents is high and it would be more effective and cheaper to use more foam than to pretreat a smaller quantity.

5.3.1.8 Plasticized Foam

AIM :

Plasticizers are defined as essentially non-volatile liquids used to modify synthetic resins - they do not chemically react with the resins but modify them through the reduction of Van der Waals forces (138).

Tributylphosphate (TBP) is a solvent with a high solvent power for dipicrylamine (see Section 5.3.3.2). It also is a plasticizer for polyurethane foam. Braun and Farag (136, 138) describe the use of TBP plasticized polyurethane foam for the recovery of materials from solution.

The aim of the experimental work was to see whether or not plasticizing polyurethane foam improves its absorption properties for dipicrylamine.

**METHOD :**

The foam was plasticized by allowing it to stand overnight in an excess of TBP (analytical reagent grade). For example, 0,96g polyurethane foam was placed in 100 ml TBP and stood for 24 hours at room temperature. The foam was then removed and squeezed dry on filter paper. The final mass was 2.9g. The foam was then equilibrated with spent seawater as described in Section 5.3.1.2.

**RESULTS :**

The plasticized foam did not show any significant improvement of absorption characteristics. Also, it was noticed that the plasticizer was leached from the foam when stirred in water.

**DISCUSSION :**

The increase in mass of the plasticized foam over that the unplasticized original mass (2.9g versus 0,96g) indicates that the plasticized foam contains about 67% plasticizer. This agrees with the results of Braun and Farag (136, 138). The loaded foam was much less dense and far softer than the unloaded original foam.

**5.3.1.9 Overall Discussion**

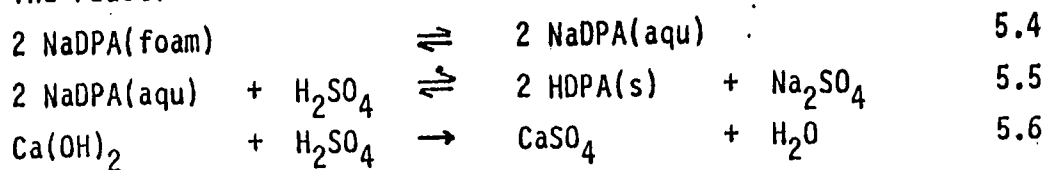
The experimental work examined several aspects of the use of polyurethane foam as an absorbent for dipicrylamine. The results of the experimental work lead one to speculate how this sorbent could be used in an industrial process. Polyurethane foam has the remarkable features that it absorbs dipicrylamine rapidly and efficiently from both seawater and bitterns and can be regenerated for re-use (with recovery of the dipicrylamine) by elution with hot fresh water.

For the case of a seawater process, where the volumes to be treated are very large, the use of polyurethane foam still presents problems. Although the kinetics are much better relative to the other solid sorbents tested (see Section 5.3.2), the time required to reduce dipicrylamine level in the seawater discharged to waste into the sea may be impracticably high. Suppose the residence time required for absorption is half an hour, then a plant which produces 100 tons potassium nitrate per day by treating 5 000 m<sup>3</sup>/hr of seawater would require an absorption vessel with a volume of 2500m<sup>3</sup>. This may be impractical. Nevertheless, one can speculate on how this method could be used in industry.

First of all, it seems clear that the simplest method of loading the foam would be to place it in a packed column or bed and pass spent seawater or bittern through it. There may be several beds in series. At regular intervals the bed which is first in the series and which is therefore contacted with the spent liquor of highest concentration should be withdrawn for regeneration when it reaches the desired loading.

One way to regenerate the foam would be to pass hot water through it and elute the dipicrylamine until the loading is reduced to a suitable level. This is likely to be inefficient as it would require large volumes of fresh water. Using the results obtained in the experimental work, one can propose a cyclical process which should use less water and may therefore be more efficient. It is shown in Fig. 5.8. Referring to this figure, hot fresh water (60°C) is passed through the foam bed where it elutes dipicrylamine. The aqueous solution leaving the foam bed now contains a high concentration of dipicrylamine (the concentration depending on the loading of the foam in the bed). It is passed to a reactor (or reactors in series) where the pH is reduced below 4 to precipitate HDPA. This HDPA is filtered off and the filtrate is neutralised with lime before being reheated and recycled through the foam bed. Thus the aqueous solution entering the bed will contain about 4 mg/l of dipicrylamine (the solubility of the HDPA).

The reactions are :



The idealised desorption reaction (5.4) takes place in the foam bed. Reaction 5.5 takes place in the HDPA settler and results in the gradual build-up with each cycle of sodium sulphate. Eventually the sodium sulphate level will rise to a point where the regeneration reaction is not efficient. Thus some of this stream will have to be purged to maintain the regeneration efficiency.

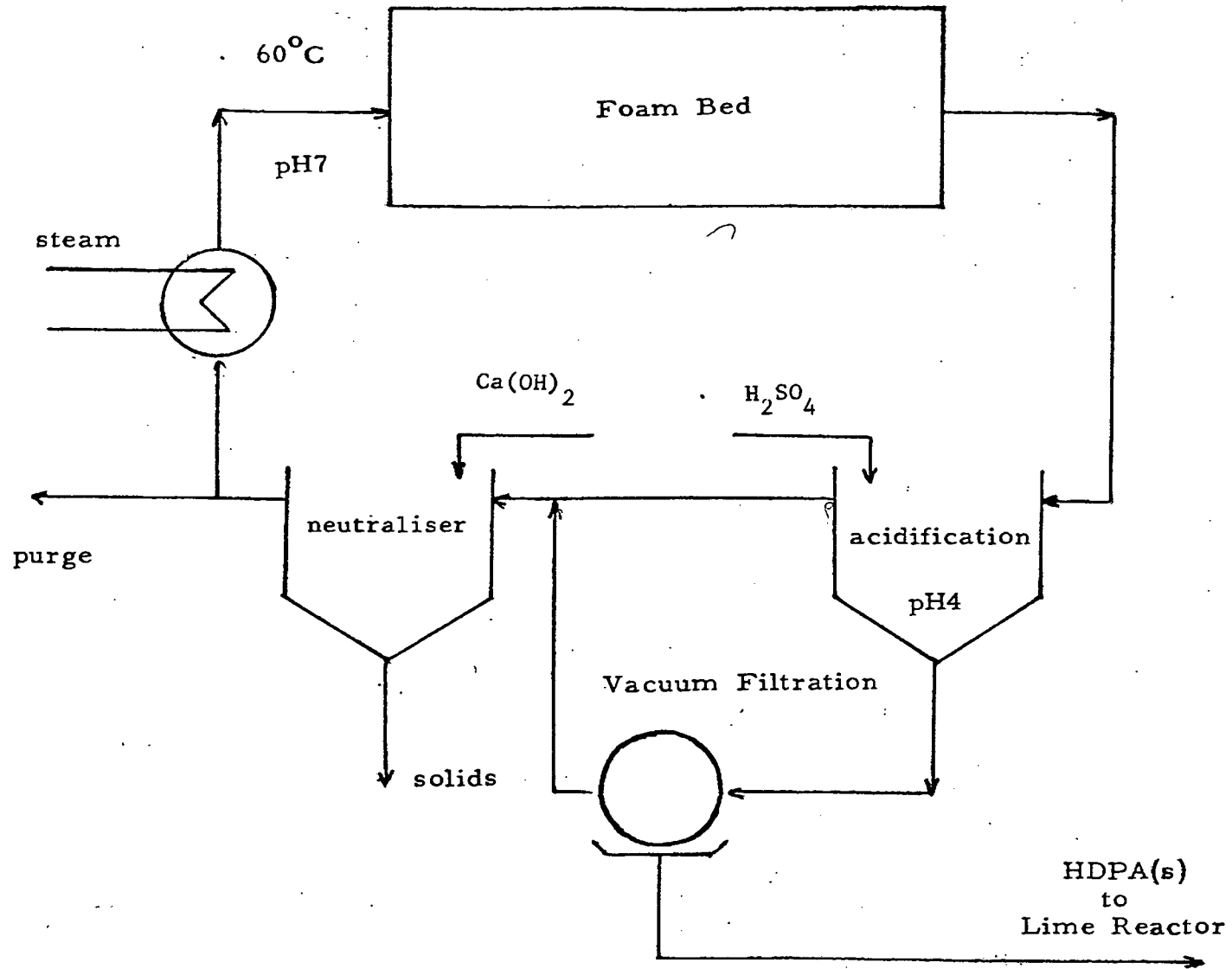


Fig. 5.8      Foam Regeneration

The third reaction occurs when the excess sulphuric acid required to lower the pH to below 4 is neutralised with lime. The level of  $\text{CaSO}_4$  will not reach saturation (2 g/l) because of the purge. However, unreacted lime solids must be recovered from the neutraliser.

If the above regeneration method is used, it should be possible to repeatedly regenerate and use the foam.

### 5.3.2 The Use of Solid Sorbents

#### 5.3.2.1 Activated Carbon, Polymeric and Ionexchange Resins

##### AIM :

The aim of the experimental work was to determine the usefulness of activated carbon, polymeric resins and ionexchange resins for the recovery of dipicrylamine. To achieve this, the loading and regeneration isotherms for these sorbents were measured.

The activated carbons tried were supplied by Klipfontein Organic Products (Pty) Limited (type KOP 40/2 and a granular carbon). There are an enormous variety of activated carbons available on the market (with widely varying properties) but it was felt that these two samples would give an indication of the suitability of the use of activated carbon for the recovery of dipicrylamine.

Three polymeric resins were Amberlite XAD-1, XAD-4 and XAD-8 manufactured by Rohm and Haas. The ionexchange resins were Amberlite IRA 35, IRA 68 (manufactured by Rohm and Haas) and A375 and ES 562 (manufactured by Klipfontein Organic Products (Pty) Ltd).

##### METHOD :

The equilibrium uptake of dipicrylamine by the sorbents was measured in the same way as that of polyurethane foam (Section 5.3.1.2) except that the resins were prepared in a special way. Also the flasks were shaken for at least 7 days (as opposed to 48 hrs) to allow equilibration.

The resins were prepared as follows. They were washed with dilute hydrochloric acid followed by distilled water and filtered off into a Buchner funnel. This was then covered with a damp cloth and a vacuum applied until all interstitial water was removed (this took about fifteen minutes). The damp resins were then accurately weighed into the flask and the experiment continued as described in Section 5.3.1.2.

#### RESULTS :

The sorption isotherm for activated carbon is shown in Figure 5.9 and the results are tabulated in Appendix A3. The isotherms for the four ionexchange resins tested are shown in Figure 5.10 and the results are tabulated in Appendix A3.

The synthetic polymer resins took up very little dipicrylamine. XAD-1 did not take up any appreciable amount of dipicrylamine while XAD-4 and XAD-8 loaded about 10% of their own mass (.1g dipicrylamine/g polymer) when equilibrated with a 200 mg/l dipicrylamine solution in seawater.

The regeneration of all the sorbents proved to be very difficult or, in the case of activated carbon, impossible. The mildest form of regeneration, heating the sorbents in distilled water, failed to regenerate them to any extent. The other two methods, stripping with hot caustic soda solution (1% m/v) and stripping with acetone, removed some dipicrylamine.

It was noticed that the kinetics of sorption of dipicrylamine by these sorbents was slow relative to polyurethane foam. The kinetics were not accurately measured but it appeared that they took some four to five times as long as polyurethane foam to reach the same degree of loading under the same experimental conditions.

#### DISCUSSION :

The experimental work described above was a cursory examination of the usefulness of activated carbon, synthetic resins and ionexchange resins for the recovery of dipicrylamine from spent seawater and bittern. From this cursory examination it appeared that they have two disadvantages compared with polyurethane foam; the relatively slow sorption kinetics and difficulty of regeneration. The synthetic polymer resins have, in addition, a low capacity for dipicrylamine.

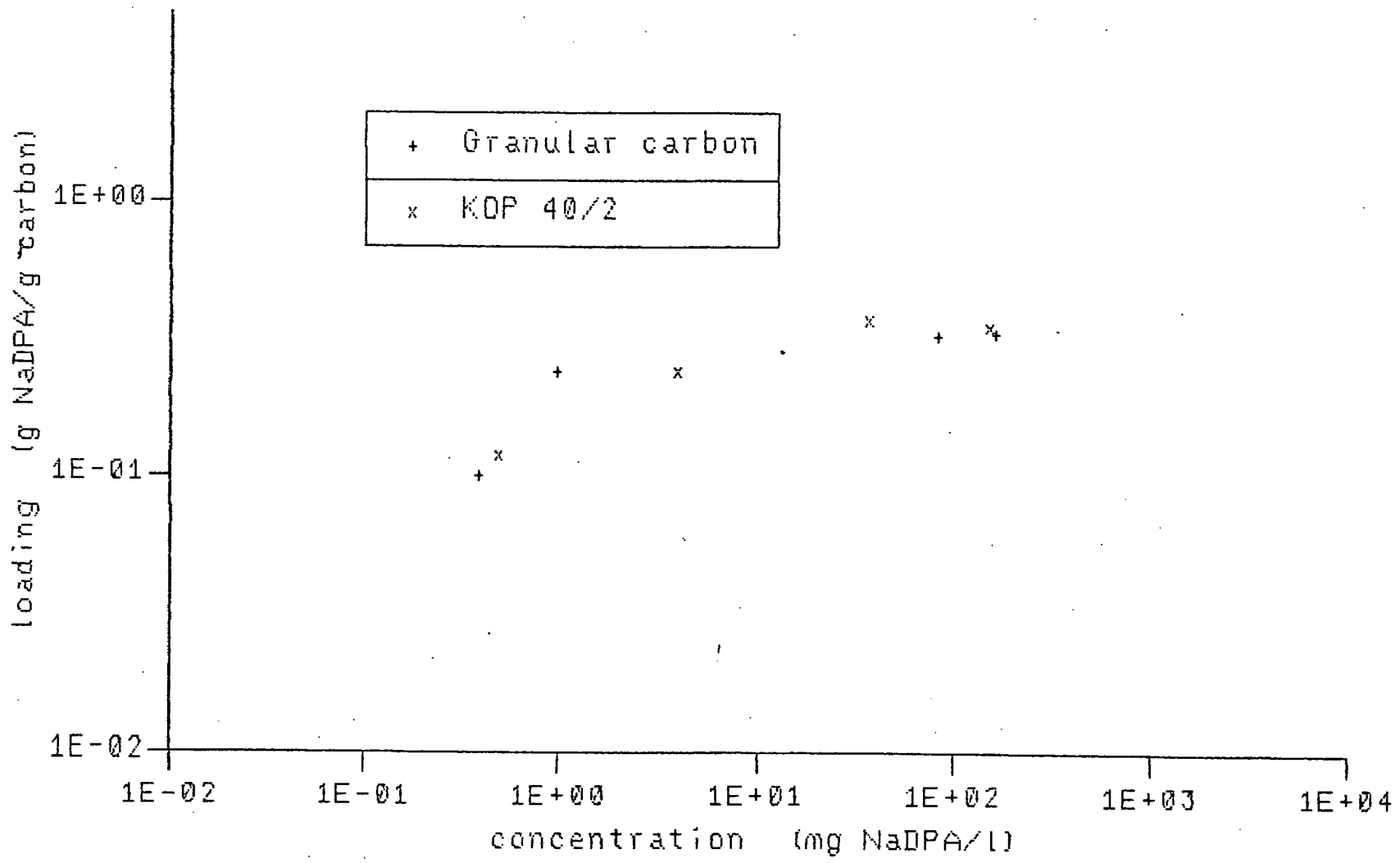


Fig. 5.9 ADSORPTION ISOTHERM FOR ACTIVATED CARBON

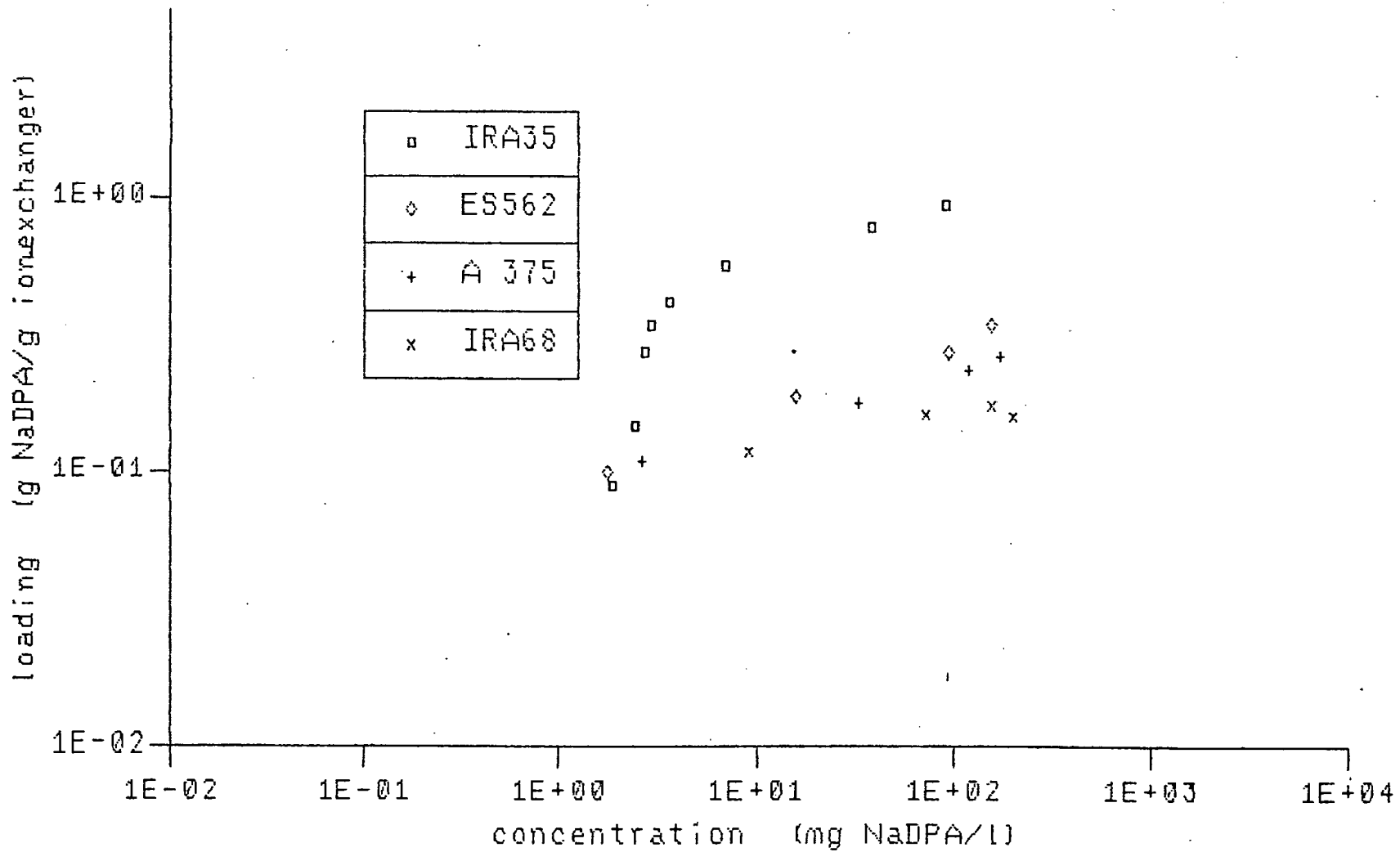


Fig. 5.10 ADSORPTION ISOTHERMS FOR IONEXCHANGE MATERIALS

### 5.3.3 The Recovery of Dipicrylamine from Spent Seawater by Liquid Extraction

#### 5.3.3.1 Overall Objective

It was seen in Sec. 5.3.1 that polyurethane foam is an effective absorbent for the recovery of dipicrylamine from seawater. However the long residence time required for the absorption step may require impractically large equipment in the seawater process in view of the large flowrates encountered in this process. On the other hand, it was felt that liquid extraction might be a more rapid method for dipicrylamine recovery.

Accordingly, the overall objective of the experimental work was to find a solvent which could be used for the recovery of dipicrylamine by liquid extraction. Certain characteristics are desirable in a solvent which is to be used for liquid extraction (140). For instance, the solvent should be selective for the compound to be extracted, insoluble in the aqueous phase and easily regenerated. Other desirable characteristics are low toxicity, non-flammability, high interfacial tension to promote phase separation and low cost. Few, if any, solvents will satisfy all these requirements. However, these characteristics were borne in mind when searching for a suitable solvent.

#### 5.3.3.2 The Solubility of KDPA in Organic Solvents

AIM :

The literature contains little reference to the solubility of KDPA in organic solvents. The aim of the work described here was to find organic solvents in which KDPA was appreciably soluble. No attempt was made to measure accurately the solubility of KDPA in the various solvents. Only an indication of the degree of solubility was required.

Since the overall objective of the experimental work was to find a solvent for use in the liquid extraction of dipicrylamine from seawater, solvents which are completely miscible with water were not investigated.

**METHOD :**

A method was chosen which rapidly gave an indication of the degree of solubility of KDPA in a solvent. Thirty two solvents were tested.

About 0,2g of KDPA was placed in a test tube. To this was added 10 ml of the solvent being examined. The tube was vigorously shaken for a few minutes. The test tube was then allowed to stand for an hour to allow any undissolved KDPA to settle. The whole procedure was carried out at room temperature. The colour of the solvent was then noted.

KDPA is a brightly coloured substance. The colour of solutions of KDPA in water vary from pale yellow to deep red according to concentration. To obtain an indication of the solubility of KDPA in the organic solvent the colour of the solvent was compared to that of standard solutions of KDPA in water with concentrations of 1,10 and 50 mg KDPA/l. The colour of these standards were quite distinct being pale yellow, orange and red, respectively.

**RESULTS :**

Table 5.4 shows an estimate of the solubility of KDPA in various organic solvents. The symbols used in Table 5.4 are as follows :

- i : KDPA is insoluble in the solvent (the colour of the solvent was paler than the 1 mg KDPA/l standard aqueous solution)
- ss : KDPA is slightly soluble in the solvent (the colour of the solvent was similar to that of the 10 mg KDPA/l standard aqueous solution.)
- s : KDPA is soluble in the solvent (the colour of the solvent was similar or a deeper red than the 50 mg KDPA/l standard aqueous solution. However, not all of the 0,2g KDPA in the test tube dissolved).
- vs : KDPA is very soluble in the solvent (all the KDPA in the test tube dissolved in the solvent).

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 TABLE 5.4 : THE SOLUBILITY OF KDPA IN ORGANIC SOLVENTS

<u>Aromatic Compounds</u>		<u>Alcohols</u>	
Benzene	ss	Amyl Alcohol	s
Aniline	vs	Octan-2-ol	s
Chlorobenzene	ss	Decanol	s
Toluene	ss		
Nitrobenzene	vs		
<u>Chlorinated Hydrocarbons</u>		<u>Esters</u>	
Dichloromethane	ss		
Carbon tetrachloride	ss	Ethylacetate	vs
Chloroform	ss	Amylacetate	vs
Trichloroethylene	s	N-Butylacetate	vs
Perchloroethylene	ss	Methylbenzoate	vs
		Dibutylphthalate	vs
		Tributylphosphate	vs
<u>Alkanes</u>		<u>Ethers</u>	
Heptane	i	Diethylether (dry)	ss
Iso-octane	i	Diethylether (wet)	s
Petroleum spirit	i	Di-n-butylether	i
Nitromethane	vs	Petroleumether	i
<u>Ketones</u>		<u>Miscellaneous</u>	
Methylethylketone	vs	Carbon disulphide	i
Methylisobutylketone	vs		
Cyclohexanone	vs		

DISCUSSION :

Table 5.4 shows that the best solvents are the ketones, aniline, nitrobenzene and the esters. How suitable are these solvents for use in a liquid extraction process for the recovery of dipicrylamine from spent seawater?

The ketones are all too soluble in water to be considered as a suitable solvent in a liquid extraction process. Their use would require an additional step for the recovery of them, in turn, from the spent seawater.

Aniline is slightly soluble in water and is toxic (61). Nitrobenzene is very toxic (61). It is too hazardous to be used in a liquid extraction process. Nitromethane is soluble in water (3) and dangerously flammable (61).

Of the esters, ethyl acetate, amyl acetate and butyl acetate are too soluble in water (141) to be useful. The other esters, methylbenzoate, ethylbenzoate, dibutylphthalate and tributylphosphate (TBP) are slightly soluble in water (141, 142) and they are all of low toxicity (61). The solubilities of methylbenzoate, ethylbenzoate, dibutylphthalate and tributylphosphate (TBP) in water are 200, 800, 400 and 400 mg/l at 25°C, respectively (141, 142). These are too high to be acceptable in a liquid extraction process for the recovery of dipicrylamine from spent seawater since the loss of solvent in the waste seawater would be prohibitive. However, TBP is commonly used with a diluent (143). Its solubility in water then drops dramatically (See Section 5.3.3.7). It was decided to investigate the use of TBP in an appropriate diluent.

#### 5.3.3.5 The Use of Tributylphosphate as a Solvent for the Recovery of Dipicrylamine - Loading Isotherm

##### AIM :

The aim of the work described below was to evaluate tributylphosphate (TBP), in a suitable diluent, as a solvent for the recovery of dipicrylamine from spent seawater by liquid extraction. In particular, the loading isotherm was determined for the uptake of dipicrylamine from spent seawater.

##### METHOD :

The TBP was diluted by mixing 10 parts by volume of TBP with 90 parts by volume of the diluent. Two diluents are recommended by the local supplier of TBP (143). These are Pegasol 3745 (an aliphatic solvent), and Pegasol R150 (an aromatic solvent). Some properties of these diluents are given in Table 5.5.

TABLE 5.5 : PROPERTIES OF DILUENTS FOR TBP (143)

	<u>Pegasol 3745</u>	<u>Pegasol 150</u>
Description	High Flash Aliphatic Solvent	High Flash Aromatic Solvent
Density (kg/m <sup>3</sup> )	800	880
Flash point (°C)	62	64
Solubility in water	Insoluble	Insoluble
Toxicity to man	Low	Moderate
Price (R/l)	0,58	0,93

The method used for obtaining the loading isotherm was to carry out a number of equilibrium experiments. In each equilibrium experiment a known volume of solvent (between 0,2 ml and 10 ml) was pipetted into a conical flask. Then 100 ml of spent seawater with an accurately measured concentration of dipicrylamine was measured into the flask. The flask was stoppered and shaken by hand for about fifteen minutes. The flask was then allowed to stand overnight to allow the phases to separate. Then a sample of the aqueous phase (about 5ml) was withdrawn using a pipette. It was centrifuged to ensure complete phase separation. The concentration of dipicrylamine in the aqueous phase was then measured in a UV/Visible spectrophotometer.

The equilibrium experiments were repeated using different volumes of solvent and varying initial concentrations of dipicrylamine in the spent seawater. All experiments were conducted at room temperature.

#### RESULTS :

The results of the equilibrium experiments are tabled in Appendix A3. The isotherm for the uptake of dipicrylamine by the 10/90 v/v TBP/Pegasol R150 solvent is shown in Figure 5.11.

It was noticed that the dipicrylamine was very rapidly taken up by the solvent phase. Although the flasks were shaken up for a full fifteen minutes it was observed that the colour of the solvent phase changed to yellow or red after a short period of shaking (about 1 minute). No change was visible after further shaking. This indicates that the kinetics of mass transfer is fast relative to that of, for example, the absorption of dipicrylamine into polyurethane foam (Section 5.3.1.5).

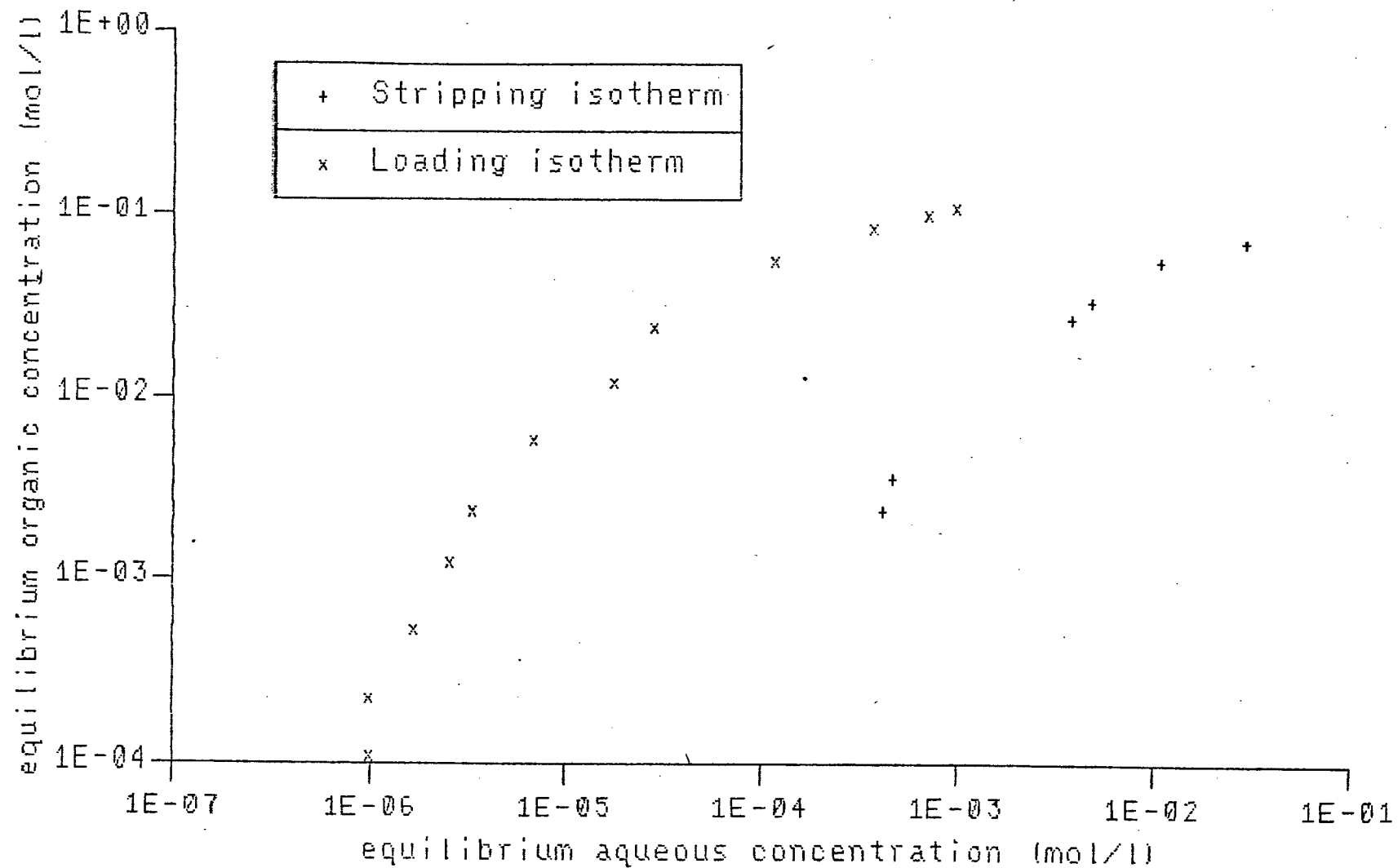


Fig. 5.11 LOADING AND STRIPPING ISOTHERM FOR TBP SOLVENT

After shaking the flasks vigorously for fifteen minutes the flasks were allowed to settle for several hours. It was observed after this settling that the aqueous phase was cloudy when the 10/90 v/v TBP/Pegasol 3745 solvent was used in the equilibrium experiments. No such cloudiness was seen when the diluent was Pegasol R150.

#### DISCUSSION :

The solvent mixtures, 10/90 v/v TBP/Pegasol R150 and 10/90 v/v TBP/Pegasol 3745, both take up dipicrylamine readily from the seawater.

The cloudiness that was observed in the aqueous phase when the diluent was Pegasol 3745 would be a problem if this solvent were used in the extraction of dipicrylamine from seawater in an industrial process since it indicates incomplete phase separation which would lead to solvent losses.

#### 5.3.3.6 The Use of Tributylphosphate as a Solvent for the Recovery of Dipicrylamine - Stripping Isotherm

##### AIM :

One of the requirements of a suitable solvent is that it must be easy to recover the dipicrylamine from the loaded solvent and regenerate the solvent for re-use. It was noticed that solvent loaded with dipicrylamine in the experimental work described in Sec. 5.3.3.5 could be stripped by shaking the solvent with distilled water. The aim of the experimental work was to obtain the stripping isotherm by conducting a number of equilibrium runs.

##### METHOD :

The method used was identical to that described in Section 5.3.3.5 except that the aqueous phase was NaDPA in distilled water (not spent seawater). The initial concentrations were varied from 304 mg NaDPA/l to 30 400 mg NaDPA/l.

##### RESULTS :

The results are tabulated in Appendix A3 and the isotherm is shown in Figure 5.11.

### 5.3.3.7 Overall Discussion

In this section the possible industrial application of the use of liquid extraction, and the problems that could be encountered with this method, are discussed. The results of the experimental work indicate that a 10/90 v/v tributylphosphate/diluent mixture should be considered as a solvent for the recovery of dipicrylamine from spent seawater by liquid extraction.

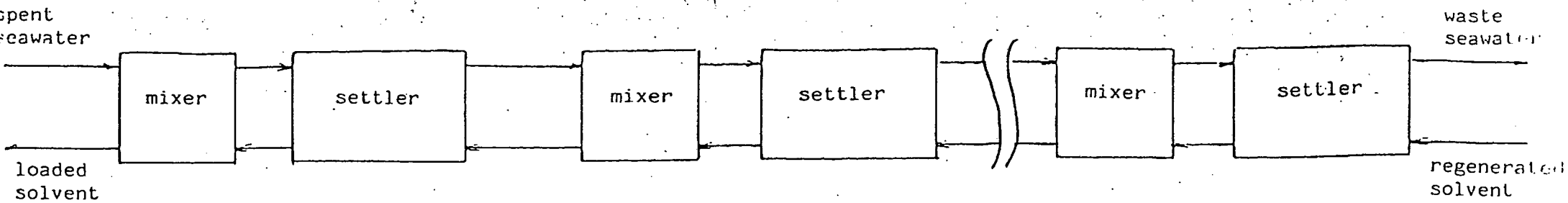
One can speculate as to how the liquid extraction method could be applied. Fig 5.12 shows one possibility.

Spent seawater containing, say, 500 mg dipicrylamine/l is pumped from the KDPA reactor/settler to a mixer/settler cascade where the seawater is contacted countercurrently with the TBP solvent. The number of mixer/settlers depends firstly, on the final desired dipicrylamine concentration of the raffinate - (the waste seawater), and secondly, on the solvent flow rate. The concentration of dipicrylamine in the seawater raffinate should be chosen so that the environmental impact of discharging it into the sea will be small.

The loaded solvent leaving the mixer/settler series will contain about 50g NaDPA/l. This loaded solvent is regenerated by stripping the NaDPA with freshwater in a cycle process which is similar to that used for the regeneration of polyurethane foam except that it operates at room temperature. This is also shown in Fig. 5.12. The solvent is stripped in a series of mixer/settlers. The concentration of dipicrylamine in the stream leaving the series would be about 5g NaDPA/l. This stream is acidified with sulphuric acid to reduce the pH to below 4 and precipitate the dipicrylamine as HDPa. This is filtered off and recycled. The filtrate is neutralised with lime and recycled to the stripping mixer/settlers. The dipicrylamine concentration in this dilute stream will be about 4mg NaDPA/l.

The regeneration process would probably be more efficient if operated at elevated temperatures. However, the temperature should be kept below the flash point of the diluent which is about 60°C.

DPA extraction:



Extractant regeneration:

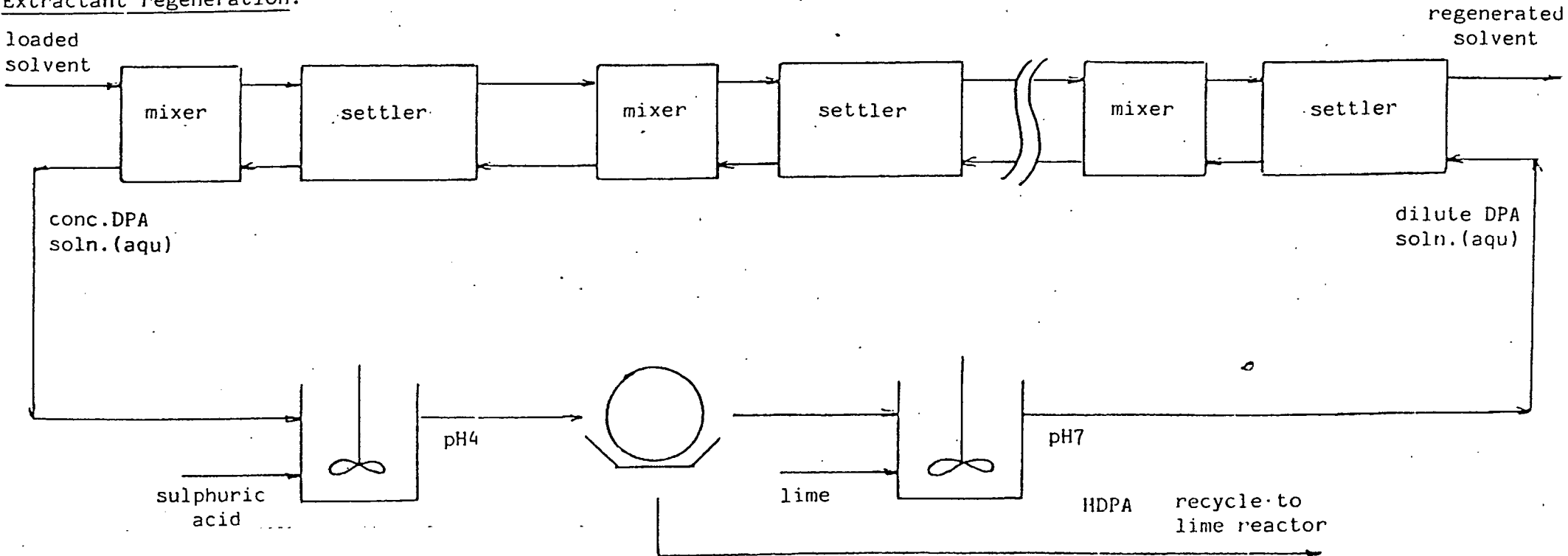


Fig. 5.12 The Recovery of Dipicrylamine from Spent Seawater Using Liquid Extraction

As in the case of the regeneration of the polyurethane foam (Sec. 5.3.1.9),  $\text{Na}_2\text{SO}_4$  is formed with each cycle of the regeneration. Thus there may have to be a purge to keep this level low.

One problem with any liquid extraction process is the loss of solvent in the raffinate. This is particularly true where liquid extraction is used for the recovery of dipicrylamine from seawater because of the high flowrates encountered in this process. Even if the solubility of the solvent is very low the total loss could be significant. An unavoidable loss of TBP will be that amount which is dissolved in the waste seawater. TBP is slightly soluble in water (the solubility is 0,4 g/l at 25°C (142)). This solubility decreases markedly in the presence of a diluent. However, the type of diluent is important. The literature gives data for the solubility of TBP in water when the TBP is mixed with various diluents (142). The concentration of TBP in water which is in equilibrium with a 10% v/v TBP/aromatic diluent is about 10 mg/l. For an aliphatic diluent the value is closer to 200 mg/l. Since the cost of the solvent loss would be very high if the solubility was the latter figure, it appears that the diluent should be aromatic, such as Pegasol R150.

#### 5.3.4 Conclusion of the Experimental Work

Flexible polyether polyurethane foam is an effective solid sorbent for recovering dipicrylamine from spent seawater and bitterns. The advantages of foam is low cost, high loading capacity for dipicrylamine and the ease of regeneration. However, the kinetics of sorption, while being much faster than for the other sorbents studied, could be too slow for use in a process for the recovery of potassium from seawater in view of the large flowrates encountered in this process. However, polyurethane foam seems well suited to the task of removing dipicrylamine from a spent bittern where the flowrates are much smaller.

The other solid sorbents tested (activated carbon, synthetic polymeric resins, ionexchange resins) do not appear, on first examination, to be suitable sorbents.

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The recovery of dipicrylamine from the spent seawater (or bittern) by liquid extraction has not been investigated in the literature. The experimental work identified a possible solvent for this extraction - tributylphosphate (TBP). The advantage of liquid extraction is the relatively high rates of mass transfer that were observed. This could be useful in the seawater process. However, the disadvantage of solvent losses in the waste seawater stream is difficult to overcome. The use of a suitable diluent for TBP, such as Pegasol R150, might eliminate this problem.

## 6. THE CONVERSION OF KDPA

### 6.1 Introduction

This chapter discusses the published data and experimental work on the conversion of KDPA to recover the potassium as an inorganic salt and to regenerate the dipicrylamine for reuse.

Four methods are given in the literature for this conversion. These are discussed in turn in Sec. 6.2.

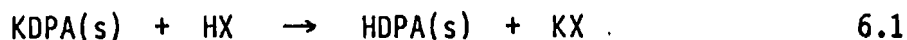
It was felt that the fourth method given in the literature, where the KDPA is converted to HDPA by reaction with an acid in the presence of an immiscible solvent, warranted further study. The experimental work studied the effect of the solvent addition on the kinetics of conversion of KDPA to HDPA. This work is described in Sec. 6.3.

### 6.2 Literature Survey

#### 6.2.1 Conversion by Reaction with an Acid

##### 6.2.2.1 Description of Method

The conversion of KDPA to HDPA by reaction with an acid in an aqueous medium is the most common method suggested in the literature (1, 107). The reaction can be written, in general, as follows :



where :

X = Cl, SO<sub>4</sub>, NO<sub>3</sub>, CH<sub>3</sub>COO for example (85)

According to Kielland (107), the production of potassium nitrate from KDPA is based on a solid phase exchange of potassium by hydrogen. He notes that the crystal habitus is unchanged by the reaction. Bakr and Zatout (109) give detailed information on the reaction kinetics. Kielland and Fleischer (85, 88) as well as Bakr and Zatout (109) studied the effect of acid concentration, mol ratio of reactants, temperature and kind of acid on the conversion of KDPA.

#### 6.2.1.2 Effect of Acid Concentration

Kielland and Fleischer (85) report that they found that the conversion of KDPA to HDPA takes place best when the nitric acid is comparatively dilute (5-20%) and the temperature is low, preferably below 30°C. At the interval of concentration between approximately 20 and 45% as well as the temperature interval of 30 to 80°C the conversion process did not give satisfactory results. However, the good results were again obtained with an acid concentration about 45% and temperature higher than 80°C.

Bakr and Zatout (109) give more detailed results which are broadly in agreement with those of Kielland and Fleischer. Figs. 6.1, 6.2 and 6.3 show their results. In all their experiments the mol ratio of nitric acid to KDPA was five to one and the temperature was 25°C.

It is not clear why the intermediate concentrations are not satisfactory.

#### 6.2.1.3 Effect of mol Ratio

The results of Bakr and Zatout (109) are given in Figs. 6.1, 6.2 and 6.3. They were obtained using a mol ratio of acid to KDPA set at five to one. Bakr and Zatout chose this ratio as further addition of acid did not influence the percentage conversion at any time for all nitric acid concentrations. The effect of mol ratio on the degree of conversion was measured by them and is shown in Fig. 6.4.

#### 6.2.1.4 Effect of Temperature

As mentioned in Sec. 6.2.1.2 temperature affects the conversion reaction. If the acid concentration used is less than 20% (3.5N) the temperature should not exceed 30°C. If the acid concentration is about 45% (9N) the temperature should exceed 80°C. Fleischer (88) reports that with high acid concentration the temperature should be high enough that the product  $\text{KNO}_3$  is dissolved.

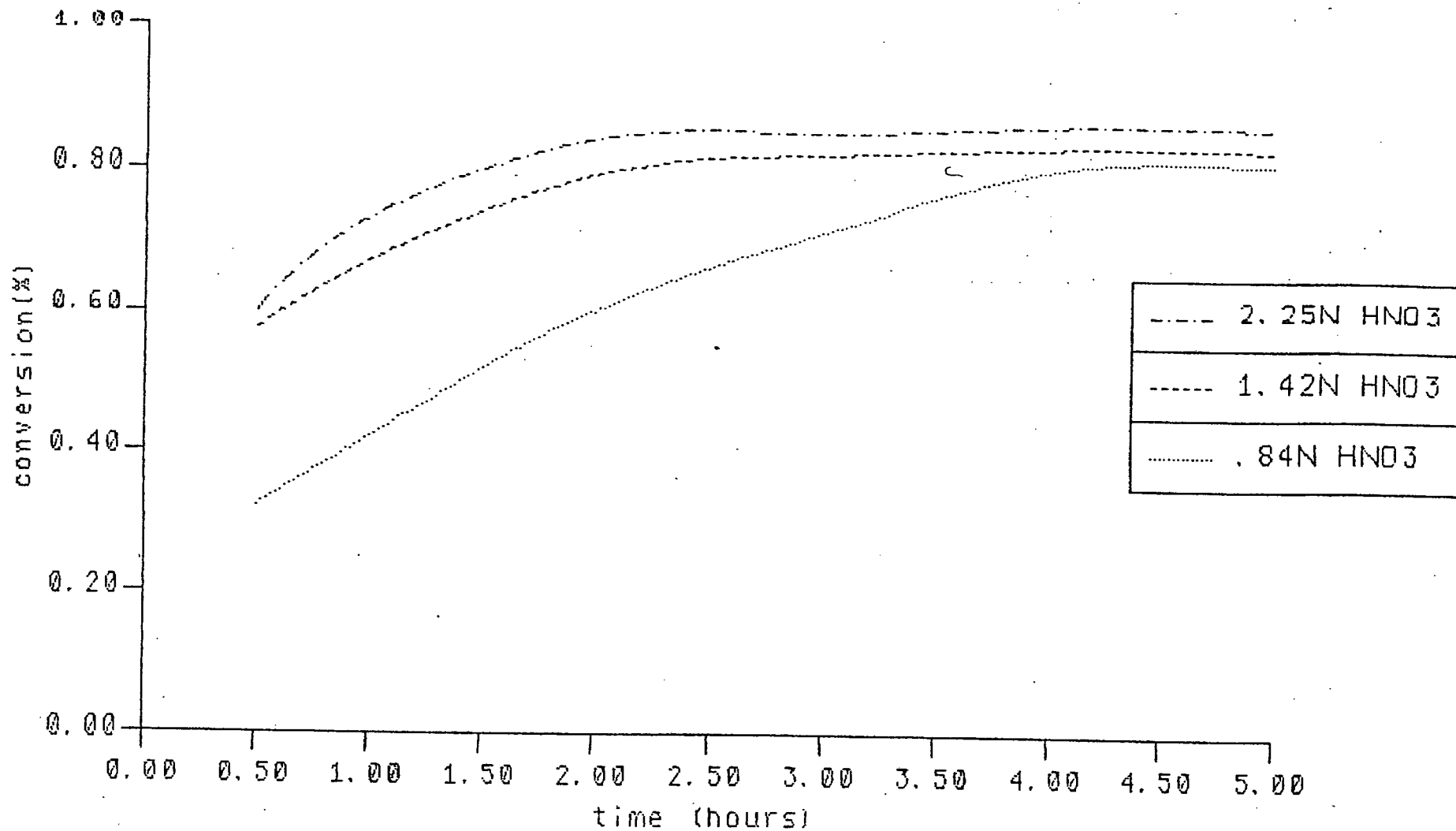


Fig. 6.1 Data of Bakr and Zatout (109)

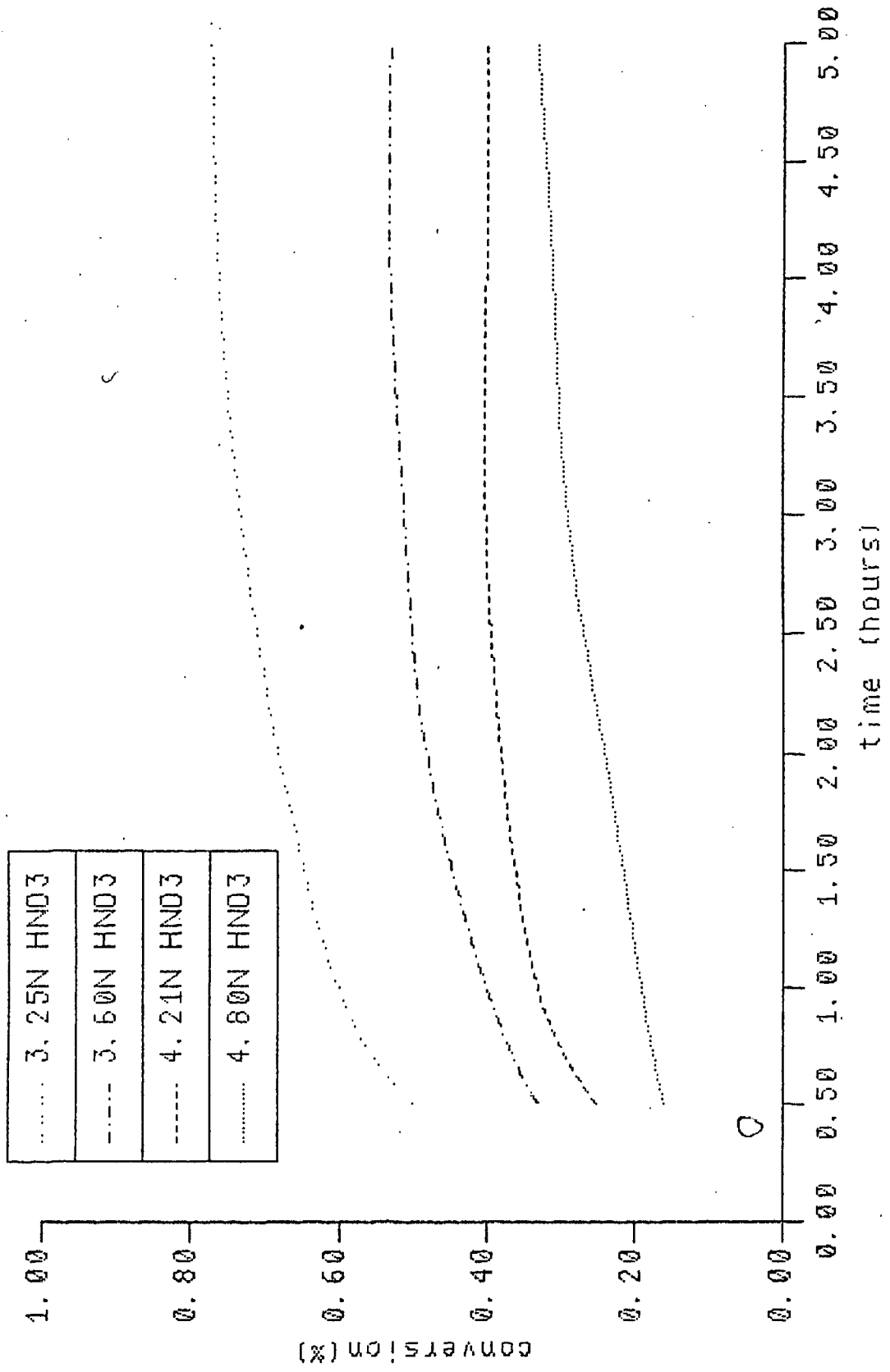


Fig. 6.2 Data of Bakr and Zatout (109)

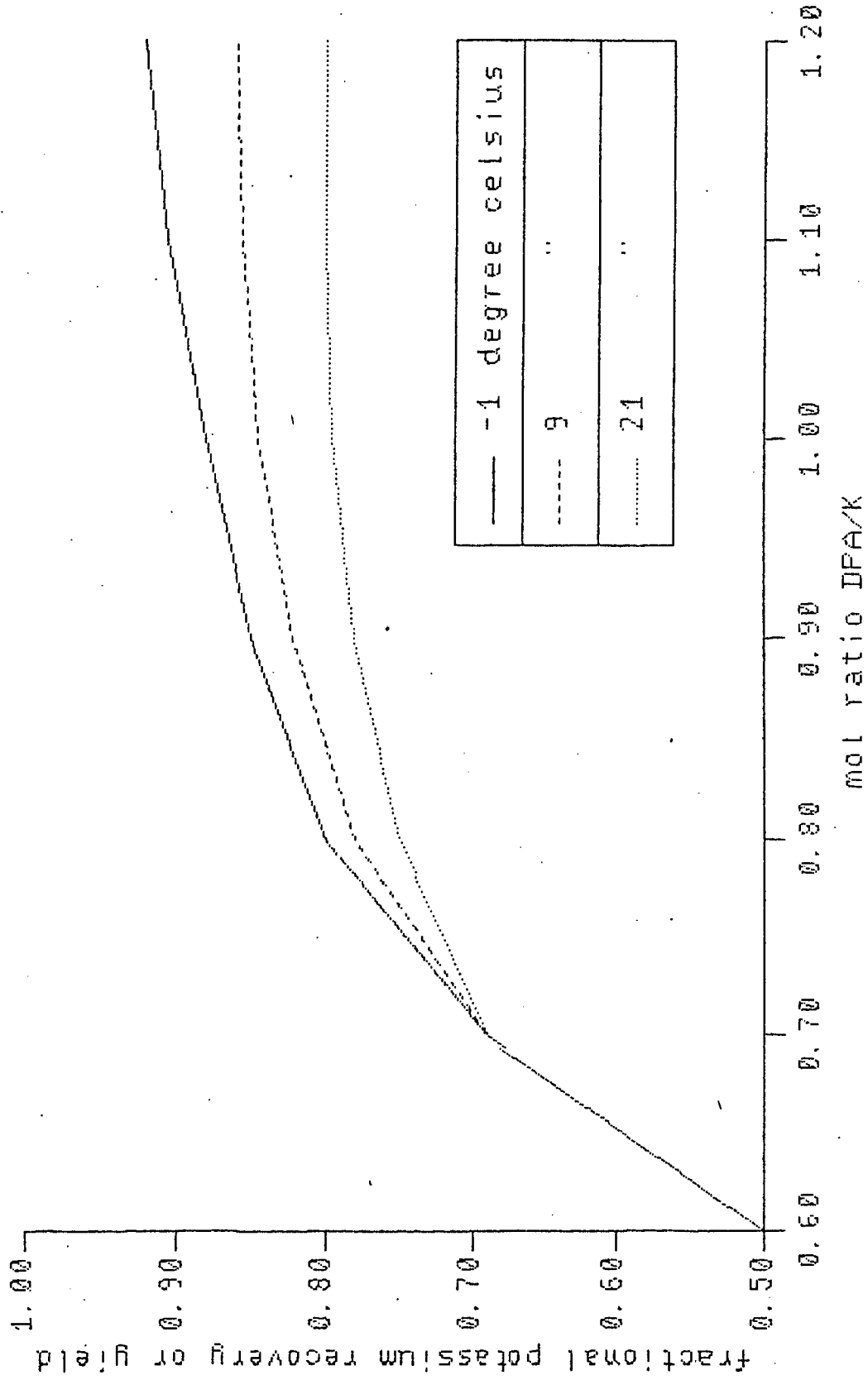


Fig. 4.1 THE YIELD OF K<sub>2</sub>PO<sub>4</sub> FROM SEAWATER (103)

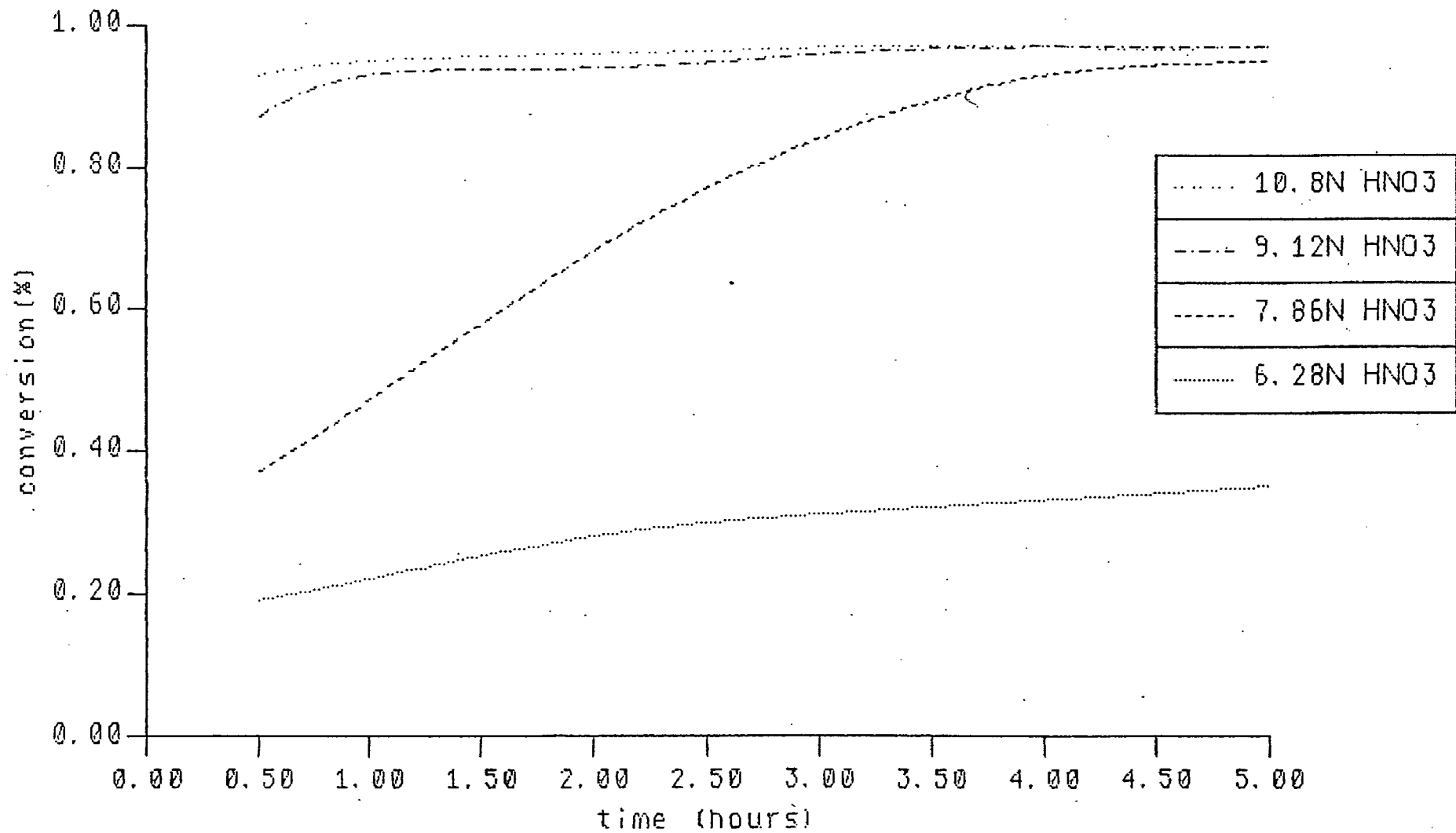


Fig. 6.3 Data of Bakr and Zatout (109)

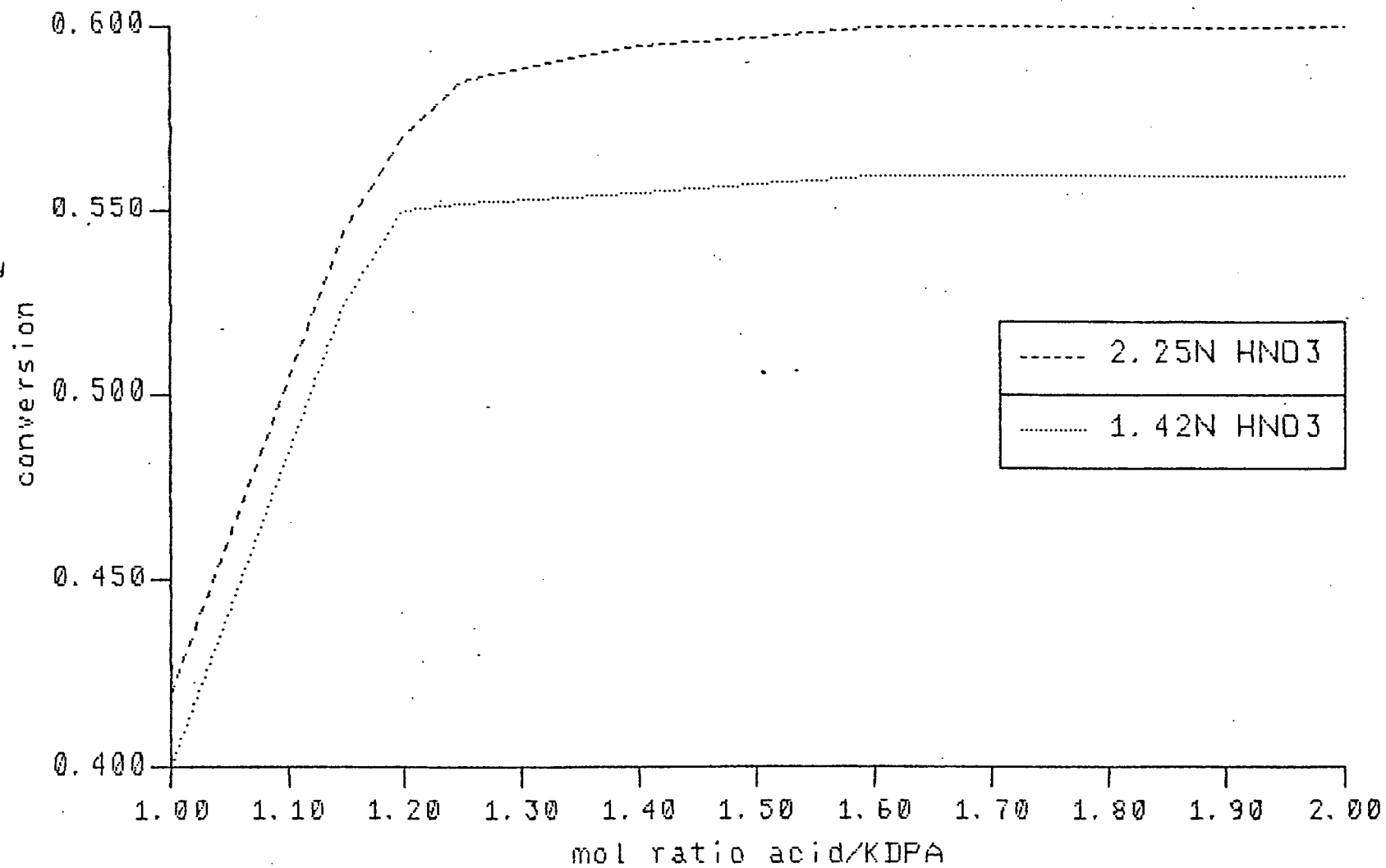


Fig. 6.4 THE EFFECT OF VARYING MOL RATIO (109)

The decrease in reaction kinetics with increasing temperature is curious and is the opposite of what is normally expected. Kielland (107) gives some data which clearly shows this effect. The data is given in Table 6.1. It shows typical values for the percentage conversion of KDPA to HDPa after 20 minutes of reaction time.

TABLE 6.1 : CONVERSION OF KDPA TO HDPa -  
TYPICAL VALUES OF % CONVERSION AFTER 20 MINUTES

Data from Kielland (107)

°C	<u>Concentration HNO<sub>3</sub> (N)</u>			
	0,5	1	2	4
15	25	45	75	20
30	8	15	18	10
45	2	2	3	4

#### 6.2.1.5 Other Acids

The use of other acids for the conversion of KDPA was studied by Kielland and Fleischer (85). Their work is described below.

They report that if acetic acid is used to convert KDPA to HDPa substantially the same conditions should be used as with nitric acid. In the case of sulphuric acid they found that the best results were obtained at comparatively high concentrations or temperatures. The concentration of sulphuric acid should be 60% or more. For hydrochloric acid the concentration should not be less than 30%.

Thus, for instance, 100g KDPA precipitated from seawater reacted with 100 ml of 36% hydrochloric acid at 20°C was 98% converted after stirring for one hour. A corresponding process with 79% sulphuric acid resulted in 99% conversion of the KDPA in half an hour (85). If higher temperatures and longer reaction times were used, satisfactory results were obtained using hydrochloric acid of concentration 100%.

### 6.2.1.6 Unconverted KDPA

Significant quantities of KDPA will remain unconverted unless the residence time in the reactor is very long. Fleischer (88) suggests that rather than using a very long residence time to convert the KDPA to a high degree of conversion it would be better to convert to a lower value (say 97%) with a shorter residence time. In this case the unconverted KDPA is carried with the HDPA to the Lime reactor. Here the HDPA solid is reacted to produce a solution of  $\text{Ca}(\text{DPA})_2$ . The unconverted KDPA remains as a solid and is removed together with the undissolved lime impurities. This solid is then acidified to convert the KDPA to HDPA. The solid, now consisting of HDPA and the lime impurities, is again treated with lime to convert the HDPA to soluble  $\text{Ca}(\text{DPA})_2$ . The solid remaining after this reaction is only the lime impurities and is discarded after washing it to remove traces of dipicrylamine.

Alternatively, Kielland (107) suggests that the solid from the Lime Reactor, consisting of unconverted KDPA and lime impurities, should be sent through a liquid cyclone where the KDPA can be separated from the other solids. This KDPA is then recycled to the original Acid Reactor.

## 6.2.2 Conversion in Acetone/Aqueous Solution

### 6.2.2.1 Reaction with Acid

This method is suggested in a U.S. patent (91) and a British patent (93). The KDPA is dissolved in a solution of acetone and water. Concentrated nitric acid is then added to precipitate HDPA and form  $\text{KNO}_3$ . The reaction is :



The solution changes from a dark red colour (unconverted) to a bright yellow suspension of HDPA on the addition of the acid. The advantage of this method is the very rapid conversion of KDPA to HDPA.

However, this method would appear to have several disadvantages. These are not discussed in the literature. Firstly, it will be necessary to distil the acetone/water phase to separate the components. This will incur an energy and capital cost.

Secondly, the HDPA which is produced must be filtered off in a vacuum filter. It may be difficult to avoid high solvent losses by evaporation because of the high volatility of acetone.

Thirdly, the KDPA in acetone/water solution may pose a health hazard as it readily stains the skin (this was found in the experimental work described in Section 4.3.6 where KDPA was dissolved in acetone for analysis). Normally it is fairly easy to scrub off any KDPA contamination from the skin. However, in the presence of acetone, the KDPA is rapidly and deeply absorbed into the skin from which it is impossible to remove (see Sec. 3.2.3 on dermatitis caused by dipicrylamine).

#### 6.2.2.2 Reaction with Inorganic Salts

A method is suggested in two patents by Klenert (96) and by Henne and Klenert (99). This method is illustrated by an example from Klenert (96).

100kg of KDPA containing 20% moisture (i.e. 80kg KDPA and 20kg water) is dissolved in 100 litres of acetone and is converted to  $\text{Mg}(\text{DPA})_2$  by mixing with a liquor containing 250 to 300 g/l of  $\text{MgSO}_4$ . This results in two phases. The acetone phase takes up Mg to convert KDPA to  $\text{Mg}(\text{DPA})_2$  and also takes up some water. The aqueous phase contains 30kg of  $\text{K}_2\text{SO}_4$ . In addition, about 5kg  $\text{K}_2\text{SO}_4$  precipitates from solution. The conversion takes place in three steps.

Klenert suggests that in place of  $\text{MgSO}_4$  one can use  $\text{CaCl}_2$ ,  $\text{Na}_2\text{SO}_4$  or  $\text{NaCl}$ . Also, instead of acetone other solvents can be used such as other ketones, aldehydes, alcohols or amines.

The advantage claimed is the use of cheap inorganic materials instead of expensive acid. Also it is not necessary to use acid-proof equipment.

Klenert does not mention the disadvantage of the energy cost for distillation. The  $K_2SO_4$  must be recovered by evaporation and crystallisation of the aqueous phase. However, this phase also contains some acetone which must be separated for reuse by distillation. In addition, the acetone phase must be evaporated so that the  $Mg(DPA)_2$  can be recycled to the KDPA Reactor/Settler.

However, this problem is taken into account by the patent of Henne and Klenert (99) who suggest the use of anhydrous inorganic salts for the conversion reaction. The heat of solution of these salts is used to distil off the acetone.

KDPA is dissolved in acetone as before. To this phase is added, for example, anhydrous  $MgSO_4$ ,  $MgCl_2$  or  $CaCl_2$ . This results in the formation of  $Mg(DPA)_2$  (or  $Ca(DPA)_2$ ) and the precipitation of  $K_2SO_4$  or  $KCl$ . The heat of the solution of the anhydrous salts is enough to drive off the acetone in the subsequent evaporation/distillation stages if a vacuum is applied.

### 6.2.3 Conversion in Ammonia Solution

A German patent by Henne and Klenert (98) describes this process in some detail. Briefly, the KDPA is dissolved in liquid ammonia under a pressure of 1.5 atm. The ammonia acts as a solvent allowing the reaction of KDPA with  $MgSO_4$  to produce  $K_2SO_4$  and  $Mg(DPA)_2$  in the same way as described in Section 6.2.2.2. The advantage is that the ammonia is not removed by distillation but by reducing the pressure whereupon excess ammonia vaporises. Any remaining ammonia is driven off by adding lime.

### 6.2.4 Conversion in the Presence of Butylether

A Japanese patent (100) suggests that KDPA should be converted to HDPA in the presence of butylether. The method is described in the patent as follows; 4g of KDPA is mixed with 80 ml of butylether and 24 ml of 0,5N HCl with stirring to form a KCl solution with solid HDPA in suspension. The HDPA is recovered by filtration and the butylether is removed in a separating funnel.

#### 6.2.5 Conclusion of the Literature Survey

The conversion of KDPA by reaction with an acid in an aqueous medium is the most commonly suggested method. The reaction proceeds at widely differing rates with varying reaction conditions. It is clear from the results of Kielland (107) and Bakr and Zatout (109) that the reaction is a slow one.

Several alternative reaction schemes have been suggested. The KDPA can first be dissolved in acetone and then reacted with acid. However, this method would appear to have the disadvantage of high distillation costs and could pose industrial health problems. Similarly, the reaction with inorganic salts in acetone solution would incur distillation costs. The reaction of KDPA with inorganic salts in the presence of ammonia is designed to avoid this problem.

The suggestion of reacting KDPA with an aqueous acid in the presence of a third phase is an interesting one. There is just one cursory reference to this idea in the literature and this method warrants further study.

## 6.3 Experimental

### 6.3.1 Overall Objective

One of the methods for the conversion of KDPA in the literature study was to react the KDPA with an acid in the presence of a solvent (Sec. 6.2.4). It was felt that this method warranted further study.

Accordingly, the overall objective of the experimental work was to study the kinetics of the conversion of KDPA to HDPA by reaction with an acid in the presence of a solvent.

To attain this objective several aspects were studied. Four solvents were tested. The solvents were chosen in accordance with the results of the experimental work given in Sec. 5.3.3.2. Some of these solvents are normally used with a diluent. The choice of diluent was examined. Other aspects studied were the amount of solvent that should be used, the effect of the concentration of the acid and the effect of the mol ratio of acid to KDPA on the reaction kinetics. Finally, the kinetics of the conversion of KDPA precipitated from seawater were compared with the kinetics of the conversion of KDPA precipitated from a bittern.

### 6.3.2 Experimental Method

The experimental conditions are tabulated for each experiment in Appendix A4. A number of solvents were used in the experimental work. These were prepared as follows : the solvent consisted of a basic component (TBP, methylbenzoate, dibutylphthalate or dibutylether) and a diluent. The diluents used were either perchloroethylene, Pegasol 3745 or Pegasol R150 (the last two are manufactured by Mobil SA (Pty) Limited, their characteristics are shown in Table 5.5). The solvent/diluent mixture was made by pipetting a volume of solvent into a 100ml volumetric flask and filling to the mark with diluent. Thus for instance a 10% v/v TBP in Pegasol 3745 mixture was made by pipetting 10 ml of TBP into a 100ml volumetric flask and filling to the mark with Pegasol 3745. The solvents were mixed at room temperature.

The kinetic experiments were conducted as follows : A sample of KDPA, precipitated from seawater and washed as described in Section 4.3.5, was placed in an oven and dried at 60°C for 3 hours. Then a portion of this KDPA (1g in most experiments) was accurately weighed into a 100 ml conical flask. A volume of solvent, prepared as described above, was then pipetted into the flask (in most experiments the volume of solvent was 2ml). The contents of the flask were then stirred for five minutes on a magnetic stirrer at room temperature to mix the KDPA and the solvent.

Then a known volume of acid (usually 10 or 20 ml of 1N HNO<sub>3</sub>) was quickly added using a pipette. The contents of the flask were thoroughly stirred with a magnetic stirrer and the reaction was carried out at room temperature (25°C). At intervals the stirrer was stopped, the phases allowed to separate and a small sample of the aqueous phase withdrawn. This took an average of about 15 seconds and the sample size was 0,1ml. The sample was diluted by the addition of an accurately measured volume of distilled water. It was then analysed for potassium on a Atomic Absorption Spectrophotometer. The stirrer was restarted after the sample had been withdrawn and the experiment was continued. In this way the change in the concentration of potassium nitrate in the aqueous phase was monitored. The concentration of potassium in the aqueous phase was used as a measure of the approach to equilibrium.

Some experiments were also conducted in the same way using KDPA precipitated from a bittern.

### 6.3.3 Results

Forty-one kinetic experiments were carried out. The conditions and results of the experiments are tabulated in Appendix A4.

### 6.3.4 Discussion of the Experimental Results

#### 6.3.4.1 General

Three interesting phenomena were noted in the experimental work. Firstly, the KDPA solid went into the solvent phase in all experiments. In other words there were two phases; a clear aqueous phase and an organic phase consisting of solid KDPA suspended (or in slurry form) in the organic solvent. Secondly, it was noticed that the large KDPA crystals (obtained from seawater) were broken down into a very fine HDPA solid as the reaction progressed. Thirdly, it was found that results of the kinetic runs were not reproducible when different batches of KDPA were used in the runs. In other words, different batches of KDPA gave different results even if they were both precipitated from the same original solution (seawater). This means that results of kinetic runs can only be compared when the same batch of KDPA is used for all the runs.

It is not clear why the results are not reproducible. It can only be assumed that batches of KDPA with quite different crystal size distributions can be produced when the precipitation reaction takes place under slightly different conditions.

The results of the investigation into different aspects of the use of an organic solvent as a third phase in the conversion of KDPA to HDPA are discussed below.

#### 6.3.4.2 Comparison of Solvents

It was decided to compare the performance of methylbenzoate, dibutylphthalate and dibutylether with the performance of TBP.

Three kinetic runs were carried out using the two esters. In the first run the solvent phase was a 50/50 v/v mixture of methylbenzoate and perchloroethylene. In the second the solvent has a 50/50 v/v mixture of dibutylphthalate and perchloroethylene. The third solvent was a 20/80 v/v mixture of methylbenzoate and perchloroethylene. The acid was 1N  $\text{HNO}_3$  and the mol ratio of acid to KDPA was 5 to 1. The ratio of solvent to KDPA was 2ml solvent to 1 gram of KDPA.

The results of these kinetic tests are shown in Fig. 6.5. For comparison the results are shown for the run where the solvent was a 10/90 v/v mixture of TBP and perchloroethylene. The 50/50 methylbenzoate/perchloroethylene solvent performs nearly as well as the 10/90 TBP/perchloroethylene solvent. Both the 50/50 and the 20/80 dibutylphthalate/perchloroethylene solvents do not work nearly as well as the other two. The 50/50 mixture works somewhat better than the 20/80 dibutylphthalate/perchloroethylene solvent.

Also shown in Fig. 6.5 is the curve for the kinetic run where no solvent was used (all other reaction conditions were identical to those in the other four runs). The use of the solvent clearly results in an improvement in the kinetics. The same batch of KDPA (precipitated from seawater) was used in all runs.

The results show that there is little advantage in using dibutylphthalate as the solvent. Methylbenzoate seems a better choice. However, this compound is susceptible to hydrolysis by acid (145) and is also expensive (143). For these reasons it could not be used industrially.

A Japanese patent (100) of Ishibashi suggests that KDPA should be converted to HDPA in the presence of butylether. Butylether is not likely to be a suitable solvent because KDPA is insoluble in it (see Section 5.3.3.2). Moreover, it is toxic, dangerously inflammable (61) and slightly soluble in water (141). Nevertheless a kinetic run was carried out using butylether as the solvent with all the other conditions being the same as for the other runs mentioned above. The result is shown in Fig. 6.5. This shows that the use of butylether slows down the reaction.

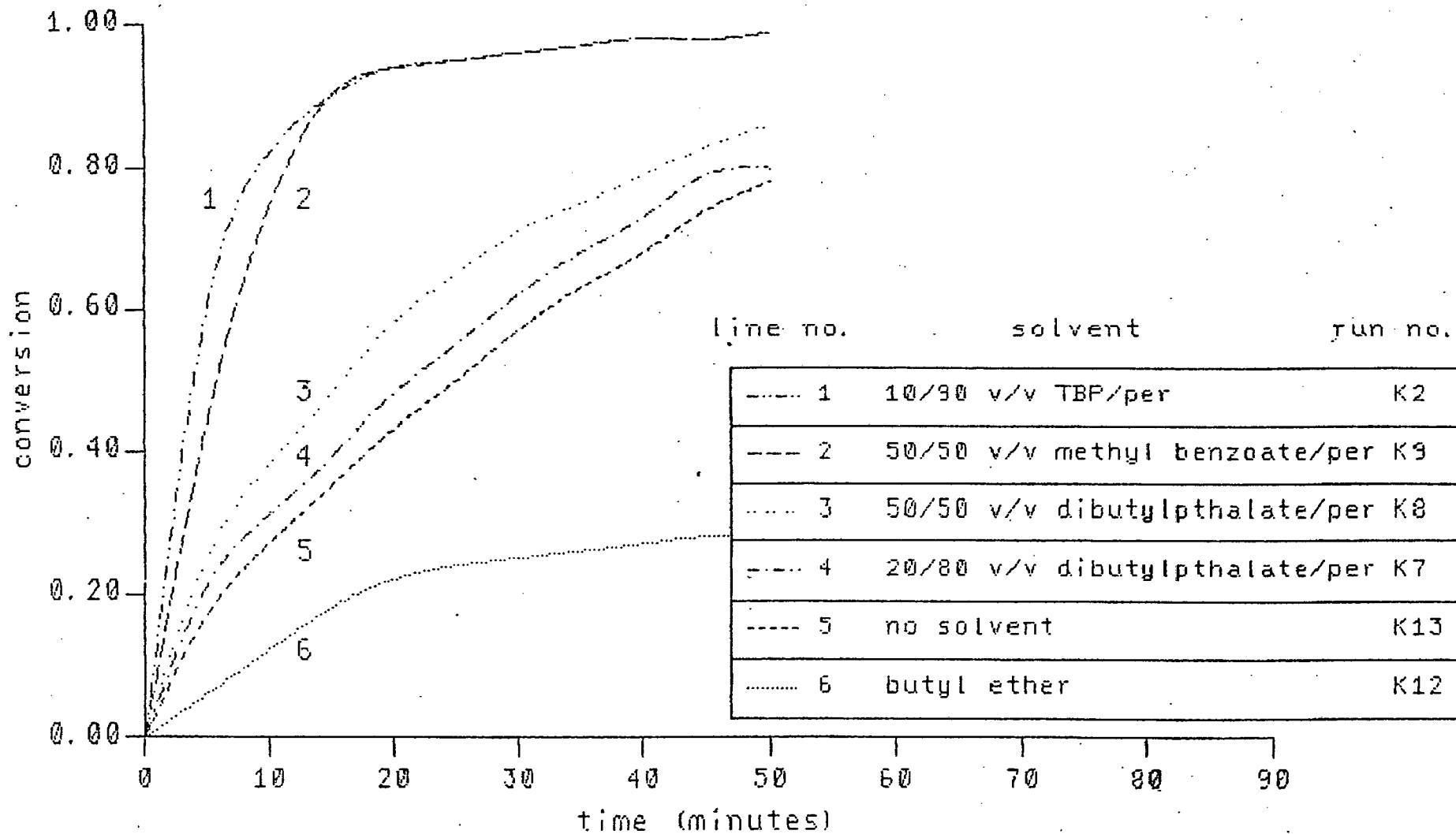


Fig. 6.5 THE EFFECT OF DIFFERENT SOLVENTS

#### 6.4.4.3 The Effect of the Diluent

Three diluents were tried : perchlorethylene, Pegasol 3745 and Pegasol R150. Perchloroethylene is a suitable diluent because it is immiscible in water, has high specific gravity and is non-flammable (4,6). It is reasonably cheap (143) and chemically stable (4). Pegasol 3745 and Pegasol R150 are products recommended by Mobil Oil Southern Africa (Pty) Limited as suitable diluents for TBP (143). Pegasol 3745 is an alipatic kerosene while Pegasol R150 is a highly aromatic solvent. Both have high flash points ( $62^{\circ}\text{C}$ ), are completely immiscible in water and are reasonably cheap (143). Some data on these diluents is shown in Table 5.5.

The effect of varying the diluent is shown in Fig. 6.6. This figure shows the result for the run where the solvent was 10/90 v/v TBP in perchloroethylene, for the run where the solvent was 10/90 v/v TBP in Pegasol 3745 and for the run where no solvent was used. As before, the acid was 1N  $\text{HNO}_3$ , the mol ratio of acid to KDPA was 5 to 1, the ratio of solvent to KDPA was 2ml per gram of KDPA and the experiment was conducted at room temperature.

Fig. 6.6 shows that the kinetics of conversion are somewhat better when perchloroethylene is used as the diluent than when Pegasol 3745 is used. This is probably because KDPA is slightly soluble in perchloroethylene (the solubility is a few mg KDPA per litre of perchloroethylene) whereas it is completely insoluble in Pegasol 3745. (Of course, KDPA is quite soluble in the TBP/diluent mixture - see Section 5.3.3.2 for the experimental investigation of the solubility of KDPA in organic solvents). This might suggest that it would be the better diluent. However it was found that it had a rather high evaporation rate which would mitigate against its use unless the whole system was enclosed.

The rapid evaporation of perchloroethylene was noticed during the kinetic experiments. A simple test was carried out to roughly compare the evaporation rates of the two diluents - perchloroethylene and Pegasol 3745. A small amount of each diluent was placed in separate but identical flat dishes of known area and allowed to stand in a fume cupboard for a couple of days at room temperature. The loss of mass by evaporation for each diluent was measured at the end of this period. The rate of solvent evaporation under these conditions was about  $1200 \text{ g/hr m}^2$  for perchloroethylene and  $10 \text{ g/hr m}^2$  for Pegasol 3745.

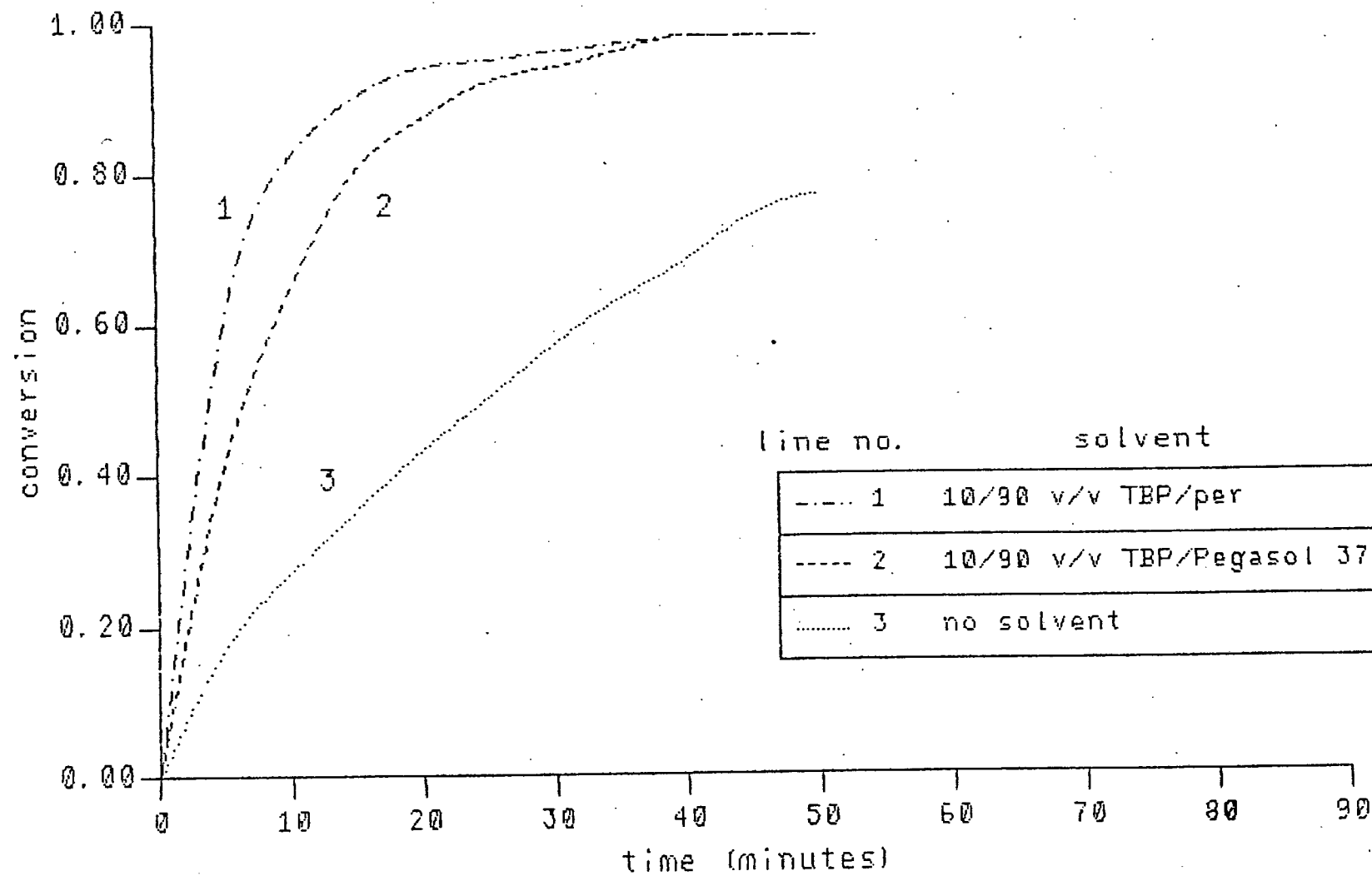


Fig. 6.6 THE EFFECT OF VARYING THE DILUENT

Unfortunately, a sample of the third diluent, Pegasol R150, was only obtained at the end of the experimental program and only one kinetic run was completed using it. Fig. 6.7 shows the results of this run where the solvent was 10/90 v/v TBP in Pegasol R150 and the results of a run where no solvent was used. The other conditions were as for the runs in Fig. 6.6 except that the mol ratio of acid to KDPA was 2 to 1 instead of 5 to 1. The same batch of KDPA was used for both runs in Fig. 6.7 but this was a different sample to that used for the result shown in Fig. 6.6. It appears that Pegasol R150 is also a suitable diluent.

The effect of varying the ratio of TBP to the chosen diluent is shown in Fig. 6.8. In this figure, curves 1 and 2 are very similar indicating that there is little advantage in using a higher ratio than 10 parts TBP to 90 parts Pegasol 3745 by volume. On the other hand, if the ratio is reduced to 5 parts TBP to 95 parts Pegasol 3745, the rate of conversion drops considerably (curve 3 Fig. 6.8). It seems that the mixture 10/90 v/v TBP/Pegasol 3745 is a suitable solvent.

#### 6.3.4.4 The Effect of Solvent to KDPA Ratio

The kinetics of conversion may be affected by the amount of solvent that is added to the reaction mixture. The effect of varying the solvent to KDPA ratio was measured in four kinetic runs. The results of these runs are shown in Fig. 6.9. The solvent was 10/90 v/v TBP in Pegasol 3745. As before, the acid was 1N  $\text{HNO}_3$ , the stoichiometric ratio of acid to KDPA was 5 to 1 and the runs were carried out at room temperature. As expected, the higher the ratio of solvent to KDPA the better the kinetics. It was found that when the solvent to KDPA ratio was low (0,5 ml solvent per gram of KDPA, curve 5, Fig. 6.9) the contents of the reaction flask were difficult to mix effectively. This explains why the kinetics of conversion shown by curve 5 are worse than when no solvent is used. If too little solvent is used, a thick paste forms which cannot be easily mixed with the acid phase.

The same batch of KDPA was used for the runs shown by curves 1 to 5 in Fig. 6.9. If we compare curve 4, Fig. 6.9 to curve 3, Fig. 6.6, both of which show the kinetics of conversion of KDPA in the absence of solvent and under identical conditions, we see the lack of reproducibility mentioned in Sec. 6.3.4.1.

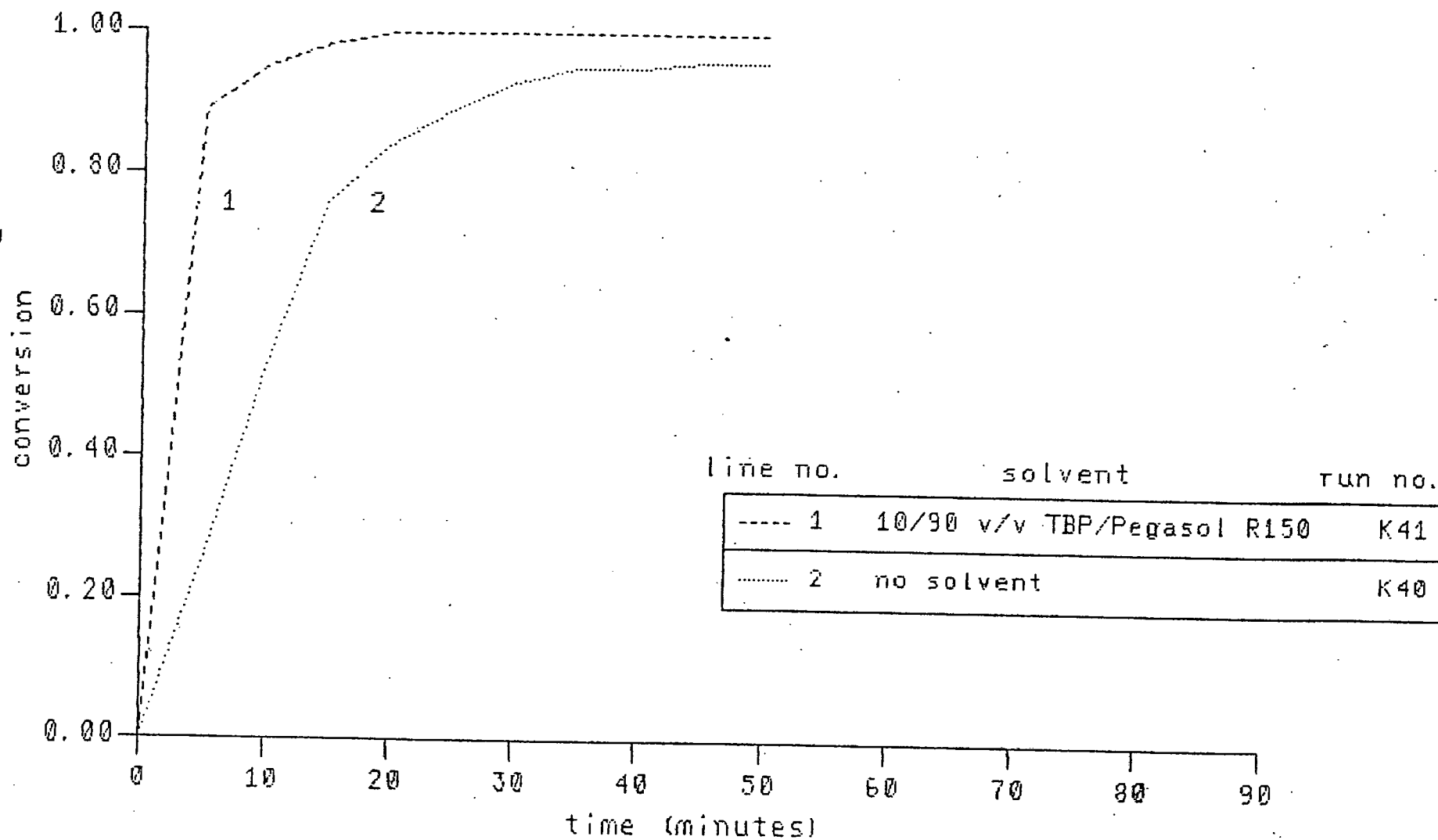


Fig. 6.7 RESULTS WHEN DILUENT IS PEGASOL R150

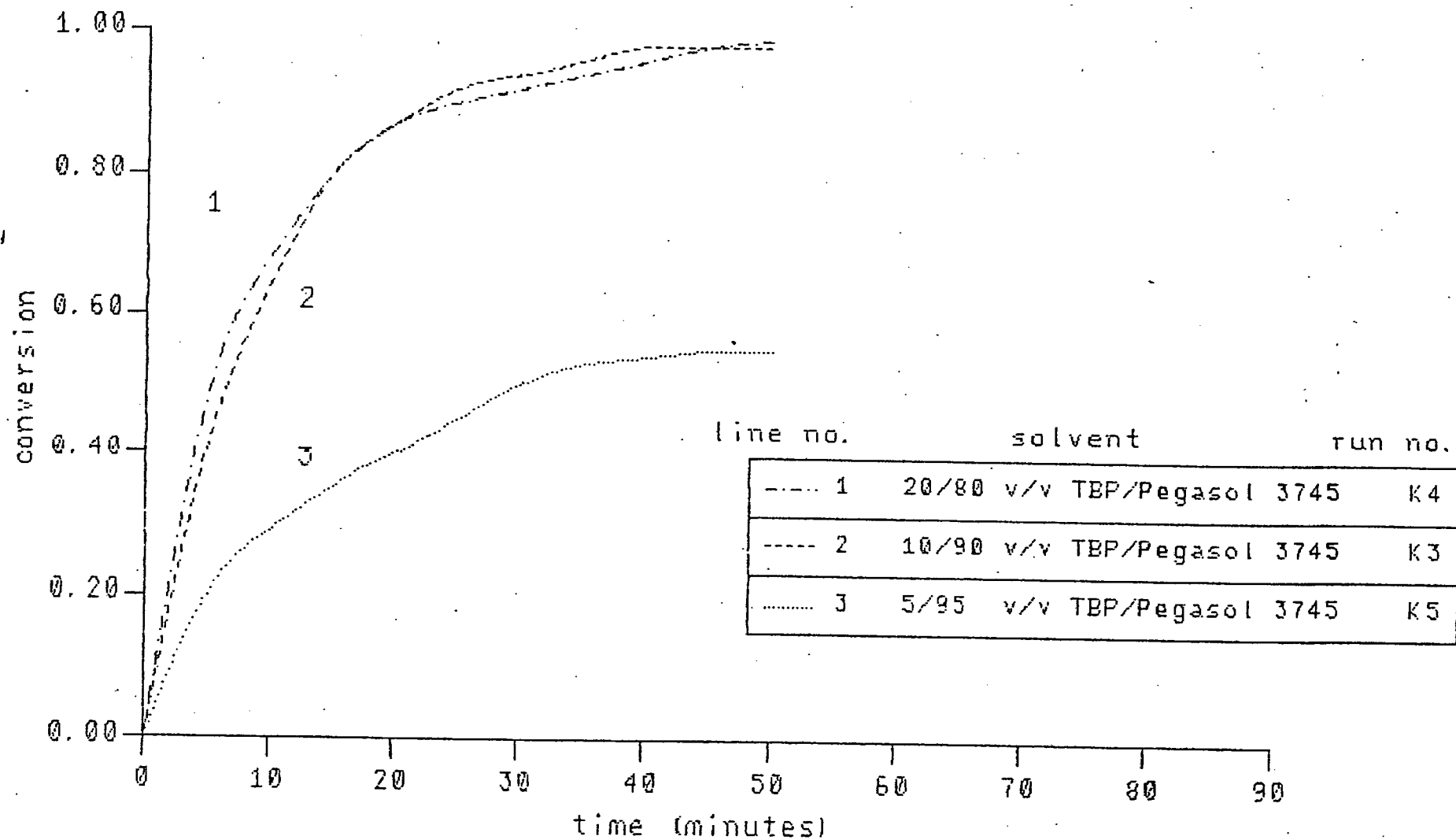


Fig. 6.8 THE EFFECT OF TBP TO DILUENT RATIO

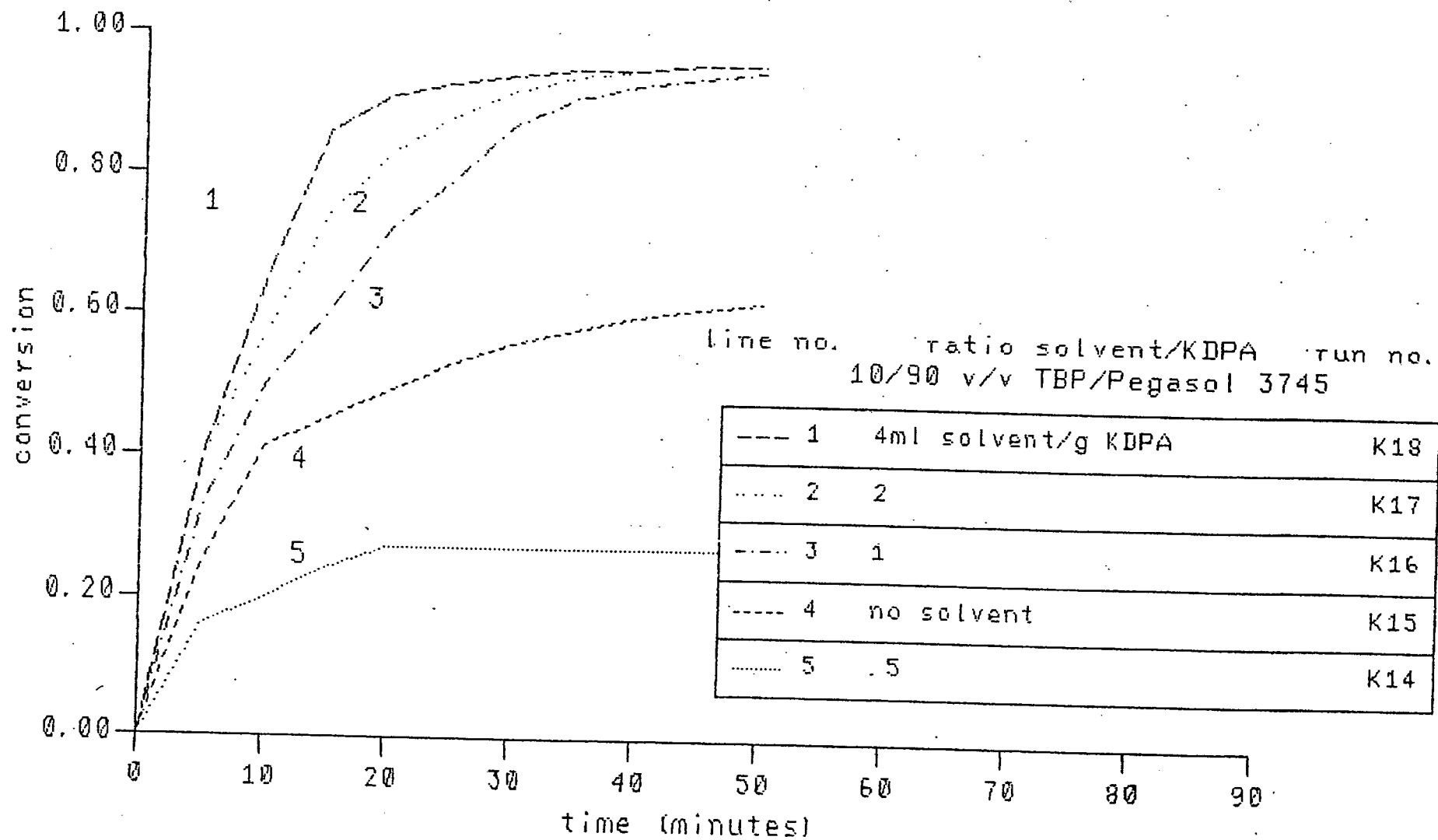


Fig. 6.9 THE EFFECT OF SOLVENT TO KDPA RATIO

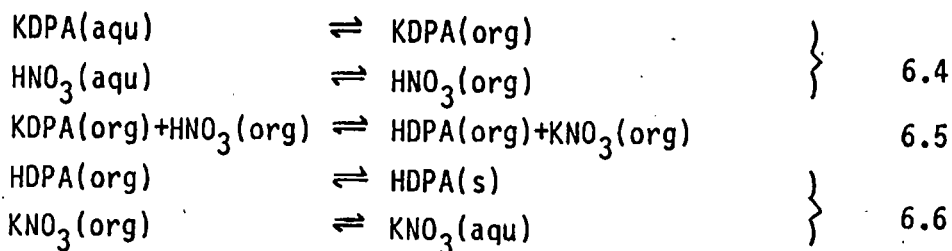
### 6.3.4.5 The Effect of the Acid Concentration

The effect of changing the acid concentration was studied in three runs using nitric acid of different concentration. The results are shown in Fig. 6.10. The acid strengths used were 1N HNO<sub>3</sub>, 2N HNO<sub>3</sub> and 4N HNO<sub>3</sub>. In all three runs the same batch of KDPA was used, the stoichiometric ratio of acid to KDPA was 5 to 1 and the runs were carried out at room temperature. Fig. 6.10 shows that there is little difference in the kinetics when 2N HNO<sub>3</sub> is used in place of 1N HNO<sub>3</sub>. The run using 2N HNO<sub>3</sub> showed slightly faster rate of conversion. However, when 4N HNO<sub>3</sub> is used the speed of conversion drops considerably.

These results are very similar to those given by Bakr and Zatout (109). Their results (see Figs. 6.1, 6.2, 6.3) show that there is little difference between the kinetics of conversion when the acid strength is 1,42N or 2,25N. However, the kinetics of conversion are very much slower (and the conversion does not proceed to completion) when the acid strength is 4,21N.

How can we explain the decrease in the kinetics and the reduction in the final degree of conversion? Firstly, the higher the acid concentration the higher the resulting KNO<sub>3</sub> concentration will be during conversion. What effect does this have?

The conversion reactions can be visualised as follows :



Obviously this is an idealisation of a complex system. However, if this simplification is valid then it is clear that a high concentration of KNO<sub>3</sub>(aqu) in Reaction 6.6 will drive the equilibrium to the left. This in turn will drive Reaction 6.5 to the left.

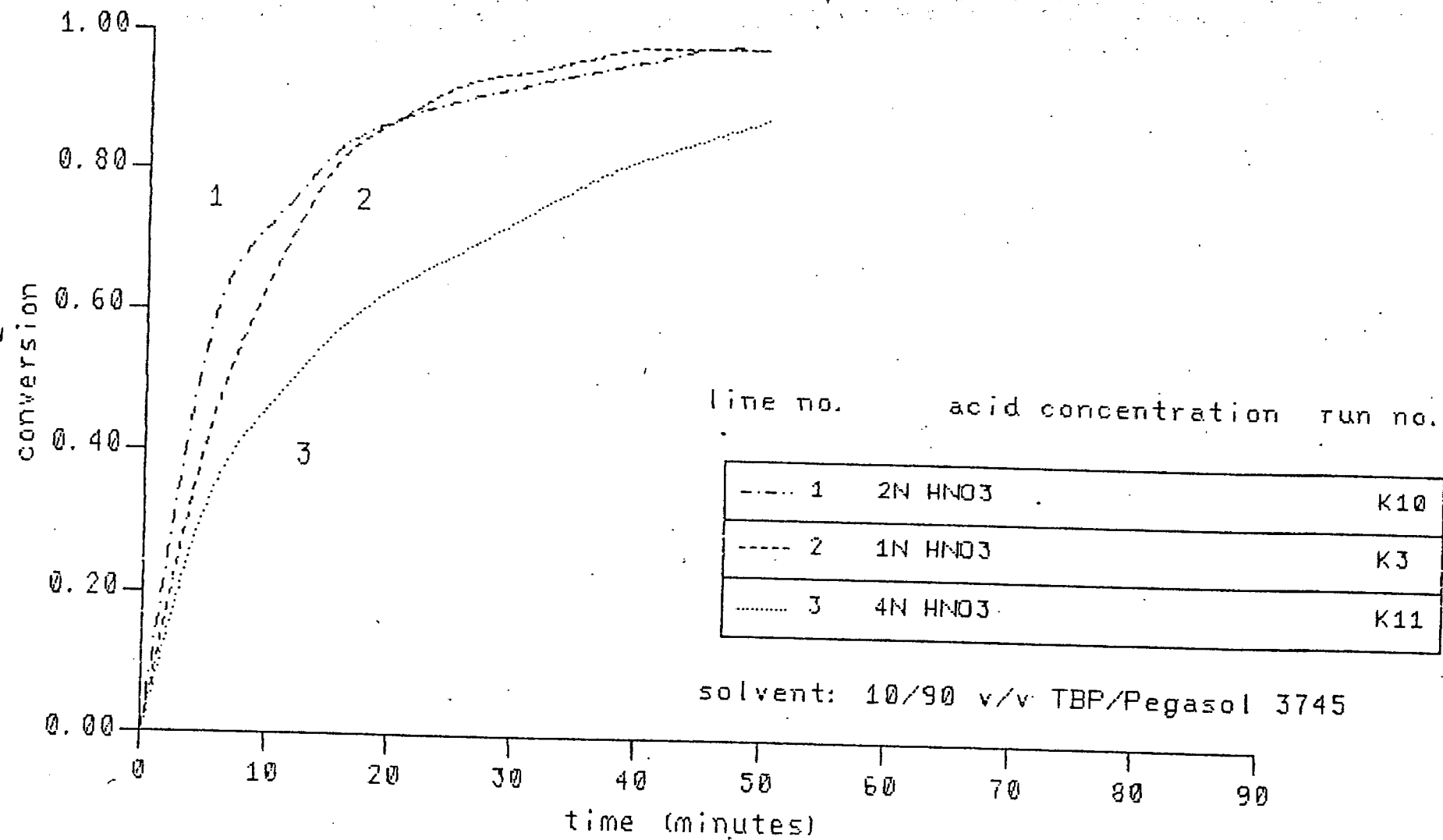


Fig. 6.10 THE EFFECT OF ACID CONCENTRATION

#### 6.3.4.6 The Effect of the Acid to KDPA Ratio

This section discusses the effect of varying the mol ratio of the acid to the KDPA in the conversion reaction. The mol ratio of acid to KDPA in the runs shown in Fig. 6.7 was reduced to 2 to 1. The rate of conversion of the KDPA is not reduced if the acid ratio is reduced. Bakr and Zatout (109) showed that the degree of conversion (as opposed to the kinetics of conversion) is not affected by the mol ratio of acid to KDPA so long as this ratio is above about 1.2 (see Fig. 6.4). In other words, the degree of conversion is not affected so long as there is a 20% or more excess of nitric acid. In the experimental work no attempt was made to find the lower limit for which the kinetics are also not affected.

The reason for this is because in practice it is quite acceptable to use an excess of acid as in the later evaporation and crystallisation step a large excess of acid is used to salt out the  $\text{KNO}_3$  (107).

#### 6.3.4.7 Comparison between KDPA Samples

In Section 4.3 a difference was noted between the KDPA crystals precipitated from seawater and a bittern. KDPA which is precipitated from seawater is a dark red crystalline solid. The KDPA which is precipitated from a bittern is a much finer orange powder.

All the kinetic runs discussed up till now have used KDPA which is precipitated from seawater. The addition of a suitable solvent to the reaction flask results in a clear improvement in the kinetics of reaction. This is not the case with the KDPA from a bittern. The rate of conversion of KDPA precipitated from a bittern is much faster than that of KDPA precipitated from seawater (see the results of runs K20 - K33 in Appendix A4). This is probably due to the relatively smaller size of the KDPA crystals precipitated from a bittern.

It proved impossible to get reproducible data on the effect of adding solvent to the reaction mixture for the conversion of KDPA precipitated from a bittern. In some runs the kinetics were improved on addition of the solvent. In others they were not.

### 6.3.5 Overall Discussion

#### 6.3.5.1 Introduction

In this section an industrial method of adding solvent to the reaction mixture for the conversion of KDPA to HDPA is proposed and possible problem areas evaluated. A flowsheet for the reaction scheme is suggested. The problem of carryover of TBP into the product  $\text{KNO}_3$  stream and the HDPA stream is also discussed.

#### 6.3.5.2 Process Flowsheet

The proposed flowsheet for the KDPA conversion step is shown in Fig. 6.11. The KDPA slurry from the KDPA reactor/settler (see Fig. 3.5) is fed to one or more Acid Reactors (one is shown in Fig. 6.11). This slurry will be a mixture of KDPA and water. Nitric acid is also added to the reactor (both acid recycled from the evaporation and crystallisation stage as well as fresh makeup acid). The concentration of this acid should be about 2N and the mol ratio of acid to KDPA should be about 2 to 1. Solvent should be added to the reactor at a ratio of 2 litres of solvent per kg of KDPA (wet) fed to the reactor. The residence time in the reactor, or reactors in series, is chosen so that the degree of conversion is high - say 97%. The rest of the KDPA is converted by second step (discussed below in Section 6.5.3). The mixture of solid HDPA, unconverted KDPA solvent and aqueous solution is fed to a vacuum filter where the solid is filtered off. This solid (HDPA and unconverted KDPA), is sent to the Lime Reactor. The liquid phases (organic and aqueous), are separated in the Settler. The organic phase is recycled to the reactor while the aqueous phase, containing  $\text{KNO}_3$  and excess  $\text{HNO}_3$ , is sent to the KDPA scavenge stage (see Fig. 3.5) where traces of dipicrylamine are removed from the solution. Then the aqueous phase is sent to the evaporation and crystallisation stage where the  $\text{KNO}_3$  is obtained as a solid by the usual process of salting out with nitric acid (107). The nitric acid used in this salting out process is recycled for use in the Acid Reactor.

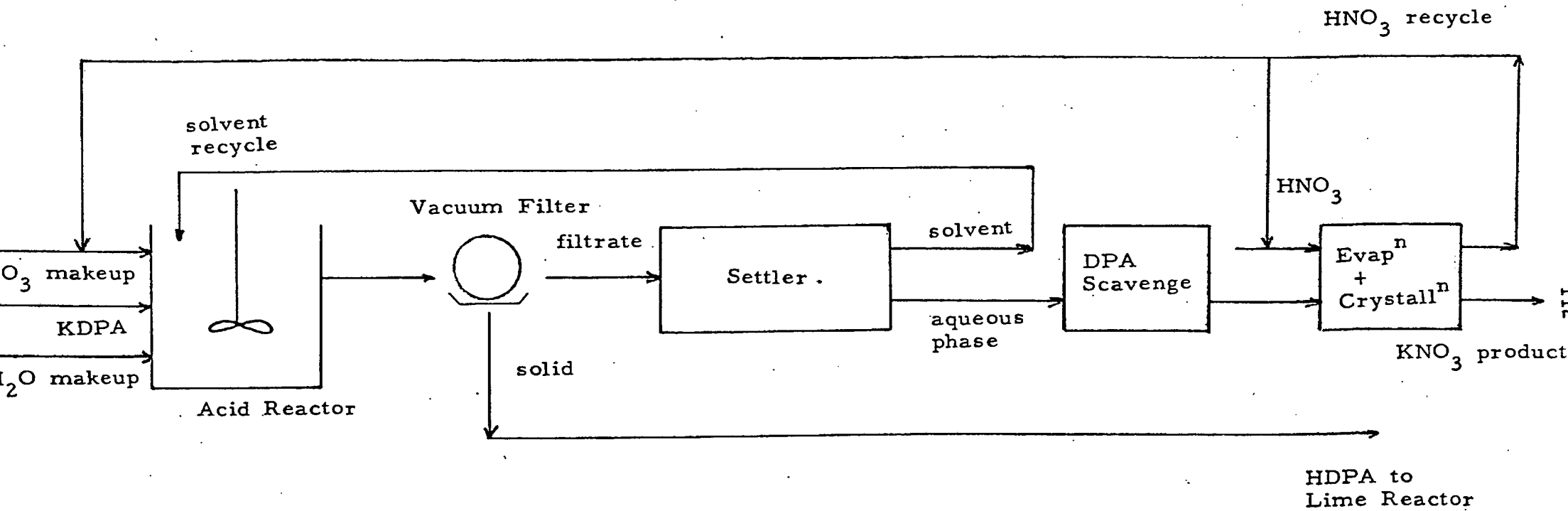


Fig. 6.11 The Application of the TBP Solvent Method

### 6.3.5.3 Unconverted KDPA

Unless the residence time in the Acid Reactor is long, some KDPA will leave this reactor unconverted. This can be recovered and recycled using one of the methods suggested in the literature (See Section 6.2.1.6).

### 6.3.5.4 Carryover of TBP with the $\text{KNO}_3$ Phase

It is to be expected that some TBP will dissolve in the aqueous  $\text{KNO}_3/\text{HNO}_3$  solution leaving the Settler in Fig. 6.11. However, according to Alcock et al (142) the solubility of TBP in nitric acid solution is less than the corresponding solubility of TBP in pure aqueous solution. Thus the concentration of TBP in the  $\text{KNO}_3/\text{HNO}_3$  will be less than 10 mg/l. Because of its low solubility, the amount of diluent in this stream will also be very low. If polyurethane foam is used in the DPA scavenger (see Fig. 3.5) then some TBP and diluent will be carried into the evaporation and crystallisation stage since polyurethane foam does not absorb these compounds. From here it will be recycled with the excess acid (recycle shown in Fig. 6.11).

### 6.3.5.5 Carryover of TBP with the solid HDPA

The solid HDPA which is removed on the vacuum filter shown in Fig. 6.11 will have some TBP/diluent solvent adhering to it. This solvent is carried with the HDPA into the Lime Reactor. If the diluent is Pegasol 3745 or Pegasol R150 the solvent is less dense than water and it can be recovered from the  $\text{Ca}(\text{DPA})_2$  solution produced by the Lime Reactor by removing it from the surface of this solution. In the experimental work it was found that the amount of solvent carried over was very small and appeared as a very thin oily layer on the surface of the  $\text{Ca}(\text{DPA})_2$  solution.

TBP is stable in the presence of a base and the high pH in the Lime Reactor will not hydrolyse it (146). If the Liquid Extraction process described in Sec. 5.3.3 is used for the recovery of dipicrylamine from the spent seawater the  $\text{Ca}(\text{DPA})_2$  solution can simply be recycled to the KDPA reactor/settler without first separating the TBP/diluent solvent from it. This solvent will be recovered in the Liquid Extraction process downstream.

### 6.3.7 Conclusion of the Experimental Work

The addition of a solvent consisting of tributylphosphate (TBP) and a diluent to the reaction mixture for the conversion of KDPA to HDPA results in improved rates of reaction when the size of the KDPA crystals are relatively large such as for KDPA precipitated from seawater (when the solvent is added a close approach to equilibrium is achieved in about one third of the time required when no solvent is used). Suitable diluents for the TBP are chlorinated hydrocarbons or kerosenes such as, for instance, perchloroethylene or Pegasol 3745 or Pegasol R150. Chlorinated hydrocarbons have the disadvantage that they are volatile and toxic by inhalation (61).

The composition of the solvent can be varied but a 10/90 v/v mixture of TBP and diluent is most suitable. The higher the content of TBP the more rapid the rate of conversion. However, the higher the content of TBP in the solvent the more expensive the solvent becomes since TBP is expensive while the diluents are cheap (143).

The rate of reaction increases as the amount of solvent added to the reaction mixture is increased. A practical amount of solvent to use is about 2 litres of solvent per kg of KDPA in the reactor.

The addition of solvent to a reaction mixture for the conversion of KDPA precipitated from a bittern does not always result in improved kinetics. The kinetics appear to depend on crystal size. If conditions in the KDPA reactor/settler are such that larger crystals are produced the addition of solvent may be useful.

Other solvents, such as methylbenzoate and dibutylphthalate, also improve the kinetics of conversion. However, they are less stable than TBP and are, being esters, subject to hydrolysis by acids and bases (145). Methyl benzoate works quite well but is unfortunately expensive (143).

## 7. THE CONVERSION OF HDPA

### 7.1 Introduction

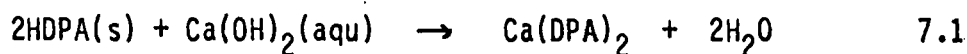
Dipicrylamine, after conversion to HDPA by one of the methods described in Chapter 6, must be converted to a soluble form so that it can be recycled to the KDPA reactor/settler. This is done by reacting the HDPA with a base.

Four bases can be used in this reaction; calcium hydroxide, magnesium hydroxide, sodium hydroxide or sodium carbonate (109). The use of the first two is discussed in the literature. The use of calcium hydroxide was further investigated in the experimental work.

### 7.2 Literature Survey

#### 7.2.1 Calcium Hydroxide

Lime is the most commonly suggested base in the literature. Kielland (107) gives a detailed flowsheet for the reaction of HDPA with lime. The reaction is :



Solutions containing up to 20% m/v  $\text{Ca}(\text{DPA})_2$  can be produced by this reaction. According to a Japanese patent (89) the reaction can be carried out using seawater as medium. This is a useful property because it dramatically reduces the quantity of freshwater required by the process. The method is as follows (102) ; 100 kg of  $\text{Ca}(\text{OH})_2$  and 1080 kg of dipicrylamine (HDPA) is added to 24 m<sup>3</sup> of seawater at 25°C. The mixture is agitated and filtered to give a solution of  $\text{Ca}(\text{DPA})_2$  in seawater. The kinetics of the reaction of HDPA with lime are not studied in detail in the literature.

#### 7.2.2 Magnesium Hydroxide

Bakr and Zatout (109) studied the use of magnesia ( $\text{Mg}(\text{OH})_2$ ) for the conversion of HDPA to  $\text{Mg}(\text{DPA})_2$  in a reaction analagous to Reaction 7.1. They found that the reaction was very slow. Figure 7.1 shows their results for the reaction of HDPA with a stoichiometric quantity of magnesia at 25°C. A conversion of 80% of the HDPA is attained after five hours of reaction.

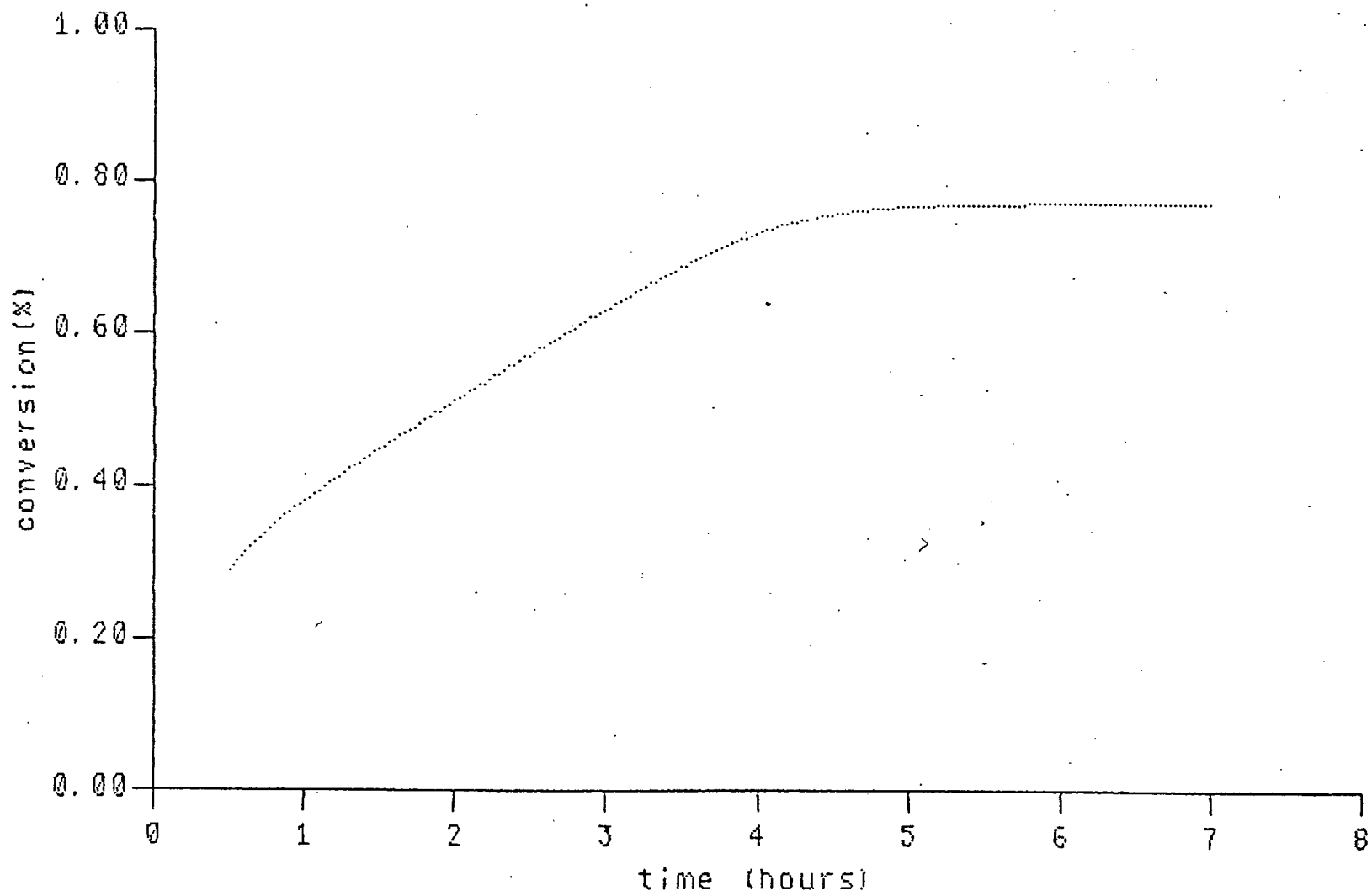


Fig. 7.1 The Kinetics of Conversion of HDPA by Magnesia

### 7.2.3 Conclusion of the Literature Survey

Lime is the most commonly suggested base for the conversion of HDPa to a soluble form. The reaction can be carried out in seawater and this will significantly reduce the freshwater requirement of the process. The kinetics of the reaction and the optimum concentration of the  $\text{Ca(DPA)}_2$  reagent produced by the reaction is not discussed in the literature.

The use of magnesia to convert HDPa would be impractical in industry as the reaction is very slow.

### 7.3 Experimental

#### 7.3.1 Overall Objective

The overall objective of the experimental work was to examine the conversion of HDPa to a soluble form from the point of view of the industrial application of this process. Thus an indication of the kinetics of the reaction was sought together with an estimate of what concentration of dipicrylamine in solution was attainable by this reaction.

#### 7.3.2 The Kinetics of the Reaction of HDPa with Calcium Hydroxide.

##### AIM:

The aim of the experimental work was to obtain an indication of the rate of reaction of calcium hydroxide with HDPa. A rigorous study of the reaction kinetics was not attempted.

##### METHOD:

A sample of HDPa was dried at 60°C for three hours. A mass of 2.3g of this HDPa was weighed into a 250ml beaker containing 100 ml of distilled water. The beaker was placed in a water bath at 25°C and the contents well stirred. The pH of the contents of the beaker was continuously monitored. The mass of 0,05g Ca(OH)<sub>2</sub> (A.R. grade) was added and the change in pH vs time noted. After about twenty minutes a further mass of Ca(OH)<sub>2</sub> was added and the pH monitored. This process was repeated a third time.

The experiment was repeated using 100 ml of spent seawater in place of distilled water.

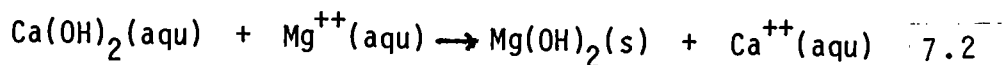
##### RESULTS:

When distilled water was used as medium the pH dropped from a value of about 11 immediately after addition of the calcium hydroxide to a final value of about 9 in less than ten minutes.

When seawater was used as a medium the reaction was very slow if carried out at 25°C. If the temperature was raised to 35°C then the reaction proceeded at a similar rate to that found when distilled water was used.

## DISCUSSION:

If seawater is used instead of distilled water, the rate of reaction drops considerably. This is probably because some of the magnesium in the seawater precipitates as  $Mg(OH)_2$ . The reaction is :



This  $Mg(OH)_2$  then reacts with the HDPa. It is clear from the work of Bakr and Zatout (109), described in Section 7.2.2, that this reaction is slow.

### 7.3.3 The Concentration of the Reagent Solution

#### AIM:

To investigate the maximum concentration of  $Ca(DPA)_2$  in seawater attainable by Reaction 7.1 without encountering two phase behaviour.

#### METHOD:

A sample of 50g of HDPa, dried for three hours at  $60^{\circ}C$ , was added to 375 ml of seawater in a 500 ml beaker. A mass of 4.2 g of  $Ca(OH)_2$  was added and the contents of the beaker were stirred at  $35^{\circ}C$ . After stirring for an hour the solution was filtered to remove solid impurities.

#### RESULTS:

The filtered solution separated on standing into two phases : an upper phase of concentration 0,12N  $Ca(DPA)_2$  and a lower phase of 1,1 N  $Ca(DPA)_2$ . The volume of the lower phase was about one fifth of the upper phase. The sodium concentration in the upper phase was about 12500 mg Na/l and in the lower phase about 8500 mg Na/l. The phases were separated and allowed to stand overnight whereupon 12.2g and 7.8g of solid precipitated from the upper and lower phase respectively. On analysis it was found that this solid was almost entirely NaDPA.

#### DISCUSSION:

The reason for this two phase phenomenon is not clear. It may be due to a relatively low solubility of NaDPA compared to  $Ca(DPA)_2$ . However, Kielland (44) found this phase phenomenon on the addition of  $Ca(DPA)_2$  to solution of  $CaCl_2$ . He could not explain this behaviour.

The experiment described above was repeated with different masses of HDPa (and corresponding masses of  $\text{Ca}(\text{OH})_2$ ) and it was found that if the final solution concentration was less than about 110g  $\text{Ca}(\text{DPA})_2/\text{l}$  then the two phase behaviour did not occur.

#### 7.3.4

#### Conclusion of the Experimental Work

Calcium hydroxide should be used for the conversion of dipicrylamine (HDPa) to a soluble form. This reagent is available cheaply in the form of lime. The reaction can be carried out in seawater and, if the temperature of reaction is  $35^\circ\text{C}$ , the reaction proceeds relatively fast compared to the rate of reaction found when magnesium hydroxide is used. About thirty minutes is required for the complete reaction of HDPa with a stoichiometric quantity of  $\text{Ca}(\text{OH})_2$  to produce a solution containing 10% m/v  $\text{Ca}(\text{DPA})_2$ .

## 8. TECHNICAL AND ECONOMIC EVALUATION OF THE DIPCRYLAMINE PROCESS

### 8.1 Introduction

This section gives a preliminary design and economic evaluation of the dipicrylamine process for the recovery of potassium from seawater and bitterns. The most important process flowrates were calculated for a plant which produces 100 tons/day of  $\text{KNO}_3$  from seawater and bittern. These flowrates were used to calculate the size of the major items of equipment. These items were then costed to give an estimate of the capital investment. Major items of the variable costs were also calculated.

### 8.2 Process Design

#### 8.2.1 Process flowrates

The major process flowrates for a plant producing 100 tons  $\text{KNO}_3$ /day from seawater and a bittern are summarised in Tables 8.1 and 8.2 respectively. The detailed calculations are given in Appendix A5.1. The flowsheets for the seawater and bittern process are shown in Figs. 8.1 and 8.2 respectively. These flowsheets are based on those given in the literature (103, 107) with several modifications prompted by the literature survey and the experimental work. For instance, it was assumed that an extraction process (using polyurethane foam or liquid extraction) would be used to recover the dipicrylamine from the spent seawater or bittern. Also, the use of reverse osmosis was assumed for the recovery and recycle of wash water.

TABLE 8.1 : FLOWRATES FOR A PLANT PRODUCING 100 TONS KNO<sub>3</sub>/DAY FROM SEAWATER

<u>STREAM</u>		<u>FLOWRATE</u>
Seawater	:	5 300 m <sup>3</sup> /hr
Reagent	: (10% m/v Ca(DPA) <sub>2</sub> )	212 m <sup>3</sup> /hr
Acid	: (70% HNO <sub>3</sub> )	3 710 kg/hr
Lime	:	1 810 kg/hr
Water	:	
Wash of KDPA	4,9	
Acid Reactor	2,0	
Foam or Solvent		
Regeneration	<u>26,0</u>	32,9 m <sup>3</sup> /hr
Solid Waste	:	250 kg/hr
Dipicrylamine loss	:	5,3 kg/hr
KNO <sub>3</sub>		4 167 kg/hr

TABLE 8.2 : FLOWRATES FOR A PLANT PRODUCING 100 TONS KNO<sub>3</sub>/DAY FROM A BITTERN

<u>STREAM</u>		<u>FLOWRATE</u>
Bittern	: (10kg K/m <sup>3</sup> )	179 m <sup>3</sup> /hr
Reagent	: (10% m/v Ca(DPA) <sub>2</sub> )	212 m <sup>3</sup> /hr
Acid	: (70% HNO <sub>3</sub> )	3 710 kg/hr
Lime	:	1 810 kg/hr
Water:		
Wash of KDPA	5.9	
Acid Reactor	<u>2.0</u>	7,9 m <sup>3</sup> /hr
Seawater	:	
Wash of KDPA	177	
Makeup Lime Reactor	<u>14</u>	191 m <sup>3</sup> /hr
Solid Waste	:	
Unreacted Lime		
and solids	250	
CaSO <sub>4</sub>	<u>3 160</u>	3 410 kg/hr
Dipicrylamine loss		Negl.
KNO <sub>3</sub>		4 167 kg/hr

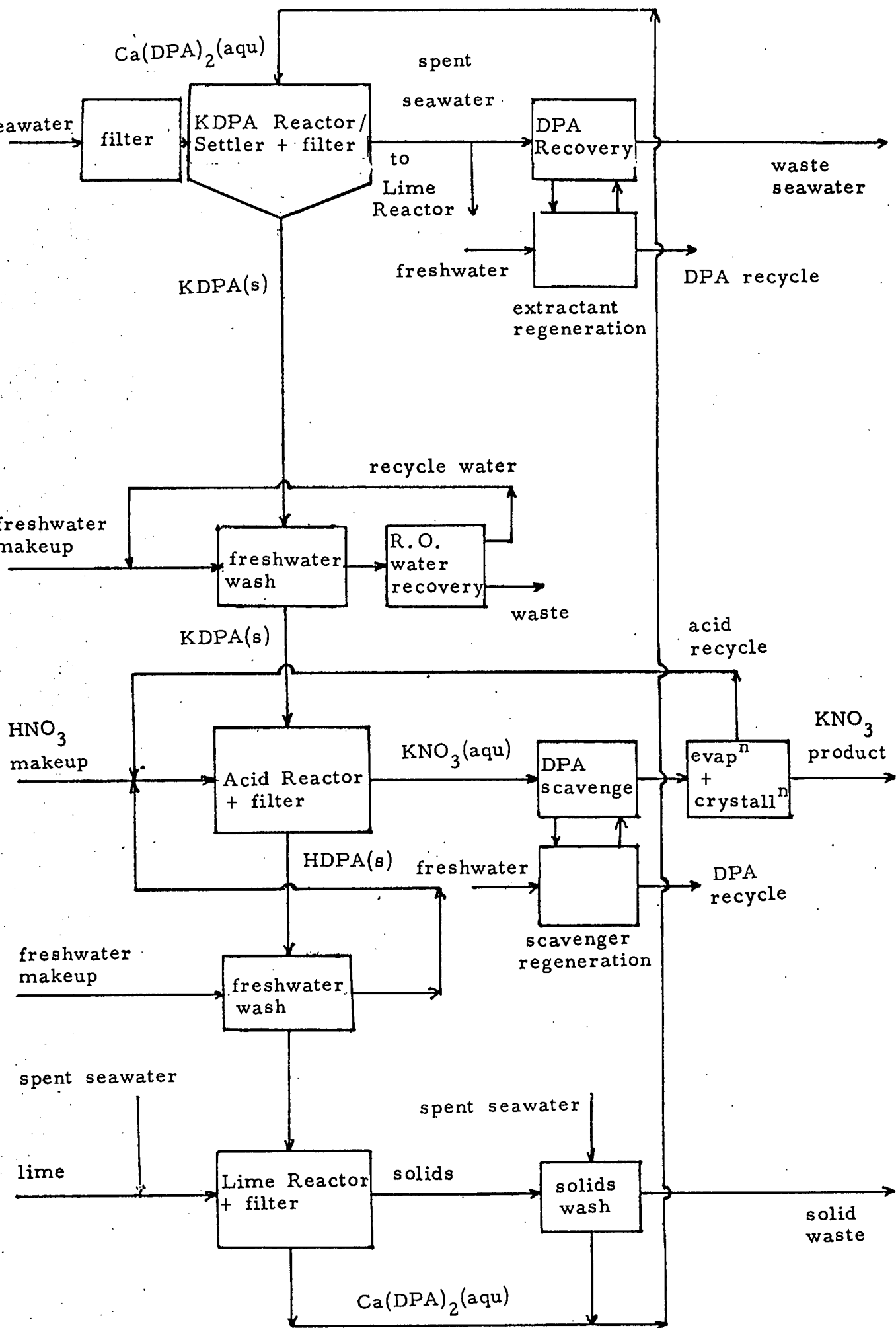


Fig. 8.1 Flowsheet for the Seawater Process

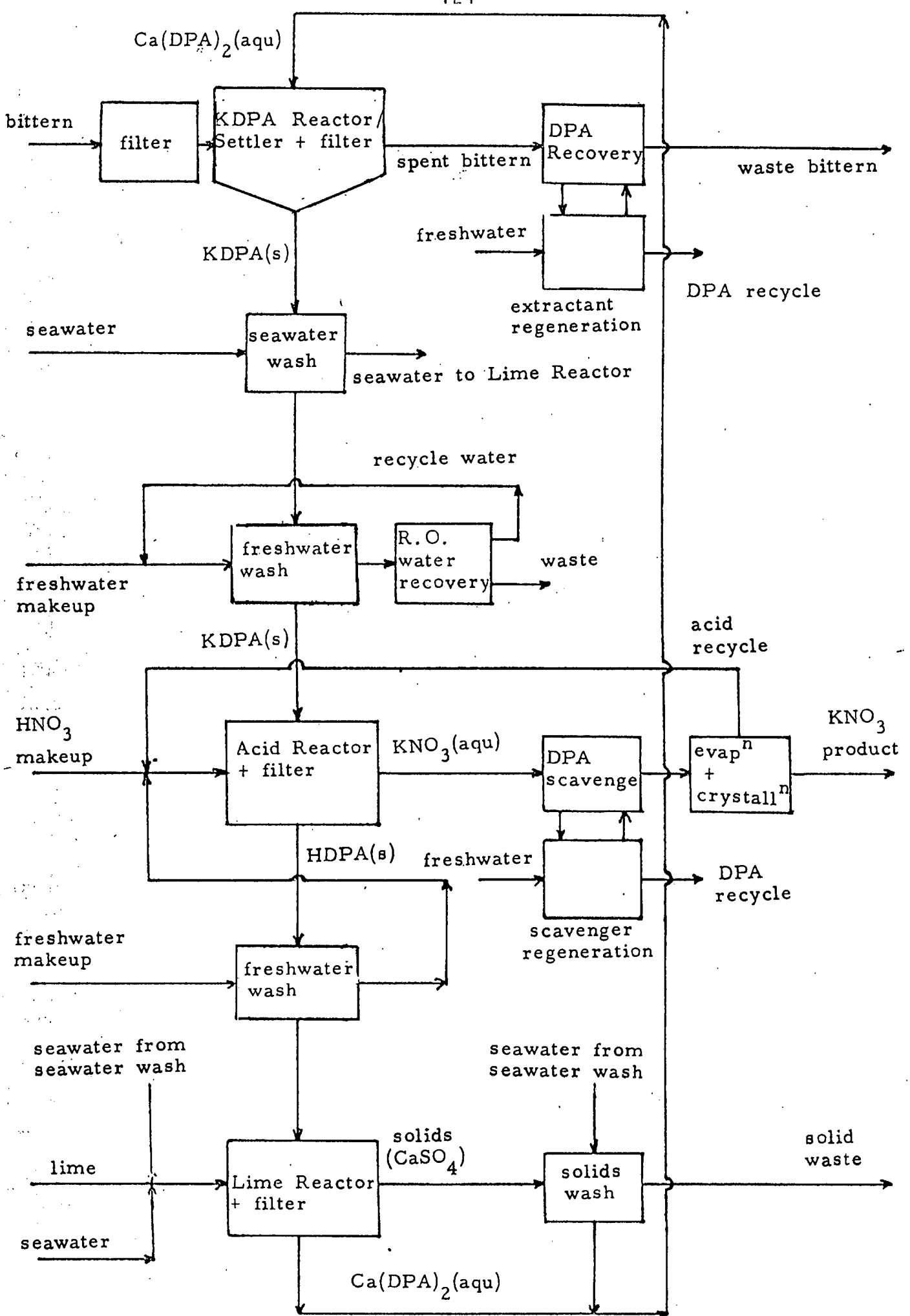


Fig. 8.2 Flowsheet for the Bittern Process

### 8.2.2 Equipment Sizing

The size and cost of the major items of equipment for the seawater process are given in Appendix A5.2.1 and summarised in Table A5.1. Similarly, for the bittern process, the size and cost calculations are given in Appendix A5.2.2 and summarised in Table A5.2. The calculations were simple and did not involve any difficulties with the exception of the sizing of the equipment for the recovery of dipicrylamine from the spent seawater. In view of the limited information available on this step, the equipment sizing must be seen as a rough estimate.

### 8.2.3 Energy Consumption

The electricity consumption of each of the major items of equipment in the seawater and bittern process is also given in Appendix A5 Tables A5.1 and A5.2.

The steam usage is calculated in Appendix A5.3. The major usage of steam is for the evaporator/crystalliser.

## 8.3 Economic Analysis

### 8.3.1 Total Fixed Capital Cost

This was calculated for the seawater and bittern process using the Lang Factor (151) which gives an order of magnitude estimate (see Appendix A5.2.1.4 and A5.2.2.3). For the seawater process the capital cost is R7,0 x 10<sup>6</sup> and, for the bittern process, R3,6 x 10<sup>6</sup>. The estimate was made using equipment prices valid in 1983.

The estimation of the capital cost of the seawater process is particularly difficult as one of the major items, the equipment for the recovery of dipicrylamine from the spent seawater, cannot be accurately designed. Only tentative solutions have been proposed for the problem of recovering this dipicrylamine.

### 8.3.2 Product Prices and Raw Material Costs

The prices of various potassium salts and some of the raw materials used in the process are shown in Table 8.3.

TABLE 8.3 : PRODUCT PRICES AND REAGENT COSTS (147 - 149)

	<u>R/Ton Cape Town</u>
Potassium Nitrate	614
Potassium Chloride	297
Potassium Sulphate	465
Nitric Acid (55%)	387
Lime	75

From Table 8.3 it is clear that potassium nitrate is the most valuable of the potassium salts. The cost of lime is largely dependent on railage charges (148). The relative price of nitric acid and potassium nitrate varies with the exchange rate as the latter is, at present, an imported product (147).

### 8.3.3 Net Present Value Calculation

One of the most common methods used to estimate the profitability of a process is to calculate the net present value of cash flows it generates over the life of the plant.

It was quickly found that the profitability of the seawater or bittern process depends on the relative price of potassium nitrate and nitric acid. Clearly if nitric acid is much more expensive than potassium nitrate the process cannot be economical. Accordingly, the net present value analysis was carried out for a number of cases with differing nitric acid and potassium nitrate prices.

A number of assumptions had to be made for the purpose of the calculation. These are tabulated in Appendix A5.4.

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The change in net present value with the change in the differential between the potassium nitrate and nitric acid price is shown in Figure 8.3. The nitric acid price used here is for hypothetical 100% nitric acid. This acid is available at a concentration range of 55 - 70% m/v commercially. Thus for 55%  $\text{HNO}_3$  costing R387/ton the cost per ton of '100%'  $\text{HNO}_3$  is equivalent to R704/ton. The assumed discount rate was 25%. Other assumptions and a simple calculation are given in Appendix A5.3. This figure shows that, when the potassium nitrate price is R600/ton the bittern process is profitable when the nitric acid price is R725/ton or less. By contrast, for the same potassium nitrate price, the seawater process is only profitable if the cost of nitric acid is less than R570/ton.

The accuracy of this analysis is, of course, limited in view of the margin of error in the estimation of the costs. However, it does serve to compare the relative potential for profitability of the seawater and the bittern process. It is clear that the bittern process has a far better chance of being an economic proposition than the seawater process.

Several factors (which could greatly influence the profitability of the process) have not been considered in this analysis. For instance, it was assumed that the nitric acid would be purchased commercially. It is probably more realistic to assume that the plant would be integrated with an existing or planned nitric acid factory in which case the nitric acid cost would be the incremental cost of production. This should be substantially lower than the commercial price. Secondly, the benefits to be gained from taking advantage of the Government's decentralisation incentives have not been assessed. These could be substantial.

#### 8.4 Conclusion

The preliminary design and sizing of a process for the recovery of potassium from seawater or a bittern is possible using information obtained from the literature and the experimental work. However, for the seawater process, the sizing of the equipment for the recovery of dipicrylamine from the spent seawater was difficult in view of the limited information available on this step.

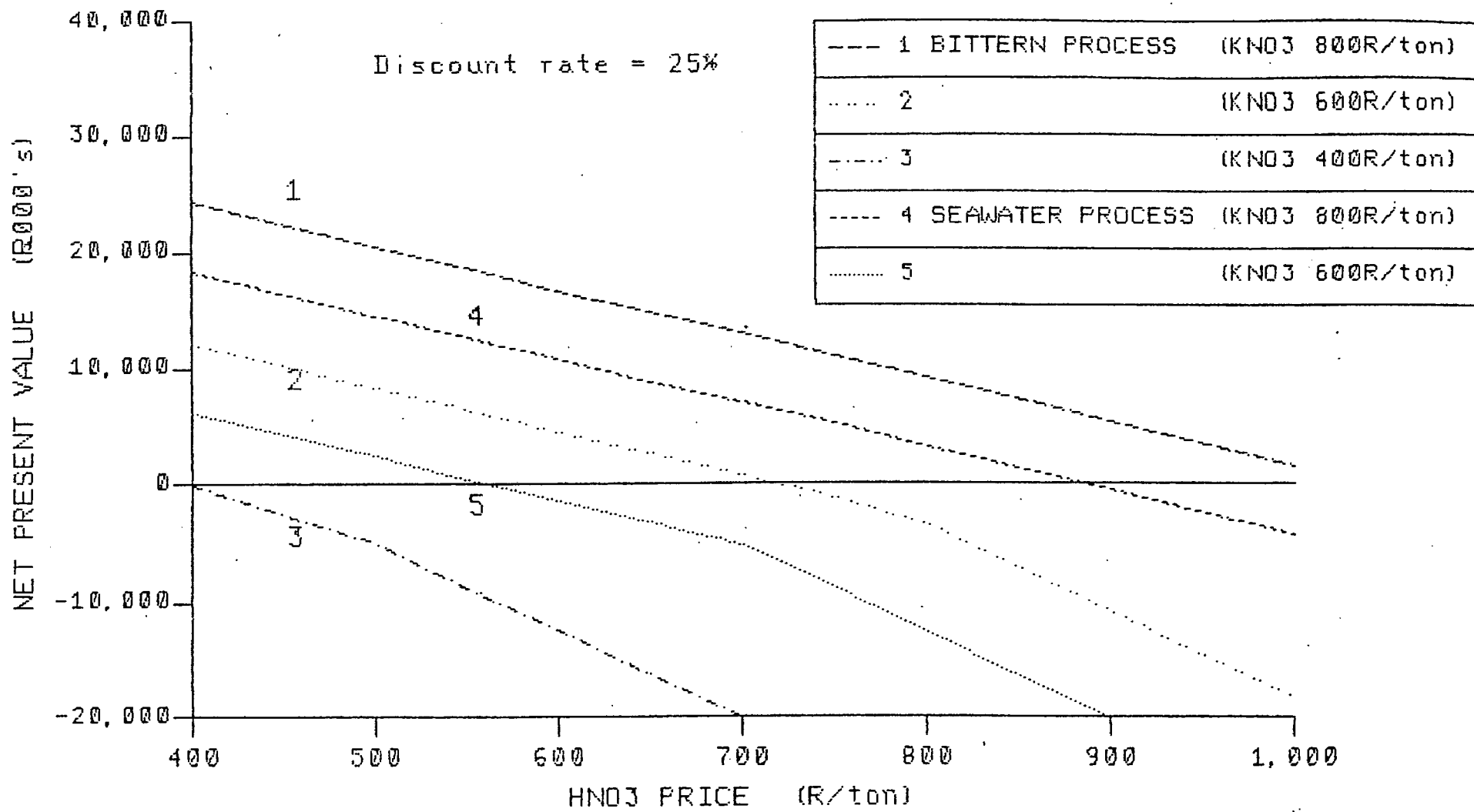


FIG. 8.3 NET PRESENT VALUE CALCULATION

The order of magnitude estimated for the capital cost of a process to produce 100 tons/day of potassium nitrate from seawater or bitterns is  $R7 \times 10^6$  and  $R3,6 \times 10^6$ , respectively.

A net present value analysis reveals that the bittern process has a far better chance of being an economical proposition than the seawater process. Indeed, this analysis shows that the bittern process is profitable with current potassium nitrate and nitric acid prices. To estimate the economic viability of this process one should include the possibility that nitric acid can be obtained at incremental production cost from an existing nitric acid factory. In addition, the impact of the Government's decentralisation incentives should be assessed.

C O N C L U S I O N S

A number of processes have been suggested for the recovery of potassium from seawater and brines. The process using dipicrylamine for the selective precipitation of potassium (as KDPA) from solution appears to offer a number of advantages, namely, that it is possible to produce a variety of potassium salts in high purity and high yield. This process is one of the few that can extract potassium efficiently from a potassium source as dilute as seawater.

The yield or fractional recovery of potassium from both seawater and bitterns has been well studied in the literature. However, other aspects which are important from the point of view of industrial design, namely the settling characteristics of KDPA and the washing of this solid have not been studied. These aspects were investigated in the experimental work and data was obtained which allows the preliminary design of a KDPA reactor/settler.

The seawater or bittern leaving the KDPA precipitation step contains some dissolved dipicrylamine. This should be recovered as the reagent is both toxic and expensive. This is particularly difficult in the process where potassium is recovered from seawater because of the high flowrates encountered when this dilute potassium source is exploited. The method most commonly suggested in the literature, namely precipitation of HDPA by acidification of the seawater is not practicable because of the difficulty of filtering the very fine HDPA flocc. An alternative method, the use of polyurethane foam, is suggested in the literature. The experimental work on the use of foam indicates that this is a much better method. It should be used to recover the dipicrylamine from the spent bittern. However, its use in the seawater process may be impractical in view of the large residence times required and the high flowrates in this process. The experimental work indicates that liquid extraction (a method not suggested in the literature) could be used to recover dipicrylamine from the spent seawater. This method is faster than the use of foam but the loss of solvent in the waste seawater will have to be minimised.

Several methods are suggested in the literature for the production of a potassium salt by the conversion of KDPA and the recycling of the reagent. The most commonly suggested method is to react the KDPA with an acid to produce the potassium salt of the acid and NDPA. However, the kinetics of this reaction are slow and an alternative reaction scheme, where the KDPA is reacted with an acid in the presence of an immiscible organic solvent, was investigated in the experimental work. This method results in improved kinetics for the conversion of the KDPA.

The HDPA produced after the conversion of the KDPA should be reacted with lime using seawater as the medium. To achieve reasonable rates of conversion (residence time about half an hour) the reaction should be carried out at 35°C. The maximum attainable reagent concentration using this method is 10% m/v  $\text{Ca}(\text{DPA})_2$ .

The information obtained from the literature survey and the experimental work can be used for the preliminary design and costing of a seawater or bittern process. The order of magnitude estimate for the capital cost of a seawater process producing 100 tons  $\text{KNO}_3$ /day is  $\text{R}7,0 \times 10^6$  while that for an equivalent bittern process is  $\text{R}3,6 \times 10^6$ . A net present value analysis of the processes indicated that the bittern process is more likely to be profitable than the seawater process. Indeed the bittern process would appear to be profitable at the current price of nitric acid and potassium nitrate.

It is concluded that the process for the recovery of potassium from a bittern and other potassium rich brines is certainly technically feasible and may be economically viable as well. The seawater process does not appear to have any major technical hurdles however certain aspects, such as the equipment for the recovery of dipicrylamine from the spent seawater, will have to be examined more closely before any judgement on the economic viability can be made.

## RECOMMENDATIONS

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1. The washing of KDPA is an important step in the process for recovering potassium from seawater and brines. The volume of fresh water required to wash the solid could probably be significantly reduced from that given in the experimental work. This would be useful as it is likely that the bittern process, in particular, would be built in an area where water is scarce and expensive.
2. The kinetics of absorption of dipicrylamine into polyurethane foam may be amenable to mathematical modelling. This could be an interesting and rewarding area to study and would be useful for design.
3. The use of liquid extraction for the recovery of dipicrylamine from the spent seawater shows promise for being the most efficient method of recovery and should be explored in further detail. There may be a better solvent than TBP or a better diluent which would reduce the losses of TBP in the waste seawater to an acceptable level.
4. The problem of industrial safety and health should be examined in detail before this process is further developed.
5. There is some uncertainty over the cost of the dipicrylamine reagent. The synthesis presents no problems and it would be useful to calculate the cost of production of this compound. So far as is known, it is not produced on a large scale anywhere and would probably have to be manufactured for use in the process.
6. The process has the best chance of being economical if it can be placed downstream of an existing or planned nitric acid and/or brine source. The economic advantages of integrating a potassium recovery plant with such facilities should be explored.

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## APPENDIX A1 : THE SYNTHESIS OF DIPICRYLAMINE

### A1.1 Synthesis Method

A method of synthesising dipicrylamine is given by Hoffman and Dame (81) and Kapoor and Sarkar (82). It has four steps and is shown in Fig. A1.1.

In the first step chlorobenzene is nitrated to 2,4 dinitrochlorobenzene with a nitrating mix of sulphuric and nitric acid. The reaction is begun at 8<sup>0</sup>C and the final nitration is carried out at 120<sup>0</sup>C. The yield of this reaction is between 95 - 100%.

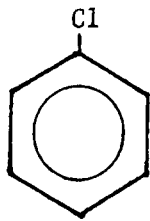
In the second step 2,4 dinitrochlorobenzene is reacted with aniline in an alcohol medium to produce 2,4 dinitrodiphenylamine. The reaction is carried out at room temperature and the yield is about 95%.

The 2,4 dinitrodiphenylamine is then nitrated at room temperature to tetranitrodiphenylamine. Again the yield is greater than 95%.

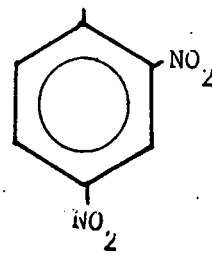
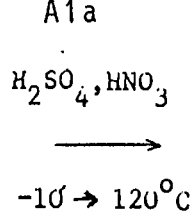
Finally, the tetranitrodiphenylamine is nitrated to dipicrylamine in a nitrating mix of fuming nitric acid and sulphuric acid at room temperature.

### A1.2 Experimental Work

It was decided to test the method given above and to synthesise the dipicrylamine for use in the experimental work given in this thesis. About 2kg of dipicrylamine was synthesised using the four step procedure described above. The dipicrylamine product was purified by washing with acetone. The melting point was measured and found to be 244<sup>0</sup>C with decomposition which agrees with the literature value. In addition, the IR spectrum of the product was obtained and compared with that given in the Aldrich catalogue (152).

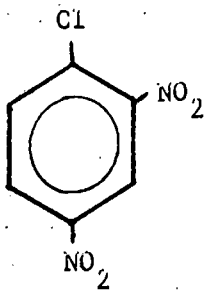


chlorobenzene

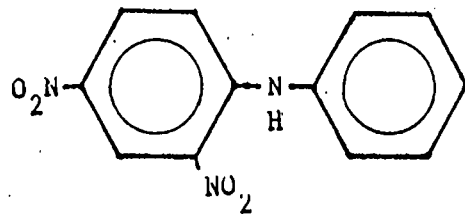
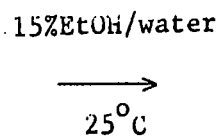
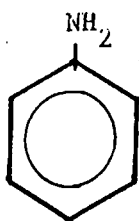


dinitrochlorobenzene

STEP 2



+

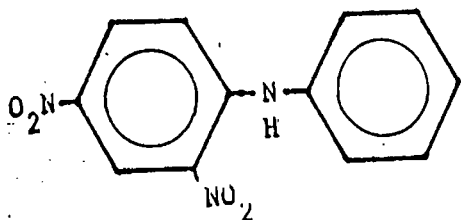


dinitrochlorobenzene

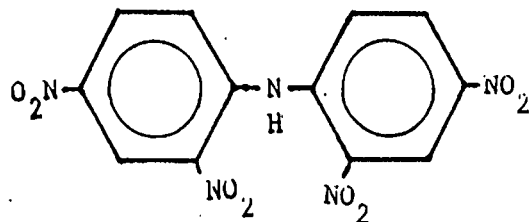
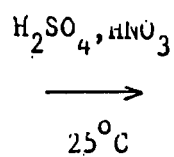
aniline

dinitrodiphenylamine

STEP 3

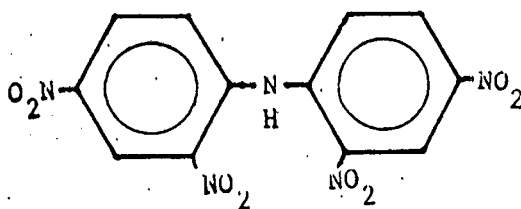


dinitrodiphenylamine

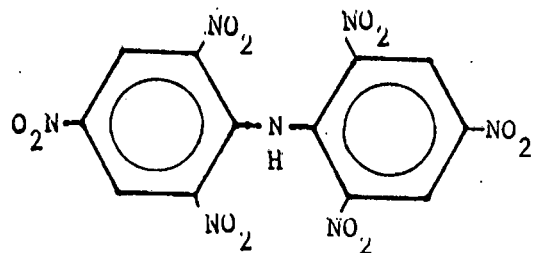
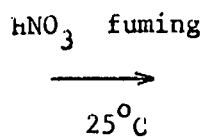


tetranitrodiphenylamine

STEP 4



tetranitrodiphenylamine



hexanitrodiphenylamine

'dipicrylamine'

Fig. A1.1    The Synthesis of Dipicrylamine

The yields were generally lower than those given in the literature. This was because problems were experienced with the first step. The product, 2,4 dinitrochlorobenzene, occurs in three isomeric forms. One of these has a melting point of about 28°C and is, according to Kapoor and Sarkar (82), undesirable. In the experimental work a large amount of this isomer was produced in the first step. Apart from this the synthesis was quite straightforward.

### A1.3

#### Alternative Method

An alternative method is given by Kuboszek et al (83). This method is claimed to produce a product with improved thermostability. According to this patent the second step given above should be replaced by a step in which dinitrochlorobenzene is reacted with aniline in the presence of a catalyst such as triethylbenzylammonium chloride. The reaction is carried out at 60°C. The yield is about 98%.

The dinitrodiphenylamine is then nitrated as before except that the nitration is carried out at 60 - 80°C. It is claimed that the product can be heated at 240°C for six hours with negligible weight loss through decomposition.

## APPENDIX A2

### A2.1 Analysis of Dipicrylamine in Aqueous Solution

#### A2.1.1 Concentrations between 0,1 and 25 mg NaDPA/1

The method given by Savage, Butt and Tallmudge (79) was used. The sample was measured directly in a Varian Superscan 3 UV Spectrophotometer at 430nm using distilled water as the blank. 1, 5 and 25mg standards of 1,5 and 25mg NaDPA/1 were used and the absorbance of the sample compared with that of the standards.

The appropriate standard was used according to which dipicrylamine salt was being measured. Thus if the sample was, say,  $\text{Mg(DPA)}_2$  in distilled water then a standard of  $\text{Mg(DPA)}_2$  in distilled water was used.

#### A2.1.2 Concentrations Greater than 25mg NaDPA/1

In this case the sample was diluted with 35g NaCl/1 solution buffered to pH8 with  $\text{NaHCO}_3$ . The sample was then analysed in the usual way.

#### A2.1.3 Concentrations less than 0,1mg NaDPA/1

A large volume of the sample (say 1 litre) with a pH above 7 was shaken with a small amount of diethylether. (10ml) whereupon the dipicrylamine was extracted into the ether phase. The ether was separated and allowed to evaporate in a beaker. Then a small amount of 35g NaCl/1 solution (pH8) was added to dissolve the dipicrylamine salt. The absorbance was then measured in the usual way.

This is an adaption of the method given by Seifert (69).

Cost of Reverse Osmosis

The cost of recovering 90% of the water from a 3g TDS/l solution is calculated below. The information was supplied by Bruce Hendry of the Department of Chemical Engineering, University of Cape Town.

The pressure required to recover 90% of the water at a maximum of 0,3g TDS/l is about 30 Bar. The cost of the production is the energy cost of pumping the water to this pressure and the amortised capital cost of the equipment which is, as a rule of thumb, about the same as the energy cost.

For a flowrate of  $60\text{m}^3/\text{hr}$  (the flowrate of wash liquor in a plant which produces 100 tons  $\text{KNO}_3/\text{day}$ ) the power requirement for pumping is (144) :

$$\begin{aligned} \text{KW} &= 8,13 \times (\text{Head}) \times (\text{s.g.}) \times (\text{flowrate}) \\ &= 8,13 \times (30 \times 10\text{m}) \times (1) \times (0,0167\text{m}^3/\text{s}) \\ &= 41 \text{ KW} \end{aligned}$$

Power Cost per  $\text{m}^3$  recovered freshwater :

$$\begin{aligned} &= 41 \text{ KW} \times 5\text{c/KWhr} = 3,8\text{c}/\text{m}^3 \\ &0,90 \times 60 \end{aligned}$$

$$\begin{aligned} \text{Total cost} &= \text{Amortised Capital Cost} + \text{Power Cost} \\ &= 2 \times \text{Power Cost} = 8\text{c}/\text{m}^3 \end{aligned}$$

APPENDIX A3 : THE RECOVERY OF DIPICRYLAMINE FROM SPENT BITTERN AND SEAWATER

A3.1 Equilibrium Loading Isotherm for Polyurethane Foam

The results of the loading experiments described in Sec. 5.3.1.3 are shown below. The mass of the foam sample used, the initial solution concentrations ( $C_i$ ), the final solution concentration and the loading are given in the Table.

Loading from Seawater :

<u>Foam Mass</u> (g)	<u>Conc.</u> (mgNaDPA/1)	<u>Loading</u> (gNaDPA/g foam)	<u>Foam Mass</u> (g)	<u>Conc.</u> (mgNaDPA/1)	<u>Loading</u> (gNaDPA/g foam)
$C_i = 250$					
.011	179	.56	.054	11.1	.43
.014	175	.48	.060	6.7	.39
.016	166	.46	.073	1.5	.33
.021	152	.43	.106	.2	.23
.029	108	.46			
.032	117	.39		$C_i = 500$	
.037	85	.42	.016	382	.64
.043	70	.40	.020	372	.56

Loading from Bittern :

<u>Foam</u>	<u>Foam Mass</u> (g)	<u>Conc.</u> (mgNaDPA/1)	<u>Loading</u> (gNaDPA/g Foam)	<u>Foam</u>	<u>Foam Mass</u> (g)	<u>Conc.</u> (mgNaDPA/1)	<u>Loading</u> (gNaDPA/g Foam)
V2	.026	1.6	.44	V7	.0099	64	.51
V4	.025	8.3	.43	V7	.014	43	.50
V6	.027	5.0	.40	V7	.016	35	.49
V8	.024	2.9	.47	V7	.020	15	.48
V10	.026	4.8	.42	V7	.026	3.7	.42
V12	.026	1.7	.44	V7	.033	1.4	.34
V7	.0053	86	.53	V7	.044	.81	.26
V7	.0061	83	.50	V7	.066	.38	.17
V7	.0075	75	.51				

### A3.2 Equilibrium Stripping Isotherms for Polyurethane Foam

The results of the experimental work given in Sec. 5.3.1.4 are given below. This table shows the NaDPA concentration in the final solution, the temperature of the solution and the calculated loading of the foam.

70°C Conc. (mgNaDPA/1)	Loading (gNaDPA/g Foam)	50°C Conc. (mgNaDPA/1)	Loading (gNaDPA/g Foam)	30°C Conc. (mgNaDPA/1)	Loading (gNaDPA/g Foam)
3550	.39	3336	.48	3155	.56
1929	.21	1691	.38	1543	.48
1014	.11	896	.23	744	.39
383	.10	334	.18	246	.31
201	.05	176	.10	106	.25
79	.025	.64	.06	39	.12

### A3.3 Loading of Activated Carbon

KOP 40/2		GRANULAR CARBON	
Conc. (mgNaDPA/1)	Loading (gNaDPA/g Carbon)	Conc. (mgNaDPA/1)	Loading (gNaDPA/g Carbon)
154	.35	164	.33
38	.37	84	.32
4.0	.24	1.0	.24
.50	.12	.4	.10

## A3.4

Loading of Ionexchange Materials

IRA 35		A 375	
Conc. (mgNaDPA/1)	Loading (gNaDPA/g Sorbent)	Conc. (mgNaDPA/1)	Loading (gNaDPA/g Sorbent)
93	.94	176	.27
39	.78	122	.24
7.1	.57	34	.18
3.7	.42	2.7	.11
3.0	.35		
2.8	.28		
2.5	.15		
1.9	.09		
ES562		IRA68	
158	.35	203	.161
97	.28	160	.176
16.3	.19	74	.163
1.8	.10	9.3	.120

## A3.5

Tributylphosphate Loading Isotherm

The results of the experiments described in Sec. 5.3.3.5 are tabulated below. The table gives the initial concentration of dipicrylamine in the aqueous phase ( $C_i$ ), the volume of solvent used, the final dipicrylamine concentration and the calculated final concentration of dipicrylamine in the solvent.

Experiment Number	Solvent Vol. (ml)	Equilibrium Aqueous Conc. (N)	Equilibrium Organic Conc. (N)
$C_i = 1,23 \times 10^{-3}N$		(570mg NaDPA/1)	
1.	.2	$1,0 \times 10^{-3}$	.11
2.	.5	0,73 " "	.10
3.	1	0,38 " "	.085
4.	2	0,12 " "	.055
5.	5	$2,9 \times 10^{-5}$	.024
6.	10	1,8 " "	.012
$C_i = 1,23 \times 10^{-4}N$		(57mg NaDPA/1)	
7.	1,0	$0,26 \times 10^{-5}$	.0012
8.	5	0,34 " "	.0024
9.	2	0,71 " "	.0058
$C_i = 1,23 \times 10^{-5}N$		(5,7mg NaDPA/1)	
10.	10	$0,10 \times 10^{-5}$	.00011
11.	5	0,10 " "	.00022
12.	2	0,17 " "	.00053

Tributylphosphate Stripping Isotherm

The results of the experiments described in Sec. 5.3.3.6 are tabulated below.

Experiment Number	Solvent Vol. (ml)	Equilibrium Aqueous Conc.	Equilibrium Organic Conc.
	$C_0 = 6,6 \times 10^{-2} N$	(30 400mg NaDPA/1)	
1.	10	.011	.055
2.	5	.030	.072
	$C_0 = 6,6 \times 10^{-3} N$	(3 040mg NaDPA/1)	
3.	10	$3,9 \times 10^{-3}$	.027
4.	5	4,9 " "	.034
	$C_0 = 6,6 \times 10^{-4} N$	(304mg NaDPA/1)	
5.	10	$4,2 \times 10^{-4}$	.0024
6.	5	4,8 " "	.0036

THE CONVERSION OF KDPA IN THE PRESENCE OF A SOLVENT

The table below gives the experimental conditions and results of the experiments discussed in Sec. 6.3.4.

The table shows the run number; the volume and type of solvent used; the volume and concentration of the acid for the reaction and the mass and origin of the KDPA sample used in each experiment. The table also shows the fractional conversion (symbol  $x$ ) vs time (in minutes) data for each run.

For each run the potassium concentration in the aqueous phase increased with time until it reached a final equilibrium value. The conversion was expressed as the fractional approach of the potassium concentration to the theoretical concentration that would be found if all the KDPA was converted to HDPK.

RUN NO.	SOLVENT	ACID	t	CONVERSION DATA			KDPA USED
				x	t	x	
K1	No measurements taken						
K2	2ml 10/90 v/v TBP/perchloroethylene	10 ml 1N HNO <sub>3</sub>	1	.23	20,5	.94	1g seawater KDPA
			3	.38	28	.95	
			5	.54	128	1.00	
			10	.83			
K3	2ml 10/90 v/v TBP/Pegasol 3745	"	1.5	.25	18.5	.87	"
			3.25	.33	25	.92	
			5	.44	40	.95	
			7.5	.54	65	.96	
			10	.62	120+	1.00	
K4	2ml 20/80 v/v TBP/Pegasol 3745	"	2	.27	21	.87	"
			3.5	.43	47	.98	
			5	.48	60	.98	
			8	.59	156	1.00	
			12	.71			
K5	2ml 5/95 v/v TBP/Pegasol 3745	"	2	.12	20	.39	"
			5	.23	30	.51	
			7.5	.27	45	.55	
			13	.34	70	.67	
K6	2ml 20/80 v/v TBP/Perchloroethylene	"	2	.31	25	1.00	"
			4	.51	45	1.01	
			7,5	.75	60	.98	
			10	.81	165	1.01	
			15	.90			
K7	2ml 20/80 v/v Dibutylphthalate/ Perchloroethylene	"	2	.12	17,5	.44	"
			5	.19	30	.63	
			10	.30	65	1.00	
K8	2ml 50/50 v/v Dibutylphthalate/ Perchloroethylene	"	2	.11	17,5	.55	"
			5	.23	43	.80	
			10	.36	156	1.00	
K9	2ml 50/50 v/v Methyl Benzoate/ Perchloroethylene	"	2	.20	20	.94	"
			5	.47	33	.96	
			7,5	.62	55	.97	
K10	2ml 10/90 v/v TBP/Pegasol 3745	5ml 2N HNO <sub>3</sub>	1	.14	9	.70	"
			2.5	.30	15.7	.83	
			4	.45	60	1.00	
			6	.55			
K11	2ml 10/90 v/v TBP/Pegasol 3745	2,5ml 4N HNO <sub>3</sub>	2	.18	12	.52	"
			4	.27	20	.63	
			7	.41	120	1.00	

RUN NO.	SOLVENT	ACID	CONVERSION DATA				KDPA USED
			t	x	t	x	
K12	2ml n-Butylether	10ml 1N HNO <sub>3</sub>	8	.10	60	.28	1g seawater KDPA
			15	.20	120	.33	
			30	.25			
K13	None	"	10	.27	75	.80	"
			20	.44	110	.86	
			30	.59	720	1.00	
			50	.75			
K14	1ml 10/90 v/v TBP/Pegasol 3745	20ml 1N HNO <sub>3</sub>	2	.08			2g KDPA placed in flask. Stirring inadequate.
			5	.16			
			10.5	.21			
			20	.27			
K15	None	"	10	.41	80	.65	2g KDPA in flask.
			20	.47	100	.67	
			30	.56	720	1.00	
K16	2ml 10/90 v/v TBP/Pegasol 3745	"	2.25	.04	18	.69	"
			4	.16	25.5	.79	
			7	.37	35	.91	
			10	.43	52	.95	
			13	.55	90	1.00	
K17	4ml 10/90 v/v TBP/Pegasol 3745	"	2	.06	18	.80	"
			4	.28	25	.88	
			7	.50	36	.93	
			10	.57	50	.96	
			13	.72	120	1.00	
K18	8ml 10/90 v/v TBP/Pegasol 3745	"	2.25	.13	15	.88	"
			4.25	.28	20	.91	
			6	.41	30	.94	
			8.25	.61	60	.98	
			11	.74	120	1.00	
K19	4ml 10/90 v/v TBP/Pegasol 3745	10ml 2N HNO <sub>3</sub>	2	.08	17	.52	
			4	.15	30	.62	
			8	.34	120+	1.00	
K20	4ml 10/90 v/v TBP/Pegasol 3745	20ml 1N HNO <sub>3</sub>	5	.76	25	1.00	2g bittern KDPA
			10	1.00	45	1.00	
			15	1.00	150	1.00	
K21	None	"	5	1.00			"
			10	1.00			
			20	1.00			
			40	1.00			
K22	4ml 10/90 v/v TBP/Pegasol 3745	"	5	.68	22	.92	1.4g Bittern KDPA dried at 110°C.
			10	.77	42	.94	
			15	.84	180	1.00	

RUN NO.	SOLVENT	ACID	t	CONVERSION DATA			KDPA USED
				x	t	x	
K39	2ml 10/90 v/v TBP/Pegasol 3745	"	2	.50	17,5	.76	1g seawater KDPA
			5	.64	30	.81	
			10	.69	90	.98	
K40	None	8.4ml 1N HNO <sub>3</sub>	15	.76			2g seawater KDPA
			30	.93			
			45	.95			
			90	.97			
K41	4ml 10/90 v/v TBP/Pegasol R150	"	3	.68	20	1.00	"
			5	.89	40	1.00	
			10	.95			

APPENDIX A5 : PROCESS DESIGN AND COSTINGA5.1 : Process FlowratesA5.1.1 The Production of KNO from Seawater

Flowrates for a Plant Producing 100 tons/day KNO

$$\frac{100\,000 \text{ kg KNO}_3}{\text{day}} \times \frac{\text{day}}{24 \text{ hours}} \times \frac{39,1 \text{ kg K}}{(39,1+14+48) \text{ kg KNO}_3} = 1611 \text{ kg K/hr}$$

$$1611 \text{ kg K/hr} = 41,2 \text{ kgmoles K/hr}$$

S1 Seawater Flowrate

Assume seawater temperature is approximately 15°C

Choose recovery of potassium (yield) = 80%

$$\frac{1611 \text{ kg K}}{\text{hr}} \times \frac{\text{m}^3 \text{ seawater}}{.38 \text{ kg K}} \times .80 = 5300 \text{ m}^3 \text{ seawater/hr}$$

S2 Reagent Flowrate

To obtain a yield of 80% at a temperature of 15°C a stoichiometric ratio of  $\text{DPA}^-$  to  $\text{K}^+$  should be about .90 (see Fig. 4.1)

$$\frac{5300 \text{ m}^3}{\text{hr}} \times \frac{.38 \text{ kg K}}{\text{m}^3} \times \frac{\text{kgmol K}}{39,1 \text{ kg K}} \times \frac{.90 \text{ kgmol DPA}^-}{\text{kgmol K}} = 46,4 \text{ kgmole DPA}$$

Assume reagent is 10% m/v  $\text{Ca}(\text{DPA})_2$  in seawater. The Molar weight of  $\text{Ca}(\text{DPA})_2$  is 916 kg/mol

$$\frac{46,4 \text{ kgmol DPA}^-}{\text{hr}} \times \frac{\text{kgmol Ca}(\text{DPA})_2}{2 \text{ kgmol DPA}^-} \times \frac{916 \text{ kg}}{\text{kgmol}} = 21250 \text{ kg Ca}(\text{DPA})_2/\text{hr}$$

$$\text{volume flowrate of reagent} = \frac{21\,250}{.10} = 212,5 \text{ m}^3 \text{ reagent solution/hr}$$

S3

KDPA Flowrate

$$\frac{41,2 \text{ kgmol K}}{\text{hr}} \quad \Bigg| \quad \frac{477 \text{ kg KDPA}}{\text{kgmol KDPA}} = 19\,650 \text{ KDPA/hr}$$

Assume 20% moisture content. Mass flowrate of moist KDPA =  
24 560 kg/hr

S4

Freshwater Wash of KDPA

Assume KDPA is washed with twice its own mass in freshwater  
(see Sec. 4.3.5)

$$\text{washwater flowrate} = (24\,560 \times 2) \text{ kg/hr} = 49,1 \text{ m}^3/\text{hr}$$

assume 90% of water is recovered by R.O. (Sec. 4.3.5)

$$\text{washwater makeup} = .10 \times 49,1 = 4,9 \text{ m}^3/\text{hr}$$

the same amount is discarded as water

$$\text{the recycle flowrate from the R.O. plant is } .90 \times 49,1 = 44,2 \text{ m}^2/\text{hr}$$

S5

Acid Flowrate

makeup  $\text{HNO}_3$  flowrate :

$$\frac{41,2 \text{ kgmol}}{\text{hr}} \quad \Bigg| \quad \frac{63 \text{ kg HNO}_3}{\text{kgmol}} = 2\,600 \text{ kg HNO}_3/\text{hr}$$

$$\text{flowrate of 70\% HNO}_3 \text{ solution (s.g. = 1,42)} = 3\,710 \text{ kg/hr}$$

S6

Freshwater Makeup for the Acid Reactor

Assume 80% of the water from the  $\text{KNO}_3$  solution is recovered from  
the Evaporator.

$\text{KNO}_3$  solution (flowrate  $41,2 \text{ m}^3/\text{hr}$ ) contains 1 M  $\text{KNO}_3$  (4 165  
kg/hr) and 1 M  $\text{HNO}_3$  (2 600 kg/hr). There the  $\text{H}_2\text{O}$  content is  
34 435 hg/hr ( $41\,200 - 4\,165 - 2\,600$ ). It is assumed that 20% of  
this is lost in the Evaporator.

$$\begin{aligned}
 \text{H}_2\text{O makeup} &= .20 \times 34\,435 &= 6,887 \text{ kg/hr} \\
 \text{But H}_2\text{O in moist KDPA} &= .20 \times 24\,560 &= 4\,912 \text{ kg/hr} \\
 \therefore \text{Freshwater makeup} &= &1\,975 \text{ kg/hr} \\
 &= &2 \text{ m}^3/\text{hr}
 \end{aligned}$$

This freshwater is first used to wash the HDPA as shown in Fig. 8.1.

### S7 Lime Flowrate

Assume Lime is 90% m/m  $\text{Ca}(\text{OH})_2$  and 10%  $\text{Mg}(\text{OH})_2$ . Ignore inert solids. Assume a 10% excess of lime is used in the Lime Reactor.

$$1 \text{ ton of Lime contains } 2 \times \left\{ \frac{900}{74,1} + \frac{100}{58,3} \right\} = 27,7 \text{ kgmol OH}^-$$

$$\text{Lime mass flowrate} = \frac{41,2 \text{ kgmol}}{\text{hr}} \left| \frac{1,10 \text{ ton}}{27,7 \text{ kgmol}} \right. = 1,64 \text{ tons/hr}$$

### S8 Seawater Flowrate to Lime Reactor

Assume 10% m/v  $\text{Ca}(\text{DPA})_2$  solution is produced by Lime Reactor.

$$\text{Seawater flowrate} = 0,90 \times 212,5 \text{ m}^3 = 191 \text{ m}^3/\text{hr}$$

This seawater is taken from the spent seawater stream.

### S9 Flowrate of $\text{KNO}_3$ Solution

Assume 2 M  $\text{HNO}_3$  is used in the Acid Reactor. Assume the mol ratio of acid to KDPA is 2 to 1. The solution leaving the acid Reactor is then a 1 M  $\text{KNO}_3$  solution in 1 M  $\text{HNO}_3$ .

$$\frac{41,2 \text{ kgmol KNO}_3}{\text{hr}} \left| \frac{1 \text{ m}^3}{\text{kgmol}} \right. = 41,2 \text{ m}^3/\text{hr}$$

Solid Waste Flowrate

$\text{CaSO}_4$  is unlikely to precipitate in the KDPA Reactor/Settler or the Lime Reactor. The solubility of  $\text{CaSO}_4$  is .014M. The high calcium level in the Lime Reactor will probably result in the solubility product of  $\text{CaSO}_4$  being exceeded. However,  $\text{CaSO}_4$  does show supersaturated behaviour so, for simplicity, the  $\text{CaSO}_4$  precipitation will be ignored.

The solid which must be removed from the  $\text{Ca}(\text{DPA})_2$  solution produced by the Lime Reactor is unreacted Lime and inert solids in the Lime.

A 10% excess of lime was used :

$$\text{Unreacted Lime} = \frac{1}{11} \times 1640 = 150 \text{ kg/hr}$$

The mass of inert solids depends on the quality of lime used. A typical value for inert solids would be about 100 kg/hr. The solid waste is washed with spent seawater to remove any adhering dipicrylamine and it is then discarded.

S11. Spent Seawater Flowrate and Composition

The flowrate of spent seawater leaving the KDPA Reactor/Settler is the sum of the seawater and the  $\text{Ca}(\text{DPA})_2$  solution, and is thus about  $5\,500 \text{ m}^3/\text{hr}$  ( $5\,300 + 191 \text{ m}^3/\text{hr}$ ). However, about  $200 \text{ m}^3/\text{hr}$  of this is sent to the Lime Reactor.

The spent seawater flowrate to the DPA Recovery Step is thus  $5\,300 \text{ m}^3/\text{hr}$ .

The flowrate of dipicrylamine added to the seawater is (from calculation S2)  $46,4 \text{ kgmol/hr}$ .

The flowrate of KDPA (calculation S3) is  $41,2 \text{ kgmol/hr}$ .

The flowrate of dipicrylamine in the spent seawater is  $46,4 - 41,2 = 5,2 \text{ kgmol/hr}$ .

The concentration of dipicrylamine in the spent seawater is then :

$$\frac{5,2 \text{ kgmol}}{\text{hr}} \Bigg| \frac{\text{hr}}{5\,300 \text{ m}^3} = 0,00098 \text{ kgmol/m}^3$$

Assuming, for simplicity, that the dipicrylamine is present as NaDPA, the concentration is :

$$\frac{0,0098 \text{ kgmol}}{\text{m}^3} \Bigg| \frac{461 \text{ kg NaDPA}}{\text{kg mol NaDPA}} = 0,452 \text{ kg NaDPA/m}^3 \text{ or } 452 \text{ ppm}$$

From Fig. 4.2 this concentration would be close to 600ppm for a seawater temperature of 25°C. The lower temperature here (15°C) results in a lower NaDPA concentration in the spent seawater.

S12

### Dipicrylamine Recovery Using Polyurethane Foam

#### (a) Rate of Foam Usage

If the dipicrylamine is recovered using polyurethane foam the mass of foam to be regenerated per hour will be, assuming that the foam takes us 0,25 kg NaDPA/kg (loaded to 0,30 kg/kg and regenerated to 0,05 kg/kg), and assuming the concentration of dipicrylamine in the waste seawater is 1 g/m<sup>3</sup> (see 12 (e) below).

$$\frac{.5\,300 \text{ m}^3}{\text{hr}} \Bigg| \frac{.452 \text{ kg NaDPA}}{\text{m}^3} \Bigg| \frac{\text{kg foam}}{.25 \text{ kg NaDPA}} = 9\,600 \text{ kg foam/hr}$$

#### (b) Freshwater for Foam Regeneration

The dipicrylamine is recovered on the foam as NaDPA. In the cyclical process described in Sec. 5.3.1.9 this NaDPA is eluted and converted to Na<sub>2</sub>SO<sub>4</sub> and HDPA. There is a purge to prevent a buildup of Na<sub>2</sub>SO<sub>4</sub> in the process. Reverse Osmosis (R.O.) can be used to recover water from this purge to reduce the water consumption of the polyurethane foam regeneration process. Assuming that the waste solution from the R.O. plant contains, say, .10 kgmol Na<sub>2</sub>SO<sub>4</sub>/m<sup>3</sup> the volume of this stream will be :

$$\frac{5,2 \text{ kgmol NaDPA}}{\text{hr}} \left| \frac{\text{kgmol Na}_2\text{SO}_4}{2 \text{ kgmol Na}} \right| \frac{\text{m}^3}{.1 \text{ kgmol Na}_2\text{SO}_4} = 26 \text{ m}^3/\text{hr}$$

Thus the R.O. plant produces 26 m<sup>3</sup>/hr of waste Na<sub>2</sub>SO<sub>4</sub> solution.

The volume of makeup freshwater to replace this waste brine will then also be 26 m<sup>3</sup>/hr

(c) Sulphuric Acid for Foam Regeneration

Sulphuric Acid is used to convert NaDPA to HDPa. The flowrate required is :

$$\frac{5,2 \text{ kgmol NaDPA}}{\text{hr}} \left| \frac{\text{mol H}_2\text{SO}_4}{2 \text{ mol NaDPA}} \right| \frac{98 \text{ kg H}_2\text{SO}_4}{\text{kgmol}} = 230 \text{ kg/hr}$$

An excess is required to reduce the pH to below 4 before the reaction occurs. Assume that 100% excess is used. Sulphuric Acid required = 2 x 230 = 460 kg/hr.

(d) Lime for Neutralisation of Excess Sulphuric Acid

Required to neutralise 230 kg H<sub>2</sub>SO<sub>4</sub>/hr to bring pH from below 4 to 7 :

$$\frac{230 \text{ kg H}_2\text{SO}_4}{\text{hr}} \left| \frac{\text{kgmol H}_2\text{SO}_4}{98 \text{ kg H}_2\text{SO}_4} \right| \frac{\text{ton lime}}{27,7 \text{ kgmol OH}} \left| \frac{2 \text{ mol OH}}{\text{mol H}_2\text{SO}_4} \right| = 170 \text{ kg/hr}$$

(e) Dipicrylamine Recovery and Loss Rates

Assume that the chosen concentration of dipicrylamine in the waste seawater leaving the foam absorber is 1 g/m<sup>3</sup> (1 ppm). Note that the use of foam does allow the attainment of a lower concentration in the waste seawater if this is desired. The rate of dipicrylamine loss is then :

$$\frac{5 \text{ 300 m}^3 \text{ seawater}}{\text{hr}} \left| \frac{1 \text{ g}}{\text{m}^3} \right| = 5,3 \text{ kgNaDPA/hr}$$

The cost of this loss is small. Essentially all the dipicrylamine in the spent seawater is recovered on the foam. The flowrate of recovered dipicrylamine is :

$$\frac{5\ 300\ \text{m}^3\ \text{seawater}}{\text{hr}} \times \frac{(452-1)\ \text{g NaDPA}}{\text{m}^3} \times \frac{\text{kgmol}}{461\ \text{kg NaDPA}} = 5,2\ \text{kgmol/hr}$$

S13

### Dipicrylamine Recovery Using TBP Solvent

(a)

#### Solvent Flowrate

Fig. A5.1, 5.2, 5.3, show the equilibrium data given in Fig. 5.11 converted to solvent free ( $x'$ ) and water free ( $y'$ ) co-ordinates. These figures show that when the solvent rate is twice the minimum (shown by a continuous line labelled 2B min in these figures), about 3 stages are needed for the extraction. If 1,5 times the minimum solvent is used (dashed line) about 4 stages are required. Choose twice the minimum.

$$\begin{aligned} \text{Solvent flowrate} &= 2B\ \text{min} = \\ &\frac{2 \times 5\ 300 \times 10^3\ \text{kg water}}{\text{hr}} \times \frac{4,5 \times 10^{-4}\ \text{kg NaDPA}}{\text{kg water}} \times \frac{\text{kg solvent}}{0,059\ \text{kg NaDPA}} \\ &= 80\ 800\ \text{kg/hr} \quad \text{or} \quad 90\ \text{m}^3/\text{hr} \end{aligned}$$

(b)

#### Freshwater for Regeneration

Fig. A5.4 shows the stripping isotherm in solvent and water free co-ordinates. From this figure the minimum water flowrate for stripping is  $640\ \text{m}^3/\text{hr}$ . Operating lines are shown for water flowrates (A) of  $1000\ \text{m}^3/\text{hr}$  and  $1\ 280\ \text{m}^3/\text{hr}$ . Even with these high flowrates the number of stages will be large. For this design assume the freshwater flowrate =  $1\ 280\ \text{m}^3/\text{hr}$ .

Fig. A5.1

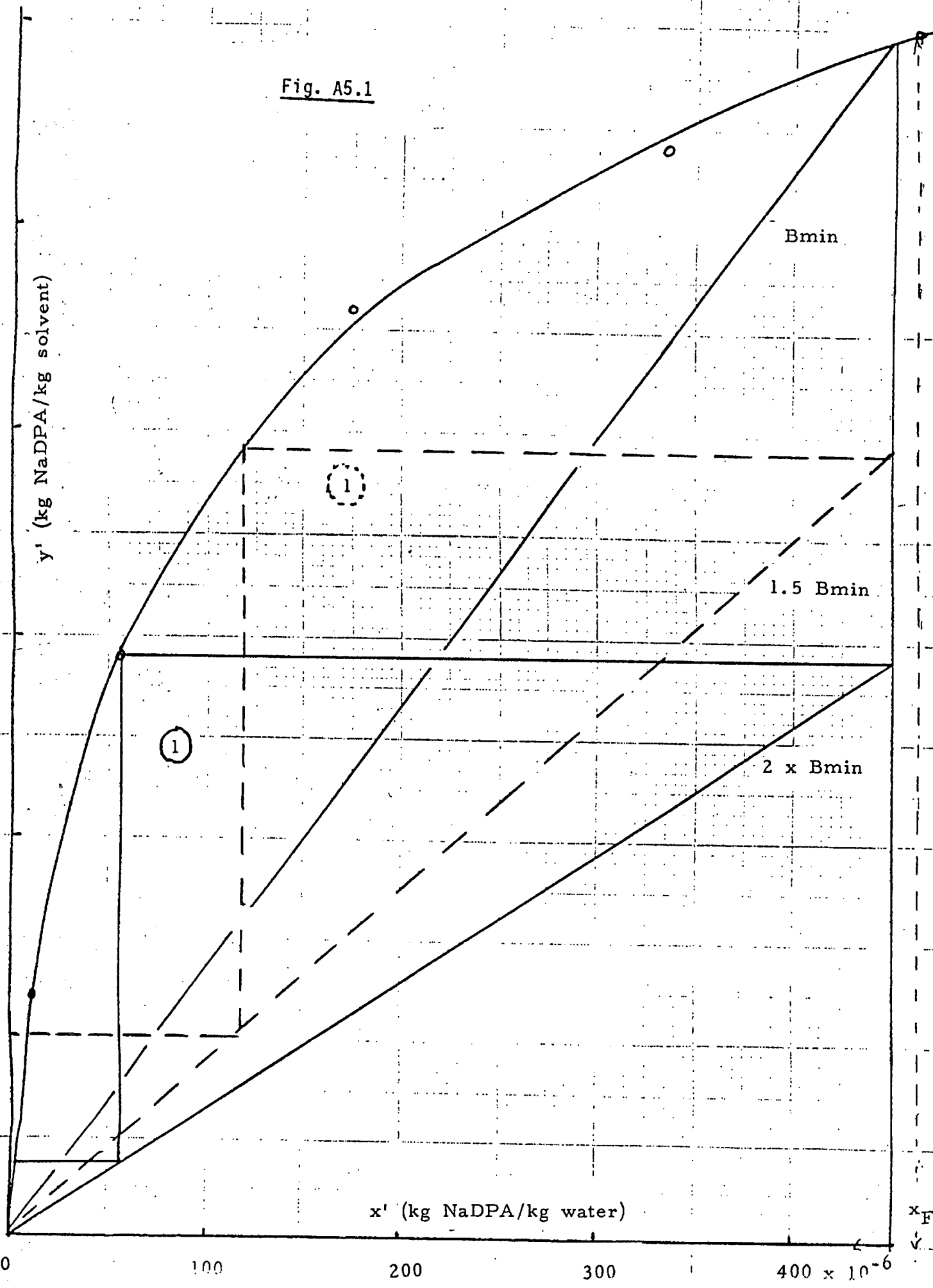


Fig. A5.2

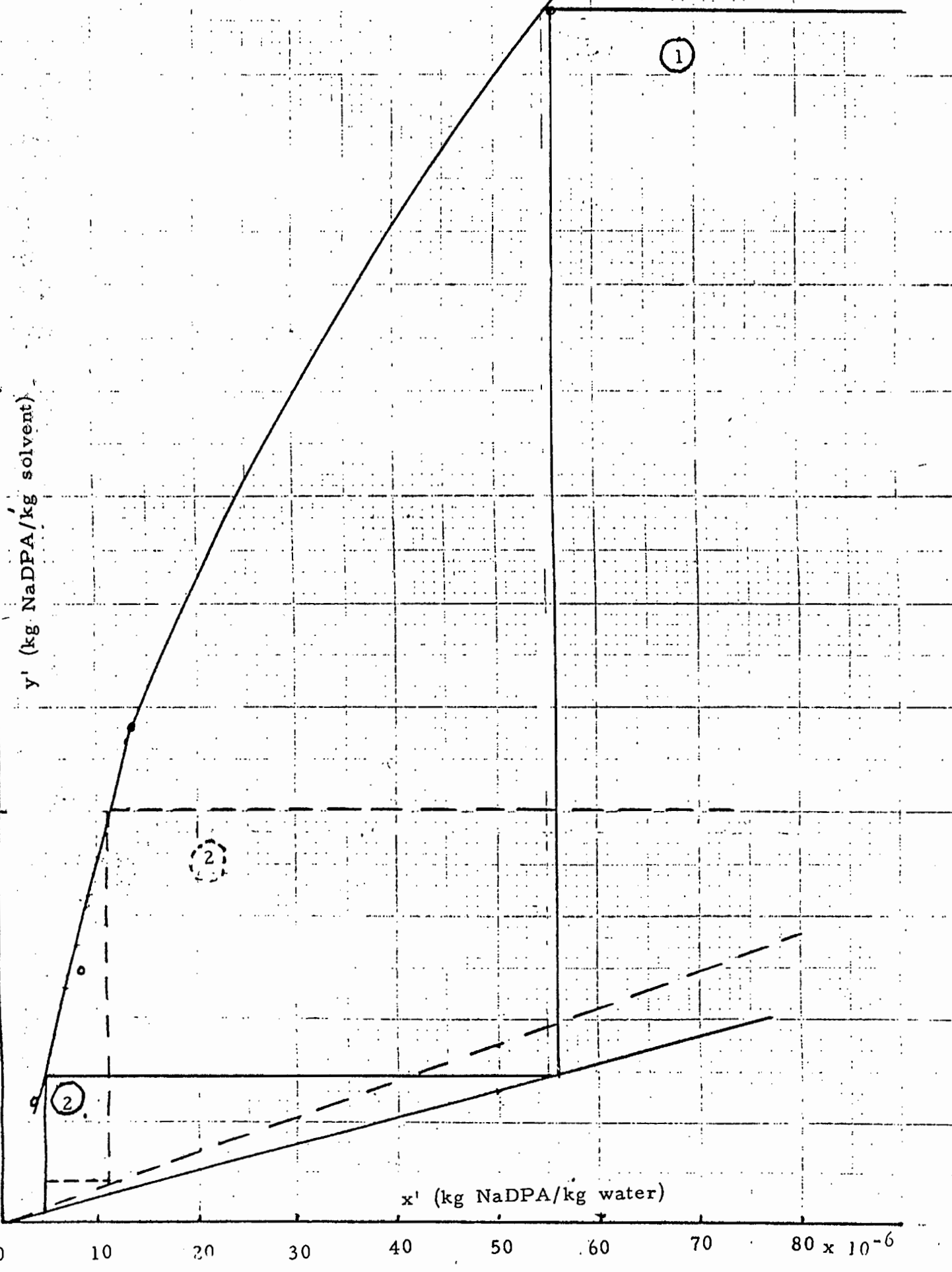


Fig. A5.3

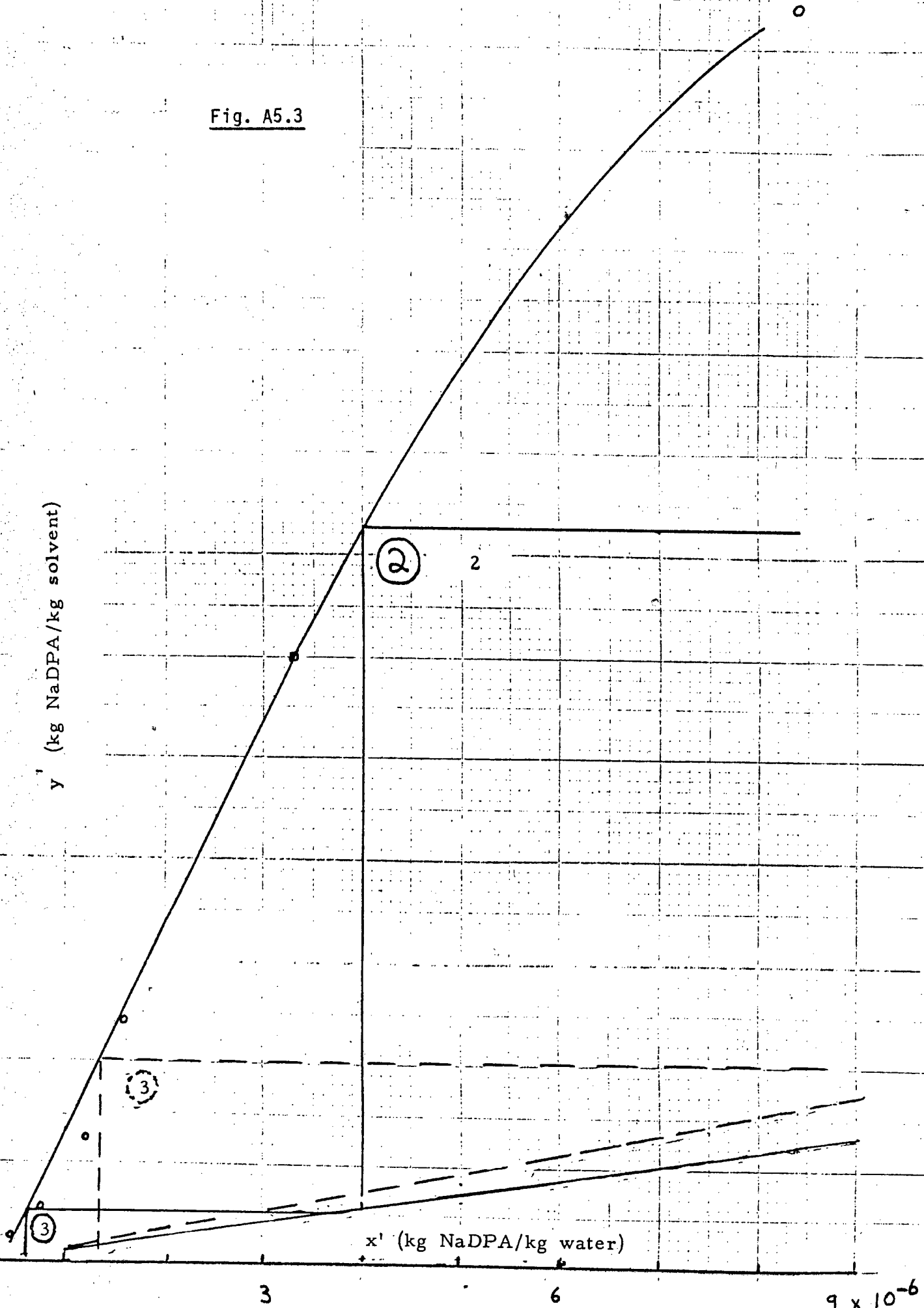
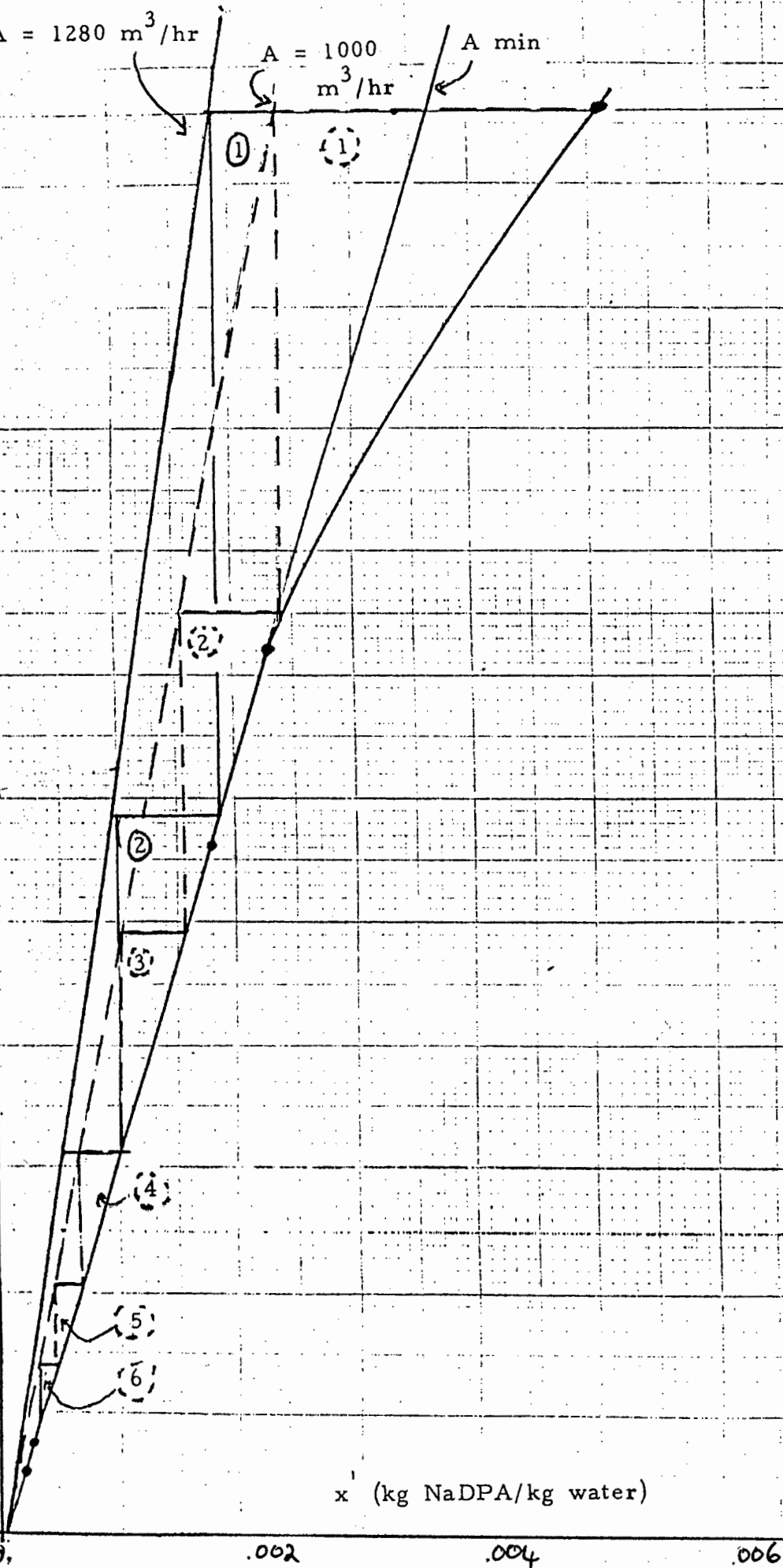


Fig. A5.4 Regeneration of TBP Solvent



As in the Foam Recovery method there will have to be a purge to keep down the level of  $\text{Na}_2\text{SO}_4$ . Reverse Osmosis can be used (as described in calculation S12 (b) above) to reduce the water consumption to  $26\text{m}^3/\text{hr}$ .

(c) Sulphuric Acid and Lime

The flowrates of Sulphuric Acid and Lime will be as calculated in S12 (c) and (d) above, namely,  $460\text{ kg/hr}$  and  $170\text{ kg/hr}$  respectively.

(d) TBP Solvent Loss

The solubility of TBP in the presence of a diluent is  $10\text{ ppm}$  (see Sec. 5.3.3.7). The loss of TBP will then be :

$$\frac{5\,300\text{ m}^3}{\text{hr}} \times \frac{10 \times 10^{-3}\text{ kg}}{\text{m}^3} = 53\text{ kg/hr}$$

A5.1.2 The Production of  $\text{KNO}_3$  from a Bittern

Flowrates for a Plant Producing 100 Tons  $\text{KNO}_3/\text{day}$

B1 Bittern Flowrate

Assume bittern temperature is approximately  $25^\circ\text{C}$ .

Assume bittern contains  $10\text{ kg K/m}^3$  and has s.g. =  $1,25$ .

Under these conditions the addition of  $0,90\text{ kgmol DPA/mol K}^+$  will give essentially a  $90\%$  recovery of K (see Sec. 4.2.2.2).

$$\frac{1\,611\text{ kg K}}{\text{hr}} \times \frac{\text{m}^3\text{ bittern}}{10\text{ kg}} \times 0,90 = 179\text{ m}^3/\text{hr}$$

$$\text{or } \frac{179\text{ m}^3}{\text{hr}} \times \frac{1\,250\text{ kg}}{\text{m}^3} = 223\,750\text{ kg/hr}$$

B2

Reagent Flowrates

As in Calculation S2 we are adding 0,90 mol DPA<sup>-</sup>/mol K<sup>+</sup>, therefore the reagent flowrate is the same, namely, 212,5 m<sup>3</sup> reagent solution/hr.

B3

KDPA Wash

(a)

KDPA Flowrate

The KDPA flowrate is, as in Calculation S3, 19 650 kg KDPA/hr on a dry basis. However, the solid contains about 33% m/m moisture, therefore the mass flowrate of moist solid is 29 500 kg/hr.

(b)

Seawater Wash

In Sec. 4.3.5 it was suggested that the moist solid should be washed with six times its mass in seawater. The seawater wash flowrate is then 177m<sup>3</sup>/hr. After it has been used to wash the solid the seawater is sent to the Lime Reactor.

(c)

Freshwater Wash

As suggested in Sec. 4.3.5 the freshwater wash flowrate is twice the mass of the moist solid or 59 m<sup>3</sup>/hr. Reverse Osmosis can be used as described in Sec. 4.3.5 and Calculation S4 above to recover 90% of the wash water and reduce the consumption to 5,9 m<sup>3</sup>/hr.

B4

Acid, Makeup Water, Lime KNO<sub>3</sub> Solution Flowrates

The flowrates of Acid, Makeup Water for the Acid Reactor, Lime and KNO<sub>3</sub> Solution will be as calculated in S5, S6 S7 and S9 respectively. The flowrates are :

Nitric Acid (70%)	<u>3 710 kg/hr</u>
Water	<u>2 m<sup>3</sup>/hr</u>
Lime	<u>1,64 tons/hr</u>
KNO <sub>3</sub> Solution	<u>41,2 m<sup>3</sup>/hr</u>

B5 Seawater Flowrate to Lime Reactor

As in Calculation S8 this will be  $191 \text{ m}^3$  seawater/hr. Of this amount  $177 \text{ m}^3/\text{hr}$  comes from the Seawater Wash of KDPA (Calculation B3 (b)) and the other  $14 \text{ m}^3/\text{hr}$  is used to wash the Solid Waste from the Lime Reactor.

To avoid the problem of precipitation of KDPA from this seawater in the Lime Reactor, it may be necessary to pretreat this water with  $\text{Ca}(\text{DPA})_2$  to remove the potassium. This should not be too difficult as the flowrate is reasonably small.

B6 Solid Waste Flowrate

The high sulphate content of the bittern will result in the precipitation of  $\text{CaSO}_4$ . For simplicity, assume all Ca in the  $\text{Ca}(\text{DPA})_2$  precipitates as  $\text{CaSO}_4$ . The flowrate of  $\text{CaSO}_4$  is then :

$$\frac{46,4 \text{ kgmol DPA}^-}{\text{hr}} \left| \frac{\text{mol Ca}^{++}}{2 \text{ mol DPA}^-} \right| \frac{136,2 \text{ kg CaSO}_4}{\text{kgmol}} = 3160 \text{ kg CaSO}_4/\text{hr}$$

B7 Spent Bittern Flowrate and Composition

The flowrate of spent bittern is the sum of the volume of bittern used and the reagent volume.

$$179 \text{ m}^3/\text{hr} + 212 \text{ m}^3/\text{hr} = 391 \text{ m}^3/\text{hr}$$

The spent bittern contains about 25 ppm NaDPA therefore the mass of dipicrylamine in the spent bittern is :

$$\frac{391 \text{ m}^3}{\text{hr}} \left| \frac{25 \times 10^{-3} \text{ kg NaDPA}}{\text{m}^3} \right| = 9,8 \text{ kg NaDPA/hr}$$

By comparison, the spent seawater in the seawater process contains about  $2400 \text{ kg NaDPA/hr}$ .

## Recovery of Dipicrylamine from the Spent Bittern

This is an insignificant problem compared to that in the seawater process. The mass of foam required per hour is, assuming a loading of 0,30 kg NaDPA/kg foam :

$$\frac{9,8 \text{ kg NaDPA}}{\text{hr}} \Bigg| \frac{\text{kg foam}}{0,30 \text{ kg NaDPA}} = 33 \text{ kg/hr}$$

### A5.2 Process Cost Analysis

#### A5.2.1 Cost Analysis of the Seawater Process

##### A5.2.1.1 Introduction

The size and cost of major items of equipment are given below for a process which produces 100 tons  $\text{KNO}_3$ /day from seawater. This is then used to estimate the Total Fixed Capital Cost for this process.

##### A5.2.1.2 Cost Data

Cost data was obtained from Ruhmer and Wilson (139) who give South African equipment costs for 1983 and from Hall, Matley and McNaughton (150) who give U.S. costs for 1982. Also consulted were Backhurst and Harker (144) and Peters and Timmerhaus (151).

##### A5.2.1.3 The Seawater Process

The major items of equipment in the seawater process are described below and summarised in Table A5.1. The major items are the KDPA Reactor/Settler, the equipment for recovering dipicrylamine from the spent seawater, the vacuum filters, the Reactors and finally the Crystalliser.

The items are sized in the paragraphs below (S1 and S16).

KDPA Reactor/Settler

The required flow velocity for a settler which removes 99% of the KDPA precipitated from seawater is 5 mm/s (see Sec. 4.3.6). The flowrate into the Reactor/Settler is 5 300 m<sup>3</sup> seawater/hr plus 212 m<sup>3</sup> Ca(DPA)<sub>2</sub> solution/hr. The underflow rate is 49 m<sup>3</sup>/hr assuming that the underflow slurry has a concentration of 400 kg KDPA/m<sup>3</sup>. Thus the overflow rate is 5 463 m<sup>3</sup>/hr (5 300 + 212 - 49). The area required for the given upflow velocity is, after including a 15% safety factor for settlers :

$$\frac{1,15 \quad 5\,463 \text{ m}^3}{\text{hr}} \quad \left| \quad \frac{\text{hr}}{3\,600\text{s}} \quad \right| \quad \frac{0,05}{0,5 \times 10^{-3} \text{ m}} = 3,500 \text{ m}^2$$

This requires either the circular settler with a diameter of 67 m or two settlers of diameter 47 m or three settlers of diameter 39 m. The cost of thickeners (or settlers) is given by Ruhmer and Wilson (139) and is given in Table A5.2. The cost is for the settler and its associated equipment.

TABLE A5.2 : COST AND POWER REQUIREMENTS OF SETTLERS

<u>DIAMETER</u> (m)	<u>COST</u> (R)	<u>POWER</u> (kW)
67	540 000	19
47	280 000	12
39	210 000	9,5

The best choice would probably be two settlers of diameter 47 m. This will allow the partial shutdown of the plant for maintenance or cleaning of one of the settlers at a time.

S2

Solvent Mixers (Loading)

The recovery of dipicrylamine from the spent seawater by solvent extraction requires a series of three mixer settlers (see A5.1.1 Calc. 13a). The flowrate of spent seawater is 5 300 m<sup>3</sup>/hr and the flowrate of solvent is 90 m<sup>3</sup>/hr. Assuming a residence time of 5 minutes in each mixer, the volume of the mixers is 450 m<sup>3</sup> each. The cost of such a mixer including agitator is R60 000 and the power required is 24kW (Ruhmer and Wilson (139) Fig. 4).

S3

Solvent Settlers (Loading)

The residence time in the settlers should be about 10 minutes. The volume required is then 900 m<sup>3</sup>. The cost of flat-bottomed cylindrical tanks of this size constructed of mild steel is R30 000 each (Ruhmer and Wilson (139) Fig. 106).

S4

Solvent Mixers (Stripping)

The solvent used for the recovery of dipicrylamine from the spent seawater must be regenerated for reuse by stripping with freshwater. The flowrate of solvent is 90 m<sup>3</sup>/hr and the flowrate of freshwater is about 1 300 m<sup>3</sup>/hr. The cycle process for this regeneration is described in Sec. 5.3.3.7. For this discussion it will be assumed that eight stages will be needed with residence times of 5 minutes in the mixer and 10 minutes in the settler. Fewer stages could be used if hot water is used in the final stages.

The volume of each mixer is then 116 m<sup>3</sup>. The cost of these mixers is R25 000 each, complete with agitator and the power required is 10kW (Ruhmer and Wilson (139) Fig. 4).

S5

Solvent Settlers (Stripping)

The volume of the settlers is 230 m<sup>3</sup>. The cost of cylindrical mild steel tanks of this volume is R14 000 (Ruhmer and Wilson (139), Fig. 106).

S6

Foam Absorption

In this design the foam will absorb dipicrylamine in six stages in series with a residence time of fifteen minutes in each stage. The volume of each stage is then  $910 \text{ m}^3$ . The cost of a cylindrical mild steel tank of this size is R40 000 (139).

S7

Foam Regeneration

While six stages are absorbing dipicrylamine three other stages will be regenerated with hot water as outlined in Sec. 5.3.1.9.

S8

KDPA Slurry Filtration

The KDPA concentration is chosen to be  $400 \text{ kg KDPA/m}^3$ . The flowrate is :

$$\frac{19\,650 \text{ kg KDPA}}{\text{hr}} \left| \frac{\text{m}^3 \text{ slurry}}{400 \text{ kg KDPA}} \right. = 49 \text{ m}^3 \text{ slurry/hr}$$

The KDPA Slurry is very easy to filter. According to Backhurt and Harker (144) a typical filtration rate for such a solid is of the order of  $1 \times 10^{-3} \text{ m}^3/\text{s.m}^2$ . With this rate the area required to filter the KDPA slurry will be :

$$\frac{49 \text{ m}^3}{\text{hr}} \left| \frac{\text{hr}}{3\,600\text{s}} \right| \left| \frac{\text{m}^2\text{s}}{3 \times 10^{-3} \text{ m}^3} \right. = 13,6 \text{ m}^2$$

A drum filter with this area will cost R75 000 (139).

S9

Freshwater Wash Filter

The KDPA solid filtered off from the seawater is washed by mixing it with  $49,1 \text{ m}^3/\text{hr}$  of freshwater and filtered again. The area of this filter will be, as before,  $13,6 \text{ m}^2$  and the cost is R75 000 (139).

S10

HDDPA Filter

Assume that the method of solvent addition is used to improve the kinetics of conversion of KDPA to HDDPA. The ratio of solvent to KDPA is chosen to be 2 to 1. The solvent flowrate is then :

$$\frac{19\,650 \text{ kg KDPA}}{\text{hr}} \left| \frac{2 \text{ kg solvent}}{\text{kg KDPA}} \right| \frac{\text{m}^3}{900 \text{ kg solvent}} = 44 \text{ m}^3/\text{hr}$$

The flowrate of  $\text{KNO}_3$  solution is (A5.1.1 Calc. S10)  $41,2 \text{ m}^3/\text{hr}$ . Assuming a filtration rate of  $1 \times 10^{-3} \text{ m}^3/\text{m}^2\text{kg}$  the filter area is :

$$\frac{44 + 41,2 \text{ m}^3}{\text{hr}} \left| \frac{\text{m}^2\text{s}}{1 \times 10^{-3} \text{ m}^3} \right| \frac{\text{hr}}{3\,600 \text{ s}} = 24 \text{ m}^2$$

The cost of a drum filter constructed with stainless steel is R120 000 (139).

S11

Solid Waste Filter

The  $\text{Ca}(\text{DPA})_2$  solution produced by the Lime Reactor will contain some solids (such as unreacted lime). This must be filtered off. This can be done by allowing the solid to settle and withdrawing it with a small amount of reagent solution, say,  $1 \text{ m}^3/\text{hr}$ . This fine solid filters at a medium rate - assume  $1 \times 10^{-4} \text{ m}^3/\text{m}^2\text{s}$ . The area required is then :

$$\frac{1 \text{ m}^3}{\text{hr}} \left| \frac{\text{m}^2\text{s}}{1 \times 10^{-4} \text{ m}^3} \right| \frac{\text{hr}}{3\,600 \text{ s}} = 2,8 \text{ m}^2$$

A disc filter of this area will cost about R30 000 (139).

S12

Acid Reactor

The residence time required in the Acid Reactor is about 30 minutes when the method of adding solvent to the reaction mixture is used to improve the kinetics. The volume of this Reactor is then :

$$\frac{1}{2} \left\{ \frac{41,2 \text{ m}^3 \text{ KNO}_3/\text{HNO}_3 \text{ solution}}{\text{hr}} + \frac{44 \text{ m}^3 \text{ solvent}}{\text{hr}} \right\} = 43 \text{ m}^3$$

The cost of such a reactor is R13 000 including agitator (139).

S13

### Lime Reactor

The residence time in the Lime Reactor is about 30 minutes if the reaction is carried out at 35°C. The flowrate of reagent is 212 m<sup>3</sup>/hr so the volume of the reactor should be 106 m<sup>3</sup>. The cost of this reactor, excluding heating coil but including agitator, is R25 000 (139).

S14

### Evaporator/Crystalliser

Very little cost data is available for this equipment. Peters and Timmerhaus (151) give a purchase cost of about \$150 000 (1979) for a crystalliser of capacity 100 tons/day but this is an order of magnitude figure. The price will have escalated to R300 000 by 1983.

S15

### Main Seawater Pumps

Three pumps, each with 1/3 of the required total capacity, are specified. The head of 20 psi is assumed to be enough to pump the seawater from the sea to the KDPA Reactor/Settler. The seawater flows by gravity flow through the rest of the process. Each pump costs R7 500 (150).

S16

### Freshwater Pump for Foam or Solvent Regeneration

The flow of freshwater in the cyclical process for the regeneration of the foam or solvent will be about 1 300 m<sup>3</sup>/hr (Calc. 13b). The water will have to be pumped through a bed of foam or through a number of stripping stages. A head of 30 psi is assumed. Each pump costs R5 000 (150).

TABLE A5.1 : MAJOR ITEMS OF EQUIPMENT FOR SEAWATER PROCESS

ITEM	NAME	NO. OF UNITS	SPEC.	MATERIAL OF CONSTRUCTION	PRICE	DATA SOURCE	COMMENTS
1	KDPA Reactor/ Settler	2	Diam. 47m	Mild Steel	R280 000 each Complete R560 000 total	(139) Fig. 111	Power required 12 kW each
2	Solvent Mixer (Loading)	3	450m <sup>3</sup>	Mild Steel	R 60 000 each R180 total	(139) Fig. 49	Complete with agitator Power required 24 kW each
3	Solvent Settler (Loading)	3	900 m <sup>3</sup>	Mild Steel	R 30 000 each R 90 000 total	(139) Fig. 106	
4	Solvent Mixer (Stripping)	8	116m <sup>3</sup>	Mild Steel	R 25 000 each R200 000 total	(139) Fig. 4	Complete with agitator Power required 10 kW each
5	Solvent Settler (Stripping)	8	230m <sup>3</sup>	Mild Steel	R 14 000 each R112 000 total	(139) (Fig. 106)	
6	Foam Absorbers	6	910m <sup>3</sup>	Mild Steel	R 40 000 each R240 000 total	(139) Fig. 106	Price excludes foam in these units
7	Foam Regeneration	3	910m <sup>3</sup>	Mild Steel	R 40 000 each R120 000 total	(139) Fig. 106	Price excludes foam in these units
8	KDPA Slurry Filter	1	49m <sup>3</sup> /hr 13,6 m <sup>2</sup>	Mild Steel Drum Filter	R 75 000 Complete	(139) Fig. 49	Power 2 kW
9	Freshwater Wash Filter	1	49,1m <sup>3</sup> /hr 13,6m <sup>2</sup>	Mild Steel Drum Filter	R 75 000 Complete	(139) Fig. 49	Power 2 kW
10	HOPA Filter	1	44m <sup>3</sup> 24m <sup>2</sup>	Stainless Steel Drum Filter	R120 000	(139) Fig. 49	Power 2,5 kW
11	Solid Waste Filter	1	1m <sup>3</sup> /hr 2,8m <sup>2</sup>	Mild Steel Disc Filter	R 30 000	(139) Fig. 48	
12	Acid Reactor	1	43m <sup>3</sup>	304 Stainless Steel	R 13 000 R	(139) Fig. 4	Power 6 kW
13	Lime Reactor	1	106m <sup>3</sup>	Mild Steel	R 25 000 R	(139) Fig. 4	Power 10 kW
14	Evaporator/ Crystalliser	1	100 tons/ day	304 Stainless Steel	R300 000 ?	(151) Fig. 13.77	Order of magnitude estimate given as \$150 in 1979. This escalated to about R300 000 in 1983
15	Main Seawater Pumps	3	1800m <sup>3</sup> /hr ea 20 psi head	Cast Iron Centrifugal	R 7 500 each	(150) Fig. 30	Price includes drive and motor. Power 60 kW
16	Regeneration Freshwater	2	700m <sup>3</sup> /hr ea 30 psi head	Cast Iron	R 5 000 each	(150) Fig. 30	Price includes drive and motor. Power 30 kW

A5.2.1.4 Total Fixed Capital Investment for Seawater Process

The total cost of the major items of equipment is as follows :

	<u>R000'S (1983)</u>
KDPA Reactor Settler	560
Dipicrylamine Recovery from Spent Seawater :	
Solvent Process (Option A)	582
<u>or</u>	
Foam Process Option (B)	360
Filters	300
Reactors	38
Evaporator/Crystalliser	300
Pumps	<u>33</u>
Total Major Item Cost Using (A)	1 813
Total Major Item Cost Using (B)	1 591

The Lang factor for a solid/fluid processing plant is 4,13 (151).  
Thus the Total Fixed Capital Investment would be :

Using A :	4,13 x 1 813	7 500
		=====
Using B :	4,13 x 1 591	6 600
		=====

## A5.2.2 Cost Analysis of the Bittern Process

### A5.2.2.1 Introduction

The size and cost of the major items of equipment are given below for a process which produces 100 tons  $\text{KNO}_3$ /day from a bittern. This is then used to estimate the Total Fixed Capital Cost for this process.

The cost data was obtained from sources given in A5.2.1.2.

The major items of equipment are the KDPA Reactor Settler, the Filters, the Acid Reactor, the Lime Reactor and the Evaporator/Crystalliser. The equipment for recovering the dipicrylamine from the spent bittern will be small and can be ignored in this discussion. The equipment is summarised in Table A5.2.

### A5.2.2.2 The Bittern Process

#### B1 The KDPA Reactor/Settler

From Sec. 4.3.1 the minimum flux is  $0,04 \text{ kg/m}^2\text{s}$  in the KDPA Settler. Thus the area required in the settler is :

$$\frac{19\ 650 \text{ kg KDPA}}{\text{hr}} \times \frac{\text{m}^2\text{s}}{0,04 \text{ kg}} \times \frac{\text{hr}}{3\ 600\text{s}} = 136 \text{ m}^2$$

In this kind of settling a safety factor of 100% is often used. Thus the area is  $272 \text{ m}^2$  which requires a circular settler of diameter 19 m. This will cost R100 000 (143).

#### B2 KDPA Slurry Filter

This will cost R75 000 (see A5.2.1.3 Calc. S8).

B3

Seawater Wash Filter

The filter cake from the KDPA slurry filter is washed by mixing it with 177 m<sup>3</sup> seawater/hr. The KDPA is then filtered off and sent to the Freshwater wash step. The filter size required assuming a filtration rate (142) of 1 x 10<sup>-3</sup> m<sup>3</sup>/m<sup>2</sup>s is :

$$\frac{177 \text{ m}^3}{\text{hr}} \left| \frac{\text{m}^2 \text{s}}{1 \times 10^{-3} \text{ m}^3} \right| \frac{\text{hr}}{3 \ 600 \text{s}} = 49 \text{ m}^2$$

This will cost R130 000 complete (143).

B4

Freshwater Wash Filter

As in A5.2.1.3 Calc. S9, this will cost R75 000.

B5

HDPA Filter

The flowrate of KNO<sub>3</sub> solution is 41,2 m<sup>3</sup>/hr. Assuming a filtration rate of 1 x 10<sup>-3</sup> m<sup>3</sup>/m<sup>2</sup>s the area required is :

$$\frac{41,2 \text{ m}^3}{\text{hr}} \left| \frac{\text{m}^2 \text{s}}{1 \times 10^{-3} \text{ m}^3} \right| \frac{\text{hr}}{3 \ 600 \text{s}} = 11,4 \text{ m}^2$$

This will cost R85 000 complete (143).

B6

Solid Waste Filter

The solid waste flowrate is 3 160 kg/hr (A5.1.2 Calc. B6). Assume that it is withdrawn with and must be filtered from 10 m<sup>3</sup> reagent solution. Assume the filtration rate is 1 x 10<sup>-4</sup> m<sup>3</sup>/m<sup>2</sup>s. The area required is then :

$$\frac{10 \text{ m}^3}{\text{hr}} \left| \frac{\text{m}^2 \text{s}}{1 \times 10^{-4} \text{ m}^3} \right| \frac{\text{hr}}{3 \ 600 \text{s}} = 28 \text{ m}^2$$

The cost of this filter is R70 000 complete (143) if a disc filter is used.

B7

Acid Reactor

As discussed in Sec. 6.3 KDPA precipitated from a bittern is rapidly converted by  $\text{HNO}_3$  to HDP. The volume of  $\text{KNO}_3/\text{HNO}_3$  solution produced by the Acid Reactor is  $41,2 \text{ m}^3/\text{hr}$  so, with a residence time of 30 minutes, the Reactor volume is  $20,6 \text{ m}^3$ . An agitated reactor of this volume will cost R8 000 complete (143).

B8

Lime Reactor

As in A5.2.1.3 Calc. S13. This will cost R25 000.

B9

Evaporator/Crystalliser

As in A5.2.1.3 Calc. S14. This is estimated to cost R300 000.

TABLE A5.2 : MAJOR ITEMS OF EQUIPMENT FOR BITTERN PROCESS

<u>ITEM</u>	<u>NAME</u>	<u>NO. OF UNITS</u>	<u>SPEC.</u>	<u>MATERIAL OF CONSTRUCTION</u>	<u>PRICE</u>	<u>DATA SOURCE</u>	<u>COMMENTS</u>
1	KDPA Reactor/ Settler	1	Diam. 19m	Mild Steel	R100 000 Complete	(143) Fig. 111	Power required 3 kW
2	KDPA Slurry Filter	1	49m <sup>3</sup> /hr 13,6 m <sup>2</sup>	Mild Steel Drum Filter	R 75 000 Complete	(143) Fig. 49	Power required 2 kW
3	Seawater Wash Filter	1	49m <sup>2</sup>	Mild Steel Drum Filter	R130 000 Complete	(143) Fig. 49	Power required 4,5 kW
4	Freshwater Wash Filter	1	13,6m <sup>2</sup>	Mild Steel Drum Filter	R 75 000 Complete	(143) Fig. 49	Power required 2 kW
5	HOPA Filter	1	11,4m <sup>2</sup>	304 S. Steel Drum Filter	R 85 000 Complete	(143) (Fig. 49)	Power required 2,5 kW
6	Solid Waste Filter	1	28m <sup>2</sup>	Mild Steel Disc Filter	R 70 000 Complete	(143) Fig. 48	Power required 3 kW
7	Acid Reactor	1	20,6m <sup>3</sup>	304 Stainless Steel	R 8 000 Complete	(143) Fig. 4	Power required 6 kW
8	Lime Reactor	1	106m <sup>3</sup>	Mild Steel	R 25 000	(143) Fig. 4	Power required 10 kW
9	Evaporator/ Crystalliser	1	100 tons/ day	304 Stainless Steel	R300 000	(50) Fig. 13.77	

### A5.2.2.3 Total Fixed Capital Investment for Bittern Process

The total cost of the major items of equipment is as follows :

	<u>R000'S (1983)</u>
KDPA Reactor Settler	100
Filters	435
Reactors	33
Evaporator/Crystalliser	<u>300</u>
Total Major Item Cost	868

Using the Lang factor (4,13 for solid/fluid operations) (50) the Total Fixed Capital Investment would be :

$$4,13 \times 868 \qquad \qquad \qquad 3\ 600$$

=====

## A5.3

Energy Consumption

## A5.3.1

Steam Usage

The major usage of steam is in the evaporator/crystalliser and, where applicable, for foam regeneration.

(a) Evaporator/Crystalliser :

Assume an economy of 2 kg evaporate/kg steam with a steam pressure of 25psig.

$$\frac{42,2 \times 10^3 \text{ kg KNO}_3 \text{ soln}}{\text{hr}} \left| \frac{\text{kg steam}}{2 \text{ kg evaporate}} \right. = 21 \text{ tons/hr}$$

(b) Foam Regeneration

Assume that the freshwater used for regeneration must be heated by 20°C before eluting the foam. The energy requirement is :

$$\frac{1300 \times 10^3 \text{ kg water}}{\text{hr}} \left| \frac{20^\circ\text{C}}{\text{kg } ^\circ\text{C}} \right| \frac{4.18 \text{ kJ}}{\text{kg } ^\circ\text{C}} = 1.1 \times 10^8 \text{ kJ/hr}$$

Use saturated steam at 25 psig (latent heat = 2200 kJ/kg).

Assume cost of this steam is R2/ton

$$\frac{1.1 \times 10^8 \text{ kJ}}{\text{hr}} \left| \frac{\text{kg steam}}{2200 \text{ kJ}} \right. = 50 \text{ tons/hr}$$

## A5.3.2

Electricity Consumption(a) Seawater Process :

The major electricity consumers are, from Table A5.1, the KDPA Reactor/Settler (24kw), the Reactors (16kw), the pumps (90kw) and, where used, the Solvent Mixers for the Solvent Extraction of dipicrylamine from the spent seawater (152kw). The total consumption is :

Option A (using Solvent for dipicryllamine recovery) 282 kw.

Option B (using Foam for dipicryllamine recovery) 130 kw.

(b) Bittern Process :

The major electricity consumers, from Table A5.2, are the KDPA Reactor/Settler (3 kw), the filters (14 kw) and the Reactors (16 kw). The total is 33 kw.

## APPENDIX

### A5.4

#### NET PRESENT VALUE CALCULATION

##### Assumptions

The following assumptions were made for the calculation :

Electricity : 3,5c/kWh

Water : 50c/m<sup>3</sup>

Steam :

R2/ton including capital cost of steam generation plant (144).

Dipicrylamine :

The cost of dipicrylamine is difficult to estimate. However, the bulk cost of chlorobenzene and aniline, the two reagents in the synthesis, is about R6/kg (51) or R675/kg mol and R560/kg mol respectively. One mol of each is required in the synthesis of dipicrylamine giving a total raw material cost of R1 235/kg mol or R2,80/kg. Assume that the total cost (including cost of manufacture) is R5/kg.

Expenses :

(Labour, maintenance, insurance, overheads, administrative costs).

These were estimated using guidelines given by Peters and Timmerhaus (151).

Depreciation :

Straight line depreciation over ten years.

Taxation :

At a rate of 50% of operating income less depreciation.

Working Capital :  
Assumed to be 10% of taxed capital.

Sample Calculation

The net present value calculation was calculated in a computer program. Samples of the output are shown for the seawater and bittern process in Figures A5.5 and A5.6

Fig. A5.5

ECONOMIC ANALYSIS OF THE DPA SEAWATER PROCESS  
=====(R000'S/YR)  
-----

SALES										
=====										
SALE OF POTASSIUM NITRATE										
-----										
KN03 (TONS/DAY)	100	100	100	100	100	100	100	100	100	100
SALE PRICE (R/TON)	600	600	600	600	600	600	600	600	600	600
-----										
SALES	20400	20400	20400	20400	20400	20400	20400	20400	20400	20400
-----										
COST OF SALES										
=====										
COST OF NITRIC ACID:										
-----										
HNO3 (TONS/DAY)	62	62	62	62	62	62	62	62	62	62
COST (R/TON)	400	500	550	600	650	700	750	800	900	1000
-----										
COST	8432	10540	11594	12648	13702	14756	15810	16864	18972	21080
-----										
OTHER COSTS:										
-----										
LIME (TONS/DAY)	43	43	43	43	43	43	43	43	43	43
COST (R/TON)	75	75	75	75	75	75	75	75	75	75
-----										
COST	1097	1097	1097	1097	1097	1097	1097	1097	1097	1097
-----										
DPA LOSSES (KG/DAY)	127	127	127	127	127	127	127	127	127	127
COST (R/KG)	5	5	5	5	5	5	5	5	5	5
-----										
COST	216	216	216	216	216	216	216	216	216	216
-----										
ELECTRICITY (KWH/DAY)	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
COST (CENTS/KWH)	4	4	4	4	4	4	4	4	4	4
-----										
COST	60	60	60	60	60	60	60	60	60	60
-----										
WATER (M3/DAY)	790	790	790	790	790	790	790	790	790	790
COST (CENTS/M3)	50	50	50	50	50	50	50	50	50	50
-----										
COST	134	134	134	134	134	134	134	134	134	134
-----										
STEAM (TONS/DAY)	1680	1680	1680	1680	1680	1680	1680	1680	1680	1680
COST (R/TON)	2	2	2	2	2	2	2	2	2	2
-----										
COST	1142	1142	1142	1142	1142	1142	1142	1142	1142	1142
-----										
TOTAL COST OF SALES	11081	13189	14243	15297	16351	17405	18459	19513	21621	23729
-----										
GROSS MANUFACTURING MARGIN										
LESS:	9319	7211	6157	5103	4049	2995	1941	887	-1221	-3329
EXPENSES:										
-----										
LABOUR	464	464	464	464	464	464	464	464	464	464
MAINTENANCE	490	490	490	490	490	490	490	490	490	490
INSURANCE	70	70	70	70	70	70	70	70	70	70
OVERHEADS	572	572	572	572	572	572	572	572	572	572
ADMIN	202	202	202	202	202	202	202	202	202	202
-----										
TOTAL EXPENSES	2262	2262	2262	2262	2262	2262	2262	2262	2262	2262
-----										
NET OPERATING INCOME BEFORE TAX										
LESS: TAX	7058	4950	3896	2842	1788	734	-321	-1375	-3483	-5591
-----										
ANNUAL CASH FLOW	3179	2125	1598	1071	544	17	0	0	0	0
-----										
ANNUAL CASH FLOW	3879	2825	2298	1771	1244	717	-321	-1375	-3483	-5591
=====										
NET PRESENT VALUE CALCULATION										
=====										
CAPITAL	7000	7000	7000	7000	7000	7000	7000	7000	7000	7000
WORKING CAPITAL	700	700	700	700	700	700	700	700	700	700
DISCOUNT RATE (%)	25	25	25	25	25	25	25	25	25	25
LIFE (YEARS)	10	10	10	10	10	10	10	10	10	10
-----										
NET PRESENT VALUE	6149	2306	504	-1378	-3259	-5141	-8844	-12608	-20134	-27661
=====										

Fig. A5.6

ECONOMIC ANALYSIS OF THE DPA BITTERN PROCESS

(R000'S/YR)

SALES										
=====										
SALE OF POTASSIUM NITRATE										
-----										
KN03 (TONS/DAY)	100	100	100	100	100	100	100	100	100	100
SALE PRICE (R/TON)	600	600	600	600	600	600	600	600	600	600
-----										
SALES	20400	20400	20400	20400	20400	20400	20400	20400	20400	20400
-----										
COST OF SALES										
=====										
COST OF NITRIC ACID:										
-----										
HN03 (TONS/DAY)	62	62	62	62	62	62	62	62	62	62
COST (R/TON)	400	500	550	600	650	700	750	800	900	1000
-----										
COST	8432	10540	11594	12648	13702	14756	15810	16864	18972	21080
-----										
OTHER COSTS:										
-----										
LIME (TONS/DAY)	43	43	43	43	43	43	43	43	43	43
COST (R/TON)	75	75	75	75	75	75	75	75	75	75
-----										
COST	1097	1097	1097	1097	1097	1097	1097	1097	1097	1097
-----										
DPA LOSSES (KG/DAY)	10	10	10	10	10	10	10	10	10	10
COST (R/KG)	5	5	5	5	5	5	5	5	5	5
-----										
COST	17	17	17	17	17	17	17	17	17	17
-----										
ELECTRICITY (KWH/DAY)	792	792	792	792	792	792	792	792	792	792
COST (CENTS/KWH)	4	4	4	4	4	4	4	4	4	4
-----										
COST	9	9	9	9	9	9	9	9	9	9
-----										
WATER (M3/DAY)	190	190	190	190	190	190	190	190	190	190
COST (CENTS/M3)	50	50	50	50	50	50	50	50	50	50
-----										
COST	32	32	32	32	32	32	32	32	32	32
-----										
STEAM (TONS/DAY)	506	506	506	506	506	506	506	506	506	506
COST (R/TON)	2	2	2	2	2	2	2	2	2	2
-----										
COST	344	344	344	344	344	344	344	344	344	344
-----										
TOTAL COST OF SALES	9931	12039	13093	14147	15201	16255	17309	18363	20471	22579
-----										
GROSS MANUFACTURING MARGIN	10469	8361	7307	6253	5199	4145	3091	2037	-71	-2179
LESS:										
EXPENSES:										
-----										
LABOUR	464	464	464	464	464	464	464	464	464	464
MAINTENANCE	252	252	252	252	252	252	252	252	252	252
INSURANCE	36	36	36	36	36	36	36	36	36	36
OVERHEADS	430	430	430	430	430	430	430	430	430	430
ADMIN	202	202	202	202	202	202	202	202	202	202
-----										
TOTAL EXPENSES	1847	1847	1847	1847	1847	1847	1847	1847	1847	1847
-----										
NET OPERATING INCOME BEFORE TAX	8622	6514	5460	4406	3352	2298	1244	190	-1918	-4026
LESS: TAX	4131	3077	2550	2023	1496	969	442	0	0	0
-----										
ANNUAL CASH FLOW	4491	3437	2910	2383	1856	1329	802	190	-1918	-4026
=====										
NET PRESENT VALUE CALCULATION										
=====										
CAPITAL	3600	3600	3600	3600	3600	3600	3600	3600	3600	3600
WORKING CAPITAL	360	360	360	360	360	360	360	360	360	360
DISCOUNT RATE (%)	25	25	25	25	25	25	25	25	25	25
LIFE (YEARS)	10	10	10	10	10	10	10	10	10	10
-----										
NET PRESENT VALUE	12074	8311	6429	4548	2666	784	-1097	-3283	-10810	-18336
=====										

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