

REMOVAL OF CADMIUM FROM WET PROCESS PHOSPHORIC
ACID BY CATION EXCHANGE

A thesis submitted for the degree of
DOCTOR OF PHILOSOPHY
in the Faculty of Engineering of the University of London

by

NICHOLAS ANTHONY BOOKER

Department of Chemical Engineering and Chemical Technology
Imperial College of Science and Technology
South Kensington
London

February, 1989

ABSTRACT

Wet process phosphoric acid (WPA), produced by the digestion of phosphate rock in strong mineral acids contains a wide range of dissolved metals (for example cadmium). The subsequent use of WPA for the production of fertilizers can result in these metal species being present in the fertilizer.

The object of this thesis was to establish the technical and economic feasibility of using commercially available ion exchange resins for the removal of cadmium from WPA.

Of the resins tested, the most suitable for removing divalent cadmium ions from phosphoric acid was Duolite C264, a macroporous, sulphonic acid resin. Competition from other divalent metal cations (in particular Ca^{2+} and Mg^{2+}) for ion exchange sites reduced this resin's cadmium capacity. The distribution coefficients for Ca^{2+} , Cd^{2+} and Mg^{2+} exchange for H^+ ions on Duolite C264 in 28% P_2O_5 were determined to be 13.0, 5.1 and 3.8 respectively.

Kinetic tests established that the rate of cadmium uptake by Duolite C264 was controlled by diffusion of cadmium through the resin particles. The diffusion coefficient was determined experimentally to be $8.7 \times 10^{-8} \text{ cm}^2/\text{s}$ at 60°C .

Successful ion exchange of cadmium from WPA was achieved once the calcium concentration of the feed acid was reduced to a concentration of less than 50 g/m^3 . This was achieved by increasing the sulphate concentration of the acid to promote precipitation of calcium sulphate. Both fixed bed and continuous counter-current column tests showed that cadmium concentrations could be reduced from about 15 g/m^3 in the feed WPA to less than 2 g/m^3 in the treated acid.

The cadmium loaded resin was effectively eluted using 5M HCl solutions with cadmium elution complete in about one bed volume of throughput. Cadmium elution efficiency was high since anionic cadmium chloride complexes were formed by the eluted cadmium in the 5M HCl eluant. The cadmium chloride complexes were successfully removed from the eluate using a strong base ion exchange resin.

A process using Duolite C264 resin to reduce the cadmium concentration of 1000 m³/day of 28% P₂O₅ WPA from 15 g/m³ to less than 2 g/m³ was estimated to increase the cost of P₂O₅ by about 13%.

ACKNOWLEDGEMENT

I wish to thank my supervisor, Dr M Streat, in appreciation of his friendly encouragement and guidance throughout my course of studies and during the period of time I spent writing this manuscript.

Special thanks go to my wife Cath for persevering with and encouraging me during the time it has taken to produce this manuscript.

I would also like to thank the staff at Albright and Wilson, Oldbury and Morton Carlisle of Rohm and Haas for their assistance during the project.

N A Booker

February, 1989

CONTENTS

	Page No.
TITLE PAGE	1
ABSTRACT	2
ACKNOWLEDGEMENT	4
CONTENTS	5
LIST OF TABLES	7
LIST OF FIGURES	9
NOMENCLATURE	12
1 INTRODUCTION	13
1.1 Background	13
1.2 Objectives	14
2 REVIEW OF RELEVANT LITERATURE	15
2.1 Significance of cadmium in fertilizers	15
2.2 Removal of cadmium from phosphoric acid	17
2.2.1 Reduced cadmium content phosphate rock	18
2.2.2 Precipitation	19
2.2.3 Solvent extraction	21
2.2.4 Ion exchange processes	25
3 THEORY	29
3.1 Ion exchange theory	29
3.1.1 Selection of a suitable ion exchanger	30
3.2 Determination of reaction kinetics	33
3.2.1 Film diffusion	34
3.2.2 Particle diffusion	35
3.2.3 Chemical reaction	37
4 EXPERIMENTAL METHODS	39
4.1 Resin selection tests	39
4.2 Batch stir tests	42
4.3 Fixed column tests	45
4.4 Multistage batch tests	48
4.5 Continuous counter-current ion exchange tests	50
4.5.1 Cadmium extraction contactor	50
4.5.2 Elution	55
4.5.3 Eluant regeneration	56
4.5.4 Overall equipment operation	56

5 DISCUSSION OF RESULTS	58
5.1 Resin selection tests	58
5.1.1 X-Ray fluorescence analysis	59
5.2 Batch stir tests	60
5.2.1 Temperature	62
5.2.2 Concentration of P_2O_5	62
5.2.3 Resin particle size	62
5.2.4 Speed of agitation	66
5.2.5 Cadmium concentration	66
5.2.6 Interruption test	70
5.2.7 Resin cross linking	70
5.2.8 Equilibrium data	71
5.3 Determination of diffusion mechanism	75
5.4 Fixed column tests	83
5.4.1 10 mm fixed columns	83
5.4.2 38 mm fixed columns	86
5.5 Multistage batch tests	96
5.6 Continuous counter-current ion exchange tests	99
5.6.1 Results of continuous counter-current cadmium extraction	105
5.6.2 Cadmium elution from C264 using 5M HCl	107
5.6.3 Regeneration of eluant	109
5.7 Process selection	114
6 CONCLUSIONS AND RECOMMENDATIONS	117
REFERENCES	120
APPENDIX 1 Analysis of phosphoric acids used in experimental work	124
APPENDIX 2 Likely metal-ion complexes in phosphoric acid	126
APPENDIX 3 Experimental conditions used in cadmium extraction tests	127
APPENDIX 4 Results from 38 mm fixed column tests	133
APPENDIX 5 X-Ray fluorescence analysis of loaded resins	143
APPENDIX 6 Cost estimates for removal of cadmium from WPA using the strong acid resin Duolite C264	145
APPENDIX 7 Estimation of errors	160

LIST OF TABLES

Table	Title	Page No.
2.1	Estimated trace element inputs to UK arable land.	16
2.2	Cadmium content of phosphate rock used in the production of phosphoric acid.	19
3.1	Selectivity scale for divalent cations in sulphonic acid resins.	32
4.1	Resins used in initial selection tests.	41
4.2	Metal species and associated ions used in resin selection batch stir tests.	42
5.1	Results of resin selection tests.	59
5.2	Raw results from a batch stir test showing calculated attainment of equilibrium.	61
5.3	Calculated ion exchange model fitting data.	75
5.4	Effect of resin diameter on particle diffusion coefficient.	80
5.5	Effect of stirrer speed on particle diffusion coefficient.	80
5.6	Effect of solution concentration on particle diffusion coefficient.	81
5.7	Effect of degree of cross linking on particle diffusion coefficient in Duolite C264.	82
5.8	Effect of temperature on particle diffusion coefficient.	82
5.9	Results of preliminary elution tests.	86
5.10a	38mm fixed bed column loading results.	94
5.10b	38mm fixed bed column elution results.	95
5.11	Progress of multistage batch experiments.	97
5.12	Results of eluted resin capacity tests.	106
5.13	Elution results using 5M HCl in fixed columns with reuse of eluate as eluant.	108
A1.1	BDH "Analar" phosphoric acid assay.	124
A1.2	Analysis of WPAs used in experimental work.	125
A3.1	Experimental conditions used in 10 mm fixed column tests	130

Table	Title	Page No.
A3.2	Experimental conditions used in 38 mm fixed column tests for extraction onto C264 from phosphoric acid.	130
A3.3	Experimental conditions used in 38 mm fixed column tests for elution of loaded C264 resin.	131
A3.4	Experimental conditions used in to extract cadmium from WPA using C264 in continuous counter-current column tests.	131
A3.5	Experimental conditions used to elute loaded C264 resin from continuous counter-current column tests.	132
A4.1,19	Results from 38 mm fixed column tests.	133,142
A5.1	Results of X-Ray fluorescence analysis of ion-exchange resins used for treatment of WPA.	144
A6.1	Estimate of capital cost of a fixed bed ion-exchange process removing cadmium from 1000 m ³ /day of WPA.	149
A6.2	Estimate of capital cost of a moving packed bed ion exchange process removing cadmium from 1000 m ³ /day of WPA.	154
A6.3	Estimate of capital costs associated with WPA pretreatment and eluant regeneration in a process to remove Cd from 1000 m ³ /day of WPA.	157

LIST OF FIGURES

Figure	Title	Page No.
2.1	Flow sheet for cadmium extraction from WPA by solvent extraction with tertiary amines.	22
2.2	Phosphoric acid extraction from WPA by solvent extraction using MIBK.	24
2.3	Flow sheet for cadmium removal from WPA by ion-exchange using anion exchange resins.	26
4.1a	Contactore tube design used in multistage batch tests.	49
4.1b	Schematic transfer sequence used in multistage batch tests.	49
4.2a	Contactore plate cross-section.	52
4.2b	Contactore bottom plate cross-section.	52
4.2c	Air actuated slider valve.	52
4.3	Cadmium extraction column control layout.	54
4.4	Schematic layout of the continuous counter-current ion exchange apparatus.	57
5.1	Cd loaded onto Duolite C264 from 40% P_2O_5 acid. Effect of temperature on loading rate.	63
5.2	Cd loading onto Duolite C264 from phosphoric acid. Effect of P_2O_5 concentration on loading rate.	64
5.3	Cd loading onto Duolite C264 from 40% P_2O_5 acid. Effect of particle size on loading rate.	65
5.4	Cd loading onto Duolite C264 from 40% P_2O_5 acid. Effect of stirrer speed on loading rate.	67
5.5	Cd loading onto Duolite C264 from 40% P_2O_5 acid. Effect of Cd concentration on loading rate.	68
5.6	Cd loading onto Duolite C264 from 40% P_2O_5 acid. Effect of interruption during contact.	69
5.7	Cd loading onto gel-type resins from 40% P_2O_5 acid. Effect of crosslinking on loading rate.	72
5.8	Cd loading onto macroporous resins from 40% P_2O_5 acid. Effect of crosslinking on loading rate.	73
5.9	Cd loading onto Duolite C264 from pure phosphoric acid. Equilibrium loadings at different P_2O_5 concentrations.	74

Figure	Title	Page No.
5.10	Ion exchange model fitting plots. Fractional attainment of equilibrium and $-\ln(1-X)$ versus time.	76
5.11	Ion exchange model fitting plots. $-\ln(1-X^2)$ and ζ versus time.	77
5.12	Arrhenius plot showing the effect of temperature on the rate of cadmium removal from phosphoric acid by Duolite C264.	79
5.13	Cadmium extraction onto Duolite C264 in 10 mm fixed bed columns. Effect of throughput rate on breakthrough.	84
5.14	Cadmium elution from Duolite C264 using sulphuric acid. Effect of acid strength, throughput rate and temperature.	85
5.15	Cadmium loading onto Duolite C264 from pure phosphoric acid. Effect of throughput rate in fixed bed columns on loading.	88
5.16	Reduction in the calcium concentration of WPA. Calcium concentration versus sulphuric acid dose applied.	90
5.17	Results of fixed column tests using Duolite C264 to treat WPA. Effect of calcium concentration of the feed acid.	91
5.18	Elution of Duolite C264 (loaded from WPA) using 5M HCl. Eluate concentration versus column throughput.	93
5.19	Relationship between metal-ion concentration in solution and on Duolite C264 for Cd, Ca and Mg in 28% P_2O_5 WPA.	98
5.20a,e	Results of continuous counter-current tests using Duolite C264 to treat WPA.	100,104
5.21	Cadmium exchange from 5M HCl eluant onto Duolite Al61. Raffinate Cd concentration versus column throughput.	110
5.22a	Elution of cadmium from loaded Duolite Al61 using 5M HCl. Eluate Cd concentration versus column throughput.	112

Figure	Title	Page No.
5.22b	Elution of cadmium from loaded Duolite A161 using water. Eluate Cd concentration and pH versus column throughput.	113
A6.1	Proposed process flow diagram for cadmium removal from WPA by cation exchange.	146
A6.2	Schematic process flowsheet for Cd removal from WPA using fixed bed ion exchange contactors.	148
A6.3	Operation of moving packed bed contactor system.	152

NOMENCLATURE

Symbol	Description	Units
a_i	Activity of ion i in solution	
$\bar{a}_i$	Activity of ion i in resin	
C	Solution concentration of metal ion	g/m^3
$\bar{C}_f$	Equilibrium metal-ion concentration on resin	mg/kg resin
C_i	Concentration of ion i in solution	g/m^3
$\bar{C}_i$	Concentration of ion i in resin	mg/kg resin
C_0	Initial metal-ion concentration in solution	g/m^3
C_t	Concentration of metal-ion in solution at time t	g/m^3
$\bar{C}_t$	Concentration of metal-ion in resin at time t	mg/kg resin
$\bar{D}$	Particle diffusion coefficient	cm^2/s
K_a	Equilibrium constant	
K_{CA}^B	Selectivity coefficient for ions B over ions A	
K_d	Distribution coefficient	
m	Mass of centrifuged moist resin	kg
q	Resin capacity in equilibrium with C	mg/g resin
r_0	Resin particle radius	m
t	Time	minutes
T	Temperature	$^{\circ}\text{K}$
V	Volume of solution in batch test	m^3
$\bar{V}$	Volume of resin in batch test	m^3
X	Fractional attainment of equilibrium	
X_t	Fractional attainment of equilibrium at time t	
γ_i	Activity coefficient for ion i	
δ	Mass transfer film thickness	m
τ	Dimensionless time function from Paterson's approximation.	

1 INTRODUCTION

1.1 Background

Phosphoric acid is produced either by dissolving phosphorus pentoxide in water or by digesting phosphate rock in a mineral acid. The majority of phosphoric acid is produced by the latter process and is termed wet process acid (WPA). In the UK, WPA is produced by digesting phosphate rock in sulphuric acid.

Geologically phosphate rock is sedimentary in origin, formed by the precipitation of dissolved phosphates from sea water. Many other compounds are also precipitated from sea water at the same time and accumulate within the same strata as the phosphate minerals.

Dissolution of the phosphate rock in mineral acids to produce WPA can release some of these compounds into the acid. An analysis of some typical WPA's is given in Appendix 1 and shows that a wide range of metallic species can be present in WPA. The actual composition of the acid will depend on the source of the phosphate rock but generally most metals present in one acid will be present to varying extents in acids produced from other ore bodies.

Over 90% of the WPA produced in the UK is used for the production of phosphate based fertilizers. Many of the metal species present in WPA will end up in the finished phosphate fertilizer and will be spread over arable land. There is increasing concern that some plants are capable of recovering heavy metals from the soil and that intensive use of fertilizers in agriculture can be a possible route to the introduction of heavy metals into the human food chain.

Cadmium is present in WPA at concentrations between about 5 and 30 g Cd/m³ and its presence in phosphate fertilizers produced from this acid may be responsible for over 50% of the input of cadmium into UK arable land. At present there are no regulations governing the discharge of cadmium to land via the use of phosphate fertilizers. However, there is concern amongst fertilizer producers that there may be restrictions on the concentrations of cadmium present in phosphate based fertilizers imposed by the European Community (EC) in the future.

1.2 Objectives

The aim of this work was to determine if it was possible to use commercially available ion exchange resins in a process to remove cadmium from wet process phosphoric acid.

This objective was achieved by: reviewing the chemistry of cadmium in phosphoric acid, performing selection tests for a range of ion exchange resins, determining the kinetic and equilibrium properties of the selected resin for cadmium sorption from phosphoric acid, develop and demonstrate a suitable process utilizing the selected resin to treat WPA and determine the economics of treating WPA using this process.

2 REVIEW OF RELEVANT LITERATURE

2.1 Significance of cadmium in fertilizers

The removal of cadmium from phosphoric acid may be required to prevent its possible release into the food chain via the phosphate based fertilizers that are used in agriculture.

Ingested cadmium compounds can be absorbed by the alimentary system (1) and can result in poisoning. Cadmium entering the body in this manner can accumulate within the liver and kidneys and has a long biological half life, accumulating with age. Cadmium interacts with other metals in the body (especially zinc) and can displace them from metal containing enzymes thus altering important biological functions.

The health effects of cadmium ingestion can be acute and in extreme cases can lead to fatal renal disorders. In Japan, the outbreak of Itai-Itai disease which resulted in irreversible renal disease was associated with high exposure to cadmium by industrial workers.

The extent of contamination of soil by phosphate based fertilizers is the subject of some conjecture and is discussed in a paper presented to The Fertilizer Society in 1984 (2). The main conclusions of their report were that:

- it is difficult to assess increases in soil cadmium as the base levels of cadmium present in the soil mask possible changes,
- cadmium from phosphate based fertilizers is not a major source of cadmium; they estimated it to be similar in magnitude to that discharged from coal fired power stations,
- increased cadmium uptake by plants is associated with increases in the cadmium concentration of soils, however, the amount the plants take up is related to the type of plant grown,

- some form of control of the levels of cadmium in phosphate based fertilizers needs to be established, the most economical method described in their paper was to use low cadmium content phosphate rock.

The conclusions made in this report are based on environmental studies within the Federal Republic of Germany and did not consider the UK situation in much detail.

Hutton and Symon (3), however, have estimated the discharge of cadmium to arable land from all sources in the UK for 1982, based on annual deposition rates in rural areas and a total arable land area of 5.12×10^6 hectares. Their estimates for heavy metals deposition are given in Table 2.1 below.

Table 2.1
Estimated trace element inputs to UK arable land.(3)

Source	Trace element input (t/year)			
	Cadmium	Lead	Mercury	Arsenic
Sewage sludge	4.9	98.3	1.0	2.5
Phosphate fertilizer	22	2.4	0.1	6.1
Atmospheric deposition	15.4	1536	5.1	102.4
Pesticides	0	ND	12	ND
Total	42.3	1637	18.2	111

Where ND indicates that the element was not detected.

The conclusion that can be drawn from the results presented by Hutton and Symon is that phosphate based fertilizers are the major contributor to cadmium deposition to arable land in the UK. They comment, however, that the levels of cadmium deposited to land from sewage sludge must be considered on a local level since only about 1% of the UK arable land is used for sludge disposal. In these areas the contribution to cadmium deposition from phosphate fertilizers is insignificant compared to that from the sludge. The same rider must be applied to these results as to the German results, that is, the

levels of cadmium that are deposited may not all end up in the food chain as this will depend on the type of crops grown.

Regulations regarding the amount of cadmium present in phosphate based fertilizers are few. The EC countries do not have a limit for the amount of cadmium present in fertilizers. The discharge of cadmium compounds must be controlled, according to EC regulations, where it may effect water resources but does not refer to the use of phosphate fertilizers. In Japan, however, it is prohibited to exceed 1.5 ppm Cd per 1% P₂O₅ present in the fertilizer.

However, the EC Directive on Limit Values and Quality Objectives for Cadmium Discharges (4) gives some indication of why no limit value has been set for discharges of cadmium arising from phosphate fertilizer manufacture, in Annex 1 of the Directive. Here the limits of discharge are given for all industries except the fertilizer industry, this is explained in foot note 7: "At present there are no economically feasible technical methods for systematically extracting cadmium from discharges arising from the production of phosphoric acid and/or phosphatic fertilizers from phosphatic rock. No limit values have therefore been fixed for such discharges. The absence of such limit values does not release the Member States from their obligation under Directive 76/464/EEC to fix emission standards for these discharges." Although this Directive relates to the discharge of cadmium to aquatic sources one must assume that the same reasoning is behind the failure to set limit values for the deposition of cadmium to arable land. It would appear from the wording of the Directive that if economically feasible processes were developed for the removal of cadmium from phosphoric acid and/or phosphatic fertilizers then the Directive may need to be ammended to include limit values for the release of cadmium from this industry.

2.2 Removal of cadmium from phosphoric acid

A number of processes have been developed or postulated for the removal of cadmium from wet process phosphoric acid. To date, no full scale process is being used to remove cadmium from WPA. Hence there is little information on the costs associated with the various

processes that have been proposed for the removal of cadmium from WPA. The following review of the proposed processes is, therefore, mainly confined to an assessment of their technical suitability.

2.2.1 Reduced cadmium content phosphate rock

Baechle and Wolstein (2) reviewed a study performed by the Batelle Institute, Geneva in which the following processes were assessed for their potential to reduce cadmium levels in WPA:

- calcination,
- precipitation,
- adsorption,
- ion displacement,
- ion exchange,
- electro-deposition,
- electro-dialysis,
- solvent extraction of the cadmium,
- solvent extraction of uranium with associated cadmium separation.

They concluded that the most economical method for reducing the cadmium content of WPA was to use phosphate rock of low cadmium content. They give a table of phosphate rock cadmium contents for a range of available phosphate ores Table 2.2.

The use of low cadmium content phosphate rock for the production of low cadmium concentration phosphoric acid must be dependent on supplies of such rock. From Table 2.2 it can be seen that the majority of phosphate ores contain high concentrations of cadmium, making this process option infeasible in the long term, if the price of phosphate rock is to remain reasonably stable. It is beyond the scope of this work to estimate the effect on the cost of low cadmium content phosphate rock of increased demand for this quality of ore.

The paper (2) reports that calcination of the phosphate rock at between 1000°C and 1150°C in the presence of 1% to 5% oxygen will remove organic matter from the rock and effect a significant reduction in the cadmium content. The cost of this calcination step must increase the overall cost of the phosphate rock. However, since no details of the energy efficiency of this calcination process are given, it is difficult to estimate accurately what this cost

increase would be. If it is assumed that the heat capacity of phosphate ore is 0.8 kJ/kg°C, the thermal efficiency of the process is about 70% and the cost of energy is 2 p/kWh, then a rough estimate of the increased cost of phosphate rock due to calcining would be about £6.7/t of ore. Since most phosphate ores contain about 33% P₂O₅, this figure results in an increased cost of about £20/t P₂O₅. This high cost will be offset to a certain extent by the reduced cost of transportation of the calcined phosphate rock (ie because of reduced weight) and the possible cost benefits seen by the phosphoric acid producer in using a low organic content phosphate ore.

Table 2.2
Cadmium content of phosphate rock used
in the production of phosphoric acid.(2)

Origin	Name	Cadmium content (mg/kg)	
		Range	Mean
USSR	Kola phosphate	1	0.3
USA	Florida pebble	3 - 12	7
USA	Nth Carolina phosphate		36
Israel	Oron phosphate		3
Israel	Nahal Zin phosphate	19 - 21	20
Morocco	Khouribga phosphate	1 - 17	12
Morocco	Joussoufia phosphate		4
Algeria	Algier phosphate		23
Span.Sahara	BuCraa phosphate		43
Tunisia	Gafsa phosphate	55 - 57	56
Togo	Togo phosphate	38 - 60	53
Senegal	Taiba phosphate	68 - 110	84

2.2.2 Precipitation

A number of workers have suggested that the cadmium concentration of WPA can be reduced by sulphide precipitation. Two processes have been patented that aim to achieve cadmium reduction by this route.

The first method (5) doses a solution of 10% calcium sulphide and calcium hydroxide (250 kg CaO/m^3) into the WPA at an excess of 25 times the heavy metal content of the acid. The sulphides of the heavy metals are precipitated and then separated by filtration. The use of calcium sulphide in the presence of acid results in the formation of hydrogen sulphide in the acid. This must be removed and may result in environmental and worker safety problems. The process removes heavy metals and sulphate from the acid to quite low levels, an example is given in the patent. Here 70% H_3PO_4 at 45°C containing 2% SO_4^{2-} , 11 g $\text{As}_2\text{O}_3/\text{m}^3$, 30 g Cu/m^3 and 41 g Cd/m^3 was treated as above and filtered after one hour. The resultant purified acid contained 0.12% SO_4^{2-} , 0.2 g $\text{As}_2\text{O}_3/\text{m}^3$, 0.4 g Cu/m^3 and 0.4 g Cd/m^3 .

The process costs are not given, however, it must be assumed that they will be high considering the fact that there is provision for one hours storage of the acid prior to precipitation, filtration of the acid and techniques for the removal of hydrogen sulphide from the acid, all of which will add to the capital cost of the process.

The other process (6) removes residual sulphate from the acid by the addition of calcium hydroxide and the subsequent precipitation of calcium sulphate. The acid is then neutralised by the addition of an alkali to an Me/P ratio of about 0.05 to 0.3 (where Me represents the number of cation equivalents in the alkaline solution used and P represents the number of phosphorus atoms in the WPA). Heavy metals are precipitated out of solution by the addition of a sulphide compound that is soluble in the WPA (eg sodium sulphide), the amount used corresponds to about 0.2 to 1 kg S^{2-}/m^3 WPA. An example given in the patent was for the treatment of 53.5% P_2O_5 containing 2% H_2SO_4 , 16 g As/m^3 , 17 g Cu/m^3 and 25 g Cd/m^3 using the above procedure. The resultant acid contained 45% P_2O_5 , 0.2 g As/m^3 , 0.4 g Cu/m^3 and 1.4 g Cd/m^3 .

Again the process costs are not given and it must be assumed that they will be high. There is no mention of the production of hydrogen sulphide in the WPA in this process, however it will probably be reduced from that of the previous method as less sulphide is added and the acidity of the WPA is reduced. It is worrying that the P_2O_5 concentration of the acid is reduced by this process. The operating cost of the process must take into account the increased cost of

evaporation required to increase the P_2O_5 concentration back to the original 53.5%.

These two processes appear to be somewhat messy in that they both require an additional filtration step (over and above that required for gypsum removal) for the removal of the heavy metal sulphide precipitates and this filter plant would need to be sized to handle the full WPA flow. Both processes will undoubtedly produce hydrogen sulphide gas to varying amounts which will present both an environmental and a safety hazard; prevention of this problem may require the installation of gas scrubbers which would add further to the capital and operating costs of the processes.

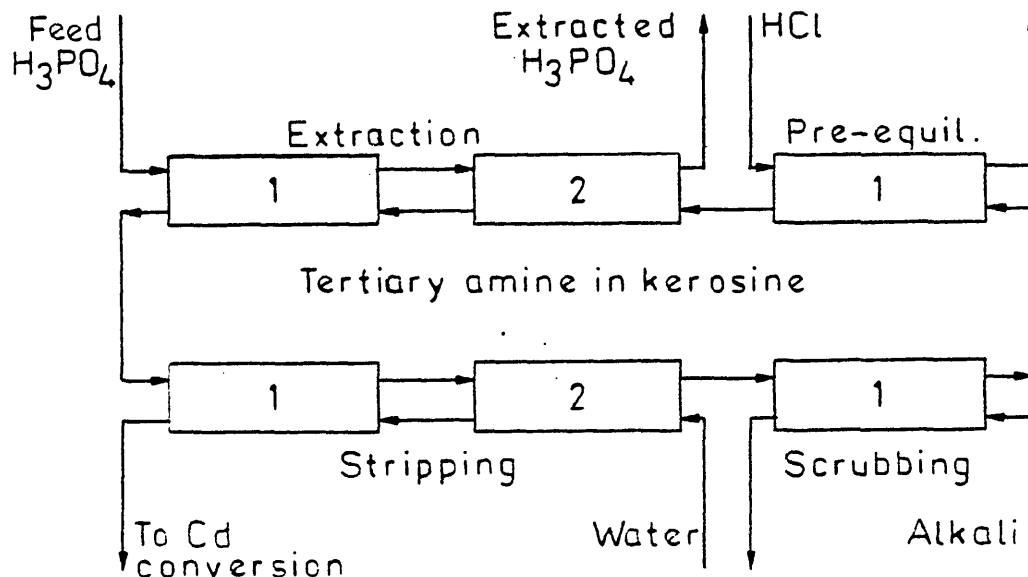
2.2.3 Solvent extraction

A solvent extraction process using dithiophosphate esters as extractants has been patented (7) and is reported to achieve good removal of heavy metals from the phosphoric acid being treated. In the process dithiophosphates of the general formula $(RO)_2PS_2H$ (where $R = 2\text{-ethylhexyl, phenyl or tetradecyl}$) are impregnated into an activated carbon or zeolite and contacted with the WPA. A case study is given where powdered activated carbon was impregnated with molten bis(2-ethylhexyl)dithiophosphate. The resultant adsorbent material was contacted for 15 minutes with 30% H_3PO_4 which contained 16 g Cd/m^3 , 33 g Cu/m^3 , 0.1 g Pb/m^3 , 0.005 g Hg/m^3 and 350 g organic carbon/ m^3 . The thioester and activated carbon used were at 0.2 and 0.1% of the solution volume respectively. The purified phosphoric acid contained <1 g Cd/m^3 , <1 g Cu/m^3 , <0.05 g Pb/m^3 , 0.001 g Hg/m^3 and 80 mg organic carbon/l. No details are given of how the adsorbent material is separated from the treated acid or how it is regenerated. Presumably some form of filtration would be required to separate the powdered carbon from the acid. If low quantities of solvent and adsorbent are required, to complete the separation of cadmium from WPA, then the regeneration step may not be required as the spent adsorbent could be separated from the WPA and disposed of to a land-fill site. However, if some form of regeneration was required because of the cost of the solvent used, organic material removed from the WPA may well pose a long term problem due to fouling of the porous activated carbon which may lead to a loss of its capacity for cadmium.

Stenstrom and Aly (8 and 9) have investigated the use of liquid solvent extraction for the removal of cadmium from WPA. The type of extractant/diluent combination used was either C₈ tertiary amines and aromatic diluents or C₁₂ tertiary amines and aliphatic diluents. These combinations did not lead to the formation of a third phase with the WPA during the solvent extraction process.

They proposed that the cadmium was extracted from the WPA as the anionic chloride complex CdCl_4^{2-} by the amine functional groups of the extractants used. They found that the distribution coefficient for cadmium extraction was strongly increased by the presence of hydrochloric acid in the WPA. Their proposed flowsheet for solvent extraction of cadmium, stripping of cadmium and scrubbing of the solvent is shown in Figure 2.1.

Figure 2.1
Flow-sheet for cadmium extraction from WPA by
solvent extraction with tertiary amines (9).



The feed WPA was pretreated to prevent crud formation by cooling and sedimentation. In the extraction section two stages and a phase ratio of 1:2 (organic:WPA) were required to achieve reduction of the cadmium content of the WPA from 7.5 g Cd/m³ to 1.1 g Cd/m³. Acids present in the WPA were extracted with the cadmium; about 0.05 to

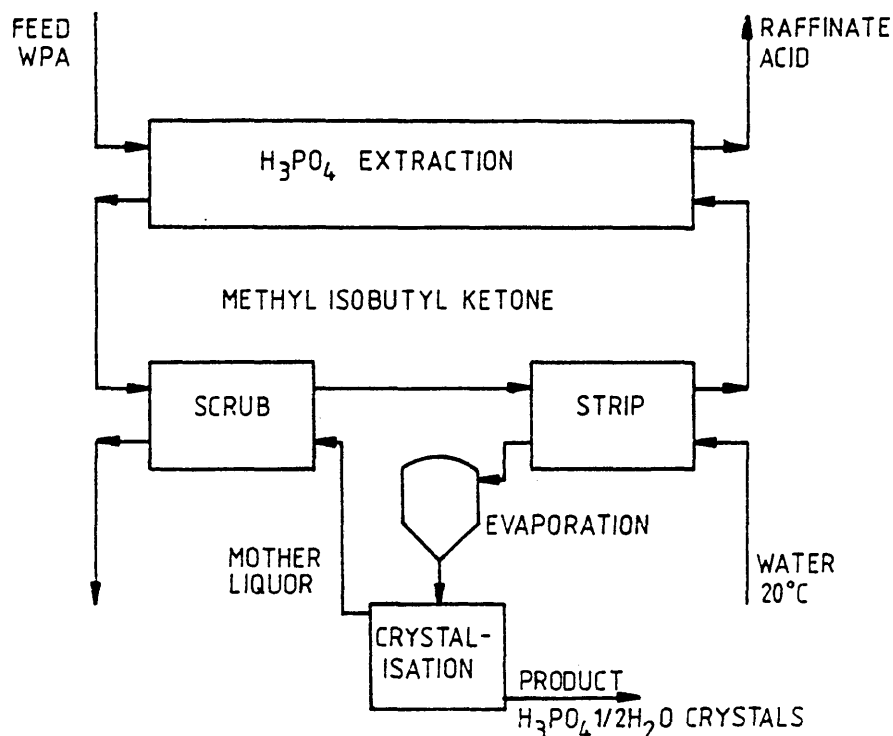
0.08% of the H_3PO_4 , 1% of the H_2SO_4 , 13% of HCl , 1% of the HF and 2% of H_2SiF_6 present in the WPA were extracted. The high extraction of HCl is associated with the formation of amine chloride salts and the formation of the cadmium-chloride complexes. The process was found to be quite selective for cadmium as no major competition was observed from the other metals present in the acid; zinc and calcium were the only other metals present that showed any degree of removal by the solvent. Crud formation was observed when treating acids of high organic content and it was felt that this would be a problem for full scale implementation of the process unless some form of pretreatment was practiced to remove the organic material. No indication of the stability of the extractant chemicals in WPA was given. The proposed process was not evaluated in terms of process economics as it is still in a state of development. It must be fair to say, however, that the process will suffer from similar problems to those encountered in the solvent extraction processes used to recover uranium from WPA. These are, crud formation and loss of extractant due to solubility in the WPA, both of which will combine to increase the operating costs for the process.

Albright and Wilson (10) has three UK patents for a process that uses solvent extraction for the removal of phosphoric acid from the impurities present in WPA. The process involves contacting WPA with ketones such as methyl isobutyl ketone (MIBK) which extracts the H_3PO_4 from the WPA. The MIBK is then scrubbed of further trace metals by a "more pure" phosphoric acid stream. The phosphoric acid product stream is recovered from the organic phase by stripping with water (or an aqueous alkali) to produce a product stream containing less than 100 ppm of metals. Further purification of the product acid was achieved by evaporation and cooling to form crystals of $\text{H}_3\text{PO}_4 \cdot \frac{1}{2}(\text{H}_2\text{O})$. These crystals when separated, washed and remelted yielded a "pure" acid containing 66% P_2O_5 and a low metal content (25 g Fe/m^3 , <1 g Cd/m^3 and <1 g Pb/m^3). The mother liquor from the crystallisation process was recycled back to scrub the MIBK from the initial extraction stage. A flow sheet for the process is shown in Figure 2.2.

A problem with the process must be, loss of solvent (MIBK) to the product acid stream. A case cited in the patents gives a product acid containing 1.7% w/w MIBK. This must presumably be removed in a

subsequent stage of either evaporation or adsorption before the acid can be used. The process removes between 75 and 80% w/w of the H_3PO_4 from the feed acid, the rest ends up in the raffinate stream. The raffinate acid also contains high concentrations of the metals present in the feed WPA and about 1.5% w/w MIBK. The disposal of this acid would present a significant environmental problem unless it was subjected to further clean up procedures. The loss of phosphate to the raffinate would increase the overall cost of P_2O_5 in the purified acid by at least 20%. Loss of solvent with the raffinate, if not recovered, will again increase the overall cost of the purified acid. It would appear from this that the process is intended to be used for the production of a higher value technical grade phosphoric acid for industrial and other uses rather than for the purification of WPA intended for fertilizer manufacture. If the raffinate acid from this process was to be used for the production of phosphate based fertilizers (which must make economic sense) then the cadmium and other heavy metals content of the fertilizer would be higher than that produced from the original WPA alone.

Figure 2.2
Flow-sheet for phosphoric acid extraction from WPA
by solvent extraction using MIBK (10).



There was no mention in the patents of the formation of crud, during the solvent extraction stages, by organics present in the WPA. Again, the presence of high molecular weight organics (such as humics) in the WPA will result in the formation of crud and result in operational problems and loss of solvent.

2.2.4 Ion exchange processes.

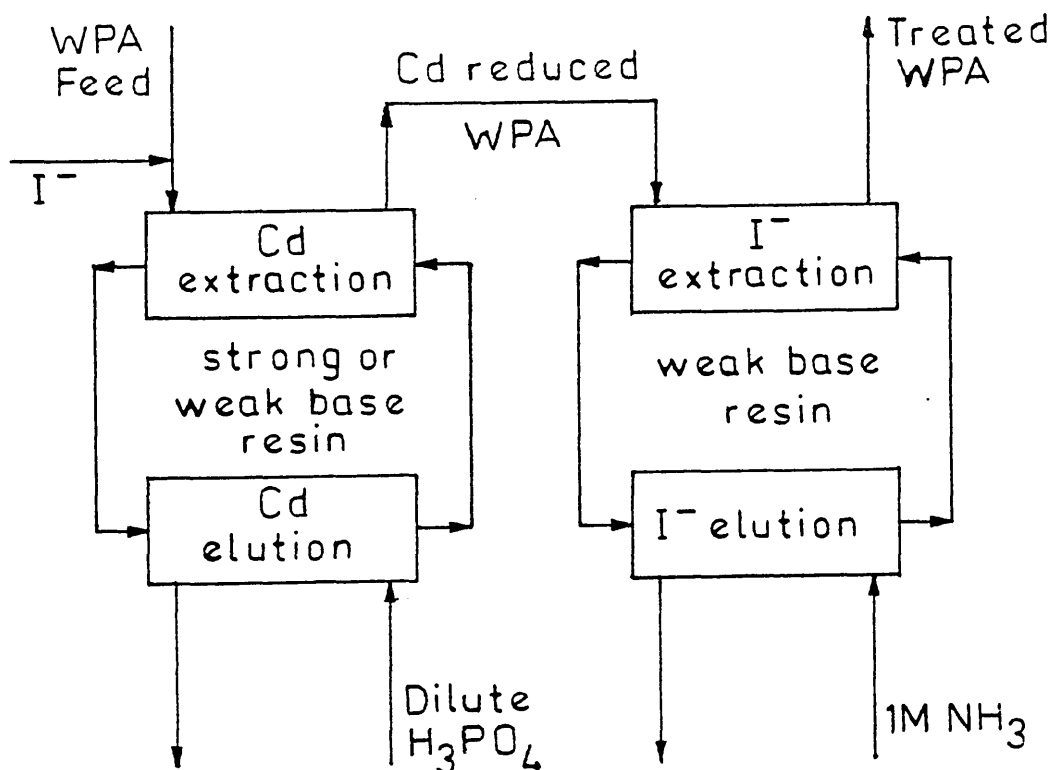
(a) Anion exchange

Anion exchange processes for the removal of cadmium from WPA are feasible because of the anionic complexes that can be formed between cadmium and halide ions in solution.

The process patented in Japan by Hiruza (11) uses chloride ions to complex with cadmium to form either CdCl_3^- or CdCl_4^{2-} in the WPA. The process then uses one of the strong base quaternary ammonium resins (IRA400) to extract the cadmium chloride complex from the WPA. The patent gives a case study where WPA containing between 35 and 55% P_2O_5 was stirred with NaCl and CaCl_2 at 40°C for 5 hours and filtered. The resultant filtrate contained 35% P_2O_5 , 250 mg Zn/l , 15 g Cd/m^3 and 25 kg Cl^-/m^3 . This was passed over IRA400 resin and the treated acid contained <1 g Cd/m^3 and <1 g Zn/m^3 . No indication was given of the methods used to regenerate the loaded resin and how the excess chloride in the WPA affected the subsequent fertilizer process. No process flow sheet or costs of treating the wet process acid in this manner were given. A process that requires an additional 5 hours storage time must incur high capital costs for large volume through-put plants. The amount of chloride required in solution to affect the formation of the cadmium and zinc chloride complexes seems to be very high and would lead to high running costs for the process.

Tjioe (12) describes a process being developed, in the Netherlands, using anion exchangers to remove the anionic complexes formed between cadmium and either bromide or iodide ions in WPA solution. The paper (12) describes the development of the process and at the Cambridge SCI conference (1988), where it was presented, Tjioe gave details of the process flow-sheet which is reproduced from memory in Figure 2.3.

Figure 2.3
Flow-sheet for cadmium removal from WPA
by ion exchange using anion exchange resins.



Tjioe found that both weak base and strong base anion exchange resins could be effective for highly selective removal of cadmium from 40 to 65% w/w H_3PO_4 acid at 90°C if the WPA contained small amounts of either bromide or iodide ions. The anion resins were more selective and had a higher capacity for cadmium iodide complexes than the cadmium bromide complexes. The capacity of the resin for cadmium was increased by increasing the halide concentration of the acid since more halide complexed with the cadmium and increased the overall negative charge on the complex. The distribution coefficient observed for cadmium removal in pure phosphoric acid solutions was higher than that seen in WPA since there was competition from other anions (possibly anionic aluminium fluoride complexes, iodide ions and anionic complexes of iron and zinc) in solution. The presence of organic impurities in the acid were not observed to affect the capacity and performance of the resin in repeated use tests. This is

a major advantage for the process when compared to the solvent extraction processes described earlier.

The distribution coefficient for cadmium decreased by at least two orders of magnitude as the H_3PO_4 concentration decreased from 65 to 2% w/w. This phenomena was employed as a means of eluting the loaded resin; dilute phosphoric acid (<10% w/w H_3PO_4) was used to elute the destabilised cadmium chloride complexes from the resin.

The authors identified the fact that iodide is an expensive reagent and loss of iodide with the treated WPA should be minimised to reduce the operating costs of the process. They propose the use of another weakly basic ion exchange resin to remove the excess iodide ions from the WPA once the cadmium has been removed. This resin was regenerated by passing 1M NH_3 solution through the resin bed. Presumably the resultant iodide containing eluate could be used to increase the iodide concentration of the feed WPA.

No indication is given of what would be done with the dilute phosphoric acid used to elute cadmium from the resin in the initial cadmium removal stage. If the solution were to be neutralised and dumped it would present an environmental hazard as it would lead to high phosphate, cadmium and iodide levels in the water course to which it was disposed.

No indication was given in the paper or at the presentation of estimated costs for the process. The use of low concentration phosphoric acid solutions for the elution of the cadmium extraction resin would result in a loss of P_2O_5 from the process which will have the effect of increasing the overall cost of the purified P_2O_5 thus produced. The authors have identified that the use of iodide for the formation of anionic cadmium complexes will result in high operating costs unless some form of iodide recovery system is employed. The inclusion of such a system in the process, that needs to treat the whole WPA stream, will increase the capital and operating costs for the process.

(b) Cation exchange

No reference to the use of cation exchangers for the removal of cadmium and other cations in phosphoric acid was found. A reference to work being performed in the USSR was found in the Chemical

Abstracts, however, attempts to access this work were not successful as it was not released from libraries in the USSR.

Holroyd and Salmon (13) indicate that neither anionic or cationic complexes of cadmium and zinc are present in phosphoric acid solutions. They propose that the Cd^{2+} and Zn^{2+} ions exist in phosphoric acid solutions as the free ion. From this it would appear possible that a process using strong acid cation exchangers should be capable of removing these ions from solution. This possibility led to the experimental work which was aimed at developing such a process and is the subject of this thesis.

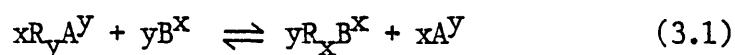
3 THEORY

3.1 Ion exchange theory

Ion exchange processes utilise solid materials, either organic or inorganic, that have bonded groups within their structure that carry an ionic charge. Early ion exchange materials were based upon the inorganic zeolite materials. In general, ion exchangers are now usually based on organic polymers. The most common of these is polystyrene co-polymerised with divinylbenzene (DVB) to provide a cross-linked resin. This resin can be sulphonated to give the resin negatively charged sites and so produce a strong acid cationic resin. Similarly, anions of weak acids (such as carboxylic and phosphonic acids) can be used to produce weak acid cation exchangers.

The use of amine functional groups within the resin matrix can yield resins with affinities for anions in solution. The type of amine group that is bound to the resin determines the nature of the anion exchanger. If a quaternary amine functional group is formed on the resin then the resin will exhibit the properties of a strong base resin. However, if a tertiary amine structure is formed then the resin will be weakly basic.

Ion exchange reactions are reversible and involve equimolar charge transfer between the resin and solution as illustrated below for the exchange of the two ions A^Y and B^X



where R denotes the stationary resin phase.

The capacity of ion exchange materials is generally expressed in milliequivalents per gram of resin. A milliequivalent is the number of millimoles of hydrogen ion equivalent to the total number of millimoles of charge on the ions taken up by the resin. Typically ion exchange resins exhibit capacities of between about 0.4 and 4 milliequivalents per gram of moist resin.

With homogeneous resin structures, as the degree of cross linking increases, the resin structure becomes more tortuous and convoluted

and the pore structure within the resin tighter. This can result in the resin becoming brittle and can reduce the rate of diffusion of the exchanging ions within the resin. However, smaller pores within the resin matrix can act to increase the selectivity of the resins for small, highly mobile ionic species.

In reality, the use of homogeneous (gel type) resins is limited to those with DVB contents of less than about 12%, since the effects of poor diffusion rates within the resin outweigh the advantages of their higher selectivity. To overcome some of the problems associated with the highly cross-linked gel type resins manufacturers have produced a range of macroporous resins. These are made up of small micro-beads of highly cross-linked resin that are bonded into larger ion exchange beads to give a kind of sintered structure to the resin. In these resins, the solute can diffuse relatively freely through the macroporous structure and gain access to micropores within the resin bead that would have been inaccessible in the gel type resins. In this way, the high selectivity of highly crosslinked resins can be achieved with reasonable rates of diffusion.

3.1.1 Selection of a suitable ion exchanger

The selection of a suitable ion exchanger for the separation of specific ions from a mixture of ions in a solute system requires a knowledge of the nature of the ionic species present in solution and the selectivity of the various types of resins for these species.

(a) Use of stability constants

The available information about the types of ionic species present in phosphoric acid systems is limited in terms of the type of metal ion and the ionic strength of the solution used to derive the information. The information that is available (14), generally presents the stability constants for the ionic species. The species that has the highest stability would be the most likely to be present in solution. However, other complexes of lower stability will be present and in equilibrium with the major species. The removal of one complex from the solution can result in a shift in the equilibrium to cause the formation of more of this species. This effect can result in the effective removal of a supposedly minor species from solution by ion exchange processes. A table of the most

likely complexes to be present in phosphoric acid solutions is given in Appendix 2.

(b) Ion exchange selectivity

The most accepted method for presenting ion exchange equilibria has been developed from the law of mass action. For the system represented by equation (3.1) earlier with the exchange of B^x ions for A^y ions originally present on the resin, the equilibrium constant for the reaction can be defined as:

$$K_a = \frac{[\bar{a}_B]^x [a_A]^y}{[\bar{a}_A]^y [a_B]^x} \quad (3.2)$$

Where $\bar{a}$ and a are the activities of the ions in the resin and solution respectively and are expressed by:

$$\begin{aligned} \bar{a}_A &= \bar{C}_A \bar{\gamma}_A \\ \bar{a}_B &= \bar{C}_B \bar{\gamma}_B \\ a_A &= C_A \gamma_A \\ a_B &= C_B \gamma_B \end{aligned}$$

The activity coefficients (γ) required to calculate the activity of each ion are difficult to determine. In practice, for dilute solutions the solution phase activity coefficient can be assumed to be one. The resin phase activity coefficients can be combined into a pseudo-equilibrium constant or selectivity coefficient K_c , which for the above system is:

$$K_c \frac{B}{A} = \frac{[\bar{C}_B]^x [C_A]^y}{[\bar{C}_A]^y [C_B]^x} \quad (3.3)$$

If the value of K_c is greater than one then the resin preferentially takes up B ions and if K_c is less than one then the resin preferentially takes up A ions. Values of selectivities have been estimated for various ions (23) in reference to lithium ion for both univalent-univalent and univalent-divalent exchange on sulphonic

acid resins. These are shown in Table 3.1 below for the divalent-univalent exchange case.

Table 3.1
Selectivity scale for divalent cations
in sulphonic acid resins (23)
(reference ion is lithium)

	4% DVB	8% DVB	16% DVB
UO ₂	2.36	2.45	3.34
Mg	2.95	3.29	3.51
Zn	3.13	3.47	3.78
Co	3.23	3.74	3.81
Cu	3.29	3.85	4.46
Cd	3.37	3.88	4.95
Ni	3.45	3.93	4.06
Ca	4.15	5.16	7.27
Sr	4.70	6.51	10.1
Pd	6.56	9.91	18.0
Ba	7.47	11.5	20.8

As can be seen from Table 3.1 the selectivity of resins for ions increases with cross linking. As the amount of DVB within the resin polymer matrix increases then the amount of cross linking between polymer chains increases. This causes the resin structure to become more convoluted and and more tightly joined. The effect of this is to decrease the size of the pores within the resin matrix which in turn makes the diffusion of ions within the resin more difficult. The net result of increases in the DVB will be the exclusion of larger and/or more highly hydrated ionic species leading to the selective ion exchange of small, highly mobile ions.

The distribution coefficient of an ion in an ion exchange system is defined as the concentration ratio of the ion on the resin in equilibrium with the ion in solution. Values of the distribution coefficient for various ions and counter ions in solution and in equilibrium with cation exchange resins have been developed by a number of workers (23). These values can be used to determine the best operating region in terms of the concentration of counter ions and type of resin required to achieve a required separation. This

information is also useful for screening for possible competing ions that may also be present in solution. Distribution coefficient data for systems involving the use of cation exchange resins and phosphoric acid solutions has not been developed and so this method could not be used to establish best operating conditions for the treatment of WPA.

3.2 Determination of reaction kinetics

The mechanisms that can control the rate of ion exchange processes can be conceived to be:

- diffusion of the counter ions through the stagnant liquid layer surrounding the ion exchanger particle (film diffusion),
- diffusion of the counter ions within the solid phase to the ion exchange sites (particle diffusion),
- chemical reaction between the counter ions and the ion exchange sites,
- diffusion of the displaced ions out of the ion exchanger particle,
- diffusion of the displaced ions through the stagnant liquid film surrounding the ion exchanger.

The two most probable rate controlling mechanisms are film diffusion and particle diffusion. Chemical reaction at the exchange sites is not usually observed to limit the rate of ion exchange except possibly for some of the chelating resins.

The rate controlling step for an ion-exchange process can be determined from the results of specific experiments or by fitting the results of batch stir tests to one of the accepted rate models. A knowledge of the mechanism controlling the ion-exchange process is useful since it can indicate where modifications to the process will result in increased rates of exchange.

The theory of the diffusional rate controlling mechanisms is well established and can be found in some detail in the Chemical Engineers Handbook, (24). Only the relevant aspects of the theory,

sufficient to explain the approach to the present experiments, are briefly discussed here.

If it is assumed that the ion exchange particles are of uniform size and spherical then Fick's first law can be used to adequately describe the diffusional processes:

$$J_i = D \text{ grad } C_i \quad (3.4)$$

Where J_i is the flux of the diffusing species i of concentration C_i and D is the diffusion coefficient.

3.2.1 Film diffusion

The diffusion of ions across the stagnant boundary layer that separates ion exchange particles from the bulk solution is termed film diffusion. If it is assumed that diffusion across the layer is one dimensional and that the flux across the boundary layer adjusts rapidly to changing boundary conditions then Fick's law (equation 3.4) can be simplified to:

$$J_A = \frac{D \Delta C_A}{\delta} \quad (3.5)$$

For isotopic diffusion of ion A through a film of thickness δ .

Applying mass balance and equilibrium constraints the rate equation can be derived to be:

$$-\frac{dC_A^*}{dt} = \frac{3CJ_A}{r_0 \bar{C}} \quad (3.6)$$

For particles of radius r_0 where C_A^* is the concentration of ion A in solution at the resin interface and $\bar{C}$ is the concentration on the resin in equilibrium with C_A^* . Equations 3.5 and 3.6 can be solved using initial and boundary conditions. Two cases of boundary condition can be applied, these are for either infinite or finite solution volume.

In the case of infinite solution, the moles of ions on the resin are far outweighed by the moles of ions in solution and equation 3.6 can be solved to give the fractional attainment of equilibrium X at any time t as:

$$X = 1 - \exp \left[- \frac{3DCt}{r_o \delta \bar{C}} \right] \quad (3.7)$$

For the other more general case of finite solution volume where the above condition does not apply, the fractional attainment of equilibrium at any time can be solved to be:

$$X = 1 - \exp \left[- \frac{3D(\bar{V}C + VC)t}{r_o \delta \bar{C}V} \right] \quad (3.8)$$

From these two equations (3.7 and 3.8) it can be seen that if film diffusion is controlling the rate of ion exchange then the rate of loading of the resin will be inversely proportional to the resin diameter and the thickness of the stagnant film. If batch equilibrium experiments are performed at different stirring speeds then the thickness of the stagnant film surrounding the particle will be different and a change in the rate of uptake of ions would be observed. Similarly if the average resin particle diameter is changed between experiments then the rate of loading will be expected to change in inverse proportion to the particle size.

If equations 3.7 and 3.8 are rearranged then it can be seen that a plot of $-\ln(1-X)$ versus time should yield a straight line passing through the origin.

3.2.2 Particle diffusion

If diffusion within the liquid film surrounding the particle is faster than that within the ion exchange particle then the concentration gradients within the liquid film level out rapidly and concentration gradients within the particle will be set up. In this case, diffusion within the particle will control the rate of exchange, this is known as particle diffusion control. The migration

of an ion within the resin particle is hindered by the tortuous nature of the diffusion paths and by the build up of charged species within the resin which can slow down the passage of the ions to the exchange sites.

Fick's first law of diffusion can again be used to describe the diffusional process which in combination with his second law and spherical geometry yields the following partial differential equation which can be used to describe the kinetics of isotopic diffusion of ions within the resin particle.

$$\frac{\partial \bar{C}_A}{\partial t} = \bar{D} \left(\frac{\partial^2 \bar{C}_A}{\partial r^2} + \frac{2}{r} \left| \frac{\partial \bar{C}_A}{\partial r} \right| \right) \quad (3.9)$$

Applying infinite solution volume boundary conditions, the fractional attainment of equilibrium can be determined from Vermeulen's approximation (23):

$$X = \left(1 - \exp \left[- \frac{\bar{D} \pi^2 t}{r_o^2} \right] \right)^{\frac{1}{2}} \quad (3.10)$$

For the more general case of finite solution volume the solution is more complex and the approximation of Paterson (23) can be used to give equation 3.11 below for cases where $\tau < 0.1$:

$$X = \frac{w+1}{w} \left[1 - \frac{1}{p-q} [p \cdot \exp(p^2 \tau) (1 + \operatorname{erf} p \tau^{\frac{1}{2}}) - q \cdot \exp(q^2 \tau) (1 + \operatorname{erf} q \tau^{\frac{1}{2}})] \right] \quad (3.11)$$

$$\text{where } w = \frac{\bar{C}_V}{C_V}, \quad \tau = \frac{\bar{D} t}{r_o^2} \quad \text{and}$$

p and q are the roots of: $x^2 + 3wx - 3w = 0$

From the two equations 3.10 and 3.11 it is apparent that the rate of diffusion is inversely proportional to the square of the particle radius. Therefore, if batch equilibrium experiments are performed using resins of different average particle size then the loading rates observed will be inversely proportional to the square of the particle size. A plot of $-\ln(1-X^2)$ versus time will yield a straight line of slope $\bar{D}\pi^2/r_0^2$ if particle diffusion is controlling the rate of loading and the infinite solution volume condition applies. In the more general case of finite solution volume, a plot of the dimensionless value ζ versus time will yield a straight line of slope $\bar{D}/r_0^2$ if particle diffusion controls. Batch stir tests should be unaffected by changes in the degree of agitation and the ion concentration in solution if particle diffusion is controlling the rate of loading.

The above descriptions of both film and particle diffusion assume that the simplified case of isotopic diffusion (that is, the exchanging and displaced ions are of equal mobility within the resin) applies. In reality, the ions will have different mobilities and an electric field will be established during the diffusion process. The effect of this will be to accelerate the diffusion of the slower moving ions and retard the diffusion of the more mobile ions. To better describe ion exchange under these conditions, the Nernst-Planck equation can be used to derive an expression, similar to Fick's first law, that takes account of the different mobilities of the counterions concerned.

Since the simple models, based on isotopic exchange, resulted in a reasonable fit to the experimentally observed rate of ion exchange, it was not felt necessary to further explore the use of these more complicated models.

3.2.3 Chemical reaction

Although it was not considered in this work, as it was assumed to be not relevant, chemical reaction kinetics can in some resins control the rate of ion exchange. This is seen to be the case in some chelating type ion exchange resins.

Two basic models of chemical reaction control can be envisaged; these are either homogeneous or heterogeneous chemical reaction within the resin bead.

In the case of homogeneous reaction, the ion exchange reaction is assumed to occur uniformly throughout the resin particle. This model will only fit in the case of resins of high internal porosity, this can allow the free passage of ions to all ion exchange sites within the resin so that the concentration of the reacting ions is uniform throughout the resin. Chemical reaction is then best described by a second order rate expression.

In the case of heterogeneous reactions the ion exchange bead is regarded as being virtually nonporous and reaction will occur at the surface boundary, that is, the interface between the unreacted core and the surrounding particle. This reaction model is similar to those developed to describe "shell progressive" or "shrinking-core" fluid/solid non-catalytic reactions (25). The model when applied to ion exchange assumes that the exchanging counterion reacts within the resin bead in spherical shells advancing into the centre of the unreacted resin particle. The progress of the reaction leaves a shell of reacted solid product in its wake. The rate of the ion exchange process can be controlled by diffusion of the counterion through the liquid film surrounding the exchanger, diffusion of the counterion through the reaction product layer or chemical reaction at the interface of the unreacted core.

4 EXPERIMENTAL METHOD

4.1 Resin Selection Tests

Small scale contact tests were performed to assist in the selection of resins suitable for the extraction of cadmium from phosphoric acid. The same small scale tests were used to assess the effects of competition on cadmium extraction by looking at the removal of other metal ions by the ion exchange resins.

The solutions used in these tests were made up by dissolving BDH "Spectrosol" standard metal solutions into 40% w/w P_2O_5 phosphoric acid. This was done by:

- pipetting the required amount of standard solution into a volumetric flask,
- adding the calculated amount of BDH "Analar" 85% w/w H_3PO_4 orthophosphoric acid to the flask (531 cm^3 /litre for 40% w/w P_2O_5),
- making up to volume with distilled water.

The solution was shaken and allowed to reach room temperature before use in the tests.

The resin samples used in the tests were conditioned before use by contacting with 2 M HCl, washing with distilled water and then contacting with 2 M NaOH. This process was repeated two more times with the resin given an alcohol wash (using absolute ethanol) during one of the water wash stages. Cationic resins were left in the H^+ form prior to use and the anionic resins in the OH^- form. Resin samples used were in the "as received" size range, generally this was between 0.3 and 1.2 mm diameter. The conditioned resins were washed into centrifuge tubes (fitted with sintered glass bottoms) using distilled water. Excess water was removed by vacuum through the porous base of the tubes and the tubes then placed in larger polythene centrifuge tubes. These were spun at about 5000 RPM for five minutes to remove surface water from the resin beads. Resin samples used for the contact tests were weighed out in this "centrifuged moist" form into 60 cm^3 polythene reaction bottles. Four to five grammes of resin were used in each bottle and 50 cm^3 of the prepared metal-ion/phosphoric acid solution added.

The reaction bottles were fitted with sealed screw caps and then gently agitated at room temperature for at least 16 hours. Twenty samples could be tested at any one time which allowed a rapid initial assessment of each resin. Fifteen different resins were used for each metal-ion solution tested, Table 4.1 gives a description of the types of resins tested. Duolite resins were used since the project was partly sponsored by Duolite (subsequently Rohm and Haas).

Once the resin/acid contact had been achieved, a sample of the final acid solution was withdrawn from the reaction bottle through a sintered glass filter. Filtration was necessary to remove small fragments of resin from contaminating the acid sample and causing possible blockages of the atomic absorption spectrophotometer (AAS) aspirator. The samples of acid were diluted by making 5 cm³ of sample up to 25 cm³ with distilled water in 25 cm³ volumetric flasks. Standard solutions for calibrating the AAS were made up using BDH "Spectrosol" metal solutions and BDH "Analar" orthophosphoric acid (85% w/w H₃PO₄). The phosphate concentration of the standards was kept in the same range as that expected in the samples to be analysed. The standards were diluted in the same manner as the samples.

The above procedure was not used for the assessment of the removal of Fe²⁺ ions from solution since contact with atmospheric oxygen rapidly results in the oxidation of Fe²⁺ to Fe³⁺ in phosphoric acid solutions. To prevent this occurring a nitrogen blanket was used to prevent air contacting the phosphoric acid. The required amount of resin was added to the reaction bottle and 50 cm³ of 40% w/w P₂O₅ acid added, a small amount of liquid nitrogen was introduced into the reaction bottle and allowed to gas off. A predetermined amount of an Fe²⁺ solution was added while the liquid nitrogen was gassing off and the reaction bottle sealed. After the acid and resin had been agitated for the required time period a sample of acid was rapidly removed from the reaction bottle once the seal was broken. Table 4.2 shows the different metal ions investigated in each test along with the other ions present in solution that were associated with the metal salt.

Table 4.1
Resins used in initial selection tests.

RESIN	FORM	FUNCTIONAL GROUP	MATRIX	STRUCTURE
Chelating				
Duolite ES465	H ⁺	mercaptane	polystyrene	macroporous
Duolite ES466	H ⁺	amino diacetate	polystyrene	macroporous
Duolite ES467	H ⁺	amino phosphonate	polystyrene	macroporous
Duolite ES346	OH ⁻	amidoxime	polyacrylic	macroporous
Strong acid				
Duolite C225	H ⁺	sulphonic acid	polystyrene	gel type
Duolite C264	H ⁺	sulphonic acid	polystyrene	macroporous
Duolite C26	H ⁺	sulphonic acid	polystyrene	macroporous
Duolite C265	H ⁺	sulphonic acid	polystyrene	macroporous
Duolite C206A	H ⁺	sulphonic acid	polystyrene	gel type
Duolite C20	H ⁺	sulphonic acid	polystyrene	gel type
Weak acid				
Duolite C433	H ⁺	carboxylic acid	polyacrylic	gel type
Strong base				
Duolite A101	OH ⁻	quat. ammonium. type 1	polystyrene	macroporous
Weak base				
Duolite A374	OH ⁻	polyfunctional amine	polyacrylic	macroporous
Duolite A30B	OH ⁻	tertiary amine	polyepoxy- amine	gel type
Duolite A561	OH ⁻	tertiary amine	phenolic	macroporous

Table 4.2
Metal species and associated ions used in
resin selection batch stir tests.

METAL	OXIDATION STATE	METAL SALT USED	INITIAL CONCENTRATION
Cadmium	Cd(II)	Nitrate	1.5 g/m ³
Zinc	Zn(II)	Nitrate	5.5 g/m ³
Iron	Fe(II)	Chloride	10.1 g/m ³
Iron	Fe(III)	Chloride	11.9 g/m ³
Chromium	Cr(III)	Nitrate	2.4 g/m ³
Chromium	Cr(VI)	Nitrate	2.5 g/m ³
Titanium	Ti(IV)	Sulphate	26.3 g/m ³
Vanadium	V(IV)	Chloride	3.7 g/m ³
Uranium	U(IV)	Nitrate	9.4 g/m ³
Uranium	U(VI)	Nitrate	11.3 g/m ³

4.2 Batch stir tests

Batch stir tests were performed on resins from the above tests that showed the best capacity for cadmium removal from phosphoric acid. These tests were performed in a 500 cm³ round bottomed glass reaction vessel. The solution in the vessel was agitated with a glass propellor type stirrer driven by a variable speed Citenco laboratory mixer. The rotational speed of the stirrer was checked using a mechanical tachometer at regular intervals during each test. Samples were withdrawn from the reactor at regular time intervals through a porous, sintered glass sample tube immersed in the reacting solution using a six inch long hyperdermic needle inserted through a rubber septa fitted to the top of the sample tube. This ensured that no resin was removed from the reactor when samples of acid were taken. The reaction vessel was kept at a constant temperature in a thermostatically controlled water bath.

Initially the batch stir tests were performed by adding a preweighed sample (normally about 15 g) of conditioned, centrifuged moist resin to 500 cm³ of the phosphoric acid containing a known amount of cadmium. The resin sample was washed into the reaction vessel with some of the phosphoric acid solution at (time = 0) the start of the test run. However, it was felt that shrinkage of the resin in the

presence of strong acid and the movement of water out of the resin into the bulk acid solution would confuse the initial stages of the batch stir test. To overcome this problem, the preweighed resin sample was agitated with cadmium free phosphoric acid solution at the temperature of the test for at least 12 hours prior to the tests starting. The test runs started with the addition (at time = 0) of an aliquot of BDH "Spectrosol" cadmium standard solution (1 kg/m^3) sufficient to give the initial cadmium concentration required in the phosphoric acid.

The test runs proceeded over 24 hours with samples being withdrawn every minute for the first 10 minutes, every 5 minutes up to the first hour, every 30 minutes up to 6 hours of elapsed time and then at the end of the run at 24 hours of elapsed time. The volume of sample taken was kept as small as possible, in the order of 5 cm^3 , the volume taken was recorded and accounted for in the subsequent calculations. The samples taken were diluted in the ratio 1:5 with distilled water and analysed using AAS and compared to standards of known cadmium concentration, made up in similar strength phosphoric acid.

Appendix 3 gives the conditions used in the various batch stir tests that were used to determine the mechanism controlling the rate of removal of cadmium onto ion exchange resins. Most of the conditions used are self explanatory, however, some of the tests performed differed from the above methodology and are discussed below.

The effect of particle size on the loading rate was examined by performing the batch stir tests with different size range resin samples. These were obtained by wet sieving the "as received" resin through brass sieves and then collecting the different size range resins off the sieves. The resins in each size range were conditioned after sieving since the strong acid resins were noticed to be corroding the brass sieve mesh, this could possibly have led to contamination of the resin by zinc. The size ranges of resin used were 0.425 to 0.6 mm, 0.6 to 0.85 mm and 0.85 to 1.00 mm. A sample of very fine resin was produced by grinding the resin beads in a mortar and pestle and the fraction that passed a 0.063 mm sieve collected. This fine resin was difficult to wash by decantation so the resin slurry was centrifuged between each conditioning stage to produce as concentrated a sludge as possible. The final conditioned

and washed resin sludge was dried in air at room temperature until friable, it was then used in this form for the batch stir tests.

An interruption test was performed to determine whether particle diffusion effects were controlling the rate of ion exchange. This was performed by withdrawing the acid from the reactor at a known time during the progress of a batch stir test. This was done by using a vacuum pump to pull the acid out of the reactor, through a sintered glass filter, into a storage vessel which was kept at the temperature of the test. The resin remained in the reaction vessel with only a minimum of acid, sufficient only to wet the surface of the resin beads. The acid was reintroduced into the reactor after a time delay of 133 minutes and the run resumed with a similar frequency of sampling as before.

Other experiments involved batch stir tests run; at different initial cadmium concentrations, using resins with different degrees of cross linking and different structures (eg gel and macroporous types) and at different phosphoric acid concentrations.

The tests performed with different starting concentrations of cadmium were used to determine the capacity of the resins used for cadmium removal from 40% P_2O_5 phosphoric acid and to develop an isothermal relationship between cadmium concentration in solution in equilibrium with cadmium on the resin. The equilibrium experiments were performed by allowing a batch stir test to reach equilibrium, sampling the final acid, adding an aliquot of standard 1 kg/m^3 cadmium solution to the reactor and allowing the new equilibrium to be attained. This procedure was followed a number of times by successive additions of cadmium solution followed by equilibration and sampling within the same experimental run. In this way the errors associated with weighing out the resin were eliminated between each test.

Some further batch stir tests were performed using a range of different functionality resins and wet process phosphoric acid for the purpose of determining what metals were taken out of solution by the various resins. The loaded resins were washed and dried and analysed by X-Ray fluorescence spectrophotometry. The resins and method used in the tests and the results of the tests are given in Appendix 5.

4.3 Fixed column tests

The strong acid macroporous resin, Duolite C264, was selected from the above tests to be suitable for cadmium removal from phosphoric acid solutions and as such the following test work was all performed using this resin.

Fixed bed column tests were performed to show that Duolite C264 could be used in columns to remove cadmium from phosphoric acid and produce treated acid of low cadmium concentration. The loaded resin from the column tests was also used to evaluate potential eluants that would be effective at removing cadmium from the loaded C264 resin.

Initial column tests were performed in glass columns that were jacketed and of 10 mm internal diameter (I.D.). The columns were jacketed so that the resin could be kept at a constant temperature throughout the tests. This was done by pumping hot water from a thermostatically controlled water bath through the jackets. About 20 g of centrifuged moist resin was used in each column, this was loaded into the columns using distilled water which was also used to remove any air bubbles from the resin bed. The backwashed and settled bed was about 26 cm high. The resin was conditioned in the column by successive 2M HCl, distilled water and 2M NaOH washes. The tests were performed with water washed resin in the H^+ form.

These small diameter columns, however, were not ideal for determining the characteristics of cadmium removal in fixed columns since the ratio of particle diameter to column diameter was low (about 1:10), leading to uncertainties caused by wall effects in the column. These uncertainties can be overcome by using particle to column ratios in excess of about 1:30 (25).

Further fixed column tests were, therefore, performed in a 38mm I.D. jacketed glass column. The resin used in this column was in the "as received" size range (0.3 to 1.2 mm) and was of similar moisture content to the centrifuged moist resin used in the previous tests. The column contained 300 cm³ of resin when full (backwashed and drained) this corresponded to 265 g of the "as received" resin. The resin was conditioned in the column by passing about a bed volume of acetone through the bed followed by a water wash. This acetone rinse was used to remove any remaining organic contaminants from the resin. The conditioning of the resin then proceeded as for the resin

used in the 10 mm I.D. column tests, using about 5 bed volumes at each stage. The interstitial water from the resin's final water wash was displaced with 30% P_2O_5 "Analar" phosphoric acid which was pumped upwards through the bed to displace the less dense water off the top of the column. The column was left standing with the resin bed in contact with this phosphoric acid for at least 24 hours to allow equilibration between the resin and acid to occur before the loading tests commenced.

The conditions used in the fixed column tests are given in Appendix 3. The feed acid used in the first three runs was "pure" 30% P_2O_5 acid (made up using BDH "Analar" orthophosphoric acid, as described earlier) which was dosed with cadmium to about 30 g Cd/m³. These runs were performed to establish the best possible loading of cadmium that could be attained when there was no competition from other metal ions in solution.

The next three fixed column tests were performed using "real" wet process phosphoric acid from Albright and Wilson, this was 28% P_2O_5 acid produced from Khouribga phosphate rock, which contained about 15 g Cd/m³. A more detailed analysis of this acid is given in Appendix 1. Four further tests were performed using Albright and Wilson WPA produced from the digestion of Zin phosphate rock, the P_2O_5 content of the acid was originally 42% w/w, this acid was diluted with distilled water to obtain 33% P_2O_5 acid which contained about 18 g Cd/m³.

The calcium concentration of all but the first "real acid" test was reduced by precipitating it out of solution as calcium sulphate. This was done by adding about 5% by volume of concentrated sulphuric acid (s.g. = 1.84) while stirring rapidly. The mixing was stopped and the acid allowed to clarify by sedimentation, the resultant acid was filtered through a porous (size 0) sintered glass filter.

The feed acid was kept in a water bath, at the temperature of the experiments (60°C), it was then pumped upwards through the resin bed from the bottom of the column using a peristaltic pump. An upward flow was used on all but the first run since it was observed that, when acid flowed downwards through the resin bed, gas bubbles were formed in the resin bed that eventually bridged the column and reduced the acid flow. Observation of the bed showed that the upflow rates used in these tests (3 to 4 bed volumes per hour) did not

expand the bed appreciably. The results of the first two runs, where similar conditions were used except for the direction of flow in the column, showed similar resin performance for cadmium removal. A total column throughput of about 30 bed volumes was used in each test.

Once loading of the resin was complete, the resin bed was washed in downflow with distilled water to displace the interstitial phosphoric acid. Elution of the resin was then performed.

The results of the 10 mm column tests showed that strong mineral acids could elute cadmium from the loaded resin. However, these tests could not show the type of elution that could be achieved with each acid. It was expected that hydrochloric acid would give good elution of cadmium because of the formation of anionic cadmium chloride complexes. However the 10 mm column runs did not show any difference between sulphuric, hydrochloric and nitric acids for eluting cadmium. Sulphuric acid was used to elute the resin loaded from "pure" phosphoric acid solutions and an attempt was made to use this acid to elute resin loaded from WPA. This resulted in the rapid formation of a calcium sulphate precipitate which cemented the resin beads together, as a result, this acid is unsuitable as an eluant. The use of nitric acid was excluded on the grounds of safety, since there is a risk of forming explosive nitrated organic compounds within the resin bed.

Hydrochloric acid (5M) was selected to elute the resin loaded from WPA in the 38 mm column. Elution of the resin was performed in downflow through the resin bed at room temperature. Only a small volume of eluant (less than 2 bed volumes) was required because the elution of cadmium was rapid and effective.

Distilled water was passed down through the resin bed to displace the interstitial eluant and to wash the resin bed; about 1 to 2 bed volumes of water was used to wash the resin.

The raffinate from the column was collected and at known volumetric throughputs the combined raffinate was sampled for analysis by AAS for cadmium, zinc, nickel, calcium and magnesium. The samples of phosphoric acid were compared to standards of synthetic WPA solutions that contained most of the major metal ions present in the WPA (at similar concentrations) made up in 30% P_2O_5 . The standards and the phosphoric acid raffinate samples were diluted in the ratio

1:5 with distilled water for cadmium analysis. Other dilution ratios were used for the other metal analyses so that the diluted concentration was in the correct range for accurate analysis by AAS. The samples of hydrochloric acid eluate were compared to standards that contained similar (known) concentrations of the metal ions expected in the eluate, made up in 5M HCl. The eluate samples and the standards were diluted in various ratios with distilled water (from 1:10 to 1:50) depending on the cadmium concentration in the eluate.

4.4 Multistage batch tests

A rough simulation of multistage counter-current ion exchange was achieved by performing a series of batch stir tests. The apparatus used in these tests consisted of five 50 cm³ tubes with sintered porous glass bases (see Figure 4.1a). These tubes could be stoppered at both ends to allow the tubes to be agitated in a bottle roller.

The Duolite C264 resin used in the tests was sieved and the size fraction 0.6 to 0.85 mm retained and used for these tests. The resin was conditioned as before and used in the H⁺ form after being equilibrated with 30% P₂O₅ "Analar" phosphoric acid for 24 hours. The equivalent of 5 cm³ of wet settled bed (4.0 g of centrifuged moist resin) was used in each tube.

The phosphoric acid used in these tests was Albright and Wilson WPA derived from Khouribga rock. The calcium concentration was reduced by sulphate precipitation as outlined before. The acid was at room temperature for these tests (23°C) and contained about 15 g Cd/m³, 62 g Ca/m³ and 2700 g Mg/m³.

At the start of the test 25 cm³ of the feed acid was added to each of the five tubes, these were stoppered and agitated on the bottle roller for 10 minutes. The agitation was then stopped and the acid drawn off from the resin by vacuum through the porous bottom of the tube. A 1.0 cm³ sample of the acid from each tube was taken before it was transferred to the next adjacent tube in the series. Fresh resin was brought into position 1 and the resin from the old position 5 discarded. Feed acid was added to the new position 5 tube and the acid from the old position 1 tube was discarded and used for further analysis, the sequence of operation is shown in Figure 4.1b.

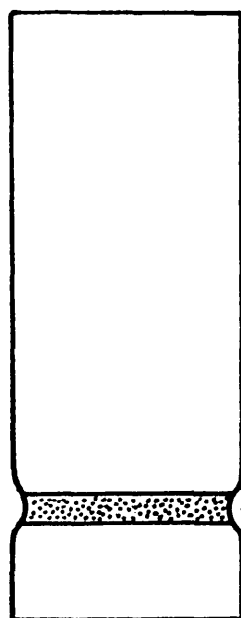


Figure 4-1a

Contactor tube design
used in multistage batch
tests.

sintered glass
filter

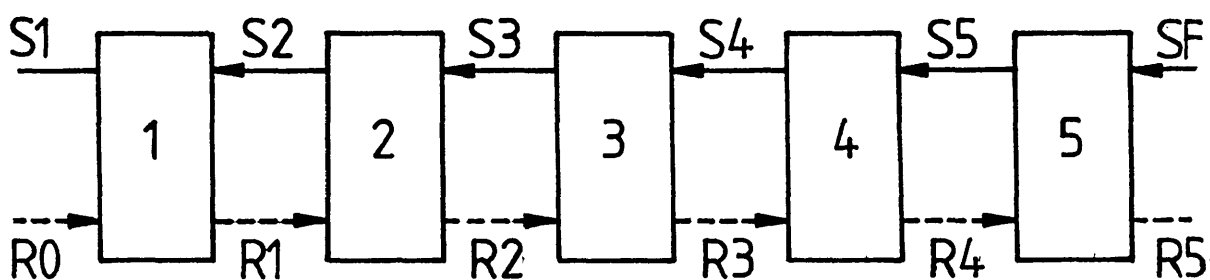


Figure 4-1b

Schematic transfer sequence
used in multistage batch tests.

S = acid flow direction

SF = feed acid

R = resin flow direction

The 1 cm³ acid samples were diluted in the ratio 1:5 with distilled water and analysed by AAS for cadmium concentration. The cadmium concentration was monitored during the tests so that the point when pseudo-steady state was reached could be determined and the experiment stopped. This occurred after about 10 cycles of the above operation. The larger samples of acid from the position 1 tubes were used to analyse for cadmium, calcium and magnesium by AAS after dilution to the required concentration for accurate analysis.

4.5 Continuous counter-current ion exchange tests

4.5.1 Cadmium extraction contactor

The selection of a suitable contactor for the extraction of cadmium from WPA depends on the kinetics and physical properties of the resin and acid used. The scale of the experiments to a certain extent also limited the choice of contactor used. The type of column chosen for these tests was a pseudo-continuous counter-current ion exchanger based on a moving packed bed principle. The eluted resin was introduced at the top of the column and the exhausted resin removed from the bottom of the column. The resin transfer occurred intermittently during pauses in the flow of acid upwards through the stationary resin bed. The conditions used in the continuous, counter current column experiments are given in Appendix 3.

The work, it was decided, should be performed in the laboratories at Imperial College since there was easy access to an AAS for the metals determinations. A 200 litre drum of 28% P₂O₅ WPA derived from Youssoufia rock was supplied by Albright and Wilson as feed for the experiments. The throughput rate for the column was planned to be in the range of 300 to 600 cm³/hour since this would lead to a realistic quantity of acid being used on a daily basis and allow for about 330 to 670 hours of column running to be performed.

The above work in fixed columns using Duolite C264 strong acid resin showed that competition with calcium and magnesium hindered the extraction of cadmium. The feed acid used was, therefore, treated with concentrated sulphuric acid (s.g. = 1.84) to precipitate calcium sulphate and so reduce calcium concentration to about 70 g Ca/m³ from the original concentration of about 4 kg Ca/m³, 5% by volume of sulphuric acid was used to treat the feed acid. The acid

flow in the column was upwards through the resin bed, counter current to the resin flowing down from the top of the column.

The resin used was Duolite C264 in the as received size distribution and the mean particle size was about 0.7 mm, as determined by sieve analysis. The previous work with this resin showed that a distribution coefficient for cadmium of about 5 in this acid could be expected. Based on this figure, and with a known feed and expected treated acid cadmium concentration an idea of the number of equilibrium stages required for each acid to resin flow ratio could be estimated.

The column diameter used was selected to be 26 mm since this would give a suitable ratio of particle size to column diameter to ensure that wall effects would not be a problem. The height of resin bed used was 700 mm. The kinetics of cadmium extraction onto C264 resin indicated that this combination would lead to about 7 equilibrium stages being established in the column. The column was therefore divided into 7 separate stages to help redistribute the flow of acid in the column and to help prevent wall effects and channelling in the resin bed.

The plates used to support the resin in each stage were made from perspex and fitted with an "O-ring" so that they could be push fitted into the glass column. The hole size in the plate had necessarily to be as small as possible to reduce the flow of acid required to support the resin bed. A hole size of 3.5 mm was shown to be too small, restricting the flow of resin down the column during resin transfer. The final plate design is shown in Figures 4.2a and 4.2b, the plates were slightly conical on the upper surface to aid resin flow. The bottom plate for the column required a baffle arrangement, as shown, to prevent resin draining down through the column during the forward acid feed periods and when the acid flow was interrupted.

The column was jacketed so that the resin bed could be kept at a constant temperature (60°C) during the experiments. This was achieved by pumping hot water from a thermostatically controlled water bath around the column jacket.

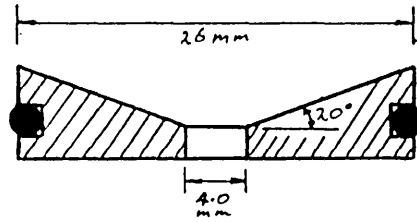


Figure 4-2a Contactor plate cross-section

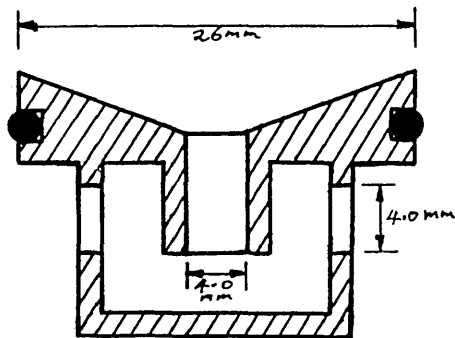


Figure 4-2b Contactor bottom plate cross-section

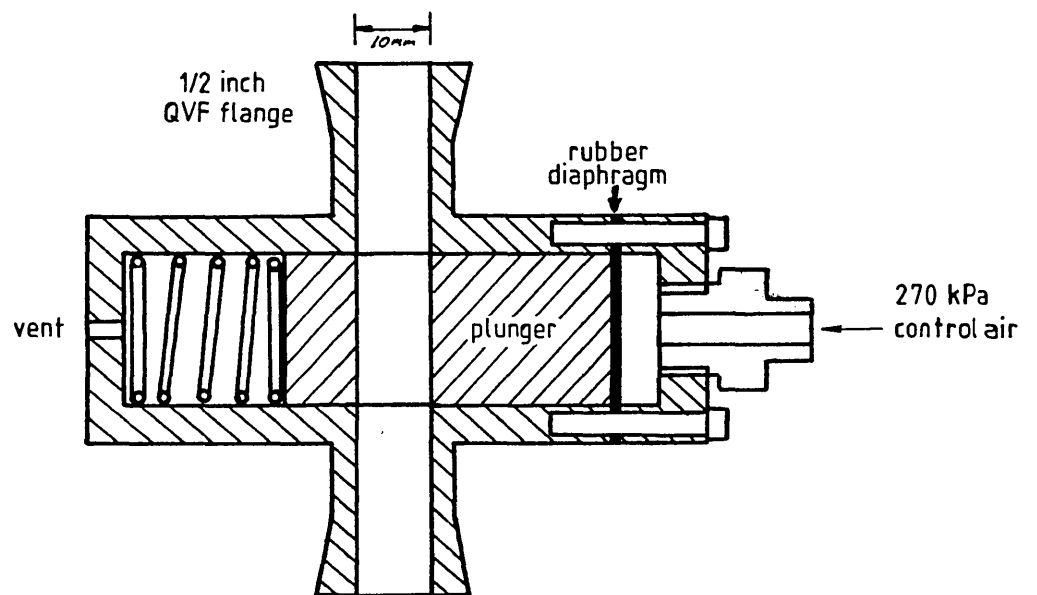


Figure 4-2c Air actuated slider valve

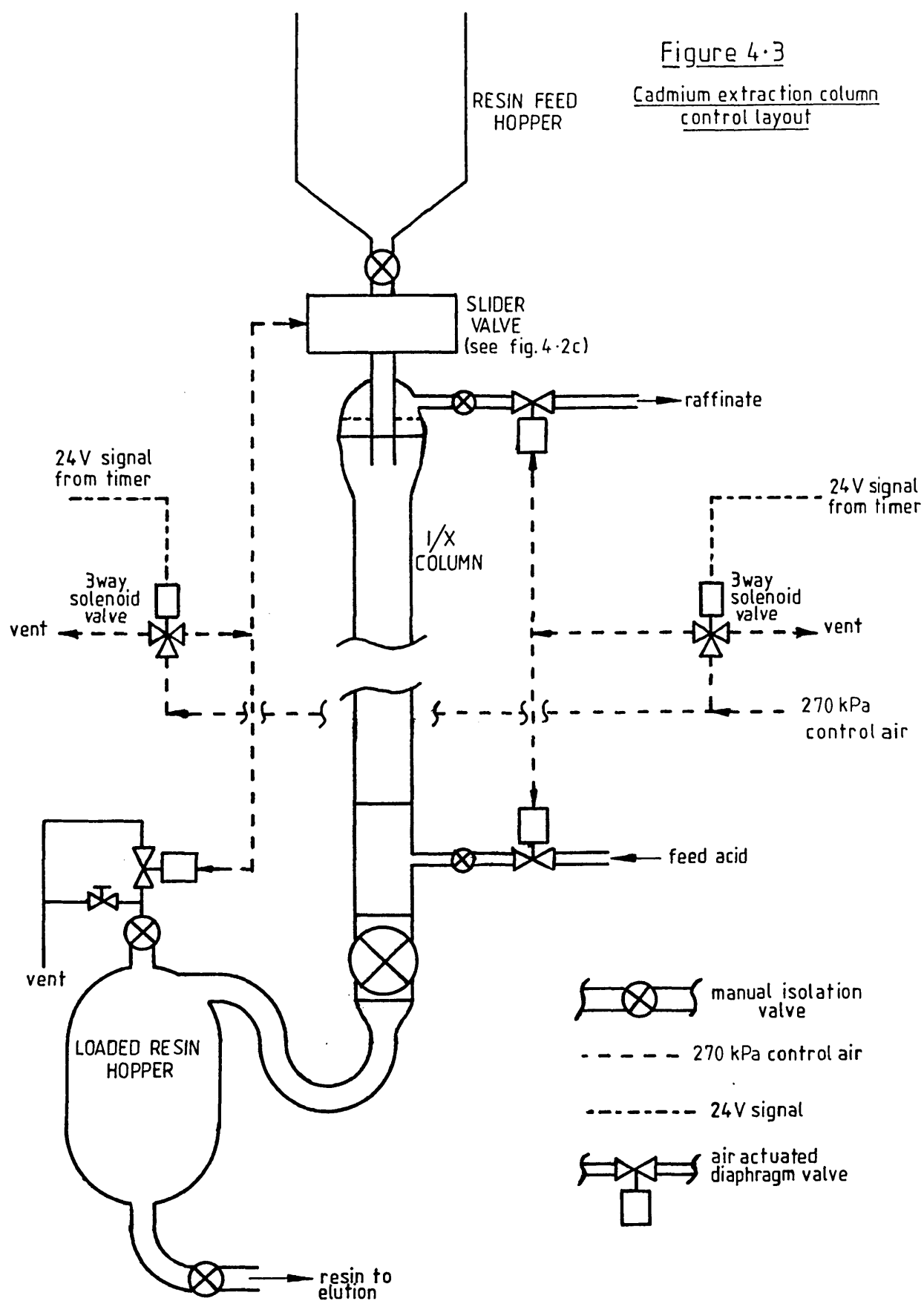
The contactor column was arranged so as to allow free flow of resin down the column by gravity during the resin transfer cycles. The column was not operated with a continuous resin flow, resin was transferred batchwise after a period of continuous acid flow upwards through the column. Solenoid valves on the resin feed and discharge and on the acid feed and discharge lines allowed for timed control of the column. The timing sequence was controlled by an "Acorn Atom" microcomputer through a set of 24 volt relays. These energised two 240 volt solenoids that controlled the 270 kPa air supply that was used to open and close the air actuated solenoid valves controlling the acid and resin flows (see Figure 4.3). The air actuated valves were air-to-close types and so manual isolation of each of the controlled flows was required to enable the column to be shut down overnight.

The flow of resin down through the column was not directly metered. Resin was allowed to flow by gravity during a timed interval, the resin flow could be altered by changing the length of time that the resin valves were open for. The quantity of resin transferred was deduced by the change in the level of the eluted resin hopper. This method proved generally reliable, however, slight variations in resin flow occurred as the level in the hopper changed. These were compensated for by adjusting the acid flow so as to maintain a constant resin to acid flow ratio. The acid flow in each cycle was adjusted on the basis of the quantity of resin transferred.

Acid flow to the column was varied by adjusting the rotational speed of the peristaltic pump used to pump the feed acid, the flow of acid was indicated on a variable area flow meter (Rotameter). The feed acid was kept at the temperature of the experiments in a storage vessel immersed in a thermostatically controlled water bath.

The treated acid was collected during each feed cycle and the volume measured. A sample of the collected treated acid was taken after each feed cycle for and kept for analysis by AAS for cadmium, calcium and magnesium.

The column was generally run for between 20 and 30 cycles of feed/resin transfer so that steady state conditions could be attained in the column.



4.5.2 Elution

Elution of the cadmium loaded C264 resin was carried out batchwise once a sufficient quantity of resin had been collected. The elution column was 39 mm in diameter and 520 mm high and was loaded and emptied of resin hydraulically through side entries to the column. Up to 600 cm³ of resin could be eluted per batch.

Resin from the loaded resin hopper, on the loading column, was drawn up into the elution column by a peristaltic pump which was used to evacuate air from the column.

The resin loaded into the elution column was present with phosphoric acid transferred with the resin from the loading column. This acid was displaced off the resin bed by a down flow of the distilled water used for washing the resin. The displaced acid was collected and returned to the loading column feed reservoir. Generally about one bed volume of water was used for this purpose and about 500 cm³ of resin eluted at any one time.

The eluant used was 5 M HCl as this was shown in previous work to give a very efficient elution of cadmium from C264 resin. The eluant was fed in upflow through the resin bed at about 600 cm³/hour, this initially displaced wash water from the resin bed voids off the top of the column. This wash water was collected until HCl was seen to appear in the eluate from the column. The volume of wash water collected was measured and a sample taken for later analysis by AAS for Cd, Ca and Mg. Samples of the column eluate were taken at known volumetric throughputs and kept for analysis by AAS for Cd, Ca and Mg. The elution continued until about two bed volumes of eluant had been pumped to the column. The eluant pump was then stopped and the resin transfer pump used to pump a distilled water wash down through the column, displacing the remaining eluate from the resin voids. The water wash continued until the pH of the water leaving the column indicated that no more acid was being released. The wash water was then displaced off the top of the column by pumping 30% P₂O₅ Analar grade phosphoric acid in upflow through the resin bed. A sample of eluted resin was kept for future evaluation of its capacity for cadmium.

Eluate from the elution procedure was collected and mixed back with any surplus eluant and used for the next elution cycle. The eluant

was supplemented occasionally with fresh 5M HCl to bring the total volume of eluant back to about 2 litres.

4.5.3 Eluant regeneration

Some small scale experiments were performed to determine whether the recycled 5M HCl could be recovered or the cadmium removed from it prior to disposal. Since the cadmium is eluted from the C264 resin as an anionic chloride complex it was assumed that an anion exchange resin could recover it. A selection of anionic ion exchange resins were tested in small batch tests with the eluate from one of the column tests. In these tests 5g of centrifuged moist resin was added to 50 cm³ of the eluate solution and agitated gently for about 12 hours. The resultant solutions were analysed for Cd by AAS. The resin selected from these tests was Duolite Al61.

The anion resin Al61 was then used in small column tests to look for possible eluants. 25 cm³ of the resin was loaded into a 12 mm diameter glass column, conditioned and used in the Cl⁻ form. A flow of the 5M HCl solution was passed down through the column and regular samples taken for analysis of cadmium concentration. The loaded resin was then water washed and eluted with a 2M NaCl solution, samples of the water wash and the NaCl eluate were collected for cadmium analysis. The subsequent eluted resin was then used for further cadmium extraction from the 5M HCl solutions.

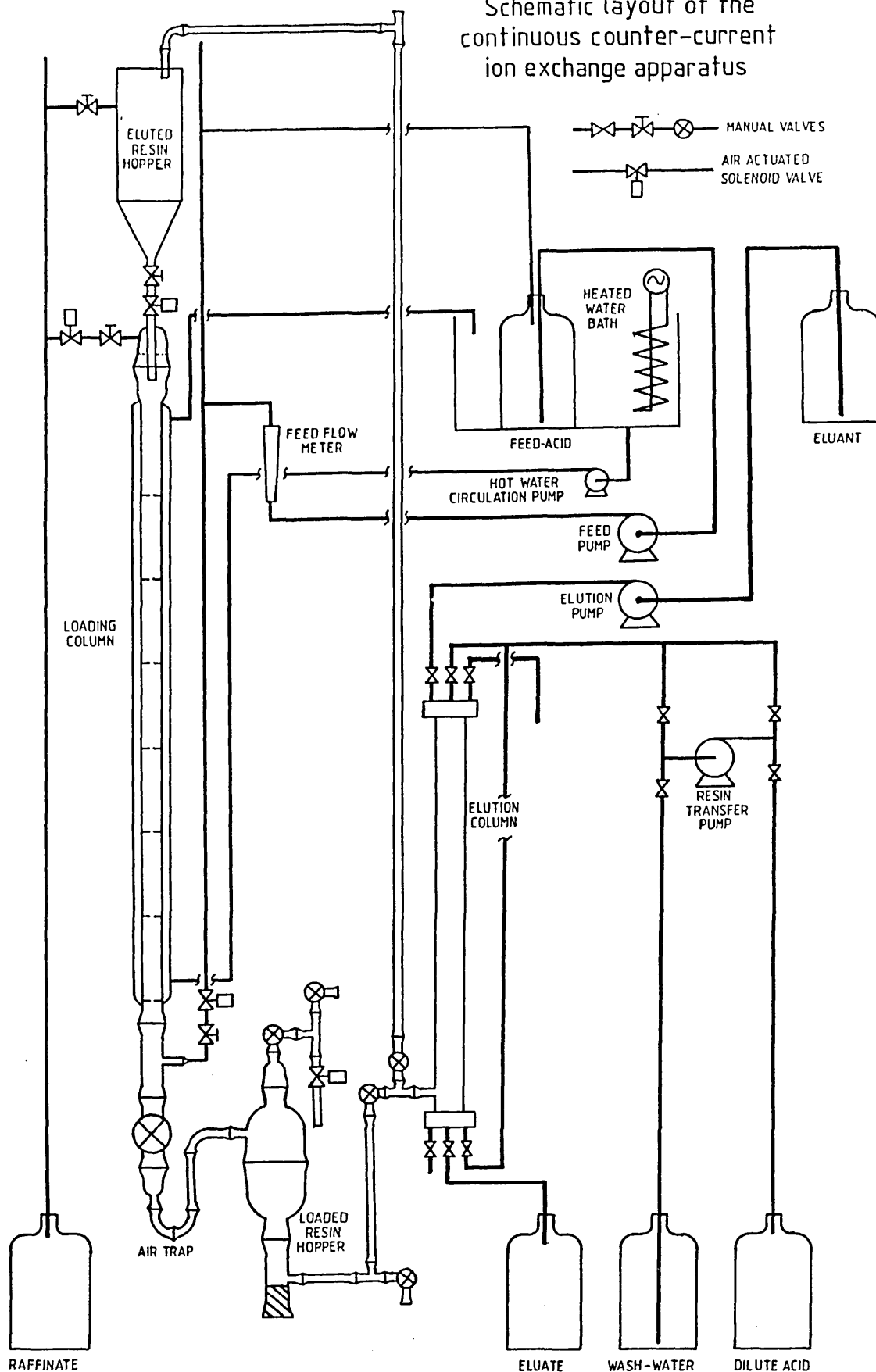
4.5.4 Overall experimental operation

Figure 4.4 shows the schematic layout of the experimental rig used.

The feed acid for the experiments was decanted into the feed tank in the water bath at the end of a days run, this allowed it to heat up to the temperature of the experiments (60°C) overnight. Resin in the column was left where it was at the last resin transfer cycle and kept at 60°C. Resin for elution was transferred at the start of the day and eluted during the day. This resin was transferred to the top eluted resin hopper late in a run. Sufficient resin inventory was kept to allow this form of operation without depleting the eluted resin stock.

Figure 4.4

Schematic layout of the continuous counter-current ion exchange apparatus



5 DISCUSSION OF RESULTS

5.1 Resin Selection Tests

The results of the resin selection tests are shown in Table 5.1 for the metal ions and ion exchange resins tested.

The ionic species that existed in the phosphoric acid as the free cation were the ones best taken up by the strong acid resins, these species included Cd^{2+} and Zn^{2+} . Of the resins tested the macroporous ion exchange resins showed the highest capacity and ones of high cross linking were best. The resin Duolite C264, with a divinylbenzene (DVB) content of 16%, was the best tested based on cadmium capacity. A conclusion that increased DVB content of resin will result in a higher capacity for cadmium cannot necessarily be drawn from this result though. The manufacturers of Duolite C264 claim that this resin is more highly sulphonated than is normally the case for this type of high DVB concentration resin. If this is the case then it would be expected to have a higher capacity based simply on the fact that there would be more potential ion exchange sites within the resin matrix. The manufacturers would not release details of how they claim to have increased the sulphonation of this resin.

The aminophosphonate chelating resin Duolite ES467 showed an affinity for complexes of Fe^{3+} , U^{4+} , Ti^{4+} , V^{4+} , Cr^{6+} and U^{6+} . This agrees with previous work (26) that used this resin for uranium removal from wet process phosphoric acid.

The mercaptane functionality chelating resin Duolite ES465 showed no ion exchange properties for the metals tested. The same was the case for the aminodiacetate resin Duolite ES466 and the weak acid resins investigated in these tests. The above resins may have shown poor performance because of the high H^+ concentration used in the tests which would lead to competition between the metal ion species and the H^+ ions present.

The strong base resin Duolite Al61 exchanged Ti^{4+} complexes in the phosphoric acid, indicating the existence of anionic phosphate complexes.

The weak base ion exchangers tested showed an affinity for the complexes of U^{4+} , Ti^{4+} and U^{6+} in phosphoric acid again indicating

the presence of anionic phosphate complexes of these metal species. The gel type anion exchanger (Duolite A30B) showed a marked deterioration of the resin beads in the phosphoric acid used, the resin fragmented into small pieces during the tests.

Table 5.1
Results of resin selection tests.

RESIN*	METAL ION LOADING ON RESINS (mg Metal/kg resin)									
	Cd(II)	Zn(II)	Fe(II)	Fe(III)	Cr(III)	U(IV)	Th(IV)	V(IV)	Cr(VI)	U(VI)
D ES465	0	0	0	0	0	0	0	0	0	0
D ES466	0	0	0	0	0	0	0	0	0	0
D ES467	0	0	101	152	0	83	238	17	12	100
D ES346	0	0	0	0	0	0	173	0	0	0
D C225	7	23	0	0	0	0	0	0	0	0
D C264	11	32	0	0	23	0	0	0	0	0
D C26	10	28	0	0	22	0	0	0	0	0
D C265	11	29	0	0	21	0	0	0	0	0
D C206A	6	17	0	0	15	0	0	0	0	0
D C20	8	22	0	0	20	0	0	0	0	0
D C433	0	0	0	0	0	0	0	0	0	0
D A101	0	0	0	0	0	0	63	0	0	0
D A374	0	0	0	0	0	26	126	0	0	34
D A30B	0	0	0	0	0	32	135	0	0	45
D A561	0	0	0	0	0	0	73	0	0	0
Initial										
Conc'n.	1.5	5.5	10	12	2.4	9.4	26	3.7	2.5	11
(g/m ³)										

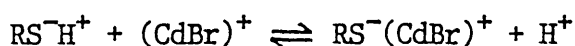
* Note "D" represents Duolite resins.

5.1.1 X-Ray fluorescence analysis

Appendix 5 shows the results of the X-Ray fluorescence (XRF) analysis performed on Duolite C264 and other resins that had been used for ion exchange from WPA derived from Zin phosphate rock.

Of the resins tested, only C264 and ES465 showed the presence of cadmium after contact with the WPA indicating that these two resins

were the most likely to succeed as resins for the removal of cadmium from WPA. The fact that no apparent removal of cadmium was seen with ES465 in "pure" phosphoric acid solutions (Table 5.1) may mean that this resin removed some complex of cadmium from the WPA. The presence of bromine in the XRF analysis may mean that this was associated with cadmium and other metal ions that were present on the resin, for example:



Where RS^- represents the mercaptane functional group.

The XRF analysis of C264 resin also shows that there are a number of other metal species that are removed from the WPA by this resin. Unfortunately the use of a tungsten X-Ray source tube meant that elements with atomic numbers of 20 or less could not be detected. This meant that the presence of calcium and magnesium on the resin was not seen in these tests.

The results of these tests indicate that this method of analysing loaded resins by XRF can be a useful tool in deciding what resins may be suitable for specific applications.

5.2 Batch stir tests

The results of the batch stir tests are given as graphs of fractional attainment of equilibrium versus time. This is a conversion of the raw results which were recorded as concentration of metal versus time. Equilibrium conditions were assumed to have been achieved once the metal concentration in solution attained a steady value. This occurred in most tests between 2 and 6 hours of contact. The resin equilibrium metal concentration was determined by performing a simple mass balance where the metals lost from solution were assumed to all be present on the resin. The fractional attainment of equilibrium at any time was determined by dividing the metal concentration on the resin by the equilibrium resin loading.

Table 5.2 shows the results from one batch test that were used to calculate the fractional attainment of equilibrium.

Table 5.2

Raw results from a batch stir test showing
calculated attainment of equilibrium at each time.

(15g of 0.6 to 0.85 mm Duolite C264 contacted with 40% P₂O₅
"pure" phosphoric acid at 60°C)

ELAPSED TIME (mins)	REACTOR VOLUME (cm ³)	CADMIUM CONC'N (g/m ³)	INCR'L Cd LOADED (mg)	RESIN Cd CAPACITY (mg/g Resin)	FRACTIONAL ATTAINMENT OF EQUILIBRIUM
0	500	14.7	—	0.0	0.0
2	493	12.6	1035	0.07	0.28
4	486	11.4	583	0.11	0.44
6	479	10.8	287	0.13	0.51
8	472	10.2	283	0.15	0.59
10	465	9.9	140	0.16	0.63
15	458	9.0	412	0.18	0.74
20	451	8.5	226	0.20	0.80
25	444	8.0	222	0.21	0.86
30	437	7.8	87	0.22	0.88
45	430	7.4	172	0.23	0.93
64	423	7.0	169	0.24	0.97
158	416	6.8	104	0.25	1.0
210	409	6.8	0	0.25	1.0

5.2.1 Temperature

The effect of temperature on the rate of loading of cadmium onto Duolite C264 resin is shown in Figure 5.1. The batch tests were performed at three temperatures, 25°C, 40°C and 60°C. The most rapid approaches to equilibrium were attained at 60°C with 90% attainment of equilibrium achieved after 30 minutes of contact, this compares to the tests at 25°C where 90% attainment was achieved after more than 70 minutes. As a result of these tests all further batch tests were performed at 60°C to ensure that equilibrium was achieved in the time allowed for the tests.

The resin Duolite C264 showed no obvious signs of deterioration when in contact with phosphoric acid at 60°C.

5.2.2 Concentration of P_2O_5

Figure 5.2 shows the results of the tests performed where cadmium was loaded onto C264 resin from phosphoric acid solutions of 30, 40 and 50% P_2O_5 . The rate of cadmium uptake by the resin was most rapid when the P_2O_5 was low. This could be due to osmotic pressure and swelling changes in the resin which would adversely affect the rate of pore diffusion. The higher concentration acids were of higher viscosity, thus affecting the liquid film mass transfer boundary layer and reducing the loading rate if film diffusion controls the loading mechanism.

No detrimental effects on the resin Duolite C264 were seen in these concentrations of phosphoric acid.

5.2.3 Resin particle size

Figure 5.3 shows the results of the loading tests performed using different size range Duolite C264 resin beads to remove cadmium from 40% P_2O_5 acid. The results indicate that the small size range resins favoured rapid attainment of equilibrium. With resin in the size range 0.425 to 0.60 mm, 90% attainment of equilibrium was achieved in about 15 minutes whereas for the resin between 0.85 and 1.00 mm it took more than 70 minutes to reach this point. This is about four times as long for about a two fold increase in particle size. This indicates that loading rate is roughly proportional to the inverse square of particle size and that diffusion within the resin bead is probably limiting the rate of reaction rather than film diffusion.

Figure 5.1 *Cd loaded onto Duolite C264 from 40% P205 acid.*
Effect of temperature on loading rate.

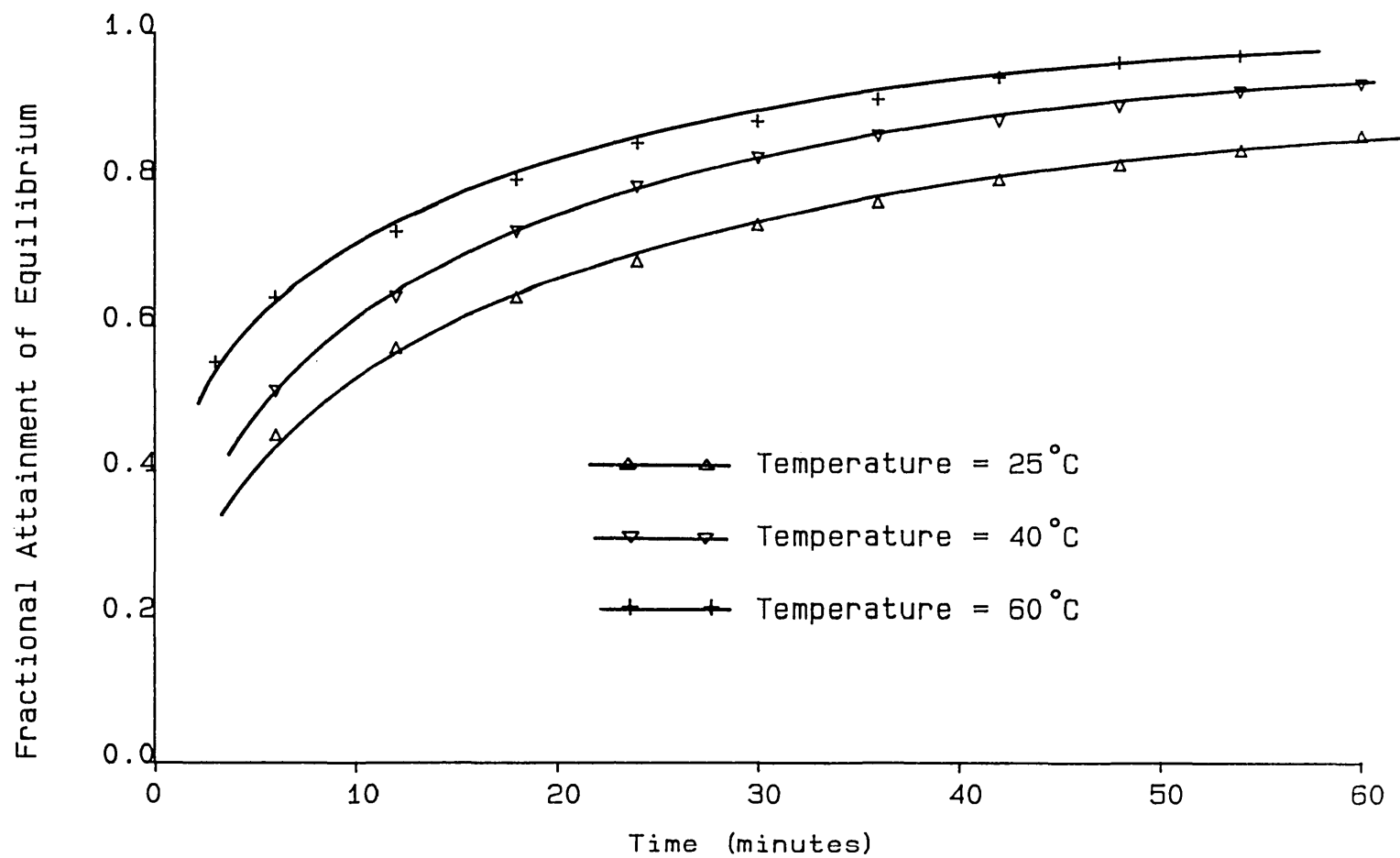


Figure 5.2 *Cd loading onto Duolite C264 from phosphoric acid.*
 Effect of P205 concentration on loading rate.

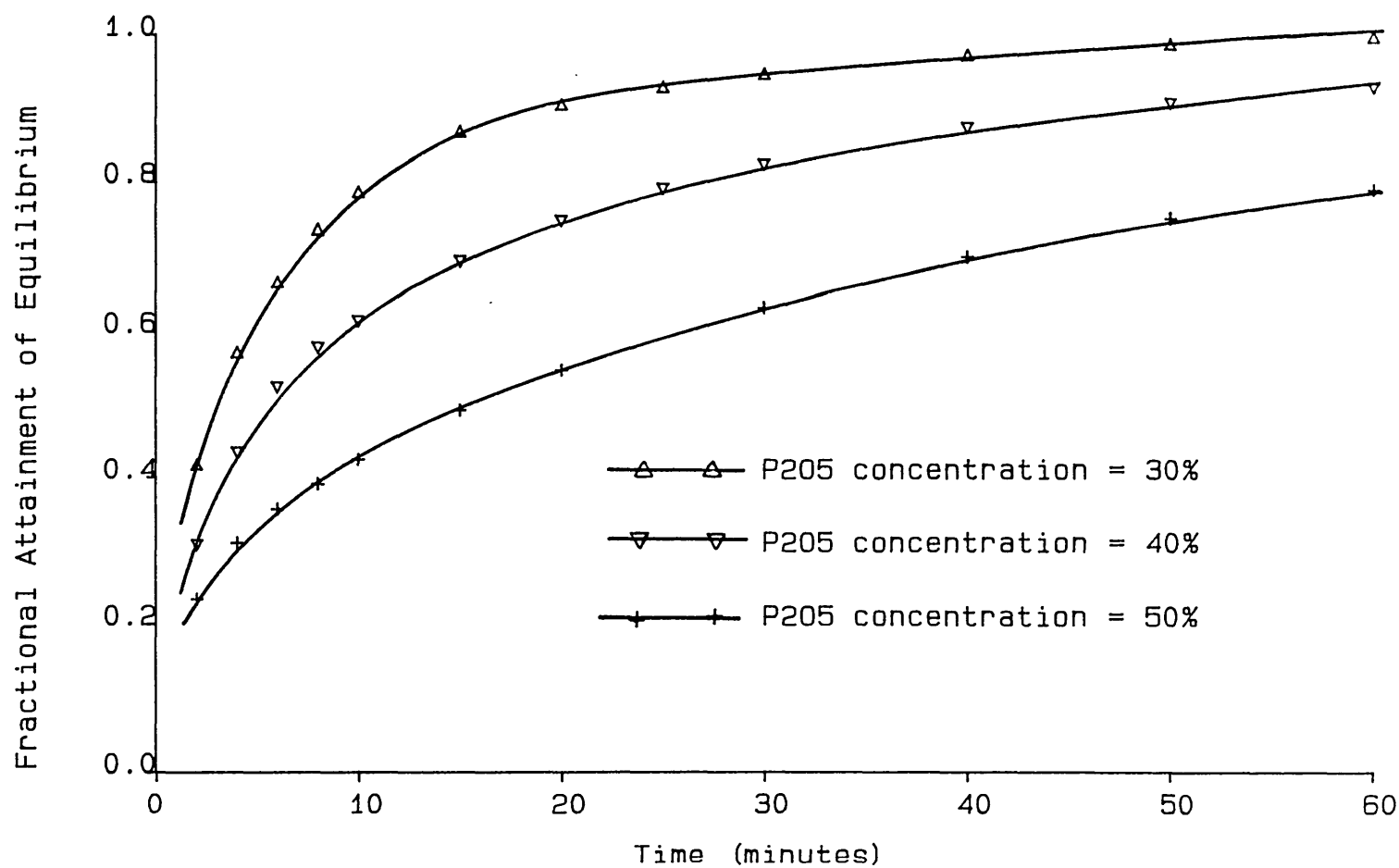
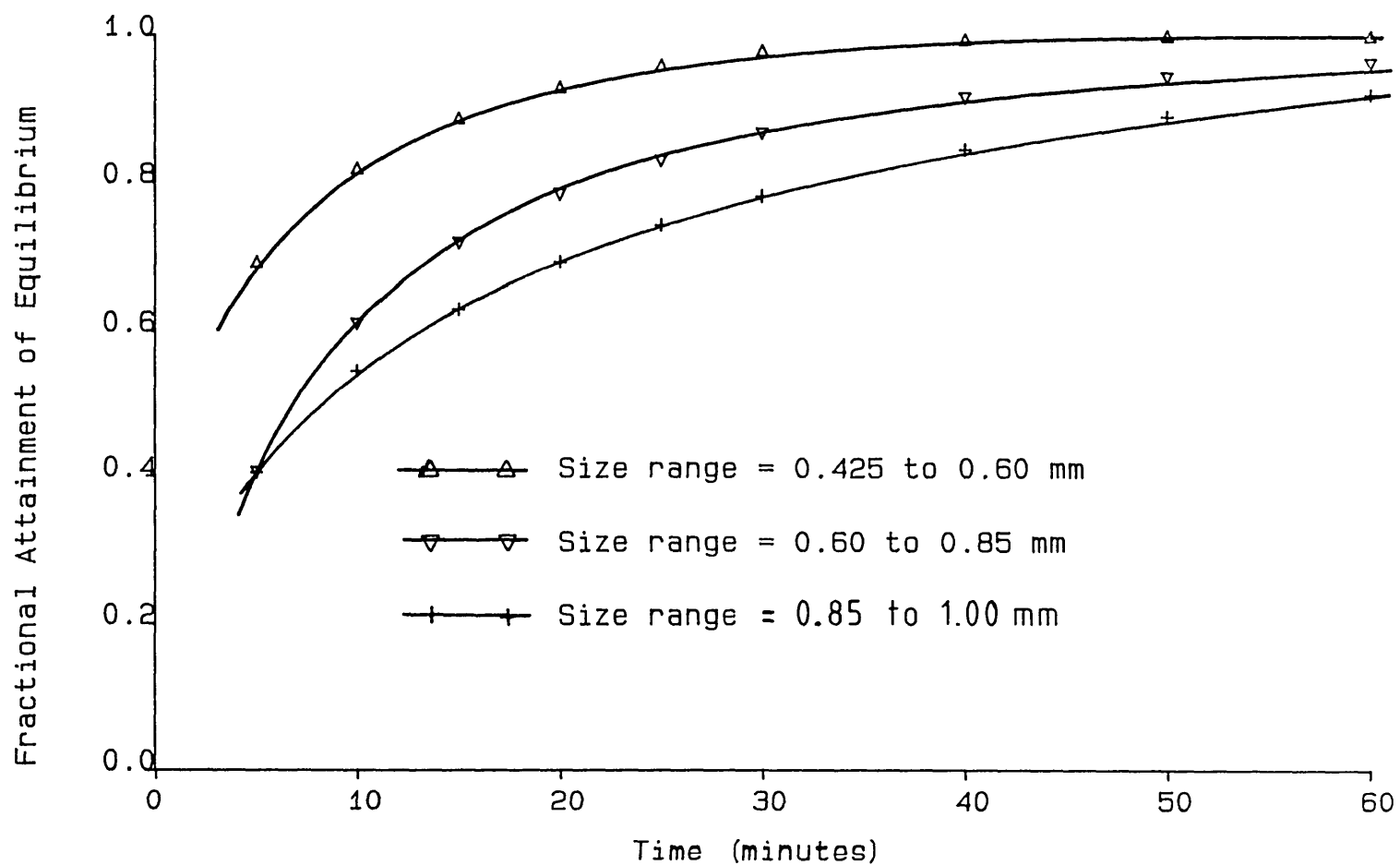


Figure 5-3 *Cd loading onto Duolite C264 from 40% P205 acid.*
Effect of particle size on loading rate.



The batch test using resin ground to less than 63 microns in size attained equilibrium extremely rapidly. The rate of sampling of the reactor was limited to once every 30 seconds because of experimental constraints. In the time it took to take the first sample from the reactor the reaction had gone to completion and equilibrium was achieved.

The relationship between particle size and reaction rate is discussed later in this chapter.

5.2.4 Speed of agitation

The speed of agitation of the reaction vessel would effect the rate of loading of the resin if the reaction mechanism is controlled by liquid film diffusion. The results of tests performed at two agitation rates are shown in Figure 5.4. There was a slight difference in the loading rates observed, after about 50% attainment of equilibrium, however this difference is within the range of experimental error expected and not considered significant.

This result would indicate that the reaction rate is probably controlled by the diffusion within the resin bead itself rather than through the diffusion layer surrounding the resin.

5.2.5 Cadmium concentration

The initial cadmium concentration used in the experiments was varied between 1.6 g/m^3 and 150 g/m^3 to determine the effect of cadmium concentration on the loading rate. The results of these tests are shown in Figure 5.5. No significant difference in the rate of attainment of equilibrium was seen in these tests for changes in cadmium concentration in solution.

If film diffusion was controlling, the rate of loading of cadmium onto the resin will be proportional to the concentration of cadmium in the solution. The results of these tests confirm that the rate of cadmium removal by C264 is not controlled by film diffusion.

Figure 5.4 *Cd loading onto Duolite C264 from 40% P205 acid.*
 Effect of stirrer speed on loading rate.

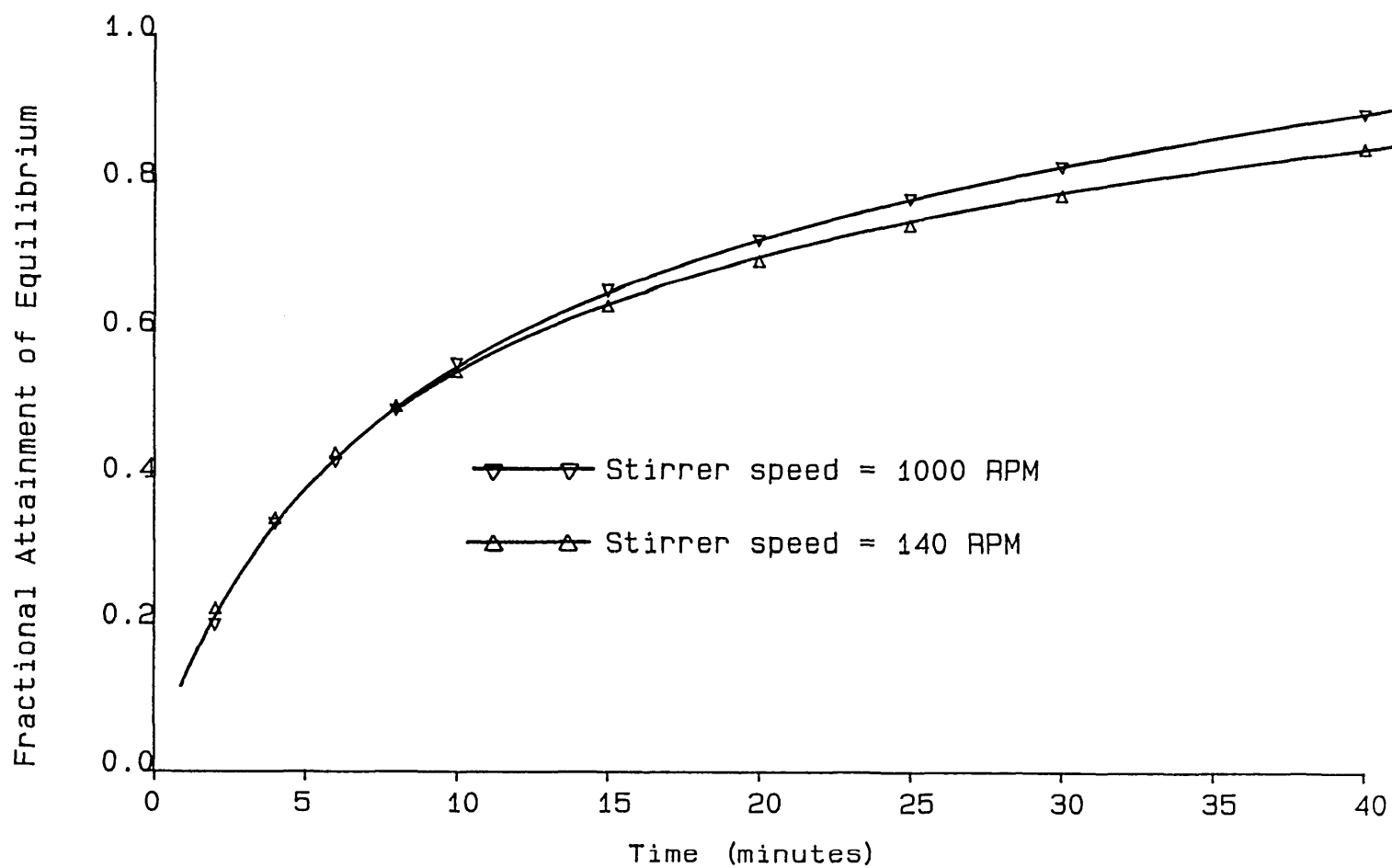


Figure 5-5 *Cd loading onto Duolite C264 from 40% P205 acid.
Effect of Cd concentration on loading rate.*

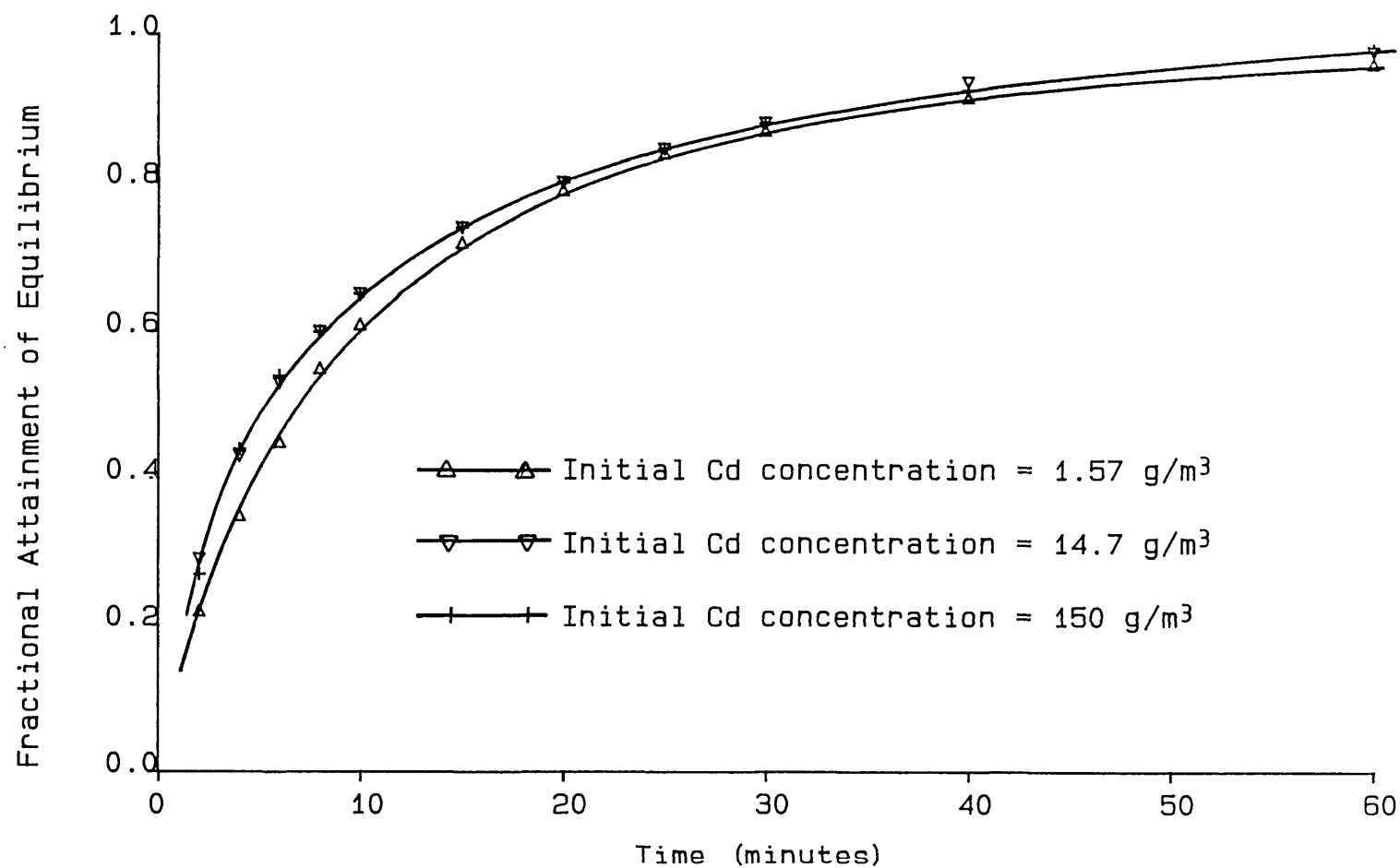
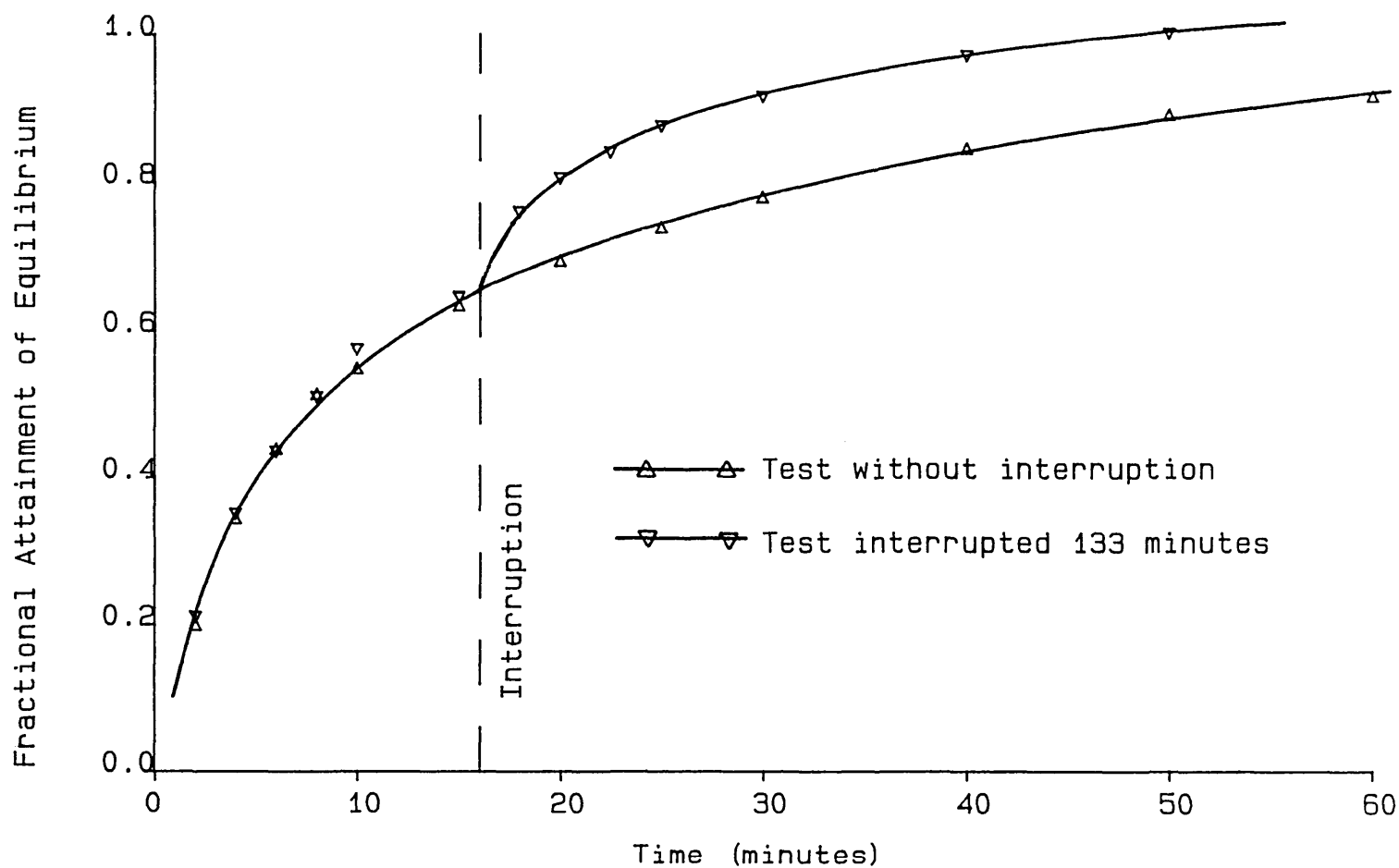


Figure 5-6 *Cd loading onto Duolite C264 from 40% P205 acid.*
Effect of interruption during contact.



5.2.6 Interruption test (27)

An interruption test should indicate whether the reaction rate is controlled by film diffusion or by diffusion within the resin bead. If the rate is film diffusion controlled then the loading curve should not show a change in slope after an interruption to the test. On the other hand, if particle diffusion is controlling the rate of loading, the interruption test should show an increased rate after the interruption. This is because the interruption period allows the diffusion process within the resin particle to continue, thus levelling out the internal concentration gradient. This results in a momentary enhancement of the rate of reaction on resuming the exchange reaction.

The results of the interruption test performed using C264 resin to remove cadmium from phosphoric acid are shown in Figure 5.6. As can be seen the rate of loading of cadmium increased markedly after the interruption indicating that the diffusion process is controlled by particle diffusion processes.

5.2.7 Resin cross linking

Figure 5.7 shows the effect of cross linking in the gel type resins tested for cadmium removal. The degree of cross linking had an effect on the rate of attainment of equilibrium seen in these tests. Duolite C225 with 8% divinyl benzene (DVB) used in its polymerisation would be less cross linked than Duolite C255 with 10% DVB in its structure. The more highly cross linked resin C255 shows a slower rate of attainment of equilibrium than the C225 resin.

Figure 5.8 shows the effect of the degree of cross linking in the macroporous resins tested. These resins showed an overall rate of loading that was higher than the gel type resins tested. Increasing the DVB content of the resins decreased the rate of attainment of equilibrium in these tests, the resin Amberlite XE386 had 12% DVB in its structure and showed the highest rate of the macroporous resins tested. The rate of loading decreased for Duolite C264 with 16% DVB and Amberlite XE383 with 20% DVB. The capacity of these resins was greatest for the C264 resin, then XE383 and then XE386. Again comparisons between Duolite C264 and the other two macroporous resins, based on capacity, is difficult since the Duolite C264 is claimed to be produced in a different manner resulting in a higher degree of sulphonation.

This considered, the trends for the resins are as expected, increased DVB content reduced the rate of attainment of equilibrium. The rate of loading is affected since the pores within the resin structure become more convoluted and tortuous for the diffusion of ions.

5.2.8 Equilibrium data

Equilibrium data was developed for cadmium loading onto Duolite C264 resin from "Analar" phosphoric acid solutions. The equilibrium relationships are shown in Figure 5.9 for cadmium removal from 30% P_2O_5 and 40% P_2O_5 "pure" phosphoric acid solutions.

The results when plotted on log-log axes yield a straight line relationship between concentration in solution and on the resin. The equilibrium relationship can be expressed as a Freundlich isotherm for the two P_2O_5 concentration solutions, as follows:

$$\begin{array}{ll} q = 0.092 C^{0.96} & \text{when } P_2O_5 \text{ concentration} = 30\% \text{ w/w} \\ q = 0.045 C^{0.95} & \text{when } P_2O_5 \text{ concentration} = 40\% \text{ w/w} \end{array}$$

where: q = equilibrium resin capacity (mg Cd/g resin)
 C = solution concentration in equilibrium with q
 (g Cd/m³)

The results show that the cadmium capacity of C264 when in 30% P_2O_5 acid was about twice that when in 40% acid. This could be due to the competition between H^+ ions and the cadmium ions increasing as the acid concentration increased. Another possibility is that the resin pore size shrinks due to osmotic pressure as the acid concentration increases thus making access to some ion exchange sites impossible at high acid concentrations.

Figure 5.7 *Cd loading onto gel-type resins from 40% P205 acid.*
 Effect of crosslinking on loading rate.

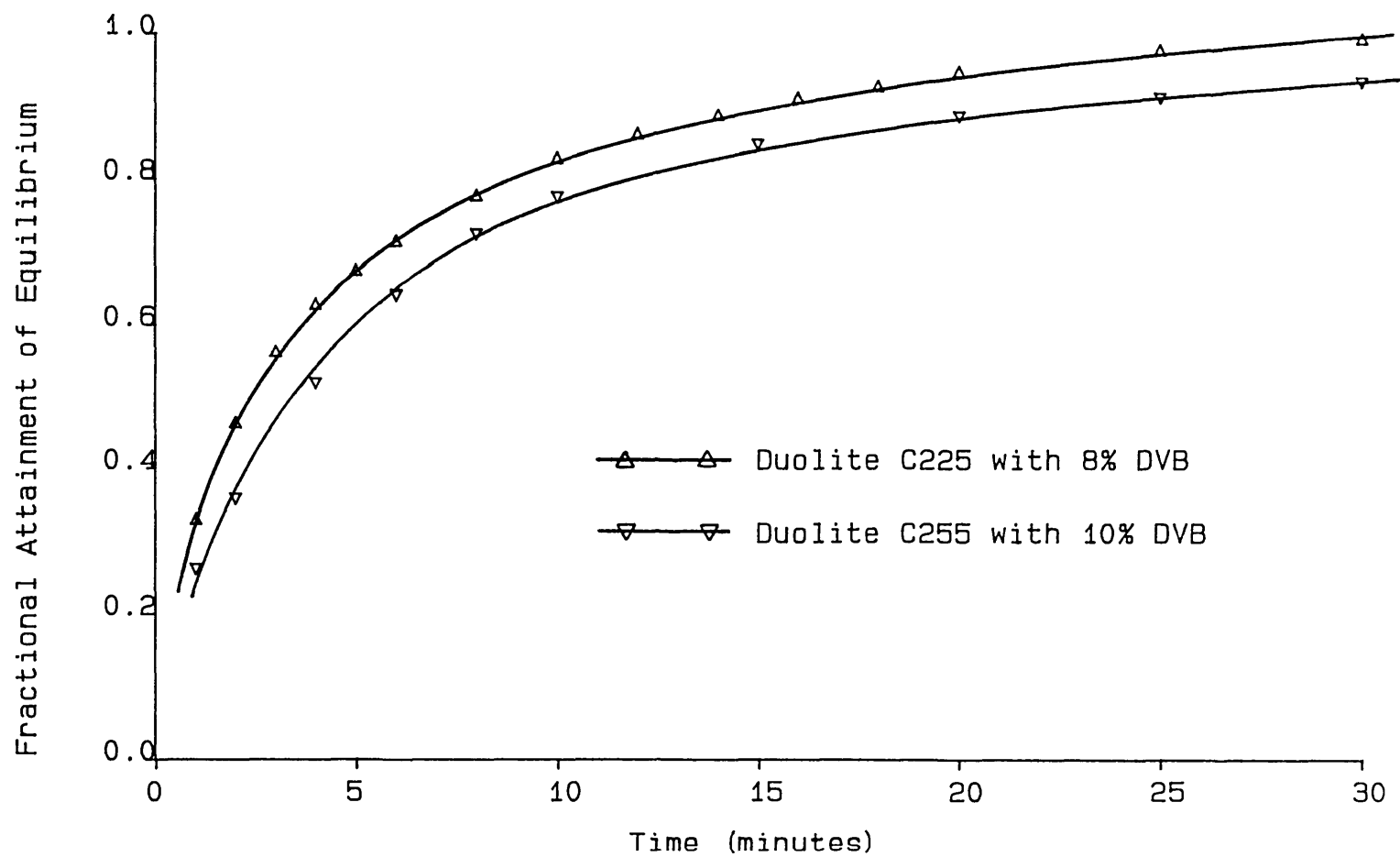


Figure 5.8 *Cd loading onto macroporous resins from 40% P205 acid.*
Effect of crosslinking on loading rate.

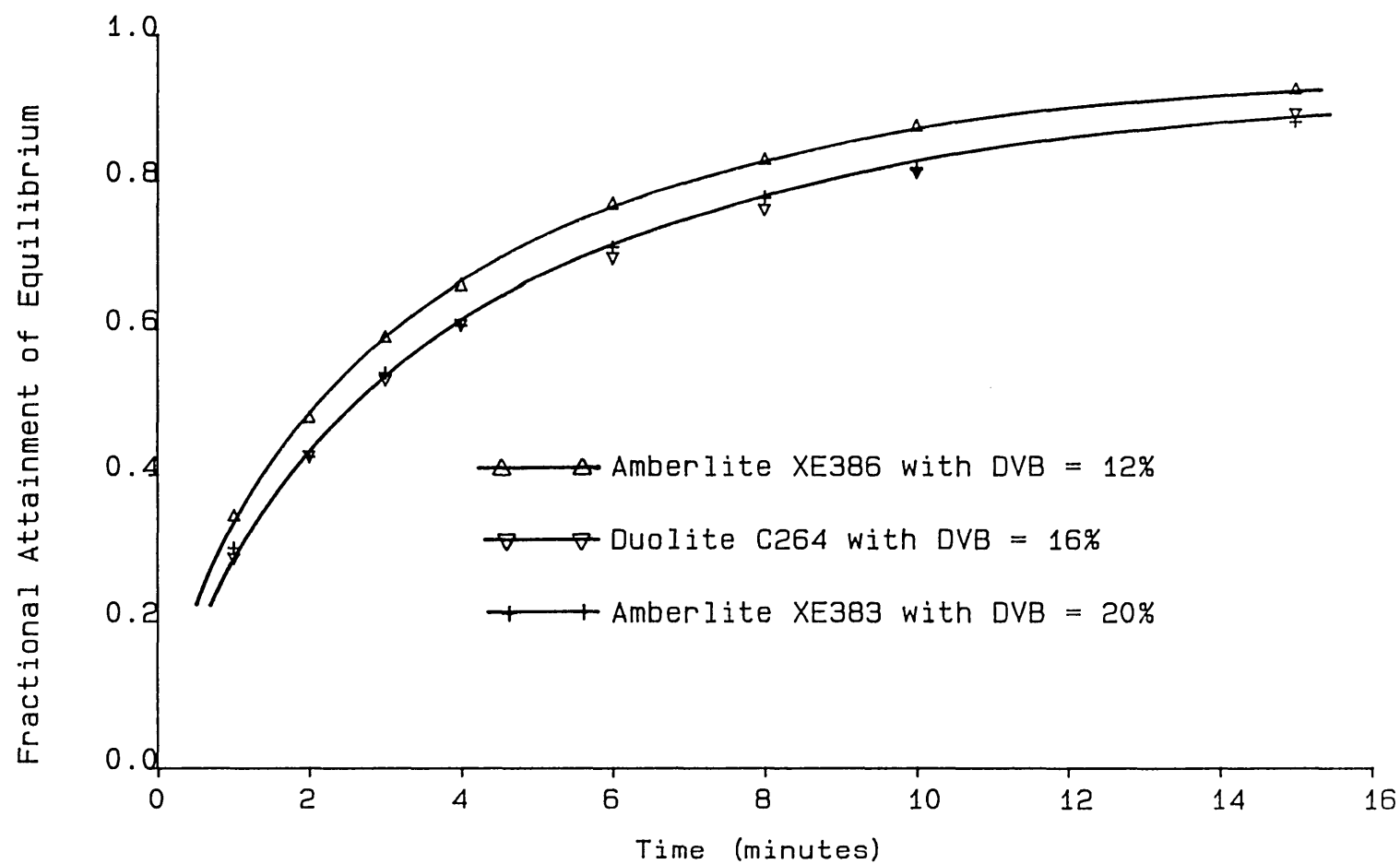
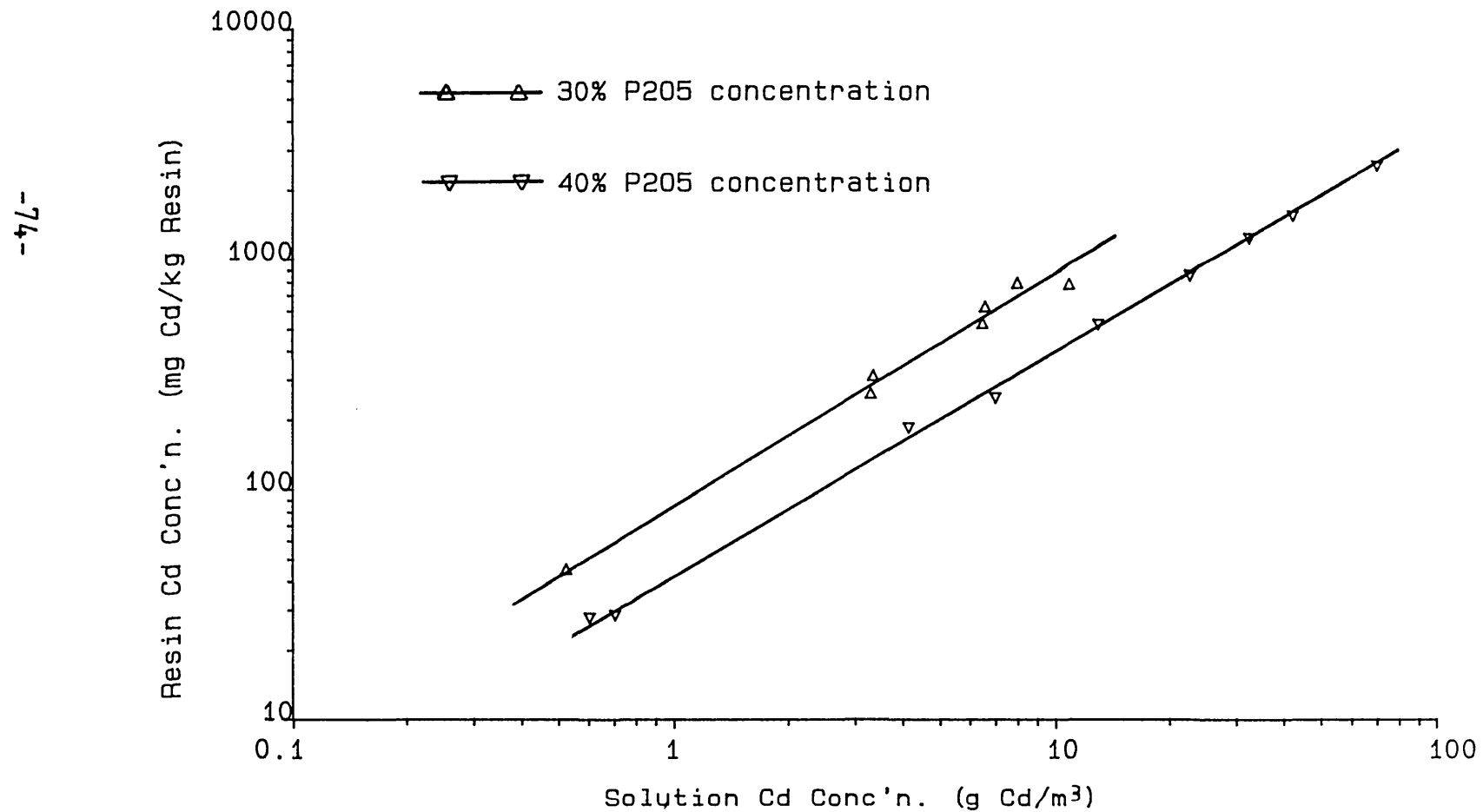


Figure 5.9 *Cd loading onto Duolite C264 from pure phosphoric acid.
Equilibrium loadings at different P205 concentrations.*



5.3 Determination of diffusion mechanism

To determine how the experimental data determined in the batch stir tests fitted the models of ion exchange processes, it was necessary to plot the appropriate functions against time to determine if there was a fit. The various functions plotted are shown in Table 5.3 for one batch stir test, the same functions are shown plotted against time in Figures 5.10 and 5.11.

The plots in Figures 5.10 and 5.11 indicate the best fit of the data was with particle diffusion controlling the rate of loading and the special case of finite solution volume giving the best fit. This result confirms the results of the various experimental tests outlined in section 5.2.

Table 5.3

Calculated ion exchange model fitting data for cadmium extraction onto Duolite C264 from 40% P₂O₅ "pure" phosphoric acid.
(Results from a run at 60°C using resin of 0.85 to 1.2 mm diameter and acid initially containing 1.5 g Cd/m³)

Time (min)	Resin Cd loading (mg Cd/kg)	X	-ln(1-X)	-ln(1-X ²)	τ
2	5.5	0.221	0.250	0.050	0.0024
4	8.6	0.345	0.423	0.127	0.0068
6	10.8	0.434	0.569	0.209	0.0120
8	12.4	0.498	0.689	0.285	0.0170
10	13.6	0.546	0.790	0.354	0.0220
15	15.8	0.635	1.008	0.516	0.0340
20	17.3	0.695	1.187	0.660	0.0455
25	18.5	0.743	1.359	0.803	0.0570
30	19.5	0.783	1.528	0.950	0.0700
40	21.1	0.847	1.877	1.264	0.0980
50	22.1	0.888	2.189	1.554	0.1270
60	22.8	0.916	2.477	1.827	0.1580
70	23.3	0.936	2.749	2.088	0.190
80	23.6	0.945	2.957	2.290	0.220
∞	24.9	1.000			

Figure 5.10 *Ion exchange model fitting plots.*
Fractional attainment of equilibrium and $-\ln(1-X)$ versus time.

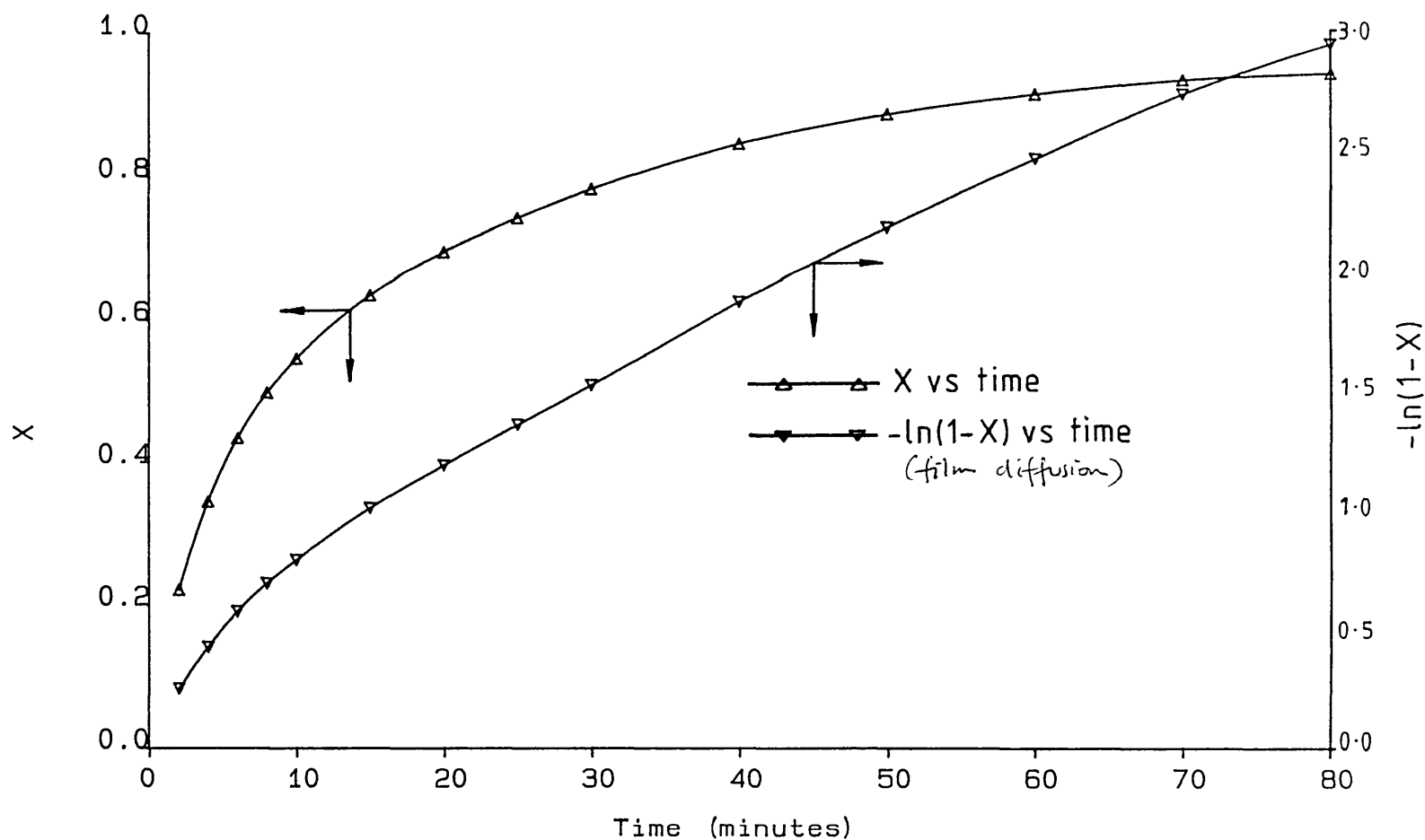
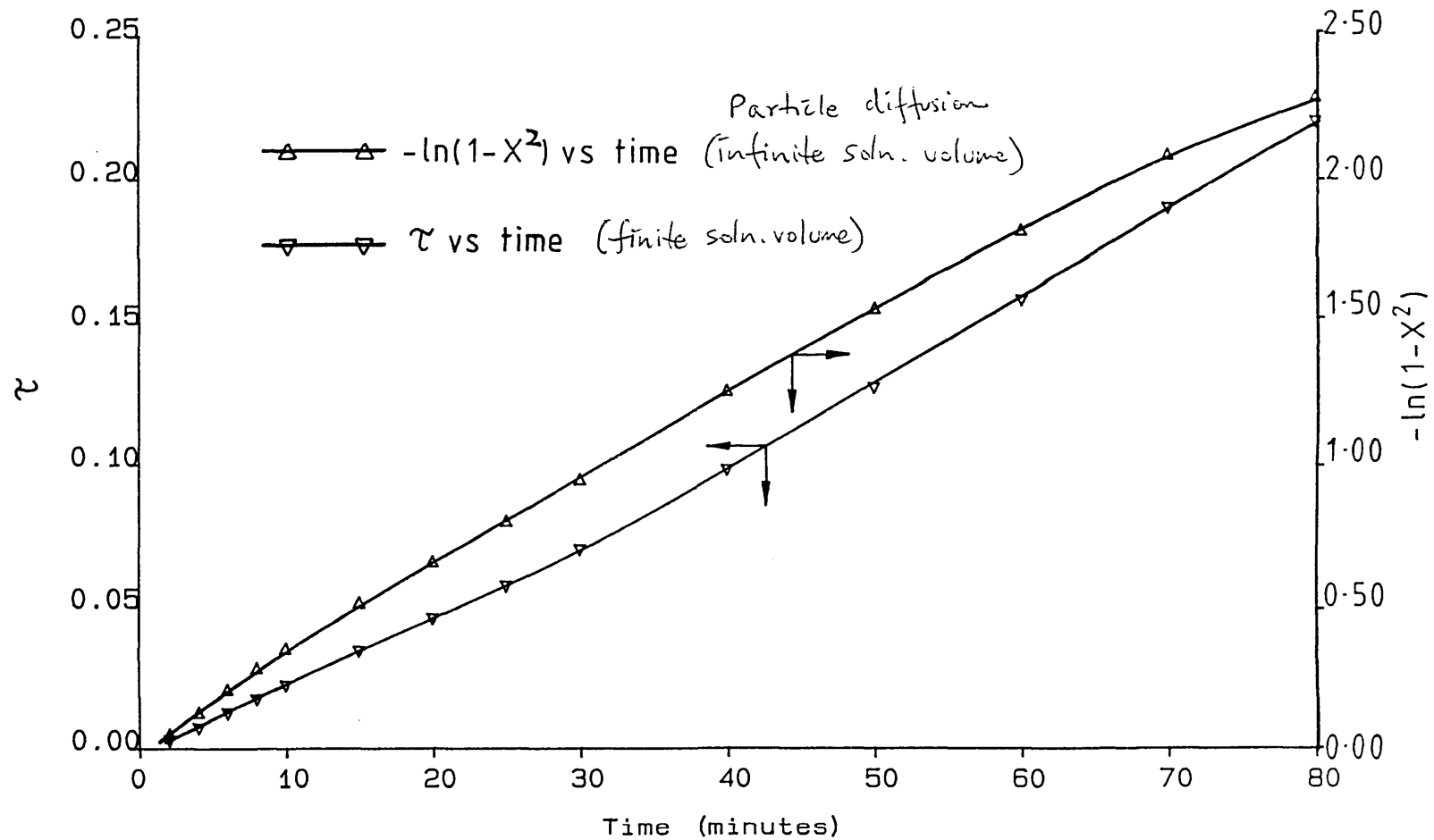


Figure 5.11 Ion exchange model fitting plots.
 $-\ln(1-X^2)$ and τ versus time.



The plot of $\mathcal{Q}$ versus time was linear between about 20 and 80% attainment of equilibrium. At less than 20% attainment of equilibrium the discrimination of the data points to give an accurate loading curve was not possible because of the experimental error expected. However, the fact that most of the experiments showed non-linearity in this period indicates that particle diffusion may not be dominating the rate of loading in the early stages of the experiment. This would be expected since the active sites in the resin are plentiful and diffusion of cadmium ions through the boundary layer around the resin beads may be limiting the rate of loading. At the end of the experiments the rate of internal particle diffusion may decrease as the easy to reach areas of the resin structure are saturated with the cadmium ions. The cadmium ions would then need to diffuse to the more convoluted areas of the resin structure and also suffer from increased electronic repulsion from the adsorbed Cd^{2+} ions already on the resin.

The slope of the straight line portion of the $\mathcal{Q}$ versus time curves were used to determine the diffusion coefficient in the system. The values of the diffusion coefficient were calculated using this technique for each experiment to determine if the value of diffusion coefficient obtained remained constant with changes in the particle size, stirrer speed and solution Cd concentration. The values of diffusion coefficient attained were expected to vary with temperature and cross linking of the resin structure if particle diffusion was controlling. The relationship between temperature and the diffusion coefficient can be used to develop an Arrhenius plot and so estimate the activation energy of Cd uptake by Duolite C264 resin in phosphoric acid. Both film and particle diffusion is expected to be influenced by the temperature of the system, however, Helfferich (27) indicates that for gel type resins activation energy should be between 25 and 40 kJ/mole for particle diffusion control and between 13 and 25 kJ/mole for film diffusion control. For the macroporous resins, activation energy of diffusion processes would be expected to be lower than the above values. The activation energy of processes dominated by chemical reaction within the resin would be expected to be greater than 60 kJ/mole. Figure 5.12 shows the effect of temperature with the Arrhenius plot, the slope of the plot yielded an activation energy of about 16 kJ/mole indicating possible particle diffusion control in this resin system.

Figure 5.12 Arrhenius plot showing the effect of temperature on the rate of cadmium removal from phosphoric acid by Duolite C264.

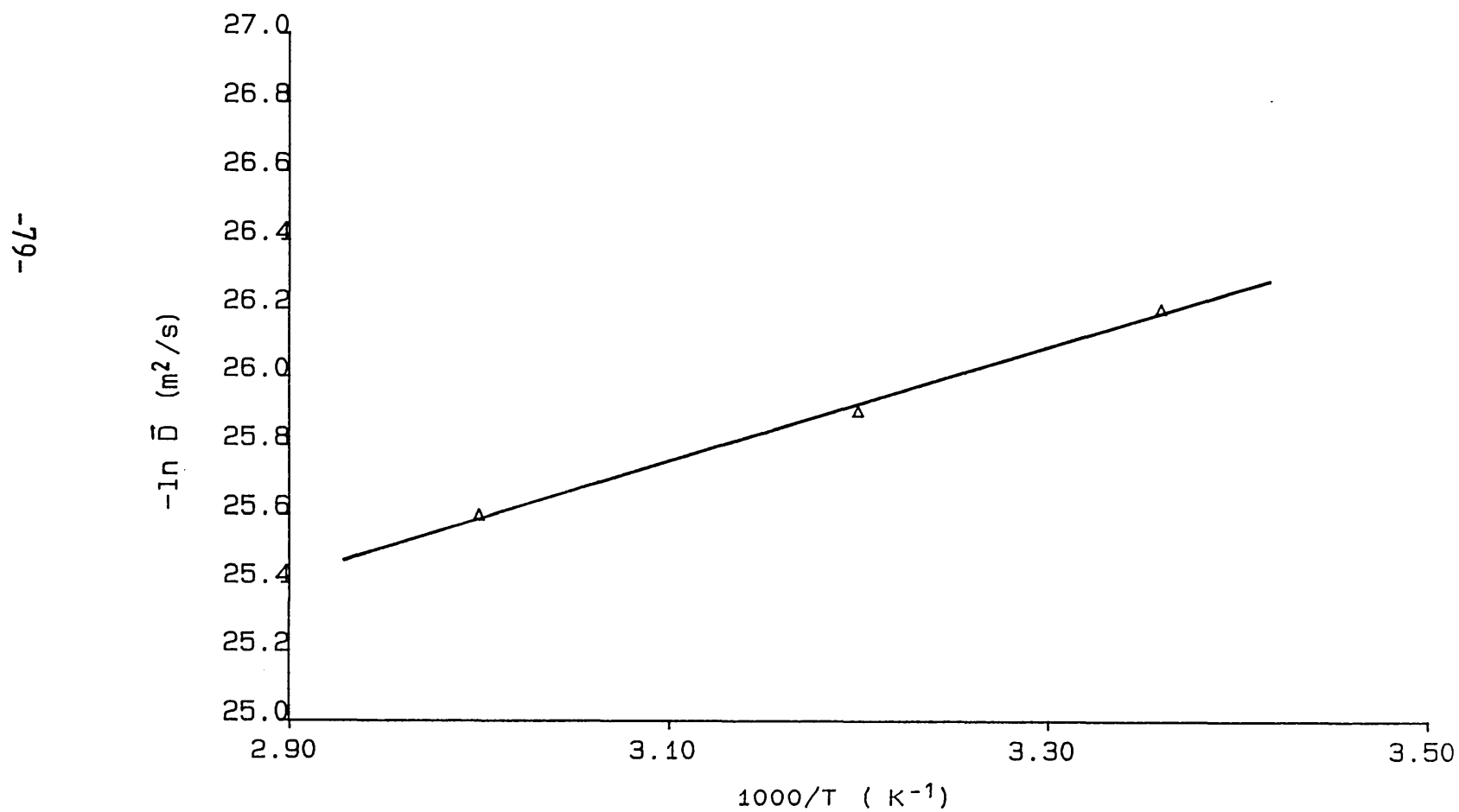


Table 5.4

Effect of resin diameter on particle diffusion coefficient.
For cadmium exchange from 40% P₂O₅ at 60°C onto Duolite C264.

RESIN SIZE RANGE (mm)	AVERAGE RADIUS r _o (mm)	r_o^2 (mm ²)	EQUILIBRIUM RESIN CAPACITY (mg Cd/kg resin)	SLOPE OF ζ vs TIME (min ⁻¹)	$\bar{D}$ (cm ² /s)
0.85-1.00	0.46	0.212	24.9	2.43x10 ⁻³	8.56x10 ⁻⁸
0.60-0.85	0.36	0.130	25.7	3.89x10 ⁻³	8.40x10 ⁻⁸
0.43-0.60	0.26	0.068	24.1	7.41x10 ⁻³	8.35x10 ⁻⁸

The results in Table 5.4 show the change in the particle diffusion coefficient with changes in the particle size. As can be seen, particle size had no significant effect on the calculated diffusion coefficient. The relative rate of loading is seen to be inversely proportional to the square of the resin radius. The equilibrium resin capacity was unaffected by the size of the resin particle.

Table 5.5

Effect of stirrer speed on particle diffusion coefficient.
For cadmium exchange from 40% P₂O₅ at 60°C onto Duolite C264.

STIRRER SPEED (RPM)	EQUILIBRIUM RESIN CAPACITY (mg Cd/kg resin)	SLOPE OF ζ vs TIME (min ⁻¹)	$\bar{D}$ (cm ² /s)
982	24.9	2.41x10 ⁻³	8.56x10 ⁻⁸
140	25.2	2.92x10 ⁻³	10.30x10 ⁻⁸

Table 5.5 shows the calculated results from experiments performed at two different stirrer speeds using C264 resin of 0.46 mm average radius. The film thickness is estimated to be different by a factor of about two as a result of changing the stirrer speed in this range, the thicker film at the lower speed of rotation. If film diffusion is controlling the rate of loading onto the resin then a change of film thickness of this magnitude should have a significant

effect on the rate. As was seen in the Figure 5.4 the effect of film thickness on the rate was insignificant. The change in the particle diffusion coefficient observed in the two tests is not experimentally significant and within the range of experimental error.

Table 5.6 shows the effect of the solution cadmium concentration on the calculated particle diffusion coefficient. As would be expected if particle diffusion was controlling the rate of loading the solution concentration had no effect on the rate of uptake of cadmium by the resin and did not effect the particle diffusion coefficient.

Table 5.6

Effect of solution concentration on particle diffusion coefficient
For cadmium exchange from 40% P₂O₅ at 60°C onto Duolite C264.

INITIAL Cd CONCENTRATION (g Cd/m ³)	EQUILIBRIUM RESIN CAPACITY (mg Cd/kg resin)	SLOPE OF C vs TIME (min ⁻¹)	$\bar{D}$ (cm ² /s)
1.57	25.7	3.76x10 ⁻³	8.40x10 ⁻⁸
14.7	245	3.77x10 ⁻³	8.15x10 ⁻⁸
150	2520	3.77x10 ⁻³	8.15x10 ⁻⁸

Table 5.7 shows the effect of different cross linkage of macroporous resins on calculated particle diffusion coefficients. The effect of the resin cross linking is not significant in the range of DVB concentrations 12% to 16%. However, there appears to be a drop in the diffusion coefficient with the resin containing 23% DVB, this would result in a drop in the apparent rate of loading of cadmium onto this resin and this was seen, as shown in Figure 5.7. The particle diffusion coefficient would be expected to drop as DVB concentration rises since the diffusion path within the resin should become more tortuous.

Table 5.7

Effect of degree of cross linking on particle diffusion coefficient
For cadmium exchange from 40% P₂O₅ at 60°C onto Duolite C264.

% DVB IN RESIN	EQUILIBRIUM RESIN CAPACITY (mg Cd/kg resin)	SLOPE OF C vs TIME (min ⁻¹)	$\bar{D}$ (cm ² /s)
12	17.9	3.95x10 ⁻³	8.53x10 ⁻⁸
16	25.7	4.17x10 ⁻³	8.40x10 ⁻⁸
23	24.2	2.37x10 ⁻³	5.11x10 ⁻⁸

Table 5.8

Effect of temperature on particle diffusion coefficient
For cadmium exchange from 40% P₂O₅ onto Duolite C264.

TEMPERATURE (°C)	EQUILIBRIUM RESIN CAPACITY (mg Cd/kg resin)	SLOPE OF C vs TIME (min ⁻¹)	$\bar{D}$ (cm ² /s)	$-\ln \bar{D}$ (m ² /s)	1/T (K ⁻¹)
25	12.1	1.52x10 ⁻³	4.06x10 ⁻⁸	26.2	3.36x10 ⁻³
40	13.1	2.04x10 ⁻³	5.44x10 ⁻⁸	25.9	3.20x10 ⁻³
60	13.2	3.00x10 ⁻³	8.00x10 ⁻⁸	25.6	3.00x10 ⁻³

Table 5.8 shows the calculated particle diffusion coefficients for Duolite C264 resin (0.60 to 0.85 mm diameter) at different contact temperatures. The value of the diffusion coefficient is seen to increase with increasing temperature, as would be expected in any diffusional process. The parameters used to plot the Arrhenius diagram in Figure 5.12 are shown in the table. The equilibrium capacity of the resin was unaffected by the temperature of the experiment.

From the above results it is apparent that the diffusion mechanism controlling the rate of loading of cadmium ions onto the resin Duolite C264 is particle diffusion. The calculated diffusion coefficient for the process was estimated to be 8.7×10^{-8} cm²/s at 60°C, the estimated error for the calculated diffusion coefficient is about 20%. This was estimated by repeating a batch test a number

of times using the same experimental conditions. The diffusion coefficient was calculated for each of the tests and the range of values obtained were within 20% of the mean value. An analytical determination of the possible error involved becomes meaningless as the amount of manipulation of data is high. An analysis of possible errors in the determination of the fractional attainment of equilibrium in each batch test is shown in Appendix 7.

5.4 Fixed column tests

The results of the work in fixed columns is split into the results of work carried out in 10 mm columns and the work in 38 mm columns.

5.4.1 10 mm fixed columns

The column work performed to assess the removal of cadmium from phosphoric acid onto Duolite C264 resin showed that the cadmium concentration could be reduced to undetectable levels when removed from "pure" phosphoric acid.

Figure 5.13 shows the effect of varying the throughput rate on the breakthrough of cadmium in the effluent from the columns. By looking at the volume of acid treated to the point when the cadmium concentration in the effluent was 10% of that in the feed, the performance of the column tests could be assessed. The 10% breakthrough point was seen to increase from 6 bed volumes treated to 23 bed volumes treated as throughput rate decreased from 12 to 3 bed volumes per hour. The relationship between throughput rate and the volume of acid that can be treated to 10% breakthrough is not well defined since the size of columns used in these tests would have resulted in significant wall effects. The size of resin particle used in the tests was 1 mm and with a column diameter of only 10 mm this gives a column to resin diameter ratio of only 10:1. Smith (25) recommends that the column to particle diameter ratio should exceed 30:1 to avoid wall effects in packed columns. The only results worth noting from these tests were that the solution cadmium concentration could be reduced to zero for a period of time and that the time to breakthrough increased with decreasing throughput rate.

The results of the preliminary column elution tests on this scale of column are shown in Table 5.9 and indicate that strong mineral acids could be used to successfully elute cadmium from the C264 resin.

Figure 5-13 Cadmium extraction onto Duolite C264 in 10mm fixed bed columns.
Effect of throughput rate on breakthrough.

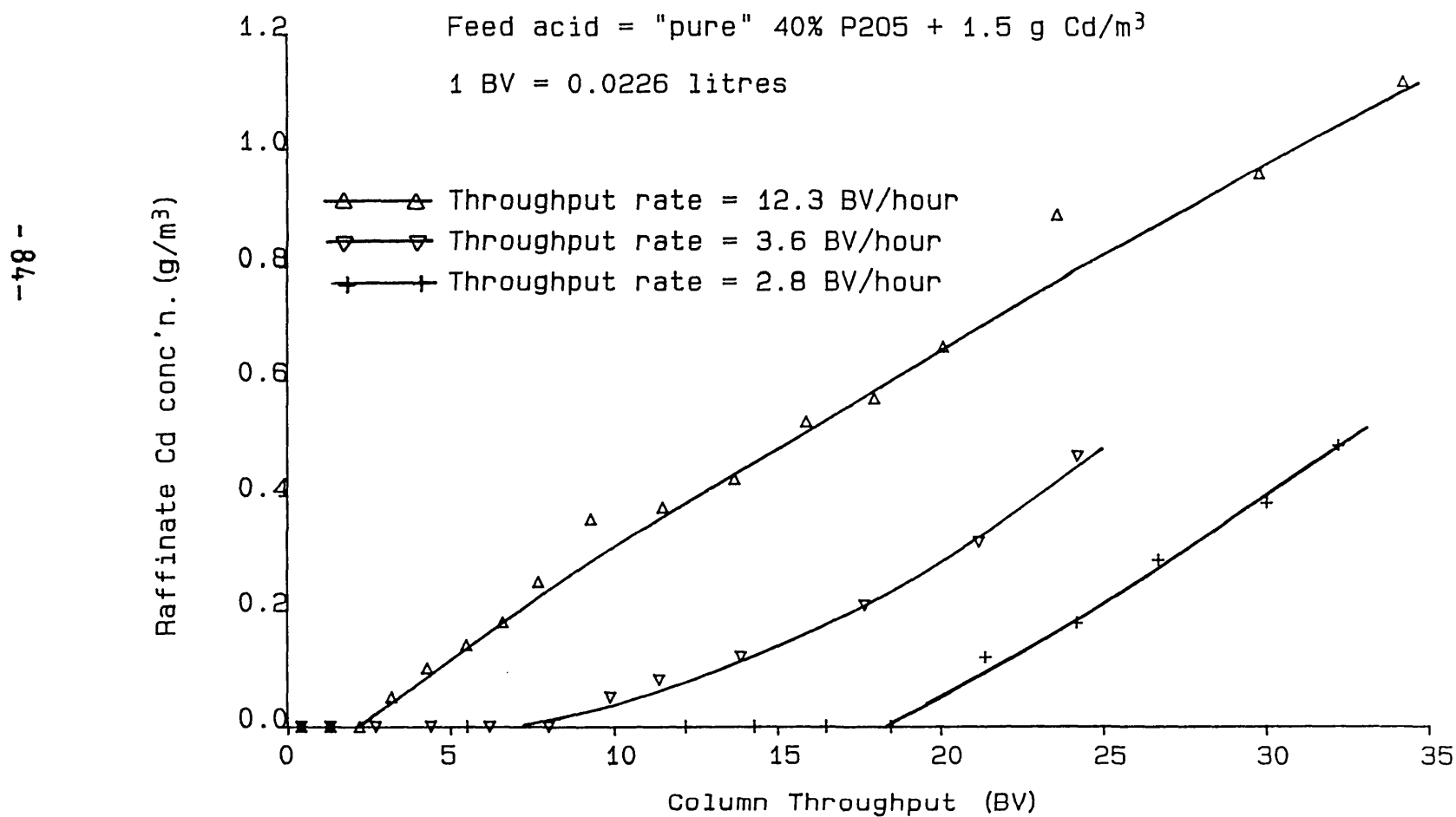
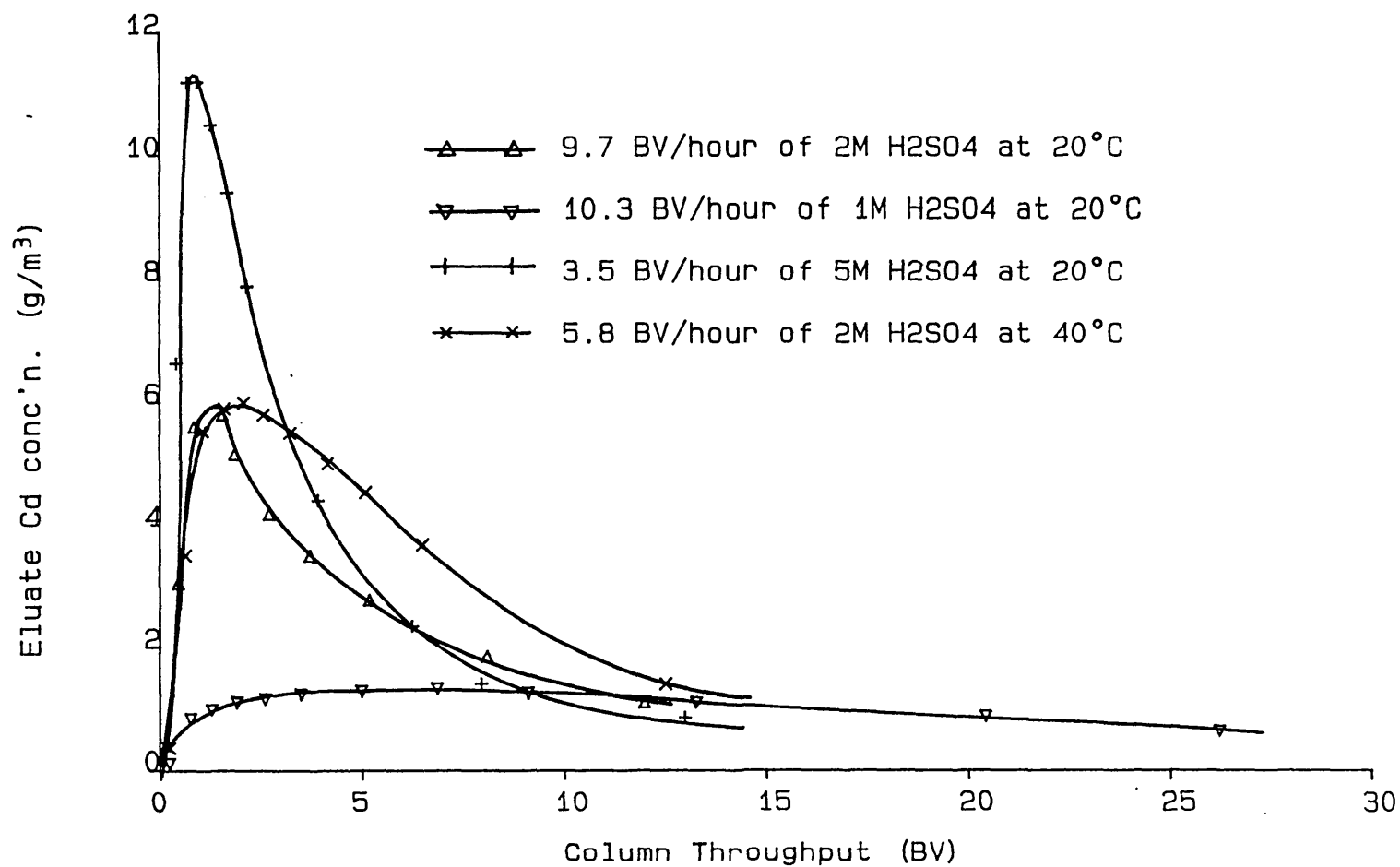


Figure 5.14 *Cadmium elution from Duolite C264 using sulphuric acid. Effect of acid strength, throughput rate and temperature.*



Sulphuric acid showed the best elution of cadmium in these tests, however, the acid used was not of the same H^+ concentration as the others used which would have biased the results in its favour.

No account for the rate of elution was looked for in these tests. Since sulphuric is one of the cheapest acids available commercially it was decided to use this acid in subsequent resin elution experiments.

Table 5.9
Results of preliminary elution tests on Duolite C264 resin
loaded with cadmium from "pure" phosphoric acid.

ELUANT USED	H^+ CONCENTRATION	Cd ELUTED
2M H_2SO_4	4M	62 %
2M HCl	2M	55 %
2M HNO_3	2M	32 %
5M NH_4Cl		56 %

Figure 5.14 shows the results of resin elution tests performed in 10 mm columns using sulphuric acid at different: acid strengths, throughput rates and temperatures. The results of these limited tests indicated that best elution was achieved at low throughput rates and with high acid concentrations and temperatures.

5.4.2 38 mm fixed columns

Appendix 4 gives the raw results of the fixed column tests performed in the 38 mm internal diameter column as elapsed time, volumetric throughput and the concentration of metal ions determined in the column effluent. Both column loading and elution results are given.

Figure 5.15 shows the results of cadmium loading onto C264 resin in the 38 mm fixed bed column tests. These tests were performed using 30% P_2O_5 "Analar" phosphoric acid at 60°C and the column feed contained 30 g Cd/m³.

The initial tests were performed with acid flowing down through the packed resin bed and resulted in the formation of bubbles of gas within the resin bed. These bubbles coalesced into large bubbles

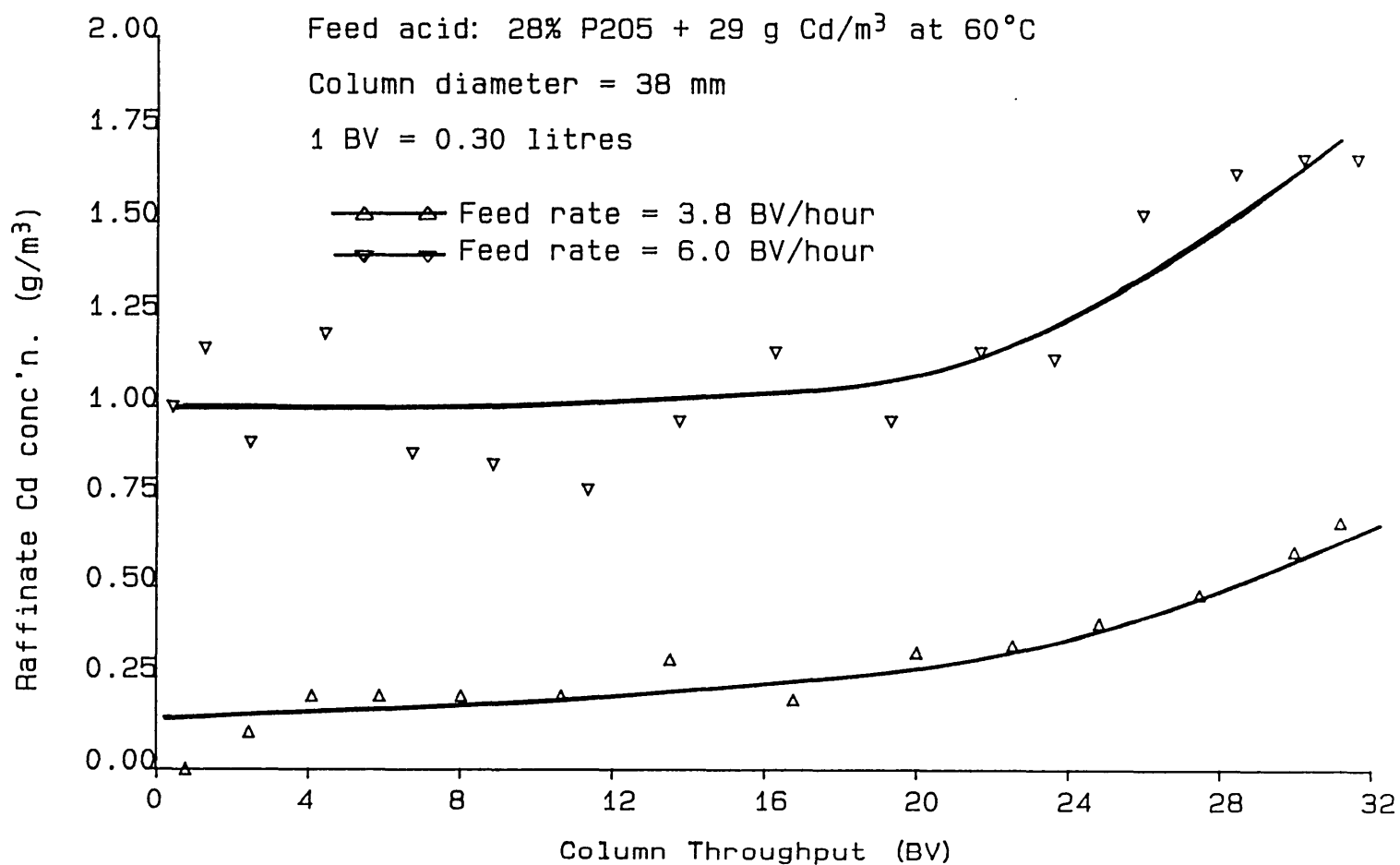
which eventually bridged the column and resulted in poor flow of the acid down the bed. The reason for the formation of these bubbles within the resin bed is not clear, however, one possibility is dissolved air in the feed acid coming out of solution. The possibility that the bubbles were formed by the degradation of the resin beads is not likely since resin performance was not seen to deteriorate significantly with age.

Subsequent tests using the 38 mm column were performed with acid flow upwards through the resin bed at velocities low enough not to cause expansion of the resin bed. The effect of running the column in upflow rather than in downflow on the loading of cadmium from phosphoric acid was observed in runs A and B, shown in Appendix 4 (Tables A4.1 and A4.2). As can be seen there was no significant difference between the two runs as regards time taken for a breakthrough of cadmium to the column effluent. The effect of increasing the upflow rate from 3.8 to 6.0 bed volumes per hour can be seen in Figure 5.15. The test at the lower throughput rate shows good removal of cadmium up to well over 30 bed volumes of treated acid, cadmium concentration in the treated acid was less than 0.5 g/m^3 . The test at the higher flow rate of 6 BV/h showed a premature breakthrough of the cadmium into the treated acid stream, this is possibly a result of slight expansion of the resin bed which would lead to a disturbance of the chromatographic profile within the bed. However, in this test the cadmium was still consistently removed to a low concentration of about 1 g/m^3 for about 20 BV at which point the cadmium concentration in the treated acid started to increase. As a result of these tests, however, further column work was performed with an acid flow of about 4 BV/hour upwards through the resin bed.

The resin used in these tests was effectively eluted using 5M H_2SO_4 at 20°C in downflow through the resin bed. Cadmium analysis of the total volume of eluant collected indicated that the mass of cadmium that had been loaded onto the resin from the phosphoric acid had been eluted by the sulphuric acid.

The phosphoric acid feed to the column was changed to wet process phosphoric acid (WPA), derived from Khouribga phosphate rock. The acid used contained 28% P_2O_5 by weight and about 15 g/m^3 of cadmium.

Figure 5-15 *Cadmium loading onto Duolite C264 from pure phosphoric acid.
Effect of throughput rate in fixed bed columns on loading.*



The resin in these tests was contacted with the acid in upflow mode at a rate of about 4 BV/h. The cadmium removal seen in the initial tests using WPA was minimal with the feed concentration of cadmium being reached after about 3 bed volumes of throughput. The effluent acid from the column was sampled and analysed for Ca, Mg, Zn, Ni, Fe, Cd and Mn by AAS to determine whether significant amounts of these species had been removed from the acid by the resin. Of the metals analysed for, concentrations of Ca, Mg, Zn, Ni and Cd in the treated acid were significantly reduced by the C264 resin in the column. Subsequent elution of the resin with 5M H₂SO₄ indicated that massive amounts of calcium had been removed from the WPA since calcium sulphate precipitated out of solution as elution proceeded. The result of this was the cementation of the resin bed by CaSO₄, this batch of resin was disposed of.

The selectivity scale for divalent cations in sulphonic acid resins containing 16% DVB (23) indicates that calcium ions ($K_a = 7.27$) are more selectively adsorbed than cadmium ($K_a = 4.95$) and magnesium ($K_a = 3.51$). Since calcium is more selectively adsorbed than cadmium ions and it is present in the WPA at higher concentrations than the cadmium ions, it is necessary to reduce the calcium concentration of the acid or alternatively, to find resins that are more selective for cadmium, to get effective removal of cadmium from WPA. Of the commercially available ion exchange resins looked at in the initial selection tests it was only the strong acid resins that showed any affinity for cadmium in phosphoric acid, therefore, it was decided that the first approach to the problem must be to try to reduce the calcium concentration of the WPA.

Increasing the sulphate concentration of the WPA will cause the precipitation of CaSO₄ from the acid and thus reduce the calcium concentration of the WPA. Various amounts of concentrated sulphuric acid (sg = 1.84) were added to the WPA in an attempt to precipitate the calcium. Figure 5.16 shows the concentration of calcium left in solution after the addition of various amounts of sulphuric acid to the WPA. Stoichiometry indicates that for every 1 g Ca/m³, 1.36×10^{-3} cm³ of concentrated H₂SO₄ is required to produce CaSO₄. Therefore for phosphoric acid containing 5.3 g Ca/m³ a dose of 7.4×10^{-4} % by volume of sulphuric acid is needed to produce CaSO₄. The results shown in Figure 5.16 indicate that an excess of sulphate is required to force the equilibrium over to CaSO₄ precipitation.

Figure 5.16 *Reduction in the calcium concentration of WPA.
Calcium concentration versus sulphuric acid dose applied.*

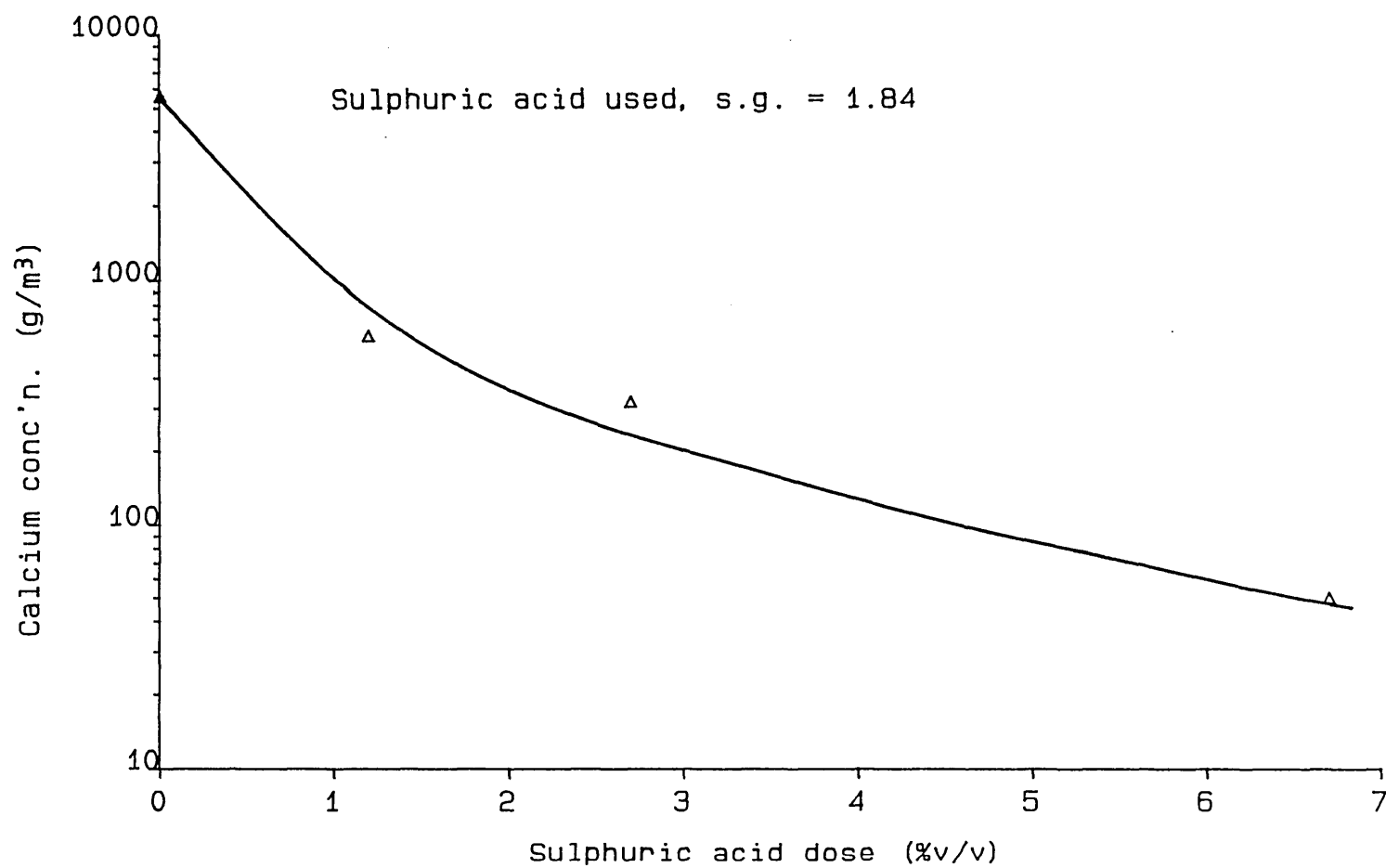
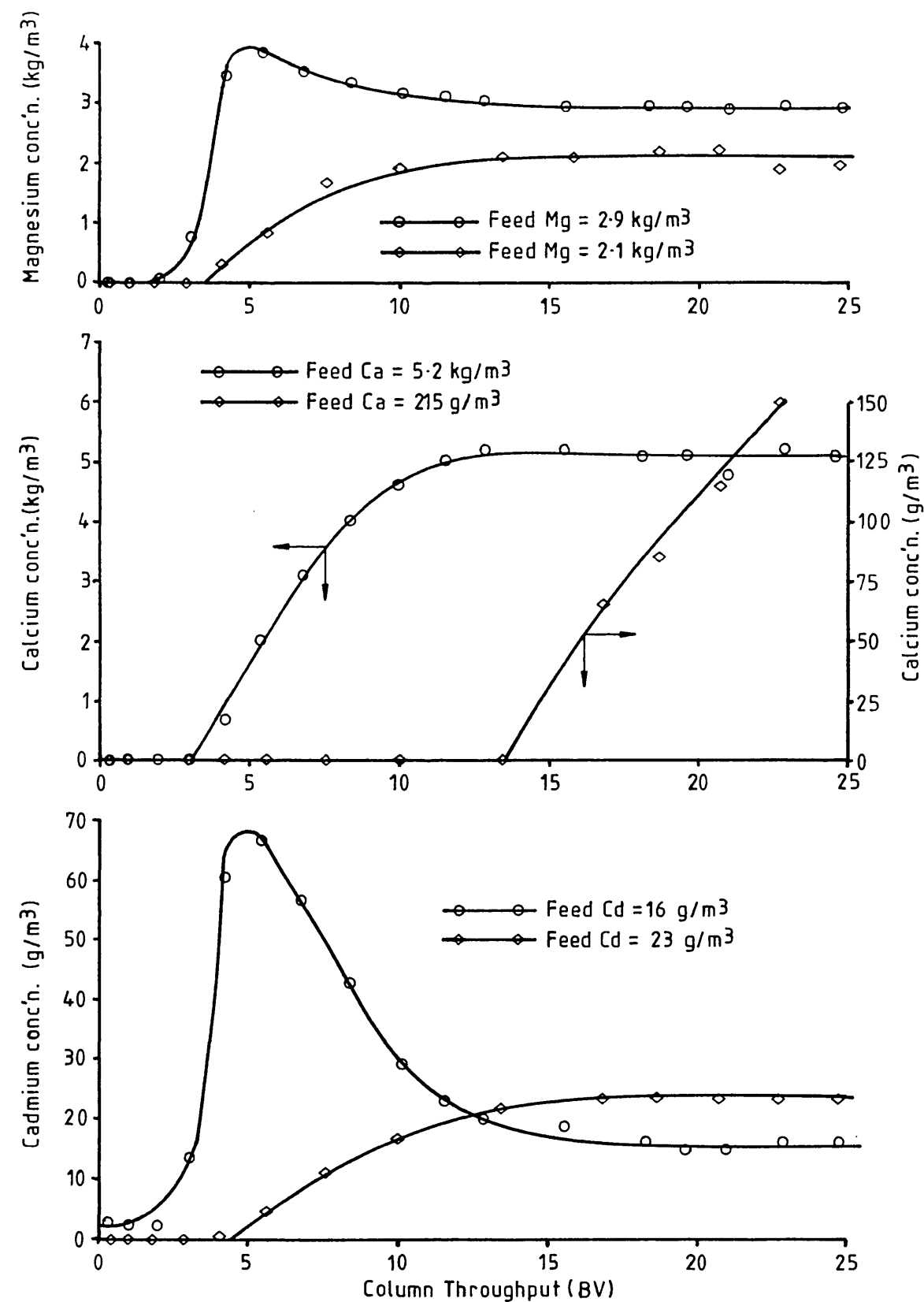


Figure 5.17 Results of fixed column tests using Duolite C264 to treat WPA. Effect of calcium concentration of the feed acid.
(Raffinate concentration versus throughput)



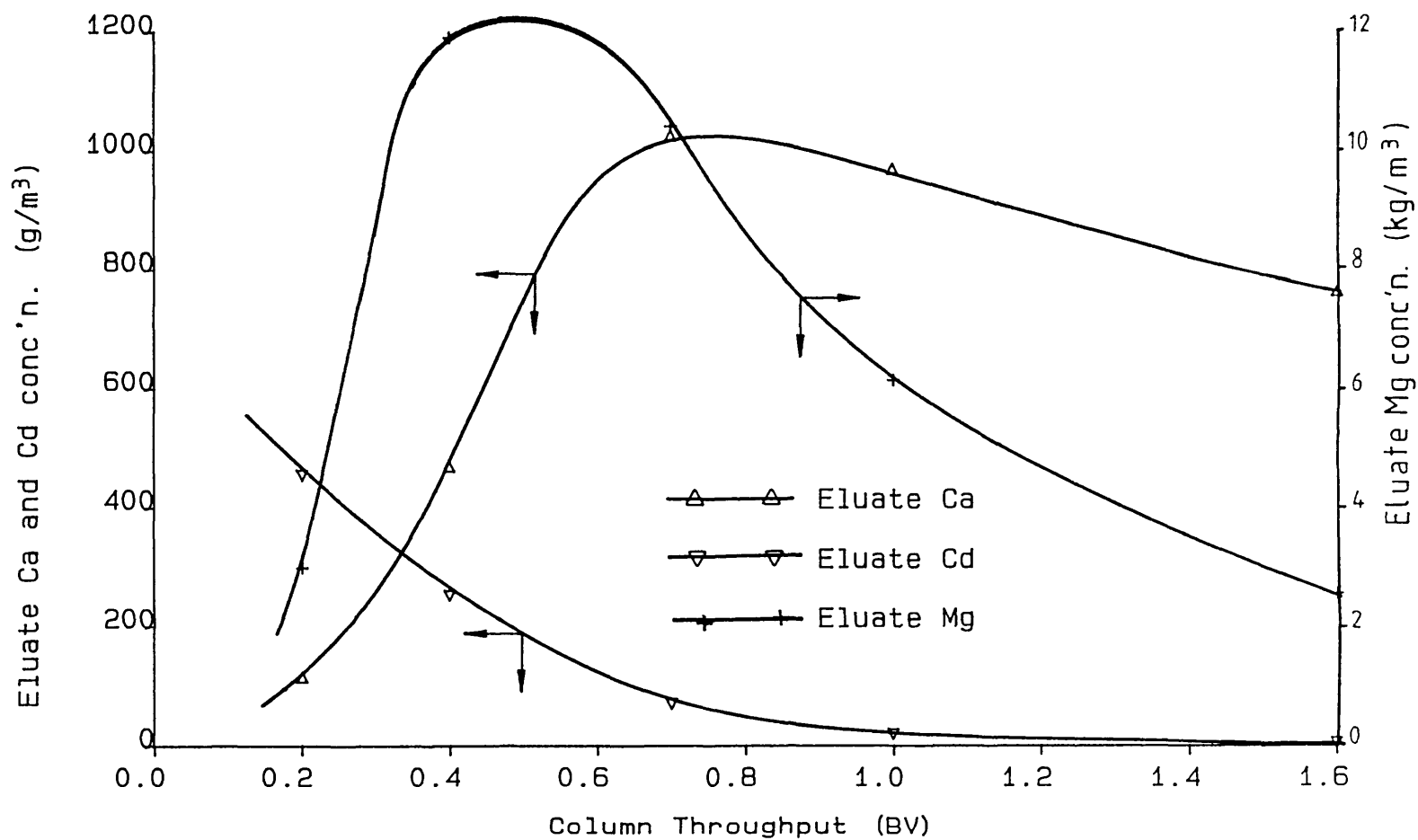
The WPA used in subsequent resin tests was treated with 3% by volume of concentrated sulphuric acid ($\text{sg} = 1.84$) and filtered to remove calcium sulphate. The initial concentration of calcium in the acid was reduced to acceptably low concentrations (about 200 g/m^3). Figure 5.17 shows the progress of the loading of Cd, Ca and Mg onto the resin at two different feed Ca concentrations, initially with the Ca concentration at that of the raw WPA (5.2 kg/m^3) and after being reduced to 210 g/m^3 .

Where the calcium concentration had been reduced the cadmium in the WPA was reduced to very low concentrations (less than 0.5 g Cd/m^3) for up to 4 BV of column throughput. The calcium remaining in the WPA was reduced to undetectable concentrations for about 13 BV and magnesium for about 3 BV. The overall performance of the resin for removal of cadmium from phosphoric acid was still inferior to that seen in pure phosphoric acid.

Elution of the loaded resin was performed with 5M HCl at room temperature (20°C). This proved to be an effective eluant for cadmium with over 90% of the loaded cadmium eluted in less than one bed volume of throughput. This is probably due to the formation of an anionic complex of cadmium with chloride ions (probably CdCl_3^-). This complex would be effectively rejected by the sulphonic acid functional groups on the C264 resin and would result in a high driving force being developed for the elution of cadmium from the resin. The elution of calcium and magnesium was typical of that expected due to an excess of counter ions (H^+). This is illustrated in Figure 5.18 where the progress of Cd, Ca and Mg elution by 5M HCl is shown. The elution was performed in downflow through the resin bed and at a flow of about 4 BV/h.

A number of runs were performed using the fixed column to assess whether there would be a deterioration in the performance of the resin for the removal of cadmium from WPA with repeated use. The results of these tests are shown in Tables 5.10a and 5.10b. Table 5.10a gives the results of the loading experiments and indicates the initial feed acid used in each test, the concentrations of metal ions in the feed and the amount of metal ion removed from the WPA. Table 5.10b gives the results of the elution experiments and indicates the type of eluant used, the initial concentrations of metal ions in the eluant and the amounts of metal ions eluted.

Figure 5-18 Elution of Duolite C264 (loaded from WPA) using 5M HCl.
Eluate concentration versus column throughput.



The type of WPA used in the tests was changed during the tests to that derived from Zin phosphate rock. The eluant used for the tests was 5M HCl, however, in some tests the eluate from previous tests was used to elute the resin.

The results from runs F and K indicate that the use of eluant from previous runs will still give effective elution of cadmium from the loaded resin. However, the elution of calcium and magnesium was not as effective when eluant was reused. The effect of these ions on the uptake of cadmium by the resin in subsequent runs was not significant.

Table 5.10a
38mm fixed bed column.
Loading results using Duolite C264 resin.

RUN	WPA FEED			RESIN METAL-ION					
	TYPE	FLOW (BV/h)	THRO'PUT (BV)	COMPOSITION (g/m ³)			LOADING (mg)		
				Cd	Ca	Mg	Cd	Ca	Mg
E	Khouribga	3.7	26	22	215	2070	45	1260	3400
F	Khouribga	3.7	29	15	78	2700	23	420	3730
G	Zin	4.0	14	18	36	1600	34	-72	1720
H	Zin	3.8	17	17	44	1600	32	31	1670
I	Zin	3.6	15	18	35	1700	53	148	3220
J	Zin	3.6	16	18	42	1700	53	180	3010

Table 5.10b
38 mm fixed bed column.
Results of elution of Duolite C264 using 5M HCl.

RUN	ELUANT USED			METAL-IONS					
	TYPE	FLOW (BV/h)	THRO'PUT (BV)	COMPOSITION (g/m ³)			ELUTED (mg)		
				Cd	Ca	Mg	Cd	Ca	Mg
E	unused	3.8	12	0	0	0	27	2977	2100
F	ex run E	5.4	11	7	850	580	18	-410	1100
G	unused	3.9	1.6	0	0	0	29	245	1710
H	unused	3.9	1.4	0	0	0	31	250	1410
I	unused	3.8	1.6	0	0	0	54	376	2970
J	ex runs G,H&I	3.8	1.4	7	150	900	49	67	1900

Repeated sequences of loading and elution using the same sample of C264 resin showed the resin to be capable of removing repeatable amounts of cadmium from the WPA.

Cadmium extraction performed in upflow mode with no bed expansion was successful in that repeatable breakthrough times could be achieved. This showed that the chromatographic profile through the bed was not being disturbed and that this was an acceptable mode of operation. In practice, this mode of operation would reduce the risk of bed blockages by the presence of small amounts of CaSO₄ in the feed acid. This may allow the process to be performed without the need for filtration of clarified WPA before the ion exchange process.

Breakthrough of cadmium to the effluent stream from the column occurred in a short number of bed volumes of WPA throughput. For the continuous removal of cadmium from a WPA stream, a frequent turnaround of resin beds would be required to maintain low cadmium concentrations in the treated acid. However, since cadmium elution occurs in such a small volumetric throughput, the elution step could be successfully performed during the time taken to reach breakthrough in the loading column. Two packed beds of C264 operating in sequence could feasibly work to continuously remove

cadmium from WPA. The size of resin bed required, however, would need to be quite large. Based on this fixed bed column work, a flow of 4 BV/h of feed acid resulted in breakthrough after about 5 bed volumes of throughput. The bed size required is therefore about a quarter of the hourly volumetric WPA flow to be treated. Therefore for a 1000 m³/day process this would mean that a bed size of 10 m³ would be required. To make the process continuous, at least two beds would be required, one bed loading while the other elutes and washes. This would result in a large inventory of resin required for the process.

A way of reducing the large inventory of resin required would be to take advantage of the rapid elution that can be achieved using HCl and to use a moving packed bed of resin. Potentially only about a quarter of the volume of the resin that is used in the loading stage is required for the elution stage, thereby reducing the overall resin inventory. The choice of process to be used depends on whether the increased capital cost of a moving packed bed process is outweighed by the cost of the larger resin inventory needed for a fixed bed process. Experimental work was, therefore, performed to show that the moving packed bed approach could be used to continuously remove cadmium from wet process acid.

5.5 Multistage batch tests

The simulation of multistage countercurrent ion-exchange in small batch reactors gave quite good results. Despite the fact that each stage probably did not reach equilibrium, a pseudo steady state was reached after about 10 cycles of operation. The change in cadmium, calcium and magnesium concentrations in the treated acid streams for each cycle of operation is shown in Table 5.11.

Once pseudo steady state had been achieved, analysis of the effluent acid from each stage was used to determine the mass of Cd, Ca and Mg that had been loaded onto the resin in each stage. The results of this are presented in Figure 5.19 as concentrations of metal in solution versus concentration on the resin for Cd, Ca and Mg. It can be seen that the distribution coefficients achieved in the experiments favour calcium exchange ($K_d = 10.4$) compared to cadmium ($K_d = 4.1$) and magnesium ($K_d = 3.0$) exchange. This agrees with the

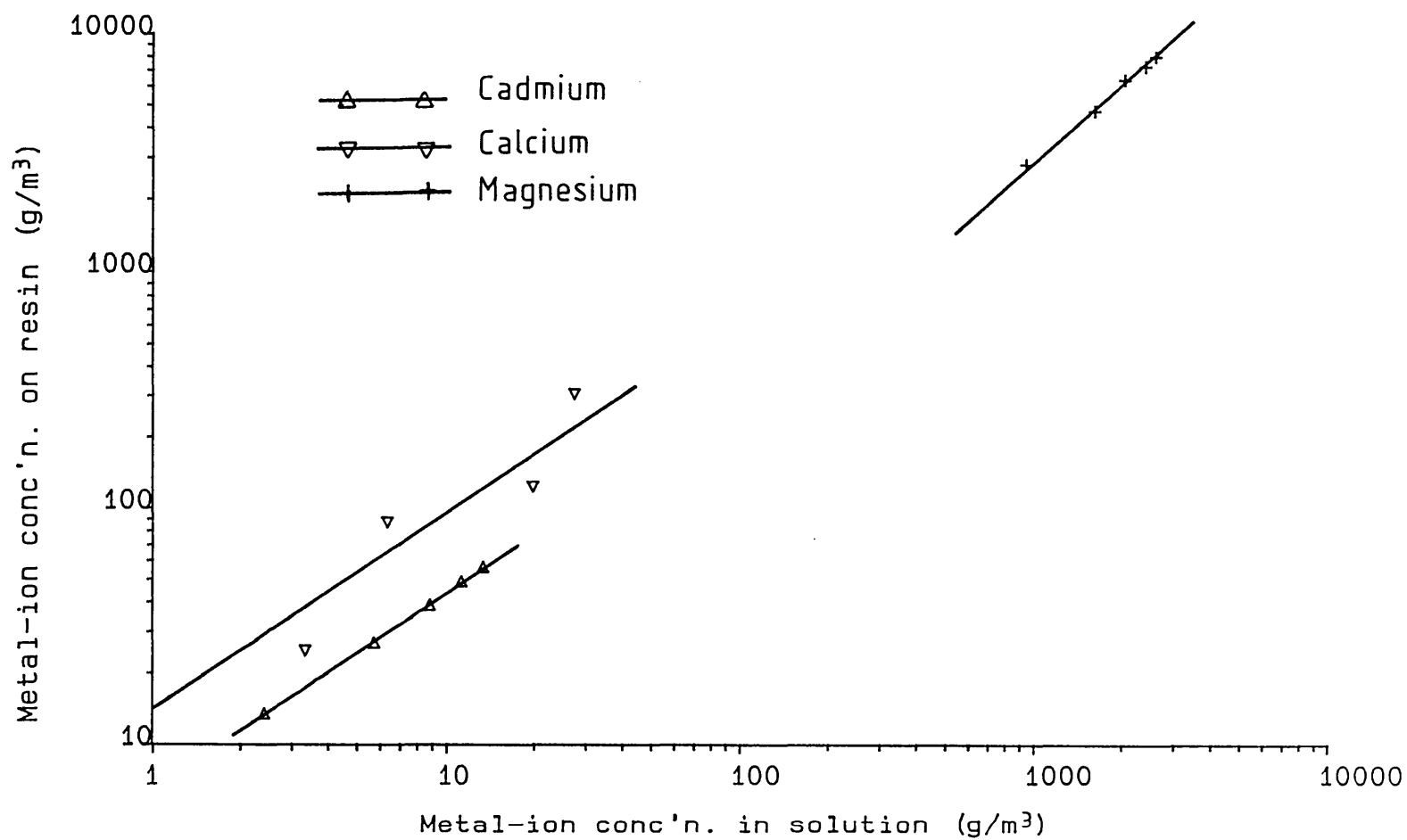
selectivity of strong acid resins for the divalent cations of these metals, discussed earlier in this chapter.

Table 5.11
Progress of multistage batch experiments with
Duolite C264 resin and WPA.

CYCLE NUMBER	TREATED ACID METAL ION CONCENTRATION (g/m ³)		
	Cd	Ca	Mg
0	15	62	2700
1	9.2	8	1900
2	5.4	3	1330
3	3.9	0	1100
4	2.2	3	820
5	1.4	6	700
6	2.5	1	880
7	2.2	1	820
8	2.5	1	900
9	2.6	1	920
10	2.3	0	930
11	2.6	1	950

In fixed column tests, cadmium in the feed WPA (15.2 g Cd/m³) came to equilibrium with a resin cadmium concentration of 77 g Cd/m³ resin. Using the K_d value for cadmium determined above, the resin capacity achieved would be about 62 g Cd/m³ resin. This indicated that only 80% of the resin equilibrium capacity was achieved in these simple batch tests. Each stage of contact was performed for only 10 minutes at room temperature (23°C). The results of the earlier kinetic tests using "pure" phosphoric acid at 25°C suggest that in 10 minutes between 70 and 80% of equilibrium would have been attained. This agrees with the findings and this implies that the actual K_d value for cadmium removal from WPA should have been about 5.1. A similar argument applies for calcium and magnesium and their respective K_d values should in effect be 13 and 3.8.

Figure 5-19 *Relationship between metal-ion concentration in solution and on DuoliteC264 for Cd, Ca and Mg in 28% P205 WPA.*



5.6 Continuous counter-current ion exchange tests

The continuous countercurrent tests were performed using the same batch of Duolite C264 resin in each test. A small amount of resin was lost through spillage though there was sufficient reserve to ensure that resin make-up was not necessary. Nine runs were performed, each until a steady concentration of cadmium in the raffinate stream was achieved.

The results of the initial four runs on the ion exchange column were not used since column control was erratic in these runs. Control of resin flows into and out of the column caused a few problems since it was difficult to find a suitable valve that could effectively shut off the resin flow. The design finally used (see Figure 4.3) shows the resin flow from the bottom of the column being controlled by venting the top of the receiver pot. The control valve, therefore, only closed against air or acid; not resin. Any design that required the valve to shut against a stream of resin resulted in the valve passing acid to some extent or unacceptable crushing of the resin in the valve. The result of a small acid leak in a column of this small size and throughput was significant. The control of resin into the top of the column was eventually achieved using the PVC slider valve illustrated in Figure 4.2c. A small amount of acid was noticed to drain from the eluted resin hopper into the raffinate acid stream, this was alleviated by raising the level of the column raffinate outlet to above the level of the eluted resin hopper.

Raining of resin down through the column and out of the bottom plate was stopped by modifying the bottom plate to include a baffle as shown in Figure 4.2b. With this modification the column could be left overnight during a run and the run started again the next day without any loss of resin from the column. In this way, runs of up to 35 cycles of resin transfer could be achieved. The overnight interruption was not severe as the resin remained undisturbed, possibly only coming into equilibrium with the acid in which it was in contact.

The column was run for a large number of resin transfer cycles so that steady state conditions could be achieved. Figures 5.20a to 5.20e show that this condition was generally reached after about 20 resin transfer cycles.

Figure 5-20a Results of continuous counter-current tests using Duolite C264 to treat WPA.

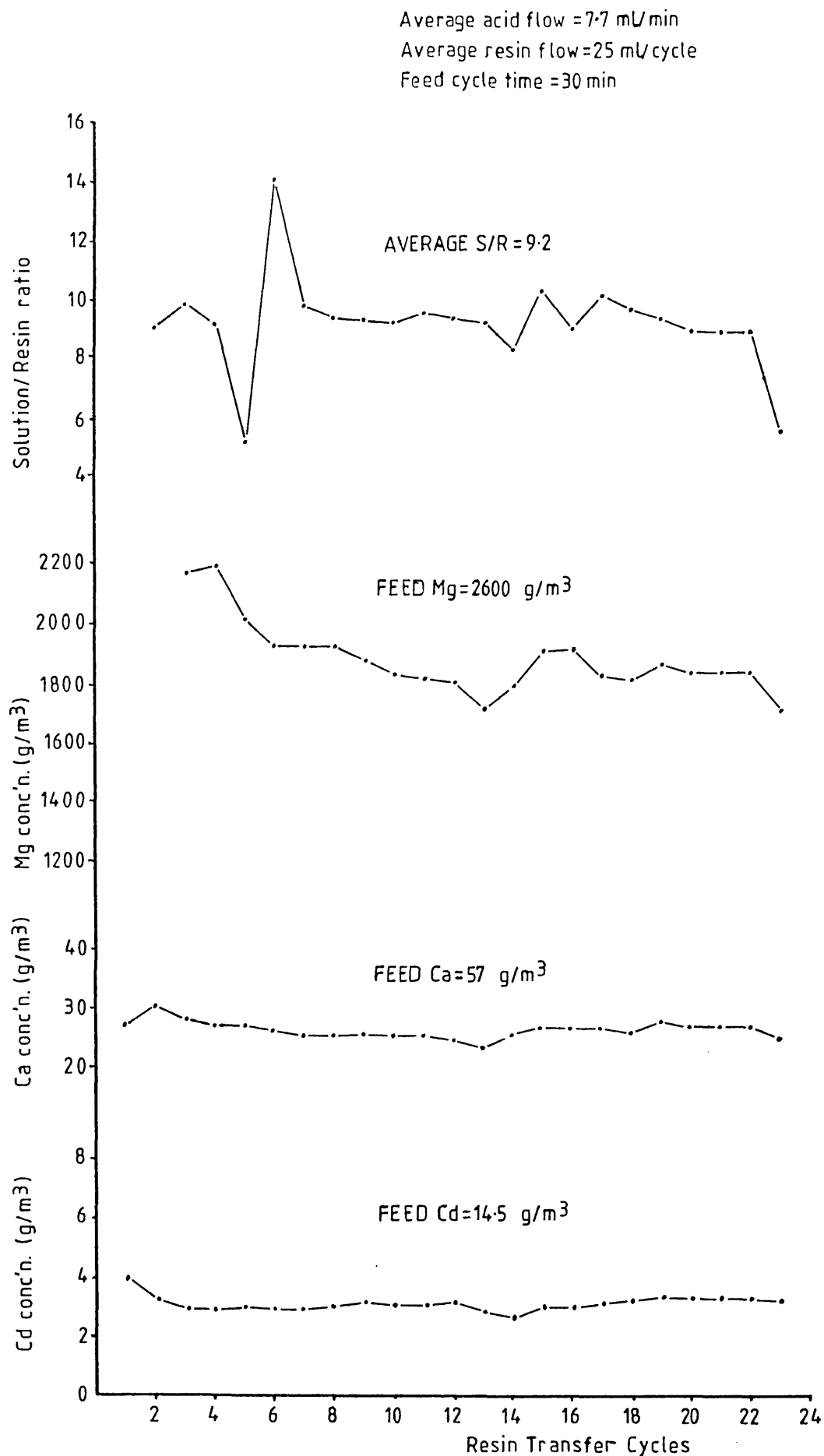


Figure 5.20b Results of continuous counter-current tests using Duolite C264 to treat WPA.

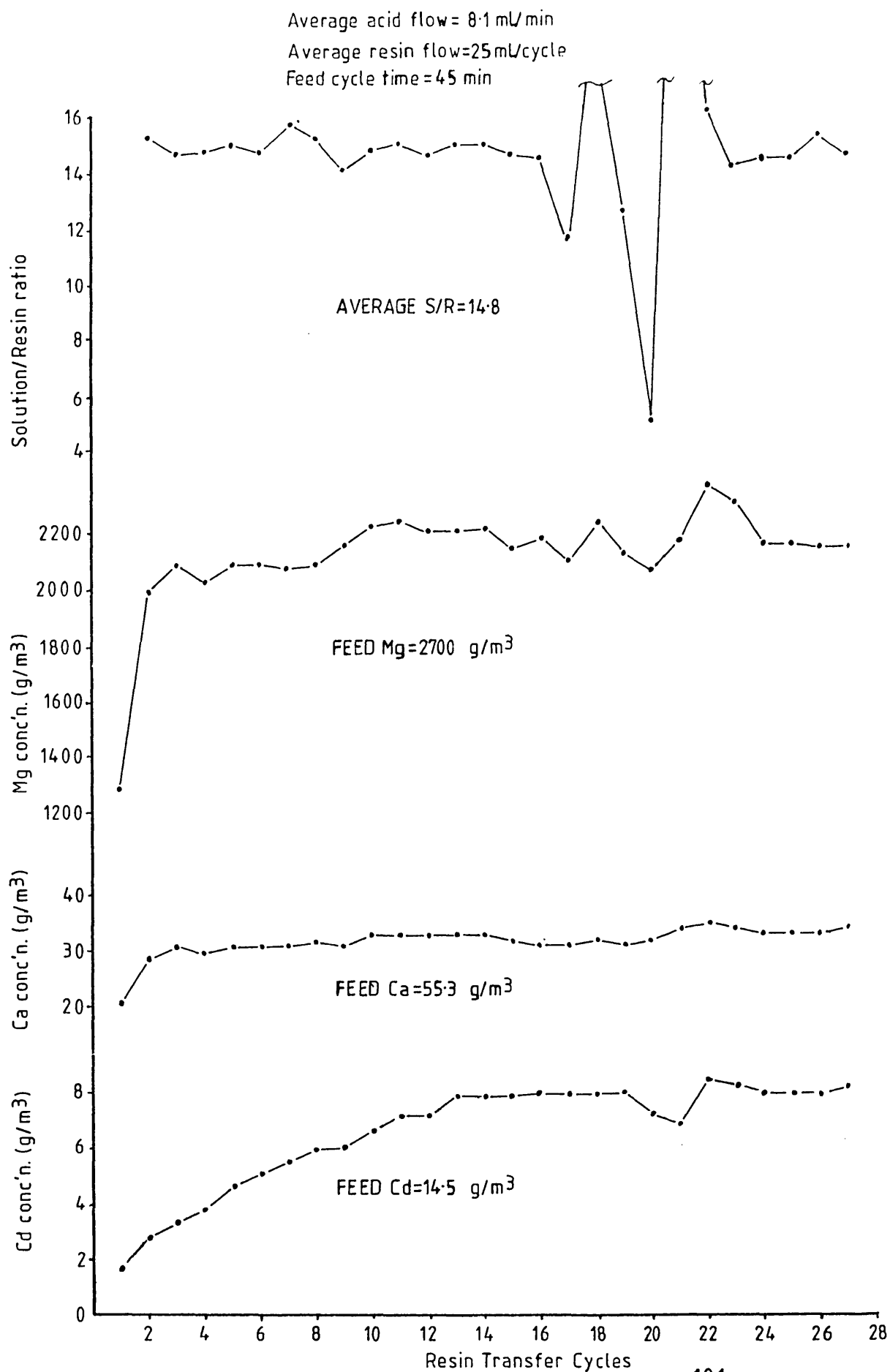


Figure 5.20c Results of continuous counter-current tests using Duolite C264 to treat WPA.

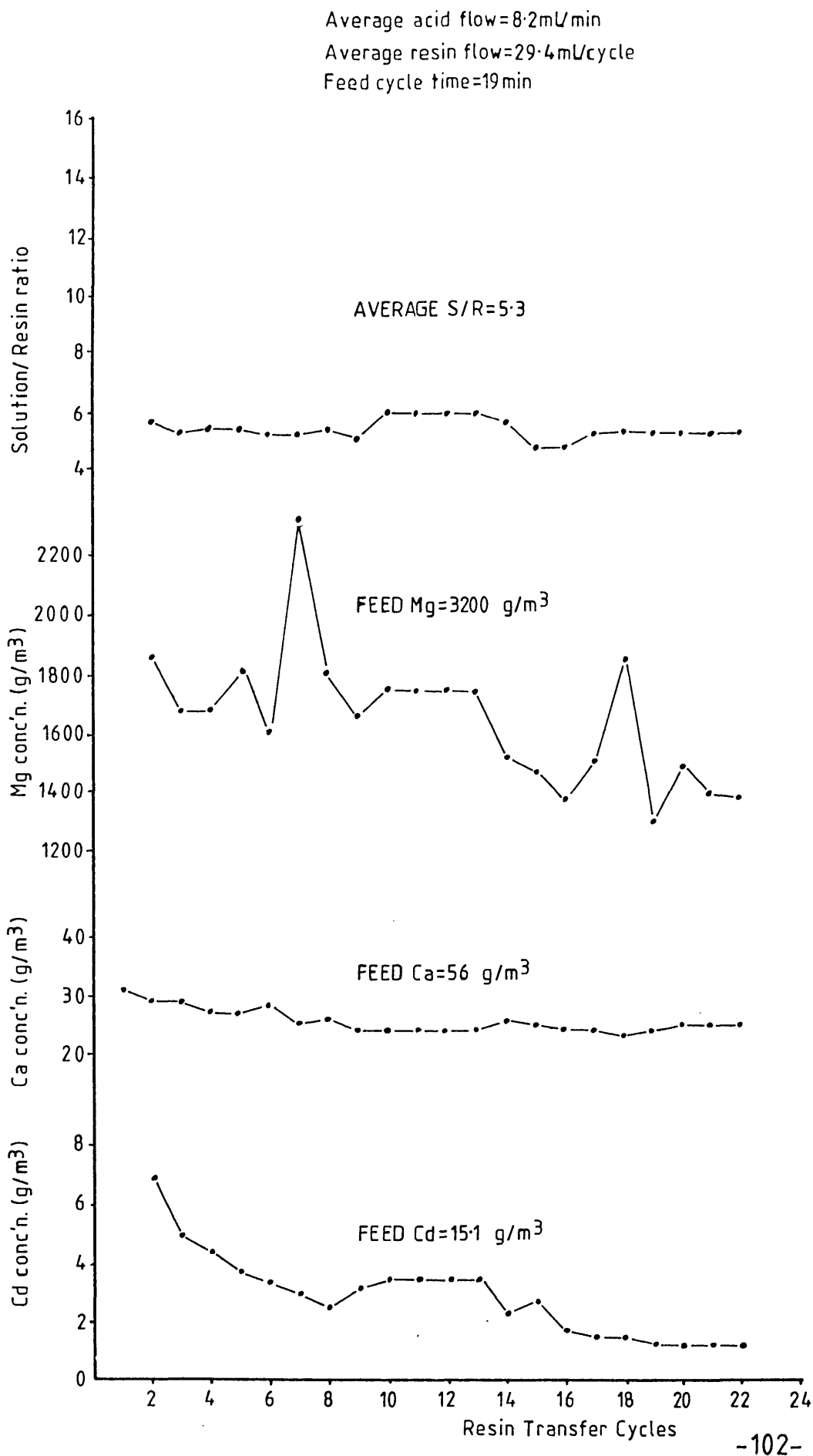


Figure 5:20d Results of continuous counter-current tests using Duolite C264 to treat WPA.

Average acid flow=8.0 mL/min

Average resin flow=25 mL/cycle

Feed cycle time=29 min

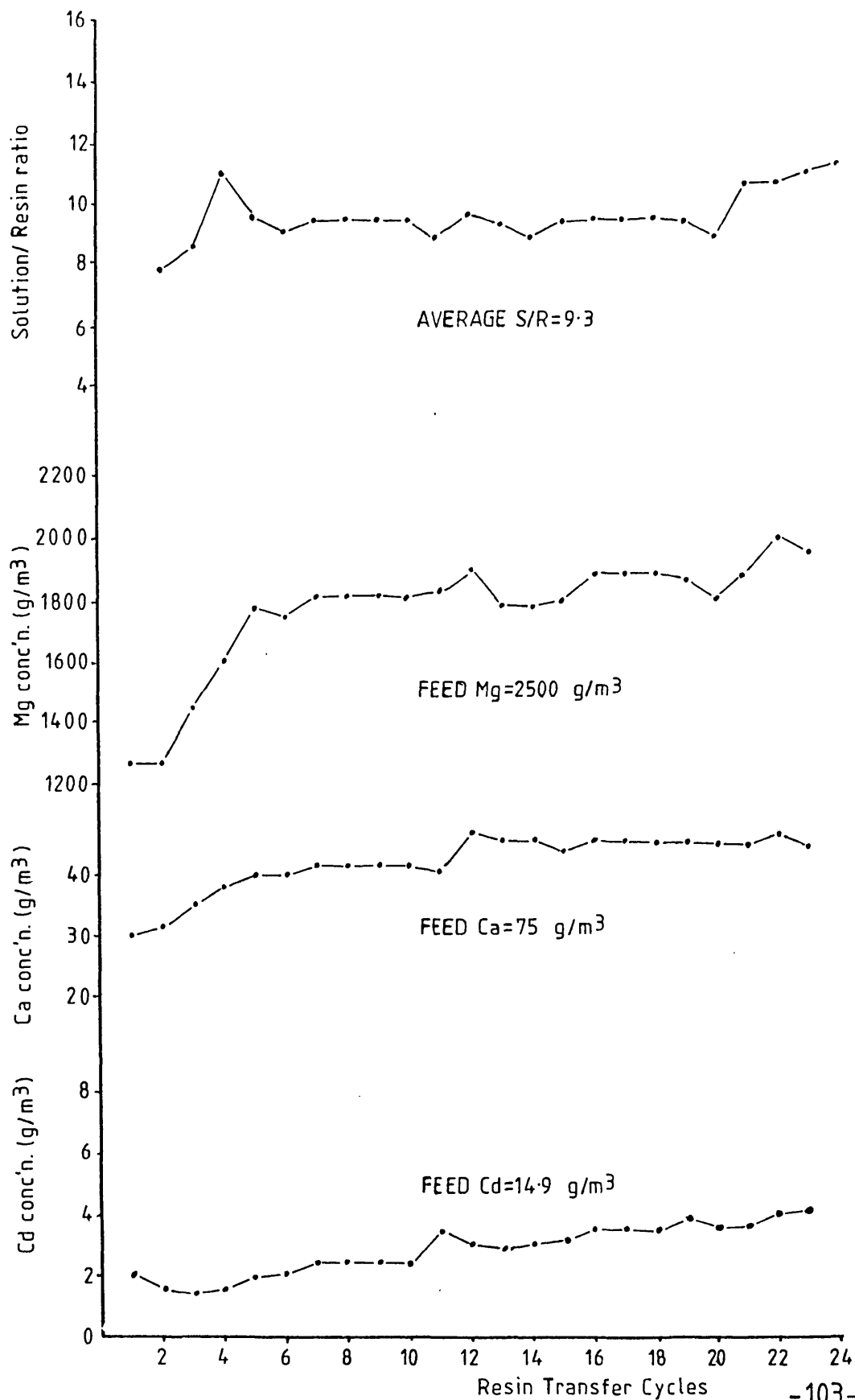
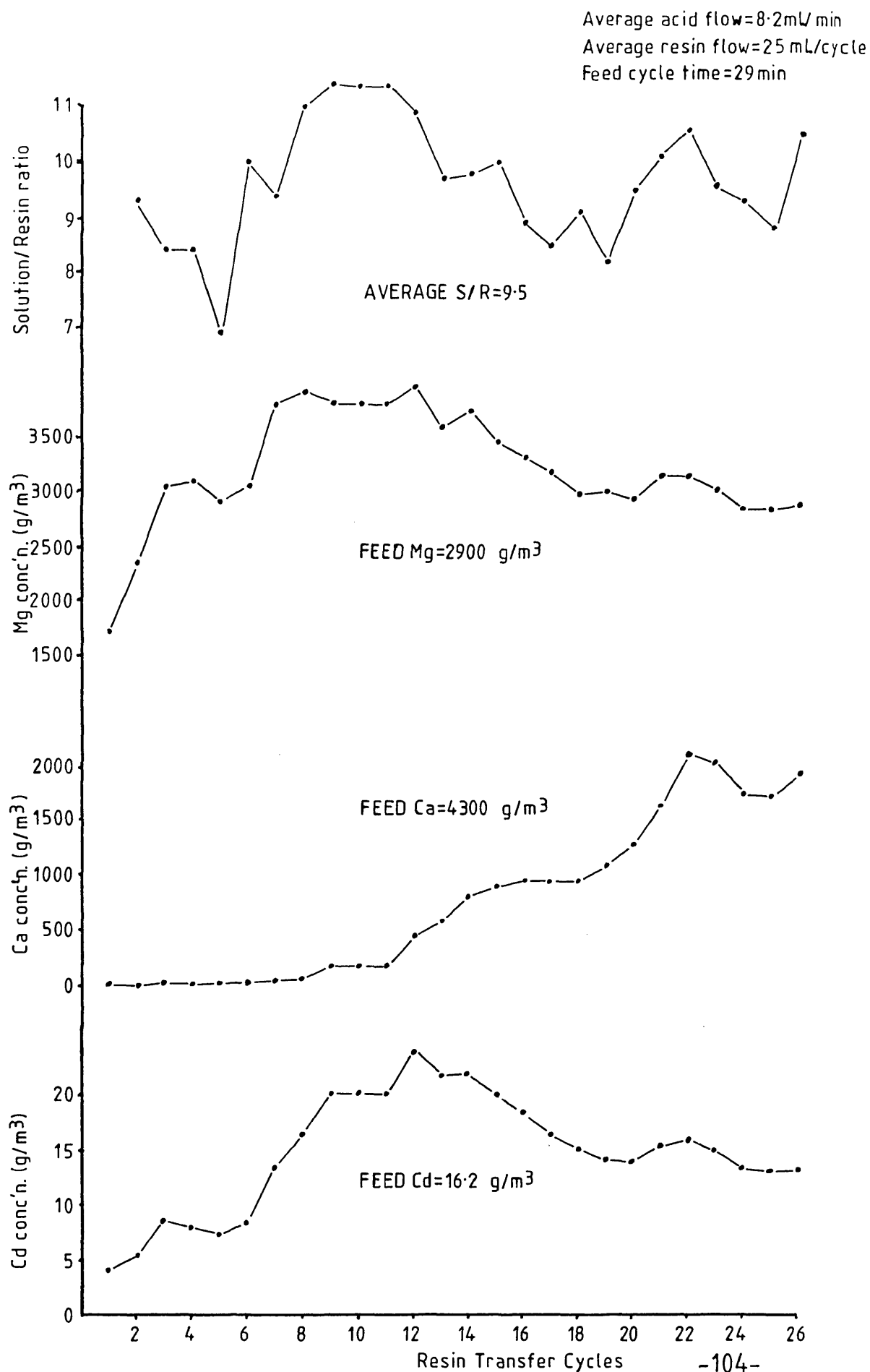


Figure 5.20e Results of continuous counter-current tests using Duolite C264 to treat WPA.



The solution to resin flow ratio (S/R) varied during the experiments, attempts to even out fluctuations by adjusting the acid flow in proportion to the resin flow after each transfer had some success. Even so, the effects of major interruptions in resin flow due to blocked valves, could not be smoothed out completely and caused some disruption to column raffinate concentrations.

5.6.1 Results of continuous counter-current cadmium extraction

The results of the extraction experiments performed using the continuous counter-current ion exchange column are shown in Figures 5.20a to 5.20e for different values of S/R.

The column raffinate cadmium concentration responded to the different values of S/R. As S/R increased, column efficiency decreased and raffinate cadmium concentration increased. The raffinate cadmium concentration increased to a steady value of about 8 g Cd/m³ with a S/R of 14.8 and dropped to a steady value of 1.2 g Cd/m³ with a S/R of 5.3.

Two runs were performed with a S/R of about 9.2, the runs were separated by two other experiments, the resultant raffinate cadmium concentrations were 3.3 g Cd/m³ initially and 4.2 g Cd/m³ finally. This result indicates that there was a slight drop in the resin capacity over the four experiments. The most probable explanation for the loss of capacity would be reduced elution efficiency. This is shown in Table 5.12 where the results of some resin capacity tests performed on eluted resin samples are given. In these tests the eluted resin sample were batch tested in 30% P₂O₅ "pure" phosphoric acid containing initially about 7.5 g Cd/m³. The final concentration achieved in these batch tests was determined and a resin cadmium capacity established. The eluted resin capacity, thus determined, was seen to drop from 63.5 to 58.1 mg Cd/kg resin.

The poor capacity seen in resins from elutions I1 and I2 is due to the fact that the resin had been loaded from WPA that had not been reduced in calcium concentration before use. The resultant poor capacity must be because of the amount of calcium present on the resin which had not been eluted thus reinforcing the need to reduce the calcium concentration of the feed WPA going to the contactor.

The reason elution efficiency dropped with repeated use of the resin could be because the eluant was recycled from run to run and needed

to be replaced with fresh 5M HCl. This is discussed in more detail in section 5.6.2.

Table 5.12
Results of capacity tests on Duolite C264 resin eluted
with 5M HCl solutions.

ELUTION NUMBER	EQUILIBRIUM CONCENTRATIONS	
	IN SOLUTION (g Cd/m ³)	ON RESIN (mg Cd/kg)
D2	1.2	63.5
E1	1.5	60.5
F1	1.2	63.0
F2	1.5	59.3
G1	1.6	58.8
H1	1.6	58.1
H2	1.8	56.8
I1	2.4	50.1
I2	2.8	46.6
New resin	0.7	67.5

The contactor was semi-continuous in the sense that resin was transferred intermittently and acid flowed intermittently. In this way the column was more like a continuous batch process. The raffinate stream coming off the top of the column was collected during the forward feed cycle of the loading sequence. The total volume of raffinate collected in each cycle was analysed for metal ion concentration, variations occurring during the cycle were therefore obscured. Some samples of the raffinate were taken during the forward feed cycle in a few cases to determine whether the raffinate concentration was changing. The results of these tests showed that the cadmium concentration of the raffinate stayed basically constant during the feed cycle. The concentrations of both calcium and magnesium increased from an initially low value to a higher value during the cycle, varying by about 30% during the cycle.

Run I was performed using acid with the original calcium concentration present. The effect of this, as shown in Figure 5.20e, was to cause the cadmium present on the resin (ie Cd not eluted from

the resin) to be displaced from the resin by the calcium that was loading onto the resin evidenced by the hump in the cadmium loading curve above the feed concentration. The same effect was seen for magnesium. As stated before this result indicates the need to reduce the calcium concentration of the feed acid.

5.6.2 Cadmium elution from C264 using 5M HCl

The elution of the C264 resin was performed batchwise once sufficient resin had been accumulated from the loading column. The eluant used was 5M HCl and the resultant eluate returned for elution of the next batch of resin. Table 5.13 shows the results of the various elution runs performed on the loaded resin from the continuous column tests.

The concentration of the metal ions in the eluant dropped from that in the eluate of the previous elution because the volume of eluant used in each run was only a part of the total volume of eluant available.

The results in Table 5.13 show that the reused eluant was still capable of eluting cadmium, calcium and magnesium after quite a number of cycles of use. The results from run I should be ignored as these were for elution of resin which had been used to remove cadmium from high calcium concentration WPA. These results and those shown in Table 5.12 indicate that the 5M HCl eluant can be recycled a number of times without having a detrimental effect on the elution of cadmium from the C264 resin. However, the process would need a bleed off from the eluate stream and a make-up of HCl: to prevent the concentration of metal ions in the eluant becoming excessively high and to keep the chloride concentration in the eluant high enough to allow the formation of CdCl_3^- . It can be seen from the results that after about elution run G1 the elution performance may have declined leading to a reduced capacity seen on the resin for cadmium. If the eluant is bled off from the eluate stream at the beginning of the elution run then the cadmium concentration of the eluate will be as high as possible.

Table 5.13
Elution results using 5M HCl in fixed columns
with reuse of eluate as eluant

ELUTION RUN	METAL ION CONCENTRATIONS (g/m ³)					
	CADMIUM		CALCIUM		MAGNESIUM	
	ELUANT	ELUATE	ELUANT	ELUATE	ELUANT	ELUATE
D2	37	79	136	544	3780	7920
E1	49	76	252	553	5000	8110
F1	57	89	340	558	6010	7280
F2	75	118	456	641	6680	8380
G1	91	129	515	626	7420	8640
H1	105	139	553	641	7930	8960
H2	115	150	573	694	8220	9000
I1	129	147	621	5297	8590	9300
I2	133	139	1960	7010	8810	8920

The amount of chloride required to be in the eluant to allow for the formation of CdCl_3^- can be estimated based on the stoichiometry of the various species assumed to be formed during elution. Assuming that calcium and magnesium only form the divalent chloride species in solution, then for the concentrations of metal ions seen in elution run G1, the amount of chloride ions required must be about 0.8 kgmoles/m^3 . The effects of the other metal ions in solution would be negligible compared to those from magnesium and calcium alone. The concentration of hydrogen ions required as a counter ion for the effective elution of these species from the resin must be of a similar order of magnitude to that of the chloride ions. The use of 5M HCl would provide sufficient of both Cl^- and H^+ for these ions not to limit the elution process seen in these tests.

Another reason for the decline in the performance of the resin with repeated use may be a result of poor elution of the calcium and magnesium on the resin. However, the loading of calcium and magnesium onto the resin must be controlled by equilibrium constraints. This would limit the cadmium capacity of the resin to a minimum value, similar to that attained in a batch test using the WPA and having final concentrations of Cd^{2+} , Ca^{2+} and Mg^{2+} similar

to those in the feed acid. Therefore the cadmium loading will not be reduced to zero as long as the concentration of both Ca and Mg in the feed acid do not rise. This can be seen from the results of run I where the Ca concentration in the feed was 4.3 kg/m^3 (compared to about 75 g/m^3 in the previous tests). This had the effect of eluting both the cadmium and magnesium from the resin as shown in Figure 5.20e.

5.6.3 Regeneration of eluant

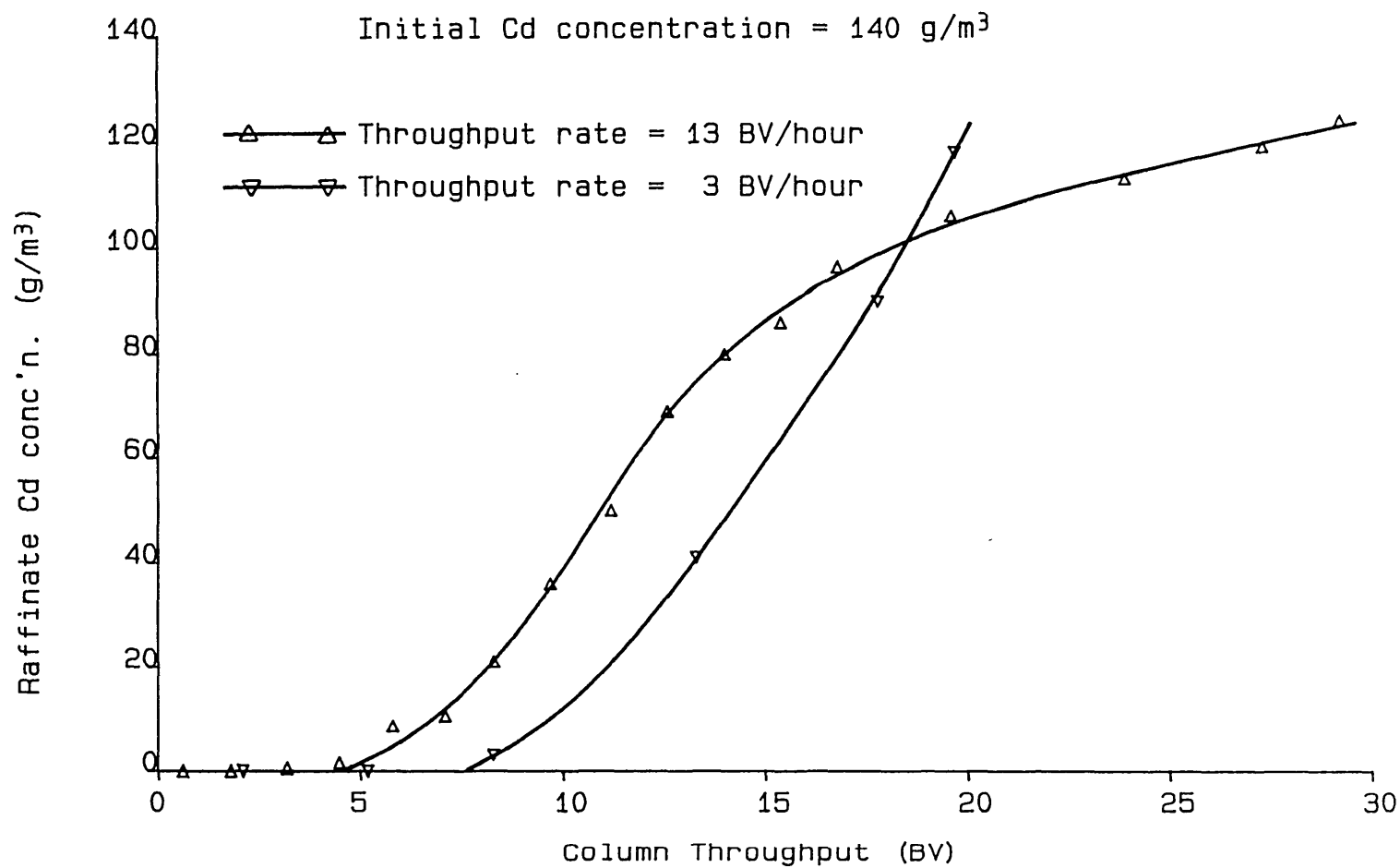
The use of hydrochloric acid as an eluant for the loaded resin presents a problem of what to do with the eluant once it is no longer effective at eluting the resin. The disposal of the acid presents an environmental problem because of the high levels of cadmium in it. A way of reducing the cadmium concentration in the eluant was sought.

The fact that cadmium will probably be in the form of CdCl_3^- in the eluant led to the idea of using a strong base ion exchanger to remove it. The results of a series of small batch tests using different strong base resins and the eluant from the continuous column tests were performed to find a suitable candidate resin for this duty. The gel type resins showed considerable evidence of degradation in the tests in that they fragmented. This was put down to osmotic shock caused by the high ionic strength of the eluant solution. The macroporous resins tested did not appear to suffer from this problem.

The resin seen to give the best capacity for cadmium in the tests was Duolite Al61, a macroporous, type one, quaternary amine, strong base resin. Figure 5.21 shows the results of two loading tests using Al61 to remove the cadmium from spent eluant solution. The tests were performed in 10 mm columns since there was only a limited amount of the spent eluant available for testing purposes. The results obtained, therefore, are for a column diameter to resin diameter (resin bead diameter = 1 mm) ratio of about 10:1 which is not ideal for avoiding wall effects in the column. The resin would be expected to perform better in cases where the criteria of column to resin diameter ratio can be met.

Figure 5.21 shows that despite the limitations of the experimental conditions the cadmium in the eluant could be removed to low levels for about 12 BV of throughput after which the concentration in the

Figure 5-21 Cadmium exchange from 5M HCl eluant onto Duolite A161.
Raffinate Cd concentration versus column throughput.



treated eluant increased above the concentration in the original WPA. The flow of eluant through the Al61 resin used was about 3.2 BV/h. Analysis of the effluent from the Al61 column for zinc and nickel showed that the zinc present in the spent eluant was removed by the Al61 resin while nickel was not. This indicates that the chemistry of zinc in the eluant was similar to that of the cadmium in that the zinc ions present associated with chloride ions to form an anionic complex that could be removed by the Al61 resin. Zinc broke through into the treated stream at about the same time as cadmium and did not appear to adversely affect the removal of cadmium from the spent eluant. This would indicate that Al61 had a similar affinity for both of these chloride complexes.

Elution of the loaded Al61 resin was attempted using a brine of 2M NaCl, a 5M HCl solution and water. The NaCl brine proved ineffective at removing the cadmium chloride from the resin. Figures 5.22a and 5.22b show the results of the elution tests performed on Al61 resin using 5M HCl and water. The elution of the resin using 5M HCl shows a long elution tail and this indicates that this elution method is inefficient. The use of another anion to elute the cadmium chloride from the resin would suffer from the fact that a sufficient concentration of the ions used to do the eluting must be present to get efficient elution performance. It was noticed that when water was used to wash the resin after an elution run that the concentration of cadmium in the water was higher than that in the eluant. this prompted the idea of using water to elute the Al61 resin. As can be seen from Figure 5.22b, water proved to be an effective eluant once the pH of the water rose above 2.0. It would appear from this that the cadmium chloride complex (CdCl_3^-) is unstable at this pH and that either neutral CdCl_2 or cationic CdCl^+ is formed leading to effective elution of the cadmium from the resin. If this is the case the chloride ions released from the cadmium chloride complex must provide the counter ions for the elution process. The cadmium concentration of the water eluate rose to well over 200 g/m^3 during the elution.

The water eluant from the Al61 resin column was neutralised using NaOH and this allowed the precipitation of cadmium hydroxide to occur. This reduced the concentration of cadmium in solution to concentrations below about 10 g/m^3 and produced a separable cadmium solid that could readily be dealt with. Although it was not tested

Figure 5.22a *Elution of cadmium from loaded Duolite A161 using 5M HCl.*
Eluate Cd concentration versus column throughput.

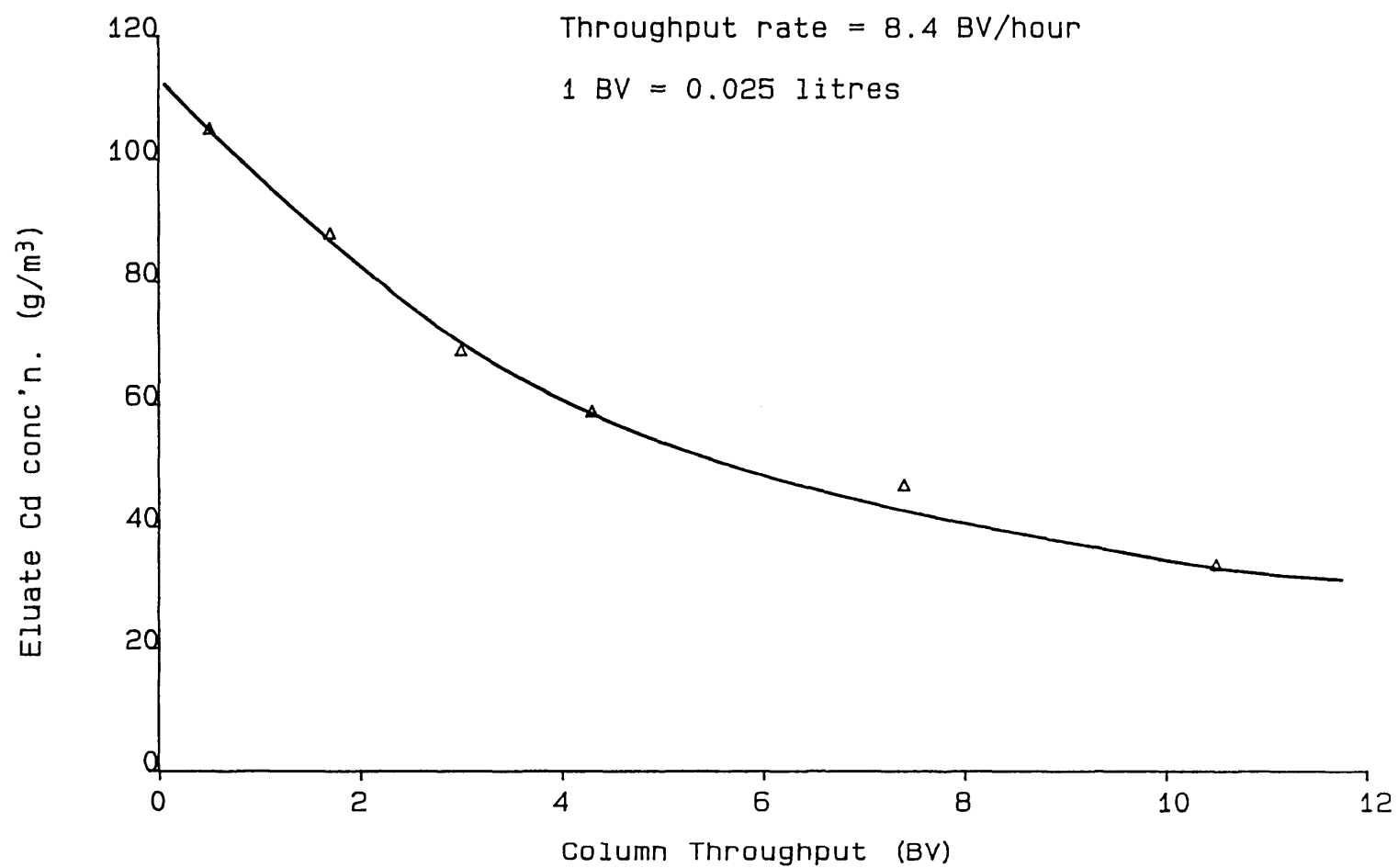
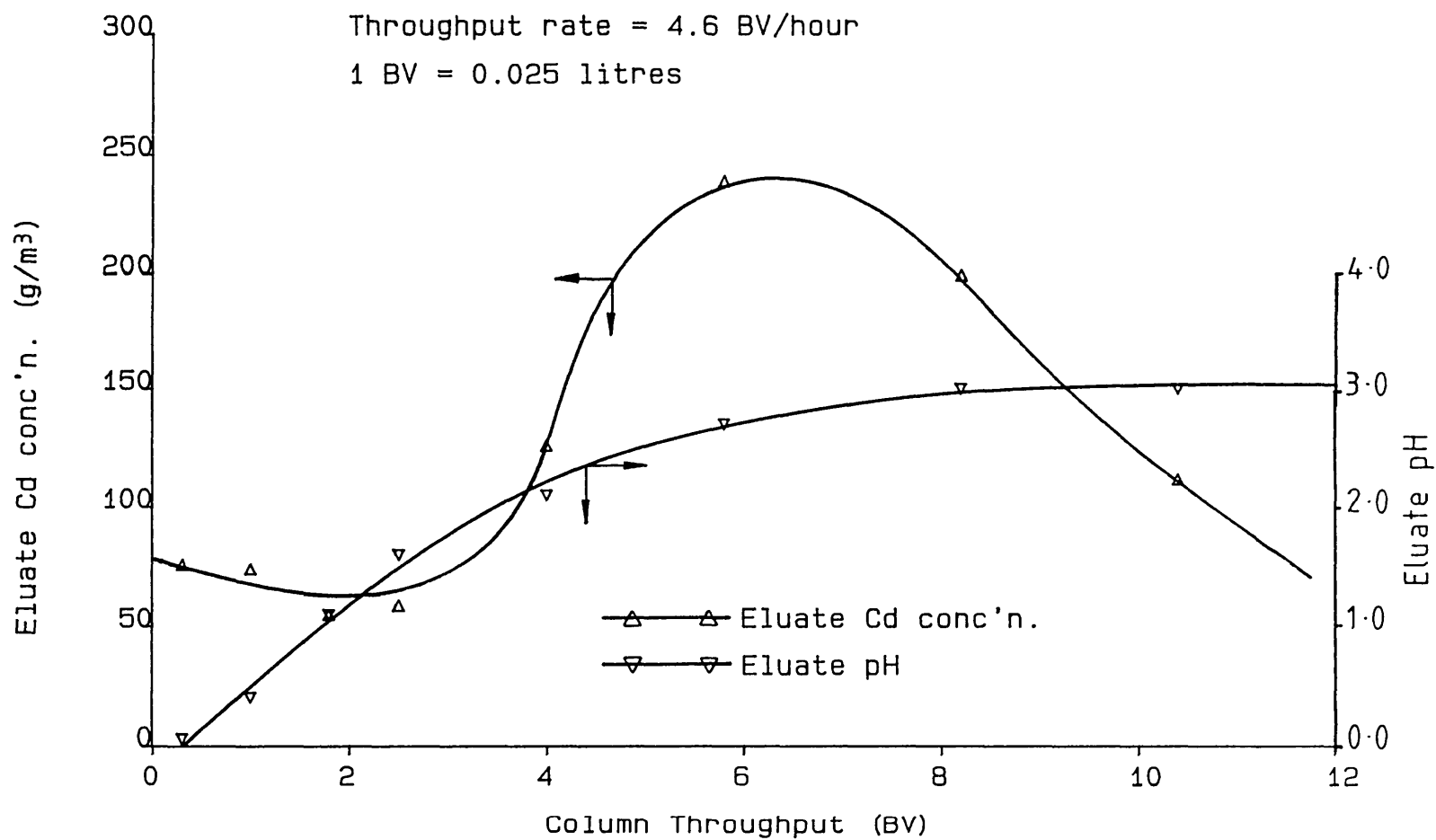


Figure 5.22b Elution of cadmium from loaded Duolite A161 using water.
Eluate Cd concentration and pH versus column throughput.



in this work, hydrogen sulphide could conceivably be used in a similar manner to precipitate cadmium sulphide from the eluant water. This would also have the effect of reducing the concentration of cadmium in the water and at the same time producing a solid cadmium waste for disposal.

5.7 Process selection

The removal of cadmium from WPA using a strong acid ion exchange resin is seen to be feasible. The process can be performed either in fixed bed ion exchange columns or in a moving bed ion exchanger. The choice of which technique to use will depend upon the economics of the two options. Estimates have been made of the capital and running costs incurred by a proposed process that could be used to continuously remove cadmium to less than 3 g Cd/m^3 from $1000 \text{ m}^3/\text{day}$ of WPA. The cost estimates are given in Appendix 6 and include the basis used for calculations in each case. In this appendix the costs associated with using either a fixed bed or a moving packed bed extraction column are calculated and the overall costs for the process utilizing either of these two techniques are compared.

The capital cost of the proposed process utilising fixed bed exchangers was only about 4% higher than that for the process using a moving packed bed exchanger design. One of the benefits of the moving packed bed process is that a smaller volume of resin is required in the elution column and consequently the size of the elution column is less. This is because this process can take advantage of the rapid elution of Duolite C264 seen using HCl solutions, whereas the fixed bed process is restricted to eluting the same volume of resin as is in the extraction column. However, the moving packed bed process requires vessels for the transfer of resin in and out of the extraction and elution columns. The cost of these vessels increases the capital cost of the process to a value similar to that of the fixed bed process. It is common practice in fixed bed processes to have a spare column of resin as a standby, the cost of this column and its resin would increase the overall capital cost of the fixed bed process to about 25% more than the cost of the moving packed bed process. However, for the purposes of comparing the two processes this spare column has not been included in the analysis.

The total capital cost of the proposed ion exchange process, including WPA pretreatment with sulphuric acid and removal of cadmium from the eluant using a strong base resin, is about £350000 at 1988 prices.

The running cost of the proposed process is estimated to be about £3.36x10⁶/year based on 365 days a year of operation. This is strongly influenced by the cost of reducing the calcium concentration of the WPA feed to the extraction column. The cost of sulphuric acid is about 80% of the calculated running cost incurred by the process. This cost may possibly be off-set by the use of another source of sulphate other than the sulphuric acid that was used in these studies. It may be that sodium sulphate or other monovalent metal sulphate salts could be used as a cheaper source of sulphate for the precipitation of gypsum from the acid. The disadvantage of using these would be, however, that the monovalent metal ion would contaminate the WPA.

The estimated usage of hydrochloric acid by the process is responsible for about 19% of the running cost of the process. This assumes that the eluate from the process can be recycled back to the eluant stream after cadmium is removed by passing the eluate through a bed of strong base ion exchange resin. A bleed stream is required from the eluate stream to reduce the build up of calcium and magnesium in the eluant. This bleed stream is responsible for the need to top up the eluant with fresh HCl.

Other costs associated with the process such as labour requirements, maintenance and resin inventory make-up are responsible in total for about 1% of the running costs of the process.

From the above cost analysis it is apparent that there is no clear cost advantage in using either fixed bed or moving packed bed exchangers for removing cadmium from phosphoric acid. However, if the quality of the feed acid were to change with time or the capacity of the resin decrease, the moving packed bed system would be more flexible in operation and thereby compensate for these changes. The time between resin transfers can easily be adjusted which results in changes to the resin throughput rate. Changing the ratio of WPA to resin flow will result in improved or reduced removal of the cadmium from the WPA. If the cycle time in the fixed

bed system becomes too short, the elution and washing of the resin in the columns will become less efficient.

The impact of removing cadmium from WPA on the cost of producing WPA can be calculated based on the above costs. Currently WPA is produced in the UK at about £200/t P_2O_5 . From the above cost analysis it can be seen that cadmium extraction will increase the cost of the WPA by about 13%. This will increase the cost of the 28% P_2O_5 WPA by about £9.2/m³.

6 CONCLUSIONS AND RECOMMENDATIONS

Cadmium in phosphoric acid is present as the divalent cation and can be removed from phosphoric acid using strong acid ion exchange resins. The macroporous, sulphonic acid resin Duolite C264 showed the best capacity for cadmium from pure phosphoric acid solutions.

The equilibrium cadmium capacity of Duolite C264 was related to the concentration of cadmium in "pure" phosphoric acid solutions by a Freundlich type isotherm.

Other divalent metal cations present in phosphoric acid can be taken up by strong acid ion exchange resins and will compete with cadmium for ion exchange sites. In particular calcium, which is present in high concentrations in wet process phosphoric acid, is more selectively adsorbed by sulphonic acid resins of high cross linking than is cadmium. For the successful ion exchange of cadmium from WPA, it is then necessary to reduce the calcium concentration of the feed acid. This was successfully achieved by precipitating it out of solution as calcium sulphate by dosing sulphuric acid into the WPA.

The rate of uptake of cadmium from phosphoric acid solutions was limited by the diffusion of the cadmium ions within the resin particles. The diffusion process was best described by Paterson's approximation of the solution of particle diffusion with the finite solution volume boundary condition. The experimentally determined diffusion coefficient for cadmium diffusion within Duolite C264 resin at 60°C was $8.7 \times 10^{-8} \text{ cm}^2/\text{s}$. Rate of loading increased with increasing solution temperatures, the activation energy for the extraction was estimated from an Arrhenius plot to be 16 kJ/mole.

Fixed column tests using Duolite C264 resin and WPA showed that cadmium concentrations could be reduced to less than 1 g Cd/m^3 in the treated acid, provided the calcium concentration of the feed acid was reduced to about 50 g Ca/m^3 .

Duolite C264 resin loaded with cadmium could be eluted using strong mineral acid solutions. Resin that had been loaded from WPA could not be eluted with sulphuric acid as this caused the precipitation of calcium sulphate within the resin bed. Hydrochloric acid proved to be a very effective eluant since cadmium eluted from the resin formed anionic chloride complexes which were electrostatically

repelled from the resin surface. Complete cadmium elution could be achieved using about one bed volume of HCl eluant solution.

Continuous, counter-current ion exchange was used to continuously produce a treated WPA stream that was below 2 g Cd/m^3 , again provided the feed WPA was reduced in calcium concentration. A solution to resin flow ratio of about 5 to 1 was required to achieve this level of treatment. As the solution to resin flow ratio increased the concentration of cadmium in the treated acid stream increased. Repeated use of the resin reduced its initial capacity to a lower value that appeared to remain relatively constant with further use. No apparent physical degradation of the resin was observed in hot WPA.

5M HCl eluate solutions could be treated with a strong base macroporous resin (Duolite A161) to remove the anionic cadmium complexes thus enabling the eluate to be returned to elute further loaded C264 resin. The loaded A161 resin was successfully eluted using water once pH in the eluate rose to above about 2.0.

Estimates of capital and running costs for a proposed process using Duolite C264 to remove cadmium from WPA showed no economic difference between performing the cadmium extraction in fixed columns or a continuous moving packed bed column. The estimated cost of removing cadmium from $1000 \text{ m}^3/\text{day}$ of 28% P_2O_5 WPA containing 15 mg Cd/l using Duolite C264 was: a capital cost of about £350000 and an annual running cost of about $£3.36 \times 10^6$. This resulted in an increased cost of P_2O_5 of about £25.5/t.

It is recommended that, since the cost of reducing the calcium concentration of the feed acid is the major contributor to annual running costs, alternative methods should be sought to cheaply reduce the feed WPA calcium concentration. Other sulphate salts, that are soluble in strong phosphoric acid solutions, such as sodium sulphate, may provide a more cost effective method for reducing the calcium concentration of the feed WPA.

The batch of Duolite C264 resin used in the continuous counter-current column work was subjected to over 10 cycles of loading and elution. During this time the resin capacity for cadmium was observed to decrease to an apparently steady value of about 57 mg Cd/kg resin, although no physical breakdown of the resin was observed. Further work should be done on a larger scale, using this

resin to treat WPA, so that the long term effects of exposure to WPA and 5M HCl eluant solutions can be fully assessed.

No attempt was made in this work to reduce the concentration of magnesium in the WPA feed to the process. It was present in the feed at high concentrations compared to cadmium and, although it was less selectively adsorbed by Duolite C264 than cadmium, its high concentration in solution meant that a large number of ion exchange sites within the resin were occupied by magnesium. The capacity of Duolite C264 for cadmium could be improved considerably if the magnesium concentration of the WPA feed was reduced before the ion exchange process. Alternatively, using sulphonic acid resins of higher DVB concentrations may increase the cadmium selectivity of the process relative to magnesium. This would need further investigation since calcium selectivity would also increase with further increases in DVB content of the resins.

Since the rate of cadmium ion exchange by Duolite C264 was controlled by diffusion of the ions within the resin particle, the volume of resin required in the contactor could be dramatically reduced by the use of smaller resin particles. This was not investigated in this work and further work would need to be performed to determine the effect on the overall process economics of using smaller size resin particles (of presumably higher cost).

REFERENCES

- 1 Guidelines for Drinking Water Quality
Volume 2, Health Criteria and Other Supporting Information
World Health Organisation, Geneva, 1984, Section 5, Cadmium.
- 2 Cadmium Compounds in Mineral Fertilizers,
Baechle,H.T., Wolstein,F.
Paper read before The Fertilizer Society of London,
October 4 1984.
- 3 The Quantities of Cadmium, Lead, Mercury and Arsenic Entering
the UK Environment from Human Activities.
Hutton,M., Symon,C.
The Science of the Total Environment,
No.57, 1986, pp 129 - 150
- 4 Council of European Communities Directive on Limit Values and
Quality Objectives for Cadmium Discharges.
26 September 1983
(83/513/EEC - OJ L 291, 24 October 1983)
- 5 Removal of Heavy Metals in Phosphoric Acid
Sasaki,H., Nakamura,M., Nakaya,M.
Japan Patent 78/75196, 4 July 1978,
- 6 A Method of Purifying Phosphoric Acid of Heavy Metals,
Berglund,H.A.L.
International Patent Classification C01B 25/237,
International Publication Number WO 80/02418
13 November 1980
- 7 Removal of Heavy Metal Ions from Wet Process Phosphoric Acid,
Gradl,R., Schimmel,G., Krause,W., Heymer,G.
International Patent Classification C01B 25/238
German Patent DE 3202658 A1,
28 January 1982,

- 8 Extraction of cadmium from phosphoric acid solutions with amines.
Part 1. Extractant selection, stripping, scrubbing and effects of other components.
Stenstrom, S., Aly, G.
Hydrometallurgy, 14 (1985), pp 231 - 255
- 9 Extraction of cadmium from phosphoric acid solutions with amines.
Part 11. Diluent selection, flow-sheet configuration, pilot plant operation.
Stenstrom, S., Aly, G.
Hydrometallurgy, 14 (1985), pp 257 - 276
- 10 Purification of phosphoric acid.
Williams, T.A., Cussons, F.M., Albright and Wilson Limited,
UK Patent specifications: 1436113, 1436114 and 1436115,
19 May 1976
- 11 Removal of zinc from phosphoric acid.
Hiruza, K. et al.
Japan patent 78/56190, 22 May 1978
- 12 Removal of cadmium by anion exchange in wet phosphoric acid process.
Tjioe, T.T., Kroon, J.A., Wesselingh, J.A., van Rosmalen, G.M.
Ion Exchange for Industry, Editor M Streat, Ellis Horwood Publishers, 1988, pp 606 - 616
- 13 Ion-exchange studies of phosphates.
Part 1. Ion-exchange sorption and pH titration methods for detection of complex formation
Holroyd, A., Salmon, J.E.
Journal of the Chemical Society, (London),
Vol. 1, 1956, pp 269 - 273
- 14 Stability constants of metal-ion complexes
Chemical Society (London)
Special Publications: #17 1964 and #25 1971

- 15 Ferrous-phosphoric acid complex
Lahiri, S.C., Aditya, S.
Journal of the Indian Chemical Society,
Vol. 41, No. 7, 1964, pp 517 - 520
- 16 Complexes involving tervalent iron and orthophosphoric acid.
Part (IV). Evidence of the formation of polynuclear complexes
from ion-exchange experiments.
Holroyd, A., Salmon, J.E.
Journal of the Chemical Society, (London),
Vol. 1, 1957, pp 959 - 963
- 17 Orthophosphato-complexes of the vanadyl (IV) ion in aqueous
acidic solution. Part 1. Ion-exchange studies
Salmon, J.E., Whyman, D.
Journal of the Chemical Society, (London),
1966, pp 980 - 985
- 18 Anion exchange behaviour of elements in orthophosphoric acid
medium.
Polkowska-Motrenko, H., Dybczynski, R.
Chemia Analityczna, 22, 1021, 1977
- 19 The formation of thorium (IV) and uranium (IV) complexes in
phosphate solutions.
Moskavin, A.I.
Russian Journal of Inorganic Chemistry,
Vol. 12, No. 12, Dec. 1967, pp 1794 - 1795
- 20 Chromium(III)-phosphoric acid complex.
Lahiri, S.C., Aditya, S.
Journal of the Indian Chemical Society,
Vol. 43, No. 7, 1966, pp 513 - 517
- 21 Chromium phosphates: Phase diagram and preliminary ion-exchange
studies of the system: chromic oxide - phosphoric oxide - water
at 0°C and 40°C.
Jameson, R.F., Salmon, J.E.
Journal of the Chemical Society, (London),
Vol. 1, 1955, pp 360 - 367

- 22 A New Guide to Capital Cost Estimating.
The Institution of Chemical Engineers and
The Association of Cost Engineers,
1986 reprint.
- 23 Ion Exchange Technology,
ICHEME Short Course,
Imperial College, May 1985
- 24 Chemical Engineers Handbook,
Perry, R.H., Chilton, C.H.
Fifth edition
- 25 Chemical Engineering Kinetics
Second Edition
Smith, J.M.
McGraw-Hill Chemical Engineering Series
- 26 Uranium Sorption from Phosphoric Acid Solutions
using Selective Ion Exchange Resins,
Gonzalez Luque, J.S.,
Thesis submitted for degree of Doctor of Philosophy,
Imperial College, London,
September, 1982.
- 27 Ion Exchange,
Helffferich, F.G.,
McGraw Hill, 1962.

APPENDIX 1

Analysis of phosphoric acids used in experimental work

A. "Pure" phosphoric acid.

"Pure" phosphoric acid refers to the solutions of phosphoric acid made up from BDH "Analar" orthophosphoric acid. This acid had the following maximum concentrations of impurities, as shown in Table A1.1.

Table A1.1
BDH "Analar" phosphoric acid assay.

SPECIES	MAXIMUM CONCENTRATION (% w/w)	SPECIES	MAXIMUM CONCENTRATION (% w/w)
H ₃ PO ₄	85.0	Cu	0.0001
Cl	0.0015	Fe	0.0015
NO ₃	0.0005	K	0.001
SiO ₂	0.005	Mg	0.001
SO ₄	0.002	Mn	0.0001
CH ₃ COOH	0.001	Na	0.01
As	0.0001	Ni	0.0005
Ca	0.004	Pb	0.0002
Cd	0.0001	Sb	0.0002
Co	0.0001	Zn	0.0002

B. "Real" wet process phosphoric acid.

All the "real" wet process acid (WPA) samples were obtained from Albright and Wilson Ltd., Oldbury, and contained various amounts of dissolved impurities depending on the original phosphate rock used for their manufacture. Table A1.2 below gives the approximate compositions of the acid samples used in the experimental work of this thesis. The analysis of the acid was provided by Albright and

Wilson and was performed on an inductively coupled plasma spectrophotometer (ICP).

Table A1.2
Analysis of WPAs used in experimental work.

SPECIES	CONCENTRATION (% w/w)		
	KHOURIBGA	YOUSOUFIA	ZIN*
P ₂ O ₅	27.4	27.2	33.0
SO ₄	0.21	0.13	NM
F	0.86	NM	NM
Cl	0.018	NM	NM
Al	0.037	0.029	NM
Zn	0.022	0.022	NM
Cd	0.0013	0.0012	0.0018
Fe	0.11	0.12	NM
Si	0.16	0.14	NM
V	0.014	0.012	NM
Cr	0.015	0.017	NM
Mg	0.24	0.24	0.18
Na	0.013	0.050	NM
K	0.023	0.019	NM
Ti	0.0026	NM	NM
U	0.0098	NM	NM
Ca	NM	0.59	0.0088

Where: NM indicates that the species was not analysed for.

* Zin acid was analysed by AAS at Imperial College

APPENDIX 2

Likely metal-ion complexes in phosphoric acid

METAL-ION	COMPLEX	REFERENCE
Fe^{2+}	$[\text{FeHPO}_4]^0$	14
Fe^{3+}	$[\text{FeHPO}_4]^+$	15
VO^{2+}	$[\text{VOHPO}_4]^0$	16
"	$[\text{HVO}(\text{HPO}_4)_2]^-$	16
"	$[\text{VO}(\text{HPO}_4)_2]^{2-}$	16
UO_2^{2+}	$[\text{UO}_2(\text{HPO}_4)_2]^{2-}$	17
U^{4+}	$[\text{UHPO}_4]^{2+}$	18
"	$[\text{U}(\text{HPO}_4)_2]^0$	18
"	$[\text{U}(\text{HPO}_4)_3]^{2-}$	18
"	$[\text{U}(\text{HPO}_4)_4]^{4-}$	18
Cr^{3+}	$[\text{CrHPO}_4]^+$	19
"	$[\text{Cr}(\text{H}_2\text{PO}_4)]^{2+}$	20
"	$[\text{Cr}(\text{PO}_4)_2]^{3-}$	20
Cd^{2+}	None	13
Zn^{2+}	None	13

APPENDIX 3

Experimental conditions used in cadmium extraction tests.

A. Batch stir tests.

1. Effect of temperature

- 45 g centrifuged moist C264 resin
- resin bead diameter = 0.60 to 0.85 mm
- 500 cm³ of "pure" 40% w/w P₂O₅
- initial Cd concentration = 1.5 g Cd/m³
- constant stirrer speed = 1000 RPM
- temperatures used = 25°C,
= 40°C,
= 60°C

2. Effect of particle size

- 15 g centrifuged moist C264 resin
- resin bead diameters = < 0.063 mm,
= 0.425 to 0.60 mm,
= 0.60 to 0.85 mm,
= 0.85 to 1.00 mm
- 500 cm³ of "pure" 40% w/w P₂O₅
- initial Cd concentration = 1.5 g Cd/m³
- constant stirrer speed = 1000 RPM
- temperature = 60°C

3. Effect of stirrer speed

- 15 g centrifuged moist C264 resin
- resin bead diameter 0.85 to 1.00 mm
- 500 cm³ of "pure" 40% w/w P₂O₅
- initial Cd concentration = 1.5 g Cd/m³
- stirrer speeds used = 140 RPM,
= 1000 RPM
- temperature = 60°C

4. Effect of P_2O_5 concentration

- 15 g centrifuged moist C264 resin
- resin bead diameter = 0.60 to 0.85 mm
- 500 cm³ of "pure" phosphoric acid with
 P_2O_5 concentration = 30% w/w,
= 40% w/w,
= 50% w/w
- initial Cd concentration = 1.5 g Cd/m³
- constant stirrer speed = 1000 RPM
- temperature = 60°C

5. Effect of cadmium concentration

- 15 g centrifuged moist C264 resin
- resin bead diameter = 0.60 to 0.85 mm
- 500 cm³ of "pure" 40% w/w P_2O_5
- initial Cd concentration = 1.5 g Cd/m³,
= 15.0 g Cd/m³,
= 150 g Cd/m³
- constant stirrer speed = 1000 RPM
- temperature = 60°C

6. Interruption test

- 15 g centrifuged moist C264 resin
- resin bead diameter 0.85 to 1.00 mm
- 500 cm³ of "pure" 40% w/w P_2O_5
- initial Cd concentration = 1.5 g Cd/m³
- constant stirrer speed = 1000 RPM
- temperature = 60°C
- after 15 minute of contact time the acid was separated from the resin, contact was resumed after a further 133 minutes of elapsed time.

7. Effect of resin cross-linking

Three different resins were used to assess the effect of resin cross-linking. The Duolite C264 resin used in all the other tests is claimed by the manufacturers to have an enhanced capacity due to a proprietary sulphonation process. Rohm and Haas claim to produce two macroporous sulphonic acid resins of different cross-linking to C264 but with similar levels of sulphonation. The three resins tested were Amberlite XE386.

(12% DVB), Duolite C264 (16% DVB) and Amberlite XE383 (20% DVB).

The other conditions used were:

- 15 g centrifuged moist resin
- resin bead diameter = 0.60 to 0.85 mm
- 500 cm³ of "pure" 30% w/w P₂O₅
- initial Cd concentration = 32 g Cd/m³
- constant stirrer speed = 1000 RPM
- temperature = 60°C

8. Effect of resin structure

Two gel type resins of different cross-linking were tested, these were Duolite C225 (8% DVB) and C255 (10% DVB). Both are strong acid sulphonic acid resins with a polystyrene matrix. The conditions used in the tests were:

- 15 g centrifuged moist resin
- resin bead diameter = 0.60 to 0.85 mm
- 500 cm³ of "pure" 40% w/w P₂O₅
- initial Cd concentration = 1.5 g Cd/m³
- constant stirrer speed = 1000 RPM
- temperature = 60°C

B. 10 mm fixed column tests.

Experimental conditions used in 10 mm internal diameter fixed column tests using Duolite C264 resin in the H⁺ form to remove cadmium from "pure" 40% w/w P₂O₅ phosphoric acid at 60°C are given in Table A3.1 below. The table also gives the conditions used for the elution of the resin from each run using sulphuric acid solutions at 20°C.

C. 38 mm fixed column tests.

The experimental conditions used in the 38 mm internal diameter fixed column tests using Duolite C264 resin to treat phosphoric acid at 60°C are given in Tables A3.2 and A3.3. The resin used was replaced after run D as the original resin was fouled by calcium sulphate precipitate. The resin had been used to treat Albright and Wilson WPA derived from Khouribga phosphate rock and had been eluted with sulphuric acid.

Table A3.1

Experimental conditions used in 10 mm fixed column tests
for cadmium extraction from pure phosphoric acid onto C264 resin.
(1 BV = 23 cm³)

RUN	FEED ACID Cd CONC'N g/m ³	RESIN LOADING		ELUANT H ₂ SO ₄ CONC'N	RESIN ELUTION	
		COLUMN THROUGHPUT			COLUMN THROUGHPUT	
		RATE	VOLUME		RATE	VOLUME
		BV/hour	BV		BV/hour	BV
A	1.5	13.8	20	2M	10.9	19
B	1.5	12.3	35	2M	9.7	14
C	1.6	5.5	28	1M	10.3	29
D	1.6	6.3	42	-	-	-
E	1.5	3.6	26	-	-	-
F	1.3	2.8	52	-	-	-

Table A3.2

Experimental conditions used in 38 mm fixed column tests
for extraction onto C264 from phosphoric acid.
(1 BV = 300 cm³)

RUN	RESIN	ACID TYPE	FEED COMPOSITION g Metal/m ³						COLUMN THRO' PUT	
			P ₂ O ₅	Ca	Cd	Mg	Ni	Zn	RATE	VOLUME
			%						BV/hour	BV
A	New	"Pure"	30	0	29	0	0	0	3.2	16
B	ex A	"Pure"	30	0	29	0	0	0	3.8	31
C	ex B	"Pure"	30	0	29	0	0	0	6.0	34
D	ex C	Khouribga	28	4800	15	2900	34	270	3.7	31
E	New	Khouribga	28	215	22	2600	31	260	3.7	26
F	ex E	Khouribga	28	78	15	2700	28	260	3.6	29
G	ex F	Zin	33	36	18	1550	NR	NR	4.0	14
H	ex G	Zin	33	44	17	1600	NR	NR	3.8	17
I	ex H	Zin	33	35	18	1700	NR	NR	3.6	15
J	ex I	Zin	33	42	18	1720	NR	NR	3.6	16

"Pure" acid was made up from BDH "Analar" orthophosphoric acid.

Khouribga acid is Albright & Wilson WPA, produced from Khouribga phosphate rock.

Zin acid is Albright & Wilson WPA, produced from Zin phosphate rock.

Table A3.3
Experimental conditions used in 38 mm fixed column tests
for elution of loaded C264 resin.
(1 BV = 300 cm³)

RUN	ELUANT USED	COLUMN THROUGHPUT	
		RATE BV/hour	VOLUME BV
A	5M H ₂ SO ₄	2.3	6
B	5M H ₂ SO ₄	4.1	8
C	eluate ex B	3.8	8
D	5M H ₂ SO ₄	2.8	-
E	5M HCl	3.8	12
F	5M HCl	5.4	11
G	5M HCl	3.9	1.6
H	5M HCl	3.9	1.4
I	5M HCl	3.8	1.6
J	eluate ex G, H and I	3.8	1.4

D. Continuous counter-current tests

The conditions used in the continuous counter-current tests during extraction are shown in Table A3.4. Cadmium extraction was attempted using C264 resin to treat, at 60°C, 28% P₂O₅ WPA produced by Albright and Wilson from calcined Youssoufia phosphate rock. The conditions used to elute the loaded resin are given in Table A3.5. Cadmium was eluted in a fixed column, batch wise using 5M HCl at room temperature. The eluate produced was returned to the eluant tank and used to elute subsequent loaded resin batches.

Table A3.4
Experimental conditions used to extract cadmium from WPA
using C264 in continuous counter-current column tests.

RUN	RESIN USED	FEED ACID COMPOSITION			FEED RESIN		VOLUME	
		Cd	Ca	Mg	FLOW	FLOW	S/R	TREATED
	EX ELUTION	g/m ³	g/m ³	g/m ³	cm ³ /hour			litres
E	D2	14.5	57	2600	460	50	9.2	5.3
F	E1 and F1	14.5	55	2700	490	50	14.8	9.5
G	F2	15.1	56	3200	490	90	5.3	3.4
H	G1 and H1	14.9	75	2500	480	50	9.3	8.3
I	H2	16.2	4300	2900	490	50	9.5	5.9

Table A3.5

Experimental conditions used to elute loaded C264 resin from
continuous counter current column tests.

ELUTION	RESIN VOLUME	ELUANT COMPOSITION			FLOW	ELUATE
RUN	ELUTED	Cd	Ca	Mg	RATE	VOLUME
	litres	g/m ³	g/m ³	g/m ³	cm ³ /hour	litres
D2	0.50	37	136	3780	2000	0.7
E1	0.54	49	252	5000	2200	0.7
F1	0.52	57	340	6000	2100	1.2
F2	0.57	75	460	6680	2300	0.9
G1	0.51	91	515	7420	2000	0.8
H1	0.53	105	553	7930	2100	0.8
H2	0.51	115	573	8220	2000	0.9
I1	0.44	129	621	8590	1800	0.7
I2	0.39	133	1960	8810	1600	0.9

APPENDIX 4

Results from 38 mm fixed column tests

A. Cadmium loading results

The following tables are the experimental results from the 38 mm fixed bed column tests used extract cadmium from both "pure" phosphoric acid and WPA using Duolite C264 resin. The run numbers referred to in the tables are the same as those given in the experimental conditions in Table A3.2 of Appendix 3.

Table A4.1

Results from 38 mm fixed column test A
cadmium extraction from 30% P₂O₅ "pure" phosphoric acid.
(Feed in downflow through resin bed)

TIME mins	COLUMN THROUGHPUT		EFFLUENT CONCENTRATION	
	INCREMENTAL cm ³	CUM ULATIVE BV	Cd g/m ³	
0	-	-	Feed =	29
23	372	1.2		0
35	166	1.8		0.5
56	345	2.9		0.2
75	304	4.0		0.1
122	565	5.8		0.1
135	432	7.3		0.2
165	500	9.0		0.1
195	443	10.4		0.2
247	887	13.4		0.1
280	525	15.1		0.1
298	289	16.1		0.1

Table A4.2

Results from 38 mm fixed column test B
cadmium extraction from 30% P₂O₅ "pure" phosphoric acid.
(Feed in upflow through resin bed)

TIME mins	COLUMN THROUGHPUT		EFFLUENT CONCENTRATION Cd g/m ³
	INCREMENTAL cm ³	CUMULATIVE BV	
0	-	-	Feed = 29
26	466	1.6	0.3
55	530	3.3	0.1
83	470	4.9	0.1
115	590	6.9	0.1
152	710	9.2	0.1
195	867	12.1	0.1
238	852	14.9	0.1
296	1104	18.6	0.1
340	832	21.4	0.1
374	682	23.7	0.1
407	675	25.9	0.1
453	920	29.0	0.1
483	575	30.9	0.1
491	142	31.4	0.2

Table A4.3

Results from 38 mm fixed column test C
cadmium extraction from 30% P₂O₅ "pure" phosphoric acid.
(Feed in upflow through column)

TIME mins	COLUMN THROUGHPUT		EFFLUENT CONCENTRATION Cd g/m ³
	INCREMENTAL cm ³	CUMULATIVE BV	
0	-	-	Feed = 29
20	520	1.7	1.2
35	440	3.2	0.9
60	740	5.7	1.2
80	640	7.8	0.9
130	1490	12.8	0.8
150	595	14.8	1.0
180	920	17.8	1.2
210	910	20.9	1.0
225	500	22.5	1.2
247	662	24.7	1.1
272	723	27.1	1.5
297	750	29.6	1.6
324	842	32.4	1.7
334	290	33.4	2.1

Table A4.4

Results from 38 mm fixed column test D
cadmium extraction from 28% P₂O₅ Khouribga WPA.
(Feed in upflow through resin bed)

TIME mins	COLUMN THROUGHPUT		EFFLUENT CONCENTRATION g Metal/m ³				
	INCREMENTAL cm ³	CUMULATIVE BV	Ca	Cd	Mg	Ni	Zn
0	—	—	Feed = 4820	15.4	2890	34	270
11	174	0.6	0	2.9	0	0	0
26	255	1.4	0	2.5	0	0	0
44	344	2.6	0	2.5	50	0	13
60	313	3.6	0	13.5	740	4	58
79	374	4.9	690	60.5	3430	29	296
96	340	6.0	2020	66.6	3730	39	339
120	460	7.5	3130	56.6	3530	41	322
146	494	9.2	4000	42.7	3340	38	302
174	547	11.0	4630	29.4	3170	35	283
189	304	12.0	5000	23.1	3100	34	280
215	470	13.6	5150	19.9	3030	35	272
277	1134	17.4	5150	18.7	2950	33	271
307	550	19.2	5100	16.4	2930	33	265
320	260	20.1	5100	15.1	2940	33	270
502	3247	30.9	5150	15.7	2900	33	261

Table A4.5

Results from 38 mm fixed column test E
cadmium extraction from 28% P₂O₅ Khouribga WPA.
(Feed in upflow through resin bed)

TIME mins	COLUMN THROUGHPUT		EFFLUENT CONCENTRATION g Metal/m ³					
	INCREMENTAL cm ³	CUMULATIVE BV	Ca	Cd	Mg	Ni	Zn	
0	-	-	Feed = 215	21.5	2070	31	260	
12	215	0.7	0	0	0	0	0	
22	188	1.3	0	0	0	0	0	
37	285	2.3	0	0	0	0	0	
55	348	3.5	0	0	0	0	4	
74	375	4.7	0	0.6	320	2	13	
100	530	6.5	0	4.5	830	10	128	
134	645	8.6	0	11.0	1690	22	240	
178	845	11.4	0	16.9	1900	29	272	
241	1200	15.4	0	21.6	2100	31	289	
285	790	18.1	65	23.4	2100	33	285	
307	397	19.4	85	23.7	2170	33	283	
349	757	21.9	115	23.4	2290	32	281	
376	490	23.6	150	23.4	1880	32	268	
414	690	25.8	170	23.4	1960	32	267	

Table A4.6

Results from 38 mm fixed column test F
cadmium extraction from 28% P₂O₅ Khouribga WPA.
(Feed in upflow through resin bed)

TIME mins	COLUMN THROUGHPUT		EFFLUENT CONCENTRATION g Metal/m ³					
	INCREMENTAL cm ³	CUMULATIVE BV	Ca	Cd	Mg	Ni	Zn	
0	-	-	Feed = 78	15.2	2700	28	259	
11	190	0.6	0	0	370	0	0	
28	297	1.6	0	0	370	0	11	
43	269	2.5	0	1.3	1130	7	71	
61	334	3.6	0	4.7	1850	15	157	
79	333	4.7	0	7.9	2120	20	213	
105	493	6.4	12	10.6	2360	24	234	
138	600	8.4	28	12.6	2390	25	243	
165	500	10.1	36	13.6	2430	27	258	
227	1130	13.8	42	14.2	2390	27	257	
262	640	16.0	44	14.7	2480	30	250	
310	875	18.9	58	13.7	2480	33	254	
366	1020	22.3	20	14.0	2520	33	257	
415	890	25.2	39	14.8	2560	33	260	
475	1068	28.8	25	15.0	2500	33	263	

Table A4.7

Results from 38 mm fixed column test G
cadmium extraction from 33% P₂O₅ Zin WPA.
(Feed in upflow through resin bed)

TIME mins	COLUMN THROUGHPUT		EFFLUENT CONCENTRATION g Metal/m ³					
	INCREMENTAL cm ³	CUM ULATIVE BV		Ca	Cd	Mg	Ni	Zn
0	-	-	Feed =	36	17.5	1550	NM	NM
8	152	0.5		34	0.4	120		
17	174	1.1		44	0.4	190		
26	173	1.7		43	0.8	400		
41	290	2.6		47	2.1	630		
57	315	3.7		56	4.6	930		
72	302	4.7		63	7.4	1140		
87	305	5.7		61	9.5	1260		
102	310	6.7		60	11.0	1370		
112	205	7.4		61	12.0	1430		
183	1445	12.2		59	14.2	1500		
213	585	14.2		57	15.4	1520		

Table A4.8

Results from 38 mm fixed column test H
cadmium extraction from 33% P₂O₅ Zin WPA.
(Feed in upflow through resin bed)

TIME mins	COLUMN THROUGHPUT		EFFLUENT CONCENTRATION g Metal/m ³					
	INCREMENTAL cm ³	CUM ULATIVE BV		Ca	Cd	Mg	Ni	Zn
0	-	-	Feed =	44	16.8	1600	NM	NM
6	102	0.3		7	0	0		
16	178	0.9		13	0	40		
26	172	1.5		17	0	210		
36	178	2.1		34	0.1	430		
51	280	3.0		24	1.9	730		
66	282	4.0		28	4.0	1060		
81	283	4.9		33	6.6	1270		
96	294	5.9		48	8.8	1390		
136	755	8.4		40	11.2	1500		
152	300	9.4		51	13.7	1540		
259	2025	16.2		47	15.2	1540		
269	207	16.9		48	15.4	1540		

Table A4.9

Results from 38 mm fixed column test I
cadmium extraction from 33% P₂O₅ Zin WPA.
(Feed in upflow through resin bed)

TIME mins	COLUMN THROUGHPUT			EFFLUENT CONCENTRATION g Metal/m ³				
	INCREMENTAL cm ³	CUM ULATIVE BV		Ca	Cd	Mg	Ni	Zn
0	-	-	Feed =	35	17.6	1700	NM	NM
5	85	0.3		0	0	0		
25	350	1.5		0	0.1	0		
45	358	2.6		0	0.2	0		
66	375	3.9		0	0.3	30		
85	345	5.1		0	0.6	200		
115	538	6.8		0	1.9	840		
185	1330	11.3		2	7.8	1500		
235	880	14.2		5	12.7	1700		
245	180	14.8		6	13.9	1690		

Table A4.10
Results from 38 mm fixed column test J
cadmium extraction from 33% P₂O₅ Zin WPA.
(Feed in upflow through resin bed)

TIME mins	COLUMN THROUGHPUT			EFFLUENT CONCENTRATION g Metal/m ³				
	INCREMENTAL cm ³	CUM ULATIVE BV		Ca	Cd	Mg	Ni	Zn
0	-	-	Feed =	42	17.7	1720	NM	NM
10	174	0.6		2	0	20		
30	355	1.8		0	0	15		
50	365	3.0		0	0	40		
70	378	4.2		2	0.6	120		
131	1090	7.9		2	2.9	940		
190	1050	11.4		5	9.2	1650		
262	1268	15.6		8	13.1	1740		
265	65	15.8		12	15.6	1730		

B. Cadmium elution results

The following tables show the results of the cadmium elution experiments performed on the loaded Duolite C264 resin in the 38 mm fixed bed column tests. The conditions used in each elution experiment are given in Table A3.3 of Appendix 3.

Table A4.11
Results from 38 mm fixed column test A,
elution of resin using 5M H₂SO₄.

TIME mins	COLUMN THROUGHPUT			ELUATE COMPOSITION Cd g/m ³
	INCREMENTAL cm ³	CUM ULATIVE BV		
0	-	-	Eluant =	0
13	174	0.6		133
27	136	1.0		345
36	90	1.3		93
56	194	2.0		77
76	197	2.6		62
93	196	3.3		43
113	208	4.0		33
133	200	4.6		27
153	212	5.4		19
160	74	5.6		15

Table A4.12
Results from 38 mm fixed column test B,
elution of resin using 5M H₂SO₄.

TIME mins	COLUMN THROUGHPUT		ELUATE COMPOSITION Cd g/m ³
	INCREMENTAL cm ³	CUM ULATIVE BV	
0	-	-	Eluant = 45
12	214	0.7	194
18	88	1.0	515
24	108	1.4	405
30	110	1.7	285
42	224	2.5	182
54	248	3.3	118
68	268	4.5	80
88	370	5.4	64
114	500	7.1	60
135	376	8.4	55

Table A4.13
Results from 38 mm fixed column test C,
elution of resin using 5M H₂SO₄.

TIME mins	COLUMN THROUGHPUT		ELUATE COMPOSITION Cd g/m ³
	INCREMENTAL cm ³	CUM ULATIVE BV	
0	-	-	Eluant = 132
4	72	0.2	478
8	74	0.5	620
13	90	0.8	538
20	127	1.2	416
27	132	1.7	336
35	171	2.2	280
49	268	3.1	230
63	260	4.0	195
79	315	5.0	180
102	453	6.5	156
116	290	7.5	146

Table A4.14
Results from 38 mm fixed column test E,
elution of resin using 5M HCl

TIME mins	COLUMN THROUGHPUT		ELUATE COMPOSITION g Metal/m ³				
	INCREMENTAL cm ³	CUMULATIVE BV	Ca	Cd	Mg	Ni	Zn
0	-	-	Eluant = 0 0 0 0 0				
8	143	0.5	1730	152	7200	154	980
15	130	0.9	2020	31	3700	74	257
26	205	1.6	2025	6	1600	30	61
45	382	2.9	1610	0	575	8	14
72	503	4.5	1085	0	75	2	10
86	277	5.5	840	0	10	0	15
135	950	8.6	430	0	0	0	15
159	484	10.2	270	0	0	0	14
189	558	12.1	195	0	0	0	0
194	56	12.3	185	0	0	0	0

Table A4.15
Results from 38 mm fixed column test F,
elution of resin using 5M HCl

TIME mins	COLUMN THROUGHPUT		ELUATE COMPOSITION g Metal/m ³		
	INCREMENTAL cm ³	CUMULATIVE BV	Ca	Cd	Mg
0	-	-	Eluant = 840 7 580		
6	112	0.4	220	100	2910
11	100	0.7	520	54	3240
16	102	1.1	480	24	2370
21	107	1.4	590	12	1710
31	198	2.1	540	9	1220
46	315	3.1	600	8	830
61	310	4.2	700	7	670
77	345	5.3	740	7	640
113	760	7.8	810	7	600
156	915	10.9	820	7	580

Table A4.16
Results from 38 mm fixed column test G,
elution of resin using 5M HCl

TIME mins	COLUMN THROUGHPUT		ELUATE COMPOSITION g Metal/m ³		
	INCREMENTAL cm ³	CUM ULATIVE BV	Ca	Cd	Mg
0	-	-	Eluant = 0	0	0
4	78	0.3	215	218	7000
9	98	0.6	480	36	6200
14	100	0.9	610	4	3000
24	194	1.6	620	0	1200

Table A4.17
Results from 38 mm fixed column test H,
elution of resin using 5M HCl

TIME mins	COLUMN THROUGHPUT		ELUATE COMPOSITION g Metal/m ³		
	INCREMENTAL cm ³	CUM ULATIVE BV	Ca	Cd	Mg
0	-	-	Eluant = 0	0	0
2	58	0.2	245	252	710
7	80	0.5	390	64	7300
13	112	0.8	540	9	4100
22	174	1.4	555	0	1500

Table A4.18
Results from 38 mm fixed column test I,
elution of resin using 5M HCl

TIME mins	COLUMN THROUGHPUT		ELUATE COMPOSITION g Metal/m ³		
	INCREMENTAL cm ³	CUM ULATIVE BV	Ca	Cd	Mg
0	-	-	Eluant = 0	0	0
3	55	0.2	115	455	3000
7	78	0.4	470	252	11900
11	80	0.7	1025	69	10400
16	93	1.0	970	19	6150
25	164	1.6	765	4	2550

Table A4.19

Results from 38 mm fixed column test J,
elution of resin using eluate from runs G, H and I.

TIME mins	COLUMN THROUGHPUT		ELUATE COMPOSITION g Metal/m ³		
	INCREMENTAL cm ³	CUM ULATIVE BV	Ca	Cd	Mg
0	-	-	Eluant = 500		
4	73	0.2	235	470	8800
7	56	0.4	635	215	13150
11	80	0.7	820	113	10500
15	78	1.0	780	77	8150
25	144	1.4	715	69	660

APPENDIX 5

X-Ray fluorescence analysis of loaded resins

The use of ion exchange resins for the removal of metal ions or metal ion complexes from wet process phosphoric acid (WPA) was investigated by examining the loaded resins using X-Ray fluorescence analysis. The analysis performed was qualitative in that no accurate assessment of the amount of each metal species on the resins could be determined, the tests were used only to see what metals were being taken up by the resins. No quantitative assessment was possible in these tests since the effects of the different resin matrices on the fluorescence observed was not established. For this reason comparisons between resins are only valid for the purpose of seeing which metals were removed rather than the extent of the metal removal.

The resins used in the tests were prepared by initially performing a batch stir test with them in the presence of WPA.

The resins used were wet sieved and the fraction between 0.6 and 0.85 mm retained, this fraction was then conditioned in the same manner as for the resins used in the initial batch selection tests. The conditioned resins were then centrifuged and 15 g of the moist resin used in each test.

The resins were each contacted with 500 cm³ of 42% P₂O₅ Zin phosphoric acid (ex Albright and Wilson) at 60°C for over 16 hours. After contact the resins were separated from the acid by filtering the acid through a porous glass filter. The resins were then washed with 500 cm³ of distilled water and centrifuged for 5 minutes at 2000 RPM. A sample of the centrifuged moist resin (about 7 g) was then oven dried at 110°C to constant weight. The dried resins were accurately weighed and stored above silica gel in a desiccator until required for X-Ray fluorescence analysis.

Samples of resin that had not been in contact with the WPA were washed, centrifuged and oven dried in the same manner as above. These resin samples were used as a comparison to the loaded resins.

The dried resin samples were each placed in a PTFE sample holder that had a 1.25 inch polypropylene membrane window in it, through which they were irradiated.

X-Ray fluorescence analysis was performed on a Philips PW1220 X-Ray fluorescence spectrophotometer. The X-Ray source was a tungsten tube set at 80 kV and 24 mA. The output from the machine was recorded as intensity of fluorescence at detector angles between 0 and 90 degrees. Elements of atomic number below calcium were undetectable using the tungsten tube and did not appear on the output from the machine. The resultant traces were analysed by Mr R Sweeny, Imperial College, and the peaks at different angles associated with different metal species. The heights of the major peaks for the 13 metals identified (and bromine) for each resin tested (when compared to the unloaded resin) are shown in the table below.

Table A5.1
Results of X-Ray fluorescence analysis of
ion-exchange resins used for treatment of WPA.

METAL	HEIGHTS OF MAJOR PEAKS FOR RESINS						
	C264	C433	A101	A30B	ES346	ES465	ES467
Titanium	ND	ND	200	280	200	ND	2200
Vanadium	410	ND	350	650	ND	ND	7400
Chromium	ND	ND	560	640	ND	ND	4100
Manganese	700	ND	ND	ND	ND	ND	ND
Iron	4100	ND	15200	14900	7500	200	OS
Nickel	8200	ND	ND	ND	ND	ND	ND
Copper	1100	ND	ND	ND	ND	3400	ND
Zinc	36000	ND	2200	140	ND	500	1640
Arsenic	ND	ND	ND	ND	ND	1800	ND
Zirconium	ND	ND	270	380	ND	ND	660
Molybdenum	ND	ND	1100	1480	1720	ND	2600
Cadmium	1100	ND	ND	ND	ND	160	ND
Uranium	ND	ND	ND	640	ND	ND	1940
(Bromine)	ND	ND	810	ND	760	720	ND

Where: ND indicates that the metal was not detected.

OS indicates that the metal was present in such high concentrations that it was off scale.

APPENDIX 6

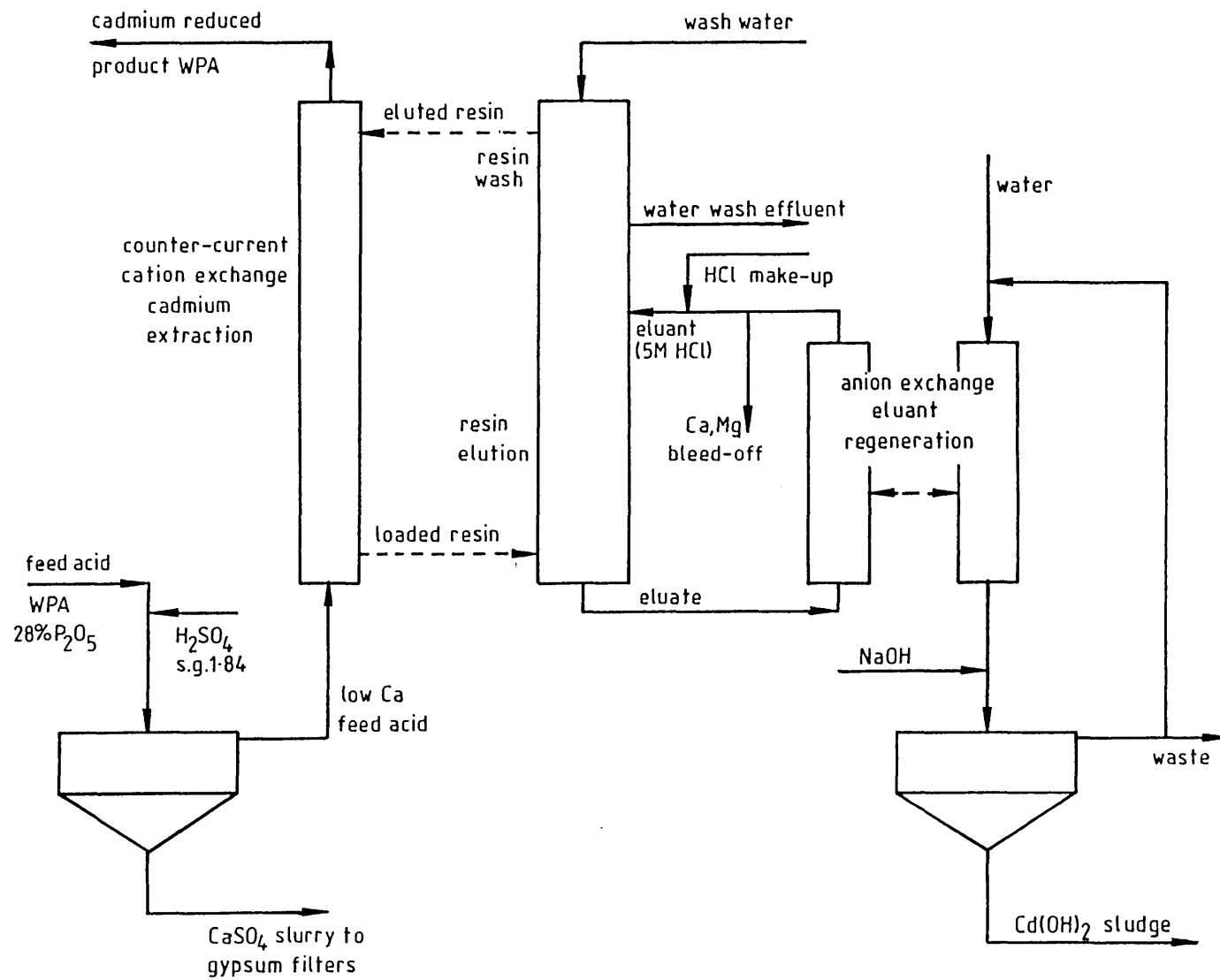
Cost estimates for removal of cadmium from WPA using the strong acid resin Duolite C264.

A. Basis

The overall process proposed for the removal of cadmium from WPA by cation exchange using Duolite C264 resin is shown in Figure A6.1. The following analysis of the costs for the process examines the effect of the type of cadmium extraction equipment used, that is, whether extraction is performed in fixed bed columns or within a moving packed bed contactor. The pretreatment and regeneration of eluant portions of the process are assumed to be similar no matter what the choice of extraction process is. For the purposes of comparing the two process options available, the capital and running costs were estimated based on the following assumptions.

- 1000 m³/day of 28% w/w P₂O₅ wet process acid at 60°C is treated.
- The feed acid contains 15 g Cd/m³.
- Calcium present in the acid is reduced by precipitation to about 50 g Ca/m³ using H₂SO₄. This pretreatment of the WPA is common to both process options and the costs associated will be the same in each case.
- The treated acid must contain no more than 3 g Cd/m³.
- The resin is eluted using 5M HCl.
- The eluate is treated by anion exchange, to recover the cadmium, and is returned to the eluant stream. This aspect is common to the two options and the costs associated with it will be the same in each case.
- Cost information is based on verbal communication with suppliers and "A New Guide to Capital Cost Estimating" (22).
- Costs have been adjusted to 1988 prices using suitable cost indexes.

Figure A6.1 Proposed process flow diagram for cadmium removal from WPA by cation exchange.



B. Fixed bed process

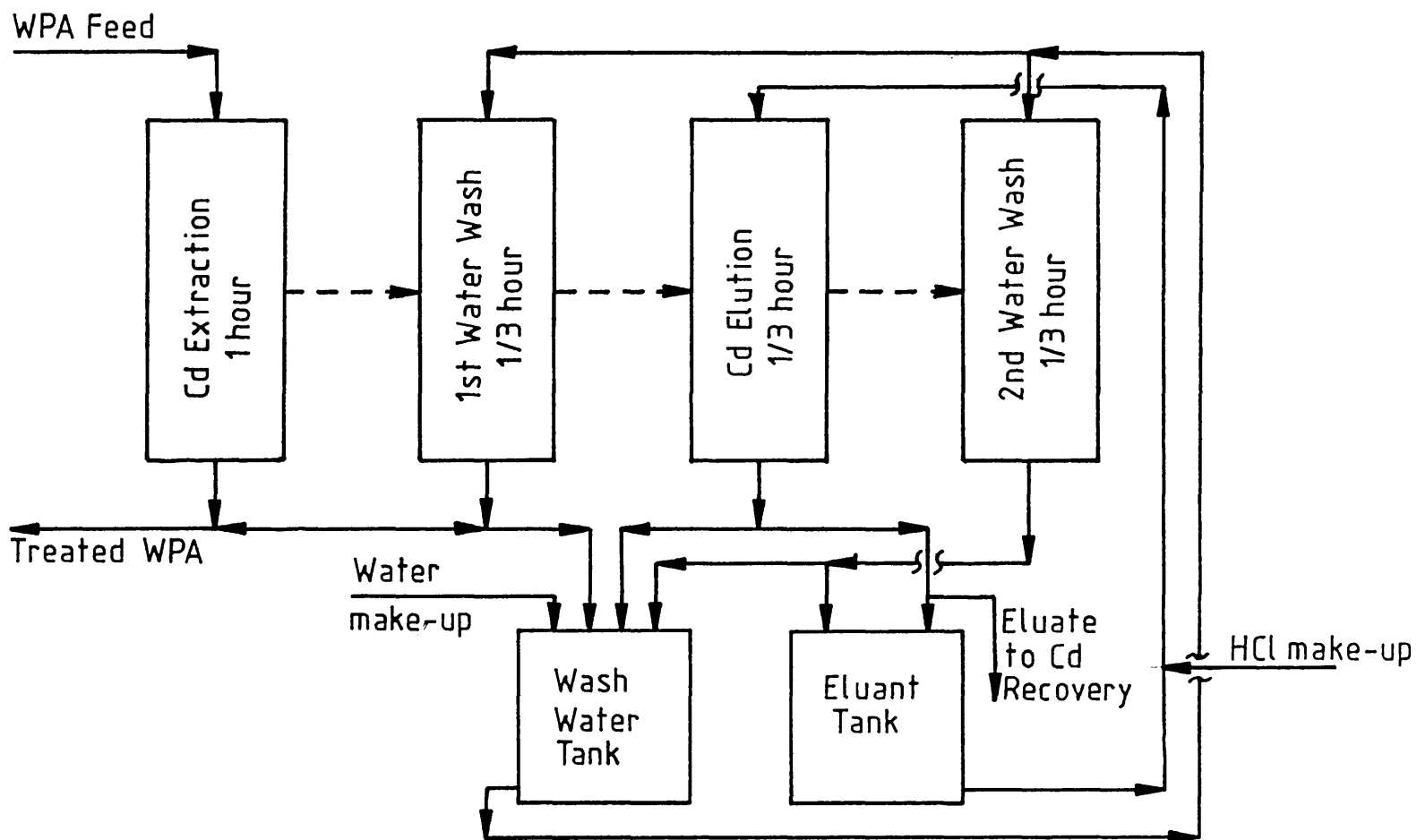
The design of the fixed bed process is based on the results of the fixed bed column work performed using 38 mm columns and WPA. The following assumptions have been used in coming to a process design.

- Column throughput rate = 4 BV/hour in downflow.
- 1 bed volume = 10.4 m^3 .
- Time to cadmium breakthrough of $3 \text{ g Cd/m}^3 = 1 \text{ hour}$.
- Column height to diameter ratio = 10:1.
- First water wash cycle = $1/3 \text{ hours}$.
- Elution cycle = $1/3 \text{ hours}$.
- Second water wash cycle = $1/3 \text{ hours}$.

The fixed bed column is operated in downflow mode since it is impractical to maintain the minimum upflow velocity, to ensure no expansion of the resin bed, as was used in the 38mm column work. If the column is operated under pressure then dissolved air in the WPA may not come out of solution and cause problems with flow through the column. Alternatively the column could be operated in upflow mode but at a sufficiently high velocity to pack the bed at the top of the column.

- Column size is dictated by the volume of acid treated and the height to diameter ratio requirement such that:
 - resin volume = 10.4 m^3
 - column diameter = 1.1 m
 - resin bed height = 11 m
- A freeboard above the resin of 1 m should be allowed, for bed expansion, this gives an overall column height of 12 m.
- If the column is constructed of GRP it should be flanged every 2 m for ease of erection and strength.
- Resin support is on wedge slot nozzles, pitched every 0.225 mm.
- The number of columns required is two, this allows for one column loading while the other column is washing and eluting.
- The estimated cost for each of these columns is £10300 allowing for; GRP construction, flanges, manhole access and distributors and nozzles.

Figure A6-2 Schematic process flowsheet for Cd removal from WPA
using fixed bed ion exchange contactors.



Other equipment required will be wash water and eluant storage tanks, HCl makeup storage tanks and associated pumps. Figure A6.2 shows the schematic process flow-sheet incorporating these items. The unit costs for each of these items has been estimated and is shown in Table A6.1 along with the factors necessary to estimate the installed cost of these units.

Table A6.1
Estimate of capital cost of a fixed bed ion exchange
process for removing cadmium from 1000 m³/day of WPA.
(1988 prices)

ITEM No.	1	2	3	4
DESCRIPTION	Loading Column	Wash Water Tank	Eluant Tank	HCl Storage Tank
NUMBER	2	1	1	1
SIZE	D = 1.1 m H = 12 m	14 m ³	20 m ³	54 m ³
MATERIALS	GRP	Polyprop.	Polyprop.	Polyprop.
UNIT COST	10300	2000	5000	31800
UNIT COST (cs basis)	6880	1700	4200	26500
FACTORS FOR				
MATERIALS	1.5	1.2	1.2	1.2
ERECTION	0.16	0.20	0.07	0.06
PIPING	1.64	1.83	1.46	1.01
INSTRUMENTS	0.77	0.60	0.34	0.39
ELECTRICAL	0.10	0.15	0.10	0.08
CIVILS	0.22	0.28	0.22	0.18
BUILDINGS	0.55	0.06	0.05	0.04
LAGGING	0.25	0.18	0.12	0.08
TOTAL FACTOR	5.19	4.50	3.56	3.04
ESTIMATED INSTALLED COST	71400	7650	14950	80600

Table A6.1 cont.

Estimate of capital cost of a fixed bed ion exchange
process for removing cadmium from 1000 m³/day of WPA.
(1988 prices)

ITEM No.	5	6	7
DESCRIPTION	Wash Water	Eluant	HCl Hose
	Pump	Pump	Pump
NUMBER	2	2	2
SIZE	0.75 kW	0.75 kW	1" hose
MATERIALS	CrMo StSt	CrMo StSt	Butyl Rubber
UNIT COST	500	500	2000
UNIT COST (cs basis)	250	250	2000
FACTORS FOR			
MATERIALS	2	2	1
ERECTION	0.3	0.3	0.3
PIPING	1.83	1.83	1.83
INSTRUMENTS	0.8	0.8	0.8
ELECTRICAL	0.8	0.8	0.8
CIVILS	0.28	0.28	0.28
BUILDINGS	0.68	0.68	0.68
LAGGING	0.18	0.18	0.18
TOTAL FACTOR	6.87	6.87	5.87
ESTIMATED INSTALLED COST	3400	3400	23500

The cost of the initial resin fill for both columns can be estimated if resin cost is assumed to be about £4000 per tonne and the bulk density is 850 kg/m³ the cost per cubic metre is £3400. Since the total resin inventory is 20.8 m³ the resin cost will be £70700.

The capital cost of the fixed bed process is then estimated to be:

Plant items = £204900

Resin inventory = £ 70700

Total capital cost = £275600

C. Moving packed bed process

The design of the moving packed bed process is based on the results of the experimental work performed using a continuous, counter-current packed bed of C264 resin to remove cadmium from WPA. The following assumptions have been used in coming to a process design.

- resin bed is packed such that expansion of the bed is not possible during acid upflow through the bed.
- eluted resin Cd concentration = 0 mg/g.
- acid to resin volumetric flow ratio = 4:1.
- elution of resin in a separate column using 5M HCl.
- 0.25 BV of resin transferred every 15 minutes for elution
- eluant flow rate = 4 elution BV/hour.

A possible process using a moving packed bed scheme is shown in the schematic diagram in Figure A6.3. Each stage of the operation of the process is shown in the Figure.

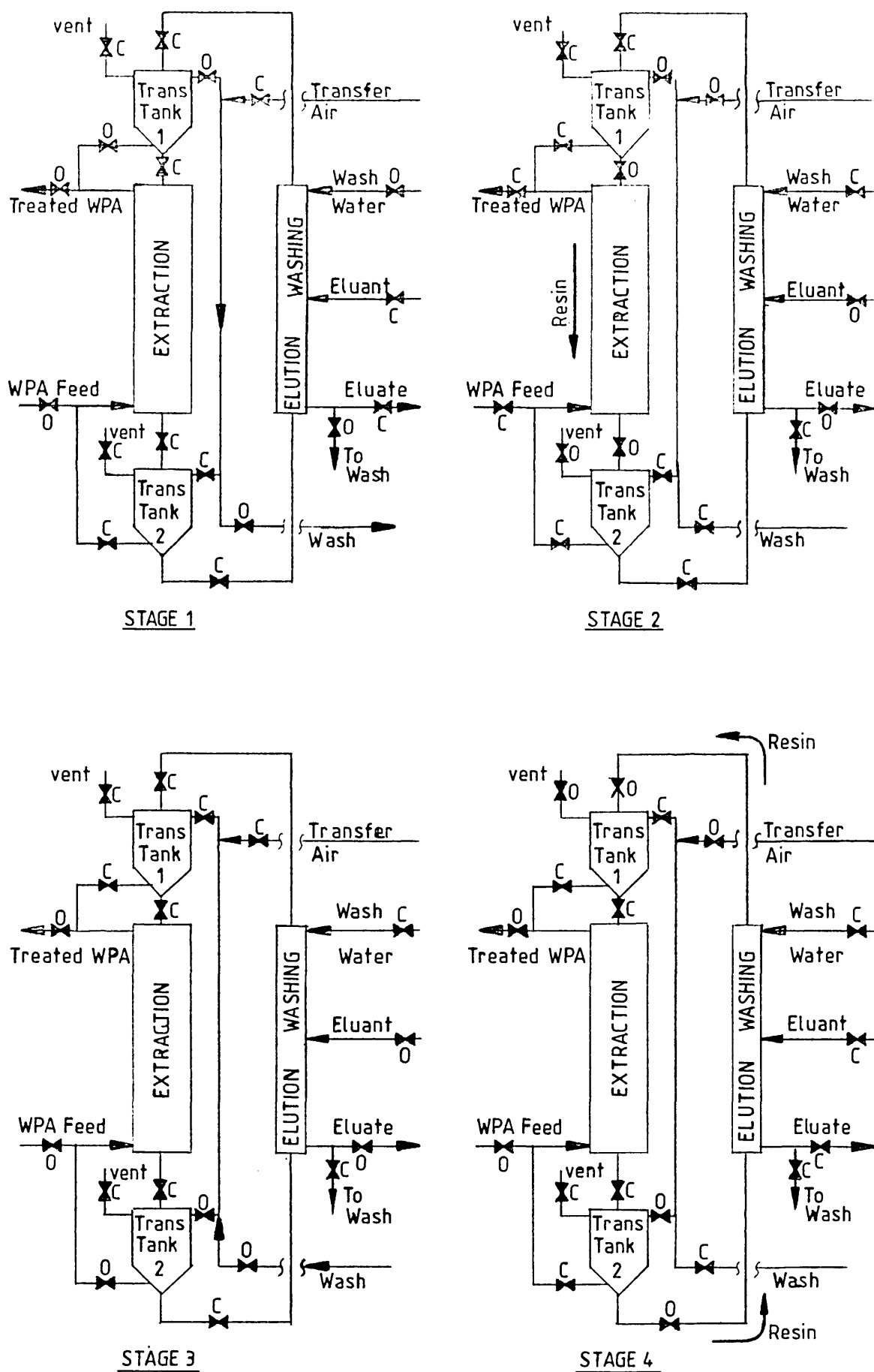
During Stage 1 the following occurs:

- cadmium is extracted from the WPA in the extraction column.
- some of the treated acid is passed upwards through the resin in transfer tank 1 (TT1) to displace the wash water back to the wash water tank (WWT).
- eluant flow to the elution column is temporarily stopped so that wash water can be used to push the eluant in the resin voids down the elution column into the next batch of resin to be eluted.
- wash water is collected from off the bottom of the elution column in the WWT.
- Time for this stage to proceed is 5 minutes per cycle.

During Stage 2:

- flow of acid to the extraction column is temporarily stopped to allow resin transfer to occur.
- fresh eluted resin is pushed out of TT1 into the

Figure A6.3 Operation of moving packed bed contactor system.



- extraction column by compressed air applied to TT1
- simultaneously an equal volume of loaded resin is pushed off the bottom of the loading column into TT2.
- wash water flow to the elution column is stopped and eluant pumped to the elution column and eluate is collected off the bottom of the column in the eluant tank.
- The initial eluate coming off the column at this stage could be sent to the cadmium recovery column for removal by anion exchange.
- Time for this stage to proceed is 2.5 minutes per cycle.

During Stage 3:

- The WPA present in the voids in the resin in TT2 is displaced off the bottom of TT2 by wash water and the WPA routed to the column feed stream.
- Elution of the resin in the elution column continues.
- Time for this stage to proceed is 5 minutes per cycle.

During Stage 4:

- The loaded resin in TT2 is pushed up into the elution column by compressed air.
- The washed eluted resin at the top of the elution column is pushed off into TT1 by the resin entering the bottom of the elution column.
- Time for this stage to proceed is 2.5 minutes per cycle.

The cycle of operation repeats at this point with the return to Stage 1 of the process.

The sizes of the various process items required for this scheme are given in Table A6.2. If the extraction column size is such that the resin bed volume is 10.4 m^3 , and with a column diameter of 1.1 m the column height would be about 11 m. The acid feed and treated acid streams from the extraction column would be taken through distributors comprising wedge slot nozzles. The column construction would need to include flanged sections to ease construction and vessel strength. The volume of the transfer tanks needs to be sufficient to contain the volume of resin transferred per cycle. The volume of the elution column needs to be twice the volume of the resin transferred per cycle to allow for resin washing in the top portion of the column. The total volume of resin in the system is then one bed volume (BV) in the extraction column, 0.25 BV in either

of the transfer tanks and 0.5 BV in the elution column making 1.75 BV of resin in total (18.2 m³). At a cost of £3400/m³ the resin inventory is worth £62000.

Table A6.2

Estimate of capital cost of a moving packed bed ion exchange process for removing cadmium from 1000 m³/day of WPA.
(1988 prices)

ITEM No.	1	2	3	4	5
DESCRIPTION	Extraction	Elution	Transfer	Wash Water	Eluant
	Column	Column	Tanks 1&2	Tank	Tank
NUMBER	1	1	2	1	1
SIZE	D = 1.1m H = 11 m	D = 0.78m H = 11 m	3.1m ³	5m ³	5m ³
MATERIALS	GRP	GRP	GRP	Polyprop.	Polyprop.
UNIT COST	9590	7900	3400	720	720
UNIT COST (cs basis)	6390	5270	2270	600	600
FACTORS FOR					
MATERIALS	1.5	1.5	1.5	1.2	1.2
ERECTION	0.16	0.16	0.30	0.20	0.20
PIPING	1.46	1.46	1.83	1.83	1.83
INSTRUMENTS	0.77	0.77	0.80	0.60	0.60
ELECTRICAL	0.10	0.10	0.15	0.15	0.15
CIVILS	0.22	0.22	0.28	0.28	0.28
BUILDINGS	0.55	0.55	0.68	0.06	0.06
LAGGING	0.25	0.25	0.30	0.18	0.18
TOTAL FACTOR	5.01	5.01	5.84	4.50	4.50
ESTIMATED					
INSTALLED COST	32000	26400	26500	2700	2700

Table A6.2 cont.

Estimate of capital cost of a moving packed bed ion exchange
process for removing cadmium from 1000 m³/day of WPA.
(1988 prices)

ITEM No.	6	7	8	9
DESCRIPTION	HCl Storage	Wash water	Eluant	HCl Hose
	Tank	Pump	Pump	Pump
NUMBER	1	2	2	2
SIZE	54 m ³	0.9 kW	0.6 kW	1" hose
MATERIALS	Polyprop.	CrMo StSt	CrMo StSt	Butyl Rubber
UNIT COST	31800	580	380	2000
UNIT COST (cs basis)	26500	290	190	2000
FACTORS FOR				
MATERIALS	1.2	2.0	2.0	1.0
ERECTION	0.06	0.3	0.3	0.3
PIPING	1.01	1.83	1.83	1.83
INSTRUMENTS	0.39	0.80	0.80	0.80
ELECTRICAL	0.08	0.80	0.80	0.80
CIVILS	0.18	0.28	0.28	0.28
BUILDINGS	0.04	0.68	0.68	0.68
LAGGING	0.08	0.18	0.18	0.18
TOTAL FACTOR	3.04	6.87	6.87	5.87
ESTIMATED INSTALLED COST	80600	3990	2600	23400

The total capital cost for the moving packed bed process is
estimated from the above Table and resin cost to be:

Plant items = £201000

Resin inventory = £62000

Total capital cost = £263000

D. WPA pretreatment and Eluant regeneration

The rest of the process items that are required are shown in Figure A6.1, these are assumed to be the same no matter what the choice of extraction process.

Pretreatment of the WPA stream is required before extraction of cadmium can be achieved. The pretreatment step is required to reduce the calcium concentration of the acid, this will be achieved by precipitating it out of solution as calcium sulphate. It is assumed that the amount of sulphuric acid required will be about 5% by volume of the feed WPA stream. The calcium sulphate crystals formed will be separated in a clarifier; an upflow rate of about 1 m/hour and a residence time of over 2 hours are assumed for the purposes of deciding on an approximate size for this unit. Sludge from the clarifier could be sent to the filters that are used for filtering gypsum (calcium sulphate) from the WPA during its manufacture. In this way WPA present in the sludge would be recovered and returned to the process.

Eluant regeneration would be required to recover the cadmium present in the eluate from the Duolite C264 elution column, this would then allow the eluate to be disposed of safely after neutralisation or returned to the eluant tank for further use. Regeneration of the eluant can be achieved by passing the HCl eluate through a bed of strong base ion exchange resin (Duolite A161 was found to be most suitable). This resin can be successfully be eluted using water; cadmium present in the eluate water can be precipitated out of solution by raising the pH to allow the formation of cadmium hydroxide. This precipitate is assumed to settle at about 1 m/hour in a suitable clarifier. The supernatant from the clarifier could be returned as eluant for the loaded A161 resin.

The size and estimated costs for these process items for a 1000 m³/day WPA throughput are given in Table A6.3. The assumptions used in deciding on the size of the eluant regeneration resin columns are given below.

- 0.5 kg Cd/hour removed from the WPA, this same amount must then be removed from the eluant stream.
- Cadmium concentration in the eluate stream reaches 150 g Cd/m³, this means that 3.3 m³/hour of eluate must be treated.

- The column throughput is 4 BV/hour, this means that one bed volume = 0.83 m^3 .
- Cadmium breakthrough after 10 BV of throughput.
- Column lasts for 2.5 hours before needing elution.
- Eluted with 4 BV of supernatant from the cadmium hydroxide clarifier at 4 BV/hour.
- Cadmium content of the eluate = 375 g Cd/m^3 .

Table A6.3

Estimate of capital costs associated with WPA pretreatment and eluant regeneration in a process to remove Cd from $1000 \text{ m}^3/\text{day}$ of WPA. (1988 prices)

ITEM No.	1	2	3	4	5
DESCRIPTION	Pretreatment Clarifier	Al61 Columns	Regen Pump	$\text{Cd}(\text{OH})_2$ Clarifier	Balancing Tank
NUMBER	1	2	2	1	1
SIZE	D = 7.5 m H = 3.0 m	D = 0.47m H = 5.0 m	0.6 kW	D = 1.3 m H = 4.0 m	5 m^3
MATERIALS	GRP	GRP	CrMo StSt	Polyprop.	Polyprop.
UNIT COST	21800	2430	380	900	720
UNIT COST (cs basis)	14500	1620	190	750	600
FACTORS FOR					
MATERIALS	1.5	1.5	2.0	1.2	1.2
ERECTION	0.06	0.38	0.30	0.20	0.20
PIPING	1.01	1.83	1.83	1.46	1.46
INSTRUMENTS	0.19	0.80	0.80	0.60	0.60
ELECTRICAL	0.08	0.15	0.80	0.48	0.15
CIVILS	0.18	0.28	0.28	0.28	0.28
BUILDINGS	0.04	0.68	0.68	0.06	0.06
LAGGING	0.08	0.18	0.18	0.18	0.18
TOTAL FACTOR	3.14	5.80	6.87	4.46	4.13
ESTIMATED INSTALLED COST	45500	18800	2600	3350	2500

The estimated total installed capital cost of the above equipment is £72750. The volume of resin needed for the column is 1.67 m^3 , which at £3400/ m^3 is worth £5660.

The total estimated capital cost of the ion exchange process for removing cadmium from WPA can be calculated for the two different designs of cadmium extractor proposed.

Fixed Bed Process = £354000

Moving Packed Bed Process = £341400

E. Running Cost estimate

The following estimate of the running costs associated with the process are based on the process being in operation for 365 days a year. If allowance is made for an annual downtime period then these costs will be proportionately less.

The major running costs associated with the process will be the cost of sulphuric acid needed for calcium reduction and the cost of hydrochloric acid needed for elution of the C264 resin.

Sulphuric acid required can be estimated assuming that 5% by volume of H_2SO_4 is needed to reduce calcium concentrations to acceptable levels.

- $2.1 \text{ m}^3/\text{hour}$ of sulphuric acid
- If s.g. of $\text{H}_2\text{SO}_4 = 1.84$, then need 3.86 t/hour
- Cost of s.g 1.84 $\text{H}_2\text{SO}_4 = £80/\text{t}$
- Cost of $\text{H}_2\text{SO}_4 = £309/\text{hour}$
= $£2.70 \times 10^6/\text{year}$

Hydrochloric acid requirements can be estimated by assuming that HCl is required to replace the chloride ions tied up with the eluted magnesium, calcium and cadmium ions

- Ca and Mg eluted as CaCl_2 and MgCl_2
- 2.1 kg Ca/hour and 62.6 kg Mg/hour eluted
- need 5.32 kgmol/hour of chloride ions
- equivalent to 194 kg HCl/hour
- Commercial HCl = 36% w/w HCl at £130/t
- Cost of HCl = $£72/\text{hour}$
= $£0.63 \times 10^6/\text{year}$

Total annual running costs will also include labour, maintenance and make-up of lost resin.

Resin loss will be minimal for the fixed bed extraction process as resin is retained within the column. For the moving packed bed system there will be a loss of resin since inevitably some resin will be trapped in valves and crushed during the transfer operations. A value of 5% by volume of resin lost per year would be reasonable for this type of process.

- 18.2 m^3 resin in system, 5% = 0.9 m^3 /year of resin loss.
- At $\text{£}3400/\text{m}^3$, Resin loss = $\text{£}3100$ /year

Maintenance costs can be estimated as a proportion of the mechanical plant cost for the process (usually about 5%). The mechanical plant cost is about 2/3 of the total capital cost which makes maintenance cost about 3.3% of the total plant cost.

- Fixed Bed maintenance = $\text{£}9160$ /year
- Moving Bed maintenance = $\text{£}9030$ /year

The labour requirements for the process would be minimal as it could be almost completely automated. If it is assumed that about half a man-years effort is required to run the process then the labour cost will be about $\text{£}15000$ /year.

The total estimated running cost for the process whether using fixed beds or moving packed beds is $\text{£}3.36 \times 10^6$ /year not including capital repayment costs.

The impact of removing cadmium from WPA on the cost of producing WPA would be to increase the cost of 28% P_2O_5 WPA by about $\text{£}9.2/\text{m}^3$ (equivalent to $\text{£}25.5/\text{t P}_2\text{O}_5$). The current cost of producing WPA is about $\text{£}200/\text{t P}_2\text{O}_5$, therefore cadmium extraction from the acid will increase the cost of the acid by about 13%.

APPENDIX 7

Estimation of errors

The following is an estimate of the errors involved in the determination of resin loading and fractional attainment of equilibrium from experimentally derived data.

1. Resin loading

The concentration of cadmium and other metals on the loaded Duolite C264 resin was determined by using the following equation:

$$\bar{C}_t = \frac{V[C_0 - C_t]}{m} \times 1000 \quad (\text{A7.1})$$

Where: $\bar{C}_t$ = concentration of the metal-ion on the resin at time = t minutes, (mg Metal/kg Resin)
 C_t = concentration of the metal-ion in solution at time = t minutes, (g Metal/m³)
 C_0 = initial concentration of metal-ion in solution at the start of the test, (g Metal/m³)
 m = mass of centrifuged, moist resin, (kg)
 V = volume of solution treated (m³).

The concentration of metal ions in solution was determined by atomic absorption spectrophotometry (AAS). The AAS was calibrated against known standard metal solutions at the start of every batch of analyses and spot checks of the standards were made after every two measurements. The standards and solutions to be measured were treated in the same manner and were each diluted using the same techniques. In this way the error in determination of the concentration of the metals in solution was reduced to less than 2%.

The mass of resin used in each test was determined by preweighing the centrifuged moist resin using a top-pan balance. The moisture content of the resin was quite constant in tests performed where the

dry weight of resin in a number of samples was determined. The estimated error in the weight of centrifuged moist resin was about 3%.

The volume of solution treated was determined by measurement in an appropriately sized measuring cylinder and estimated error in volume was within 1%.

Applying these errors to equation A7.1 the estimated error in the concentration of metal-ion on the resin was determined to be in the order of 9%.

2. Fractional attainment of equilibrium

The fractional attainment of equilibrium on the resin was determined by performing the following calculation:

$$X_t = \frac{\bar{C}_t}{\bar{C}_f} \quad (\text{A7.2})$$

Where: X_t = the fractional attainment of equilibrium at
time = t minutes.

$\bar{C}_f$ = the equilibrium metal-ion concentration on the
resin, (mg Metal/kg Resin).

The same errors apply to the determination of the value of $\bar{C}_f$ as to the determination of $\bar{C}_t$, that is about 9%. This leads to a possible error in the determination of X_t of about 18%. This possible error was reduced by plotting the experimentally determined values of $\bar{C}_t$ against time and drawing a smooth line of best fit through the data points. The values of $\bar{C}_t$ and $\bar{C}_f$ used to calculate X_t were then taken from this graph. The determined values of X_t were then plotted against the corresponding time value and a smooth line of best fit drawn through the points. This curve was then used for the subsequent determination of the particle diffusion coefficient for the experimental system being investigated.

3. Determination of particle diffusion coefficient

The diffusion coefficient for cadmium diffusion within the ion exchange resins tested was determined by using tabulated values (27)

of τ versus X, at the correct value of w for the system, to solve Paterson's approximation (equation 3.11) in the following manner.

(a) Calculate w

$$w = \frac{\bar{C}_m}{CV} \quad (A7.3)$$

Where: m = mass of resin in system (kg)

$\bar{C}$ = concentration of cadmium ions in the resin phase (mg/kg)

V = solution volume in system (m³)

C = concentration of cadmium ions in solution in equilibrium with C, (mg/m³)

(b) Plot X versus τ from tabulated values (27) at the appropriate value of w.

(c) At equivalent values of X determine values of time and τ from the experimentally determined plot of X versus time and the plot of X versus τ (from (b) above) respectively.

(d) Plot τ versus time and draw a straight line of best fit through the points.

(e) Calculate the slope of the graph and use it to calculate the value of the particle diffusion coefficient based on the known resin particle size using the following equation.

$$\text{Slope} = 6 \times 10^{-3} \frac{\bar{D}}{r_o^2} \quad (A7.4)$$

Where: Slope = slope of τ versus time graph (minutes⁻¹)

$\bar{D}$ = particle diffusion coefficient (cm²/s)

r_o = resin particle radius (m)