DESALINATION AND TERTIARY TREATMENT OF WASTEWATER BY CONTINUOUS COUNTERCURRENT ION EXCHANGE UTILIZING SULPHURIC ACID AND LIME AS REGENERATING CHEMICALS

by

BRUCE ALEXANDER HENDRY

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The most patient person was surely the typist, Philippa Coetzee.

bed stages of the CCIX contactor. Improved lime regeneration system stability permits greater anion waste solutions to be attained. This system has not yet been fully developed and its potential and anticipated limitations are discussed.

It is concluded that desalination and tertiary treatment of municipal (domestic) wastewater by the CCIX process using sulphuric acid and lime as regenerants is feasible and economically attractive. Water produced in the pilot plant from humus tank effluent was suitable for many industrial purposes. Further treatment of this water by chlorination and carbon adsorption produced a water meeting all present potability standards. Water quality data are presented in an appendix.

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NOTATION

SYMBOL	QUANTITY DESCRIBED	USUAL UNITS
α_B^A	selectivity factor for ions A and B	-
c	liquid phase concentration	meq/mℓ or
c'	liquid phase concentration of regenerating ion	eq/ℓ
$\bar{c}$	resin phase fixed group concentration or technical volume capcity	"
x,y	ion fractions	-
d	desalination duty	meq/mℓ
D	degree of desalination or conversion	fraction or %
F	fractional attainment of equilibrium	-
K_a, K_b	acid or base equilibrium constants	(as appropriate)
L	liquid phase equivalent flow rate	eq/hr
R	resin phase equivalent flow rate	"
	(or total equivalents of the phase present)	(eq)
V	volumetric flow rate	ℓ/hr
	(or volumes of liquid and resin contacted, V_L, V_R)	(ℓ)
η	CCIX stage efficiency	fraction or %

Subscripts

A,B	ions in a multicomponent system
o, t, ∞	times in a batch contact process
t,b	top and bottom of countercurrent column
n	number of CCIX column stages
f	feed solution
p	product solution
r	regenerant solution
w	waste solution

Superscripts

*	denoting value at equilibrium condition

ABBREVIATIONS

BE	bed expansion
CCIX	continuous countercurrent ion exchange
COD	chemical oxygen demand
HTE	humus tank effluent
NIM-CIX	National Institute for Metallurgy - continuous ion exchange (contactor patent)
TDS(TDIS)	total dissolved (inorganic) solids

Various drinking water standards are compared in Appendix 1. As a general guide the T.D.S. of drinking water for a large city should not exceed 500 mg/ℓ (W.H.O. standard) although 250 mg/ℓ may be a preferred limit. Smaller communities in arid areas such as South West Africa apply less stringent standards out of necessity. The T.D.S. of various water supplies and corresponding wastewaters are given in Table 1.1.

TABLE 1.1

AVERAGE TOTAL DISSOLVED SOLIDS (T.D.S.) IN VARIOUS WATER SUPPLIES AND WASTEWATERS

	PERIOD	TOTAL DISSOLVED SOLIDS mg/ℓ			REF.
		SUPPLY	WASTE WATER	INCREASE	
Cape Town:					
Athlone - treatment works	1980	50-100	773	673	4
- reclamation plant	1980	50-100	914	814	4
Cape Flats	1980	50-100	692	592	4
Mitchells Plain	1980	50-100	500	400	4
Milnerton	1976*	50-100	1200	1100	6
Milnerton	1980	50-100	750	650	-
Windhoek - reclamation plant	1971-75	170	640	470	1
Walvis Bay	1980*	900	2200	1300	5

Note: * Saline groundwater infiltration

The percentage by which existing fresh water supplies can be incremented before exceeding a specified maximum salinity in any part of the overall supply system has been calculated for the situations above and presented in Table 1.2. In most cities, especially those being supplied from more than one existing fresh water source it would not be possible to mix evenly the reclaimed sewage water with all of the fresh water. The reclaimed water may be supplied to only one part of the city. It can be generally assumed that all the effluent is treated in one sewage works, however.

TABLE 1.2

MAXIMUM INCREMENT OF RECLAIMED WATER (AS % OF TOTAL EXISTING SUPPLIES) BEFORE EXCEEDING SPECIFIED BLENDED WATER SALINITY

	CAPE TOWN	WINDHOEK	WALVIS BAY
T.D.S. of fresh water (mg/ℓ)	100	170	900
Salinity increase (mg/ℓ)	600	640	600
Specified maximum blended water T.D.S. (mg/ℓ)	500 250	500	1000
Maximum increment if all of the fresh water is used for blending	67% 25%	51%	17%
Maximum increment if half of the fresh water is used for blending	44% 14%	-	-

From Table 1.2 it may be seen that Cape Town could not increment its present water supplies by more than 67% with reclaimed water before exceeding the W.H.O. standard of 500 mg/ℓ T.D.S. in the blended water but by only 25% if a standard of 250 mg/ℓ was set. To do this, however, all the fresh water supplies would need to be brought to one point and equally blended together with the increment of reclaimed water. This would be difficult in practice since the various supplies are separated by large distances and feed separate service reservoirs. If only half the fresh water could be blended with reclaimed water (e.g. at one of the larger service reservoirs), the maximum increment would be only 44% for a 500 mg/ℓ standard and 14% for a 250 mg/ℓ standard. In order to recycle more water desalination of the reclaimed water would be necessary.

In Cape Town during 1980 152 000 Mℓ of fresh water was treated[4]. (Some of this was sold outside the municipal area.) The Cape Flats wastewater treatment works produced 32 000 Mℓ with a T.D.S. increase of 600 mg/ℓ. If all of this were reclaimed it would provide an increment of at least

21% and Table 1.2 shows that a T.D.S. of 250 mg/ℓ would be exceeded unless almost all the water supplies were evenly blended. Consequently, if only one or two fresh water sources were located where they could be blended with the reclaimed water it would be necessary to apply some desalination in order to recycle all the available effluent. On the other hand, an alternative to the expense of desalination would be to provide the civil works and incur the operating costs to divert more of the fresh water sources for blending and redistribute them again. The choice depends mainly upon the relative costs and benefits to be derived from the alternatives. The CCIX technology is now available to perform the desalination reliably. This was shown by Giddey[6] and is reconfirmed in the developments reported in the present volume.

1.2 CONTINUOUS COUNTERCURRENT ION EXCHANGE (CCIX) FOR DESALINATION

In the case of Windhoek, because of low sewage return flows resulting from high consumptive use of water, it is unlikely that the limiting increment of 51% shown in Table 1.2 could be attained at all.

The development of the CCIX process for wastewater desalination using nitric acid and ammonia as regenerants has been reported in detail by Giddey. In the case of Walvis Bay although the T.D.S. increase is high (1300 mg/ℓ) about 700 mg/ℓ reduction can be envisaged by lime softening since the fresh water supply is very hard. Possible improvement in the sewage collecting network further eliminating saline ground water infiltration would also help to offset the accumulation of salt resulting from recycling. Also in Walvis Bay it would be feasible to combine all the water sources in one existing reservoir and obtain even blending. The result is a highly flexible process in which various operations such as recovery of by-products can be efficiently achieved.

Choice of desalination process

In those cases where desalination is required, between 300 and 1000 mg/ℓ T.D.S. must be removed from the reclaimed water. This desalination duty falls well within the range in which ion exchange is usually more economical than alternative desalination processes such as evaporation or reverse osmosis. The removal of salt from the water supply system is in most cases best achieved by desalinating the reclaimed water since it is the smaller volume and because removal of organic matter is also achieved which reduces the problem of attaining potable water standards for chlorinated hydrocarbons and other organic-related parameters.

CHAPTER 2

THEORETICAL BACKGROUND AND DESCRIPTION OF THE CCIX DESALINATION PROCESS

2.1 INTRODUCTION

A thorough study of ion exchange fundamentals and applications has been presented by Helfferich[9] while Giddey[6] has covered the mass transfer performance of CCIX columns in comprehensive detail. Only those aspects of the theory which are of direct importance in understanding the results presented in this report are discussed in this chapter.

2.2 ION EXCHANGE REACTIONS FOR DESALINATION USING SULPHURIC ACID AND LIME AS REGENERANTS

The desalination process is carried out in four separate contacting columns linked as shown in Figure 2.1. Additional columns can be included to allow conversion of waste solutions to useful by-products or recovery of regenerant chemicals.

2.2.1 Cation and anion loading reactions.

Neutral salts such as sodium chloride and magnesium sulphate are converted into their corresponding strong acids using a strong cation resin in the hydrogen form:

$$R\text{-}H + NaCl \rightleftharpoons R\text{-}Na + HCl \qquad (2.1)$$

and in the case of divalent cations such as calcium or magnesium:

$$2R\text{-}H + CaCl_2 \rightleftharpoons R_2Ca + 2HCl;$$
$$2R\text{-}H + MgSO_4 \rightleftharpoons R_2Mg + H_2SO_4.$$

The cation resin (Zerolit 625) has a total capacity of 1,6 meq/mℓ while the feedwater used in this work (humus tank effluent) has an average ionic strength of 0,014 N. Therefore one litre of resin can treat up to 114 litres of feedwater.

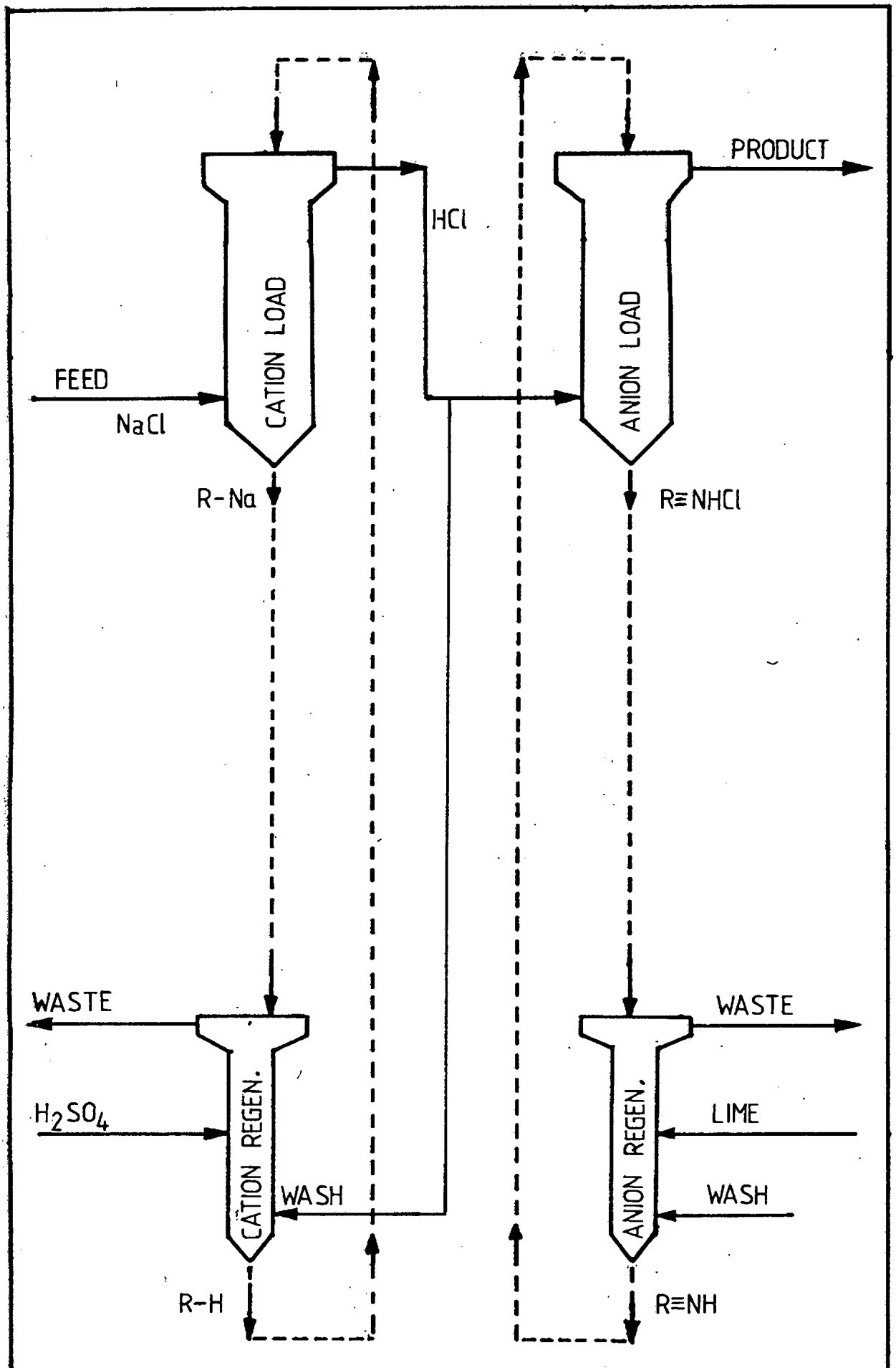

FIGURE 2.1 FOUR-COLUMN CCIX DESALINATON PLANT

$$2R - Na + H_2SO_4 \rightleftharpoons 2R - H + Na_2SO_4 \qquad (2.3)$$

or in the case of calcium form resin:

$$R_2Ca + H_2SO_4 \rightleftharpoons 2R - H + CaSO_4 \qquad (2.4)$$

The solubility of $CaSO_4:2H_2O$ in water is 0,025N[14]. This gives a saturation ion product of $0,22*10^{-3}(mole/\ell)^2$ which is almost always exceeded on account of the high sulphate ion background in regenerating solutions of sulphuric acid. However, precipitation does not necessarily occur immediately because supersaturated solutions of calcium sulphate are metastable and remain so for long periods. Kunin[10] has pointed out that this is the main reason why sulphuric acid can be widely used (although with care) in fixed bed regeneration. Were this not the case only dilute solutions and an uneconomical excess of regenerant solution would be necessary to avoid precipitation which would have serious consequences in a fixed bed operation. Nucleation is promoted by high supersaturation levels, agitation, presence of solid surfaces and by steep concentration gradients[11] such as may occur along the diffusion pathway of calcium ions from the resin beads into the bulk solution. (Precipitation of $CaSO_4$ within the pores of the ion exchanger is unlikely in normal operation because the sulphate ion is largely excluded by the Donnan effect - see Sections 2.3.2 and 2.3.4.

Certain operating conditions will lead to precipitation and scaling of equipment surfaces, ultimately causing blockage of stage separator orifices and failure of the regeneration column. Controlled precipitation, (e.g. by seeding) would have the beneficial effect of promoting the regeneration reaction by removing one of the reaction products. Control of precipitation would be aimed at avoiding supersaturation conditions and at producing fine crystals of $CaSO_4$ which could be washed out of the fluidized beds. This is discussed further in Chapter 4. Following regeneration the resin is washed with decationized water (or with feedwater) in order to desorb sulphuric acid from the pores. The resin is then ready for the next loading cycle.

thus easily carried out of the column but can be settled before discharging or reusing the waste solution.

After rinsing with desalinated water (anion load column product) to desorb electrolytes from the resin pores and physically to disengage lime and organic sludge from the voids, the regenerated anion resin is ready for the next loading cycle.

2.3 RESIN PROPERTIES AND ION EXCHANGE CONTACTING

2.3.1 Ion exchange capacity

The ion exchange resin matrix contains a fixed number of ionogenic groups. This results in a well defined capacity for attracting counter-ions (ions of opposite charge to the active groups on the ion-exchanger). The "technical volume capacity" is expressed as equivalents per litre (or meq/mℓ) of free settled resin. This quantity is affected by the swelling effects due to the nature of the counter-ions present in the ion exchanger and factors such as size distribution of the resin beads. The capacity is therefore usually referred to a specified grading and ionic form of the resin. The advantage of this measure is that it can be easily determined in the laboratory for any form or batch of resin.

Effective working capacity. Because of ion exchange equilibrium limitations it is usually uneconomical to regenerate the strong cation resin completely since large excesses of regenerant are required to do this. Thus after regeneration a significant fraction of the resin's capacity may still be occupied by counter-ions other than the regenerating ion (H^+). Calcium usually remains on the regenerated cation resin even though most of the other cations are removed. That portion of the resin capacity which is in the hydrogen form after regeneration is the "effective working capacity" since it is usually the only portion available for loading ions from the feedwater. Any improvement in efficiency of the regeneration process will result in a greater effective working capacity, which will allow less resin to be cycled for a given desalination duty.

2.3.3 Expression of resin and liquid compositions in terms of ion fractions

Ionic concentrations are expressed in equivalents per litre or milli-equivalents per millilitre using the symbol C for the liquid phase and $\overline{C}$ for the resin phase. Because $\overline{C}$ is the fixed ion exchange capacity of the resin and C remains constant in a liquid stream in which ions are exchanged stoichiometrically, the ion fractions, y for liquid phase and x for resin phase, can be used to indicate the compositions:

$$y_A = \frac{C_A}{C_A + C_B + \ldots} = \frac{C_A}{C} \qquad (2.6)$$

$$x_A = \frac{\overline{C}_A}{\overline{C}_A + \overline{C}_B + \ldots} = \frac{\overline{C}_A}{\overline{C}} \qquad (2.7)$$

for ions A, B, etc.

Hence in a two component system of ions A and B, $x_A = 1 - x_B$; $y_A = 1 - y_B$.

2.3.4 Ion exchange equilibria and selectivity

The equilibrium of a binary system may be expressed as a separation factor, α:

$$\alpha^{H}_{Na} = \frac{x_H}{y_H} \Big/ \frac{x_{Na}}{y_{Na}} = \frac{x_H(1-y_H)}{(1-x_H)y_H} = \frac{1}{\alpha^{Na}_{H}} \qquad (2.8)$$

Hence

$$x_H = \frac{\alpha^H y_H}{1 + (\alpha^H - 1)y_H} \qquad (2.9)$$

Using equation (2.9) the composition, x, of the resin phase in equilibrium with a liquid phase of composition, y, can be calculated if the separation factor is known. The resin phase is usually selective to ions of greater size and valency so that α^{Na}_{H} is > 1 for example.

resin, uptake of anions will proceed to completion and the loading equilibrium is very favourable. No real counter-ions which could compete for the active sites are being removed from the resin during loading. In the regeneration reaction, removal of anions will continue to equilibrium as long as the solution pH is high enough. The hydroxyl ion concentration, which is affected by the solubility of the alkali used and its base strength, clearly influences the equilibrium. In regeneration the anion being removed from the resin phase may remain within the ion exchanger due to sorption and may move the equilibrium to the left in equation (2.5) (section 2.2.3).

Sulphate, phosphate and nitrate ions are even more favourably taken up than chloride and are almost completely removed in the loading column in most situations.

Uptake of organic matter. Equilibrium relationships for organic species on the anion resin have not been studied in any detail owing to the difficulty of isolating pure species for study and analysis. Uptake of pure acids such as butyric and propionic acids has been studied by Kennet[12] but it remains difficult to relate these to the substances in wastewater. Experimental evidence indicates that both uptake and regeneration are favourable in spite of the large molecular sizes of the colour and humic substances involved: removal of C.O.D. from the feedwater has been adequate for most industrial reuse purposes; fouling (irreversible uptake) has not been observed in long term resin use. Because no difficulties were experienced the chemistry and equilibria of the organics have not been studied. However, later work in producing potable water has highlighted the potential advantages of improving the removal of organics by the resin and this is discussed further in Appendix 1.

ion exchanger is smaller so that only a small concentration of co-ion in the pores will result in a greater Donnan potential and electrostatic counter-effect);

(c) valency of the co-ion is increased (the electrostatic counter-effect will be established at lower co-ion concentrations in the ion exchanger).

The exclusion is of importance with the cation resin. In the weak anion resin in contact with a strongly basic electrolyte such as $Ca(OH)_2$ there is no counter-ion on the free base form of the resin and $Ca(OH)_2$ would diffuse freely (as would $CaCl_2$) and be sorbed into the resin pores. Consequently washing of the weak anion resin is a greater problem than washing of the strong cation resin. However, the concentration of $Ca(OH)_2$ in solution at the bottom of the regeneration section of the column is low due to its low solubility. Therefore sorption of $Ca(OH)_2$ is not as great as with NH_4OH which is used in higher concentrations. On the other hand, when using lime, $CaCl_2$ is sorbed by the resin at the top of the regenerating section and desorbed lower down and in the wash section. If washing is incomplete, both $CaCl_2$ and $Ca(OH)_2$ are carried over into the anion load column and desorbed by the final product water thus contaminating it. With only a few washing stages this happens to some extent and although calcium is usually completely removed from the feed water in the cation load column, the final product usually contains up to 20 mg/ℓ of calcium. Because of the effect (c) above, H_2SO_4 is expected to be more effectively excluded from the cation resin than HNO_3. In summary, therefore, there are no additional problems with the wash section of either the cation or the anion regeneration columns as a result of using sulphuric acid and lime as regenerants instead of nitric acid and ammonia. The same number of stages and other conditions which were suitable with the HNO_3/NH_4OH system can be expected to perform as well or better with the new regenerants. The expectation has been confirmed in the present experiments.

2.3.5 Batch contact between resin and liquid phases

Figure 2.5 illustrates on an equilibrium diagram a batch contact process with the cation resin. Liquid of composition y_o and resin x_o are brought together at time t = 0. At any later time, t, the compositions are y_t and x_t and if the system is allowed to reach equilibrium y_∞ and x_∞ correspond to a point on the equilibrium line. If the total equivalents of liquid and

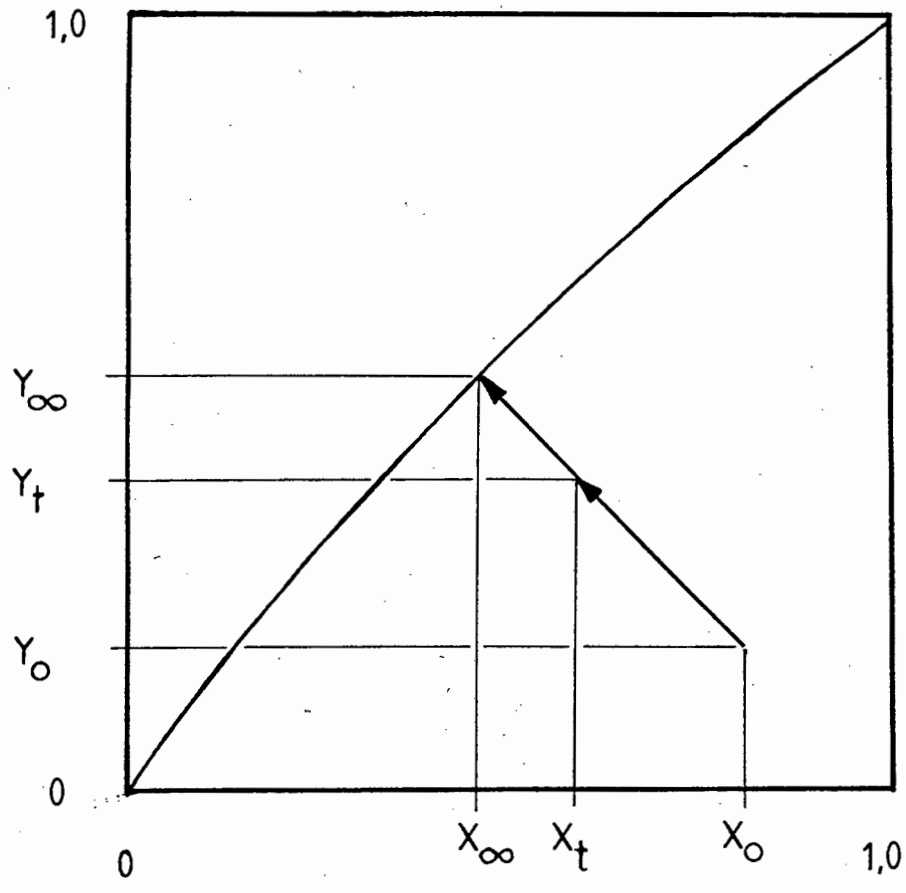

FIGURE 2,5 BATCH CONTACT PROCESS

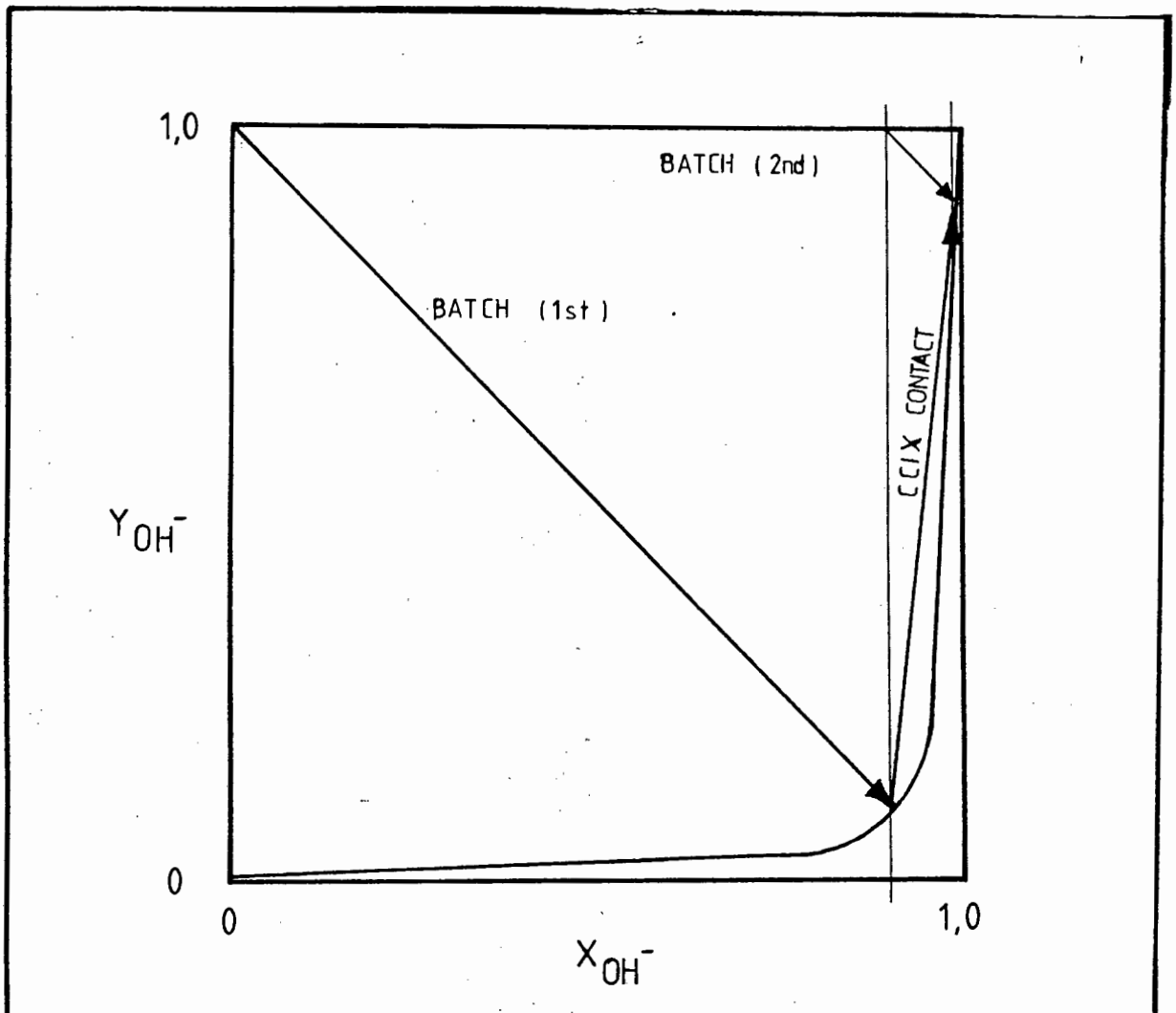

FIGURE 2,6 BATCH REGENERATION OF ANION RESIN

In this way it is possible to achieve a fairly high degree of regeneration of the weak anion resin in a batch contactor. This would incorporate recirculation of the liquid through a settler to remove precipitated organic material as it is formed. This eliminates interference with resin fluidization due to the accumulation of sludge. A CCIX column would be employed only for the washing step (electrolyte desorption). Operating without large quantities of lime and organic sludge its efficiency would be at its best.

In order to obtain maximum conversion of the resin in the regeneration system a small amount of lime could, however, be introduced into the CCIX column. Since most of the regeneration duty is performed in the batch regenerator, the amount of lime needed in the subsequent CCIX column would be small enough not to present as great a fluidization problem as found when all the regeneration must be done in a CCIX column.

2.3.6 Ion exchange kinetics

The batch contact of equation (2.11) and Figure 2.5 can be followed with respect to time by measuring the liquid or resin composition changes. The fractional conversion at any time, t, may be defined:

$$F(t) = \frac{x_o - x_t}{x_o - x_\infty} \qquad (2.12)$$

F(t) approaches unity asymptotically since equilibrium is theoretically never reached. Figure 2.7 shows the kinetic curves for the exchanges of interest in the desalination process. Experimental curves use for x_∞ the constant value reached after a number of hours for a relatively fast exchange or a matter of days for a very slow one.

In general, desorption of electrolytes from the resin pores occurs more rapidly than the ion exchange processes. Cation exchange rates are faster than anion exchange and the larger the exchanging ions the slower the rate. Greater liquid phase concentration of exchanging ion results in faster kinetics. This fact is particularly important when using sulphuric acid to regenerate a calcium form resin. At higher acid concentrations faster exchange results in larger concentration gradients of calcium ions diffusing from the resin beads into the bulk solution as well as the increased sulphate ion concentration. Both of these increase the likelihood of $CaSO_4$ precipitation.

The presence of calcium chloride in the anion regenerant waste solution retards the rate of regeneration. This may be due to one or both of the following:

retarded kinetics. This means that longer regeneration contact times will be needed requiring larger equipment to be used.

It is interesting to note that if the anion resin were loaded with sulphate ions the regeneration reaction product, $CaSO_4$, would precipitate negating both of the above effects (a) and (b). $CaSO_4$ solubility is 0,026 N compared to $Ca(OH)_2$ solubility of 0,05 N. Should, however, $CaSO_4$ in precipitating coat the particles of free lime their rate of solution may be retarded and limit the regeneration kinetics. However, this has not been investigated, since no problems were encountered in the present application.

Ion exchange kinetics in all the concentration ranges encountered in this process of desalination are pore diffusion controlled with the exception of the top (product water) end of the anion load column. Here the acid concentrations fall to very low levels as complete conversion of the liquid phase is approached. In this region film diffusion may begin to limit the rate. Because pore diffusion is the major factor in most of the anion load column stages total concentration changes do not significantly affect the validity of using the kinetic data of Figure 2.7 for the design of contactors (dealt with in Section 2.4.4). In all the other columns total liquid phase concentration is constant and the composition differences do not significantly affect the kinetics.

Because the desorption rates are faster, wash section stage efficiencies are greater than the ion exchange stage efficiencies. Thus the ion exchange stage efficiencies are determined mainly by kinetics and contact time while it is the sorption equilibria which mainly determine the limiting performance of wash stages.

2.4 DESIGN OF CCIX CONTACTORS

2.4.1 Continuous countercurrent contactor operation

Figure 2.8 is a diagram of a fluidized bed CCIX contactor as described by Giddey[6] and used by the present author. A regeneration column with a side stream inlet distributor stage for the regenerant chemical is depicted.

Loaded resin enters the top stage via the enlarged section. This acts partly as a storage hopper and partly as a liquid-resin separator to prevent loss of resin particles in the liquid stream leaving the top of the column.

A well-defined interface between the fluidized resin bed and the leaving liquid is formed since the resin beads have a fairly narrow size distribution (0,5 to 1,2 mm, uniformity coefficient = 1,4). The flow of resin into the top of the column is regulated to restore the required resin inventory after each resin transport operation.

Constant solution concentration and R/L ratio. The feed resin slurry is dewatered before it enters the hopper. Feedwater pulled down with the resin from the bottom of the load column must be separated from the resin before the resin is introduced into the top of the regeneration column. Thus dilution of the regeneration waste solution and unnecessary wastage of feedwater is avoided. (The quantity of feedwater present within the resin pores has a negligible effect under most operating conditions.) In the regeneration column electrolytes sorbed by the resin during passage through the regeneration stages are desorbed in the wash stages and thus remain in the liquid phase. Consequently the liquid phase total concentration is unaltered and the equivalent flow rate, L, is constant within the regeneration section.

Likewise the resin composition is altered stoichiometrically and the resin capacity is constant so that R is constant. Hence R/L is constant in the countercurrent contactor. (In the wash section, of course, the liquid concentration does change and the design approach is somewhat different.)

Cyclic operation and resin transport. Upflow of liquid fluidizes the resin in each stage. At the base of each stage is a multi-orifice separator plate which redistributes the liquid flow and prevents backmixing of resin between stages. Resin is moved downwards in plug flow from stage to stage by temporarily interrupting the liquid upflow and allowing the fluidized resin in each stage to settle followed by withdrawal of an appropriate amount out of the bottom stage. Optical or ultrasonic level sensors may

be employed to measure and control the volume of resin pulled down. After resin has been pulled down upflow is restarted. The upflow period in this cycle may be as short as 20 minutes in a regeneration column or a matter of hours in a load column. The time required for the resin settling and pull-down operations may be from 2 to 5 minutes. The total cycle time thus consists of three distinct periods:

$$\text{cycle time} = \text{upflow time} + \text{settle time} + \text{pull-down time}$$

The average liquid flow rate,

$$V_L = \text{flow during up-time} * \frac{\text{up-time}}{\text{total cycle time}} \qquad (2.13)$$

The average resin flow rate,

$$V_R = \frac{\text{volume of resin pulled down each cycle}}{\text{total cycle time}} \qquad (2.14)$$

2.4.2 Overall material balances

To facilitate ionic material balances the equivalent flow rates of liquid and resin are used: $L = C.V_L$; $R = \overline{C}.V_R$. As pointed out above R/L is set by the average flow rates and concentrations entering the column and remains constant. The resin flow rate depends on cycle time and the resin volume pulled down which in turn depends on the resin inventory of the stages (it is usual to pull down not more than 90% of the inventory of the stage in order to prevent backmixing of the resin). The stage inventory depends on stage volume and resin bed expansion which is determined by the liquid velocity. Thus:

$$BE = \frac{\text{stage volume} - \text{settled resin volume}}{\text{settled resin volume}}$$

and the stage inventory,

$$\text{settled resin volume} = \frac{\text{stage volume}}{BE + 1} \qquad (2.15)$$

Fluidization properties depend on resin bead diameter and density (material, swelling and ionic form), bead size distribution and solution density. Thus it is necessary to measure the bed expansion characteristic for each resin-liquid system. Data applicable to the desalination process are presented in Appendix 4.

From the above discussion it is clear that altering the liquid velocity (column diameter or liquid flow rate) and altering the cycle time will both affect the R/L ratio as will altering the liquid concentration (for example in a regeneration column). In order to maintain a constant R/L ratio a change made to one of these must be accompanied by appropriate changes to one or more of the other parameters. Iterative calculations can be carried out to arrive at optimum column diameters and cycle times for specified values of R/L, resin capacities, liquid concentrations and feedwater flow rates. The resin flow rate in a load column and its corresponding regeneration column must obviously be equal so that each column in a pair must be designed with the other in mind.

2.4.3 Component balance for CCIX contactor.

Figure 2.9 presents a model of a CCIX contactor. The ion fraction of one of the components may be used to follow the process, subscripts t and b referring to the conditions at the top and bottom respectively of the column. From a material balance for one component over the entire contactor:

$$y_b L + x_t R = y_t L + x_b R \qquad (2.16)$$

$$\therefore \quad y_t = y_b + R/L(x_t - x_b) \qquad (2.17)$$

For any stage, n,

$$y_n = y_{n-1} + R/L(x_n - x_{n-1}) \qquad (2.18)$$

between the resin phase and liquid phase at that point is extremely long, i.e. the stages would need to be extremely long, physically, or the liquid flow rate almost zero. In this situation (which could be approached in a practical, though cumbersome, experimental reactor), there is still a well-defined composition profile in the CCIX column as well as in each stage since the process remains a countercurrent contact.

Thus the stage efficiency, η_n, is given by:

$$\eta_n = \frac{x_n - x_{n-1}}{x_n - x_{n-1}^*} \qquad (2.19$$

where x_{n-1}^* is the resin composition which would be in equilibrium with liquid of composition y_{n-1}.

Fractional conversion. The fractional conversion in batch contact, Equation (2.12), has been defined in a similar way and is the actual composition change at any time divided by the maximum change that could occur. The maximum change possible corresponds to the two phases having reached equilibrium, which requires a very long contact time. Equation (2.12) can be rewritten:

$$F(t) = \frac{x_o - x_t}{x_o - x^*} \qquad \text{where } x^* = x_\infty$$

which is the resin composition in equilibrium with y_∞.

Equivalence of batch (F(t) and CCIX $\eta(t)$ for equal-contact times.

By considering the composition profile in a CCIX stage plotted against liquid contact time (which is directly related to the length of the stage through the superficial liquid velocity) it may be seen that the closeness of approach to equilibrium of the composition profiles of two passing phases in a CCIX stage with a given contact time (length) can be directly compared with the closeness of approach to equilibrium to two phases in the batch contact at a corresponding contact time providing that in both cases the

same kinetics apply (e.g. pore diffusion and the concentrations are similar). The analogy has been discussed by Giddey[6] and it has been shown that the stage efficiency $\eta(t)$ with a given contact time, t, in the CCIX stage is equal to the fractional attainment of equilibrium, F(t), in a batch contact after the same time, t:

$$\eta(t) = F(t) = \frac{x_n - x_{n-1}}{x_n - x_{n-1}^*}$$

Hence,

$$x_n = \frac{x_{n-1}\left(F(t) - x_{n-1}^*\right)}{F(t) - 1} \qquad (2.20)$$

The analogy may be illustrated by the composition-time diagrams in Figure 2.11 in which the contact time, t, is proportional to the length of the stage, ℓ. By a suitable scale factor the F(t) versus time curve of a batch contact can be directly related to the composition-length profile and hence the composition change over a CCIX stage. The limiting conditions at t=0 and t=∞ define the scale factor. In Figure 2.11 the assumption is made, for simplicity of the representation, that α in the exchange is 1,0, i.e. x_{n-1_∞} or x_{n-1}^* is equal to y_{n-1} the liquid composition with which it reaches equilibrium in an infinitely long contactor stage. When η=1,0 the liquid and resin composition profiles coincide while the smaller η becomes the further apart they lie.

2.4.5 Stagewise calculations and graphical construction for design of a CCIX contactor

Equations (2.9), (2.18) and (2.20) can now be used to calculate the compositions of the streams entering and leaving any stage for which the contact time is known if a suitable kinetic relationship is available. For example, the steps are stated below and illustrated in Figure 2.12.

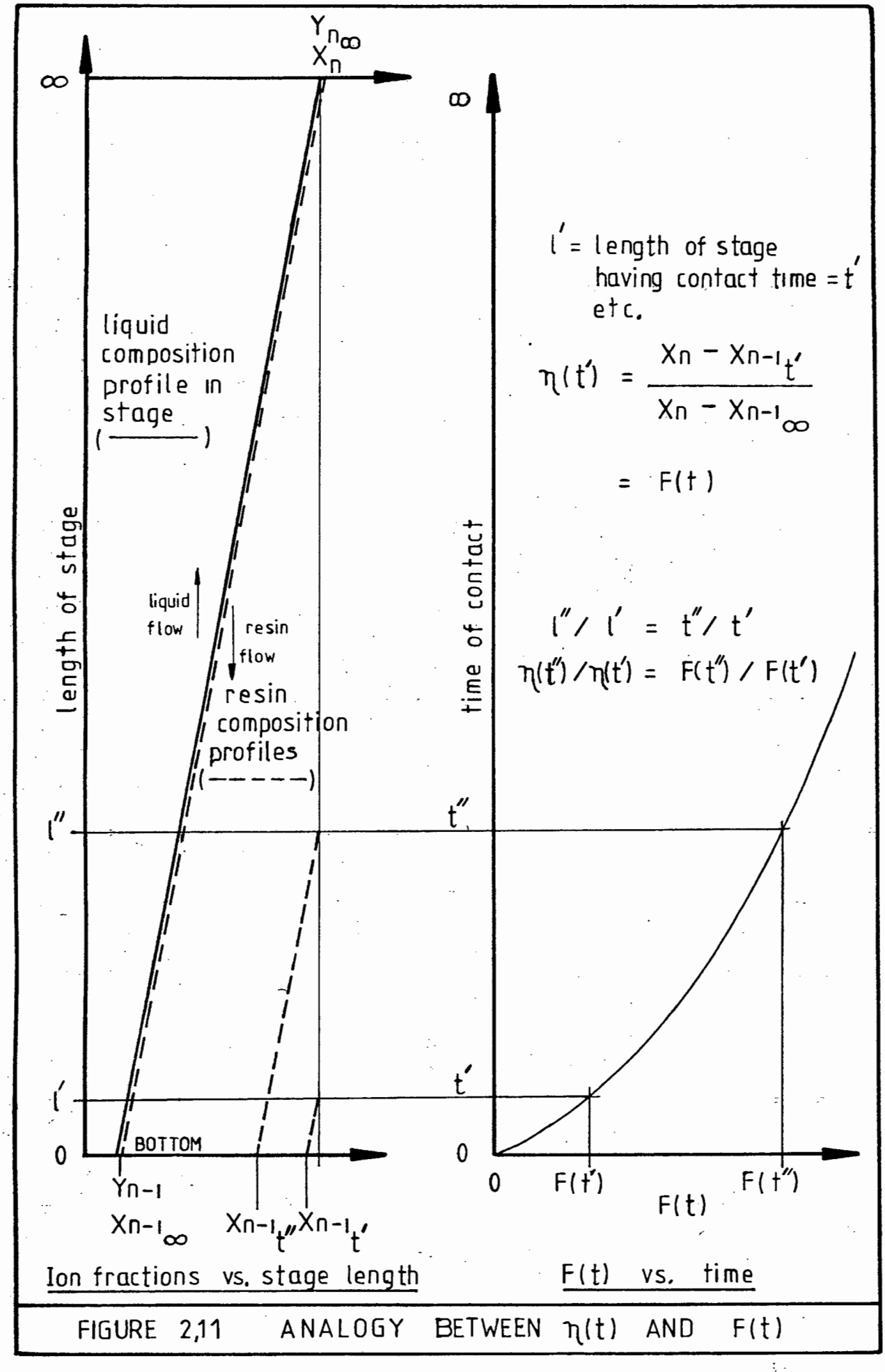

FIGURE 2,11 ANALOGY BETWEEN $\eta(t)$ AND $F(t)$

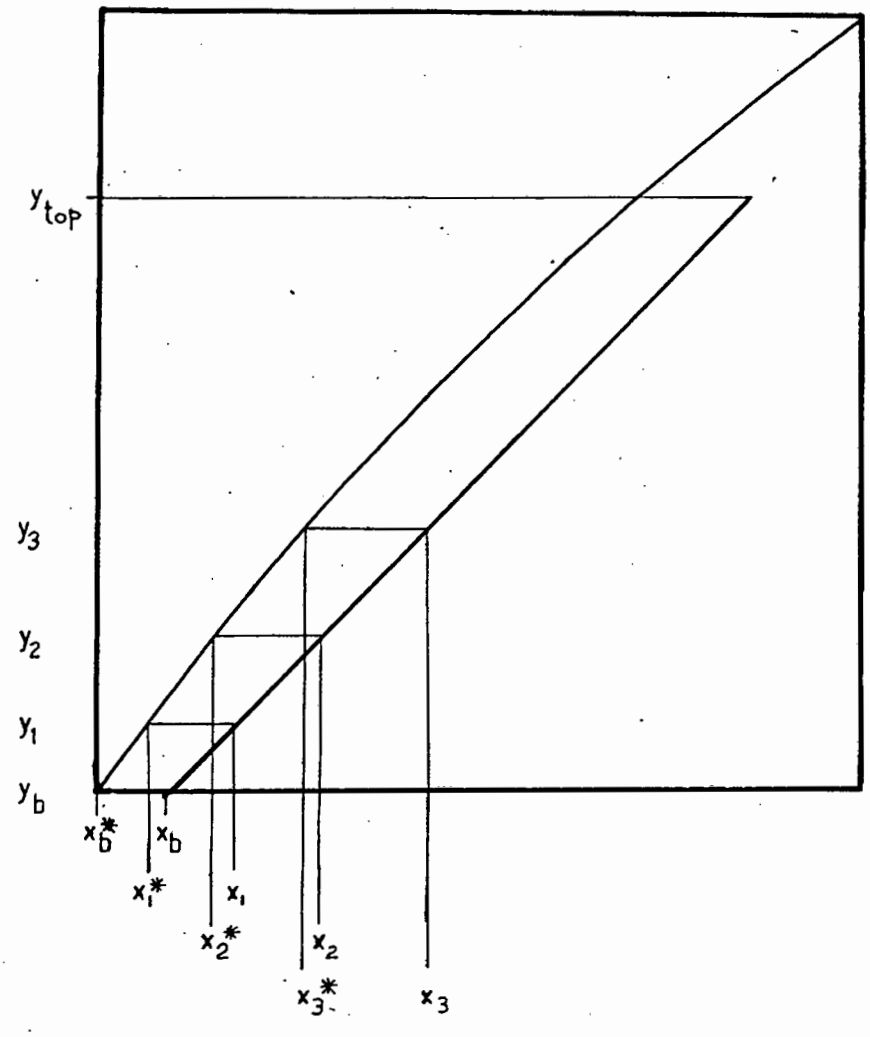

FIGURE 2,12 STAGEWISE CONSTRUCTION

Given x_b, y_b and x_t, y_t (or any three of these and R/L) and the stage efficiency and equilibrium data, α, then

from Equation (2.9) $$x_b^* = \frac{\alpha y_b}{1 + (\alpha-1)y_b}$$

from Equation (2.20) $$x_1 = \frac{x_b\left[F(t) - x_b^*\right]}{F(t) - 1}$$

(F(t) is obtained from an experimental kinetic curve)

concentration and also the cation of most concern in desalination the multi-component problem reduces to attaining the specified removal of sodium. If this is achieved the other ions will automatically be taken care of. In most cases (e.g. at 75% or greater required removal of sodium), calcium and magnesium are completely removed. Thus the calculation of stages for the load column should utilize the sodium/hydrogen equilibrium relation.

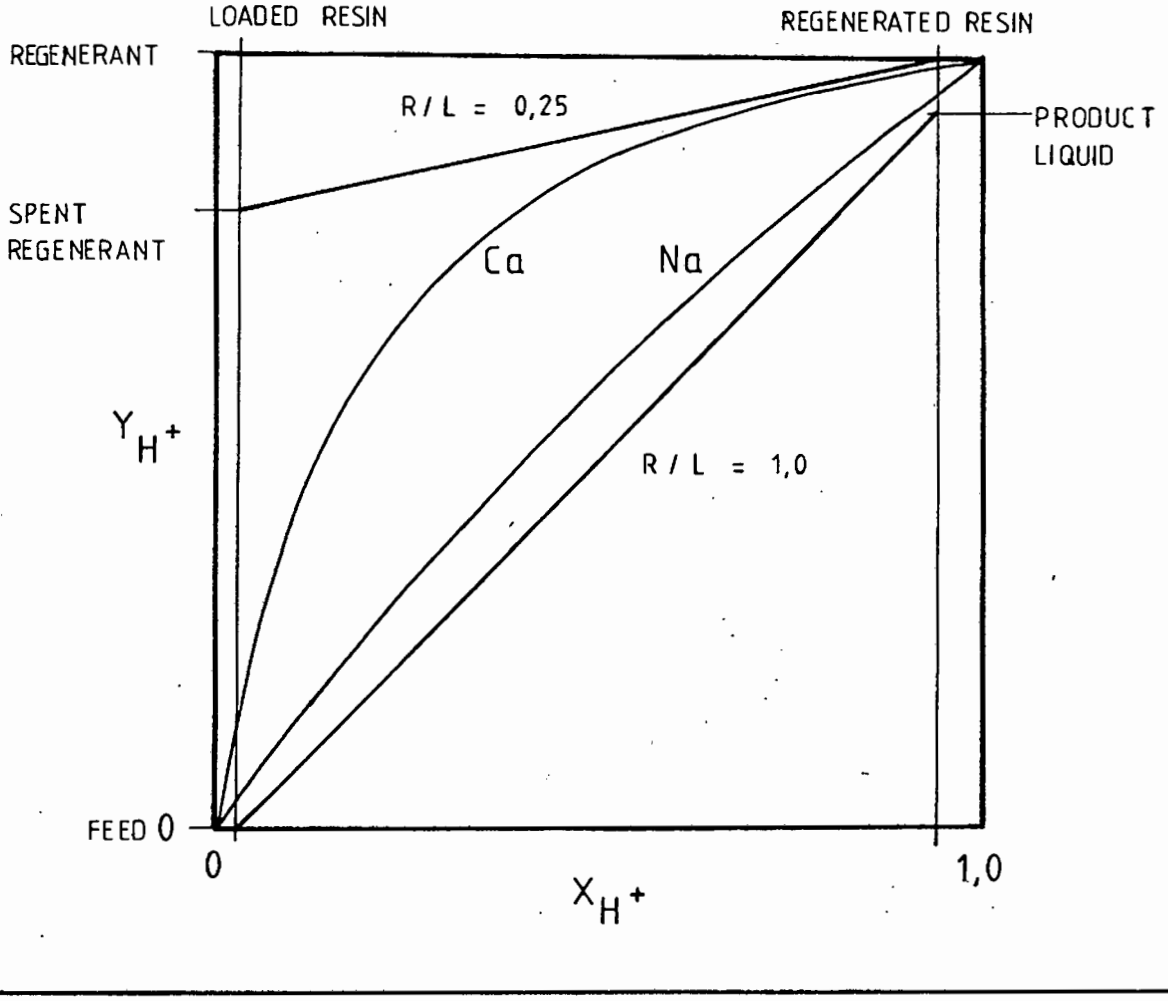

FIGURE 2,13 TWO-COLUMN DESIGN USING α^{Ca} AND α^{Na}

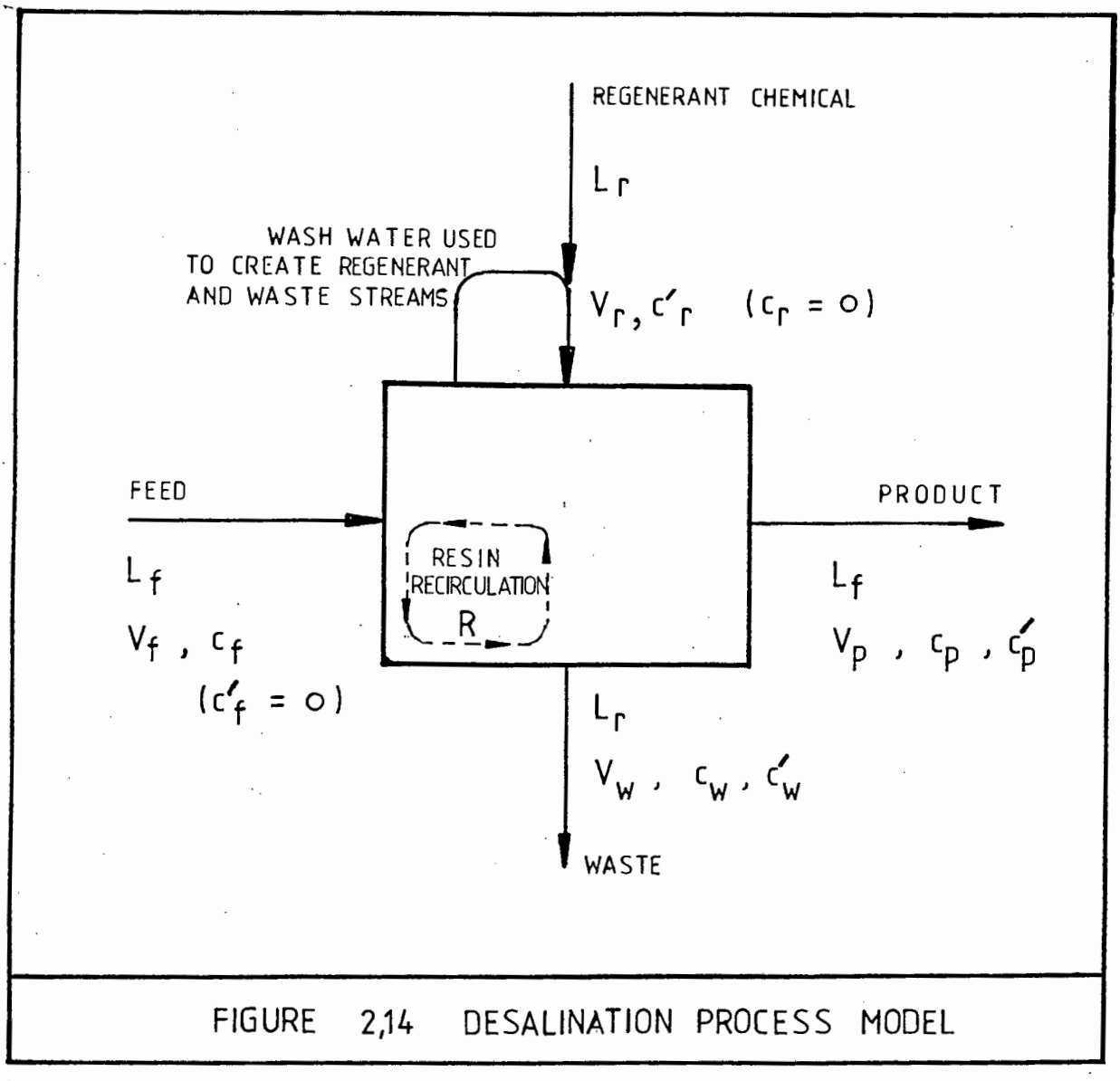

FIGURE 2,14 DESALINATION PROCESS MODEL

chemical. Subscripts refer to the feed, f; product, p; regenerant solution, r; and waste solution, w.

No regenerant ions are present in the feed ($c'_f = 0$) and no exchanging salt ions are present in the regenerating solution ($c_r = 0$). Resin is recirculated within the process with equivalent flow rate R. The following basic statements may be made:

$c_f = c_p + c'_p$, since exchange is stoichiometric

$c_w + c'_w = c'_r$, ditto.

$L_f = c_f V_f$ and $L_r = c'_r V_r$

$= c'_r V_w$, since $V_w = V_r$ because no water enters with the regenerant chemicals.

Certain terms may now be defined:

Degree of desalination, $D = \frac{c_f - c_p}{c_f}$ (2.21)

Desalination duty, $d = L_f D = c_f V_f D$ (2.22)

Concentration factor of salts removed, $\frac{c_w}{c_f}$

Water recovery ratio, $\frac{V_p}{V_f}$

From an overall flow balance:

$$V_p + V_w = V_f \tag{2.23}$$

From a component balance for the exchanging salt ions:

$$c_p V_p + c_w V_w = c_f V_f \tag{2.24}$$

From equations (2.23) and (2.24):

$$\frac{V_p}{V_f} = \frac{c_w/c_f - 1}{c_w/c_f - c_p/c_f} \tag{2.25}$$

Substituing $c_p/c_f = 1 - D$ from Equation (2.21):

$$\frac{V_p}{V_f} = \frac{(c_w/c_f - 1)}{(c_w/c_f - 1) + D} = \frac{1}{1 + \frac{D}{(c_w/c_f - 1)}} \qquad (2.26)$$

Equation (2.26) shows that for a given degree of desalination, D, the water recovery, V_p/V_f, can be increased if the concentration factor can be increased. Also, increasing D or c_f or both (i.e. increasing the desalination duty, d) will result in reduced water recovery unless c_w, the concentration of rejected salt in the waste solution can be increased at the same time. The implication is that where only low waste concentrations can be used, as found in the use of sulphuric acid or lime, the water recovery of the process will suffer.

Now $c_w = \frac{d}{V_w}$ since all the rejected salt ions removed from the feed water appear in the waste solution. Since $V_w = L_r/c'_r$,

$$c_w = \frac{d\ c'_r}{L_r} \qquad (2.27)$$

Equation (2.27) shows that the waste concentration (or c_w/c_f) can be increased by increasing the concentration of the fresh regenerant solution and by increasing the ratio d/L_r.

2.5.2 Effective regeneration R/L and effective working capacity

Since the ions exchanged are transported by the resin flow,

$$V_R = \frac{d}{\overline{c}_{effective}}$$

where $\overline{c}_{eff}$ is the effective working capacity of the regenerated resin (see Section 2.3.1).

Hence $$d = V_R \cdot \bar{c}_{eff}$$

$$= R_{eff}$$

where R_{eff} is the effective equivalent flow rate of exchangeable hydrogen ions on the regenerated resin.

Thus $$\frac{d}{L_r} = \frac{R_{eff}}{L_r} \qquad (2.28)$$

d/L_r or R_{eff}/L_r may be termed the effective R/L ratio (effective stoichiometric ratio) for the regeneration column. It is simply the stoichiometric ratio calculated using the resin's effective capacity instead of the total capacity and its value is determined by the efficiency of the regeneration process and is different under different operating conditions. The value of R_{eff}/L may be used as an indication of the efficiency of the regeneration process. For a given resin flow rate the inverse ratio, L_r/d, gives the ratio of regenerant applied to effective capacity gained or the regenerant consumption factor.

2.5.3 Water recovery and regenerant consumption

It is desirable to attain the highest possible water recovery for two reasons:

(a) if product water is used for washing the regenerated resin it is necessary to minimize its consumption owing to the cost of producing this water;

(b) the waste solution volume must be minimized in order to minimize the cost of evaporting pans or other waste disposal method. Disposal of the waste solutions is a problem in ion exchange desalination because the spent regenerating chemicals must be discarded in addition to the salts rejected from the feedwater. In some situations the feasibility and cost of waste disposal may be the overriding factor in deciding on ion exchange as a treatment system.

Use of feedwater for washing regenerated resin. It can be shown that if feedwater is used to wash the regenerated cation resin instead of product water washing, the increased desalination duty of the cation load column resulting from sorption of feedwater salts and contamination of the load column product water is smaller than the improvement in product water output gained by saving of product water. This is true even at quite high feedwater concentrations. No ill effects on the product water or regeneration efficiency would be expected except where extremely high purity product water is required (80% desalination is typically adequate). Thus feed water wash is economically attractive and recommended for the cation system. However, use of feedwater for anion wash will result in partial loading of the anion resin in the lower wash stages. Consequent reduction of the effective capacity will tend to reduce the performance of the load column. Thus feed water washing in the anion regeneration column is not recommended.

The regenerant consumption factor has a direct effect on the operating cost of the desalination process. This factor is also improved by attainment of high regenerant (or waste) solution concentrations.

2.5.4 Limiting regenerant concentration

The benefit to be gained from higher regeneration concentrations is due to both equilibrium and kinetic advantages with the lowered separation factor α_H^{Ca} being a major one:

Concentration	0,02 N	0,25 N	0,5 N	5,0 N
α_H^{Ca}	12	7,3	6,2	4,7

The effect on α_H^{Ca} due to increased concentration is most marked up to about 0,5 N after which only very high concentrations make further significant change to its value. Extremely high concentrations such as the last one are needed to make the same difference to α_H^{Ca} as the increase from 0,25 N to 0,5 N. It is not practical to use such high concentrations because they lead to the sorption capacity of the resin exceeding the ion

exchange capacity (1,5 N). This means that more water would be needed for the wash than for regeneration. Higher capacity resins must be used in order to allow greater regenerant concentrations if the objective is to reduce water consumption. As long as sorption capacity is proportional to solution concentration (see straight line equilibria in Figure 2.4), the minimum wash water volume will always be a fixed fraction of the volume of resin to be washed if the regenerant is made up of spent wash water only. The minimum wash water consumption is that at which the wash water plus desorbed regenerant is at the same concentration as the regenerant solution from which the sorption took place.

As the solution concentration is increased the volume required to satisfy a given R/L ratio in the regeneration section decreases but the wash water required increases. At about 4,5 N the two quantities are equal and any further increase in concentration may require some spent wash water to be discarded wastefully. (In the reverse situation at lower concentrations more wash water is used than necessary but only means wash stages are more efficient and this is beneficial.) With very high concentrations the number of wash stages needed may become excessive.

Also at higher concentrations a shorter cycle time is necessary to attain a given R/L ratio and the flow of water pulled down out of the column with the resin increases. At some point the average flow out at the bottom of the column will exceed the average upflow which would require raising the upflow velocity to attain a net positive upflow in the column. This would increase bed expansion and reduce resin flow rate which would need a further shortening of the cycle time to correct the R/L ratio. A stage will be reached where the column operation becomes unstable or impossible.

In normal applications there is no incentive to raise waste solution concentrations above about 2 N. However, where very high feed water concentrations are to be desalinated a 2 N waste solution may well result in low water recovery. Higher capacity resins may then allow higher waste concentrations to be practically attained.

CHAPTER 3

PILOT PLANT EQUIPMENT

3.1 INTRODUCTION

The equipment used in the experiments was a 6 kℓ/day pilot plant constructed during 1976/1977 and described in detail by Giddey[6]. Later improvements included microprocessor controlled sequencing of the cyclic operations of the columns and monitoring of the cation and anion product water quality using conductivity and pH instruments. This information was used in a computer control system to adjust automatically plant operation to maintain optimum plant performance. Details of these important improvements and related development of the process have been described in a report to the Water Research Commission[7]. This chapter presents photographs showing the physical arrangement of the various CCIX columns and the pumps, intermediate storage tanks, catchpots and ancillary equipment used during the experiments discussed in this report. Most of this work was carried out using the simple electromechanical timing controls manually adjusted to obtain altered operating conditions. During potability tests where the plant was operated under one condition for long periods automatic control was used toward the later stages when it became available. Details of column operation are given in Figure 2.8 and Section 2.4.1

3.2 GENERAL ARRANGEMENT OF COLUMNS

Table 3.1 gives some of the important dimensions of the columns. Figure 3.1 is a view of the ground floor of the Chemical Engineering Building within which the pilot plant was housed, showing the columns and electromechanical timer boxes to the left of each column. The columns are of "Perspex" and the fluidized resin beds are visible. The 0,5 m long stage segments are clearly distinguished by their flanged connections in-between which the multi-orifice stage separator plates are clamped. At the base of each column is the conical resin outlet and liquid inlet segment leading to the pull-down valve and the resin catchpot surrounded by a metal safety screen. Transport of resin takes place under air pressure of 1,8 bar and the screens are for

TABLE 3.1

PILOT PLANT COLUMN DIMENSIONS

Column	Diameter (ID) mm	No.of 0,5 m stages	Overall height m
Cation load	100	12	7,5
Anion load	200	8	5,5
Cation regen	50	12	7,5
Cation intermediate	50	12	7,5
Anion regen			
Original	50	12	7,5
Later unit	100	12	7,5
Batch regenerator	200	(1 x 1,2 m)	3

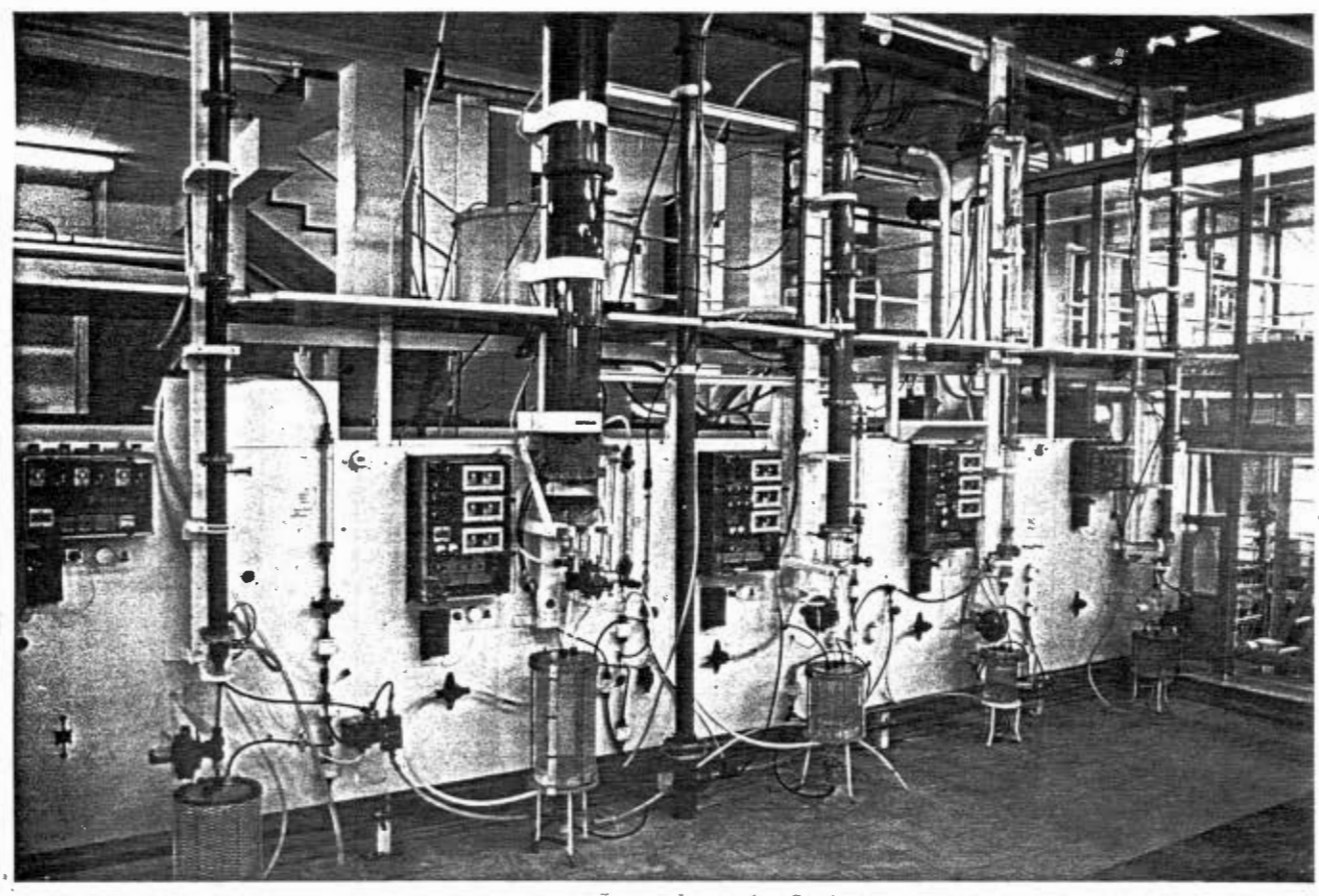

FIGURE 3,1 6 Kl/d CCIX DESALINATION PILOT PLANT

protection in case of failure of the "Perspex" catchpots. On a small plant visual observation of vessel contents was extremely important to the operator since other methods of gauging contents would be too costly and difficult to adapt to so small a scale. Later development of optical resin sensors made automatic gauging and control possible. These inexpensive and extremely versatile devices were constructed in the Chemical Engineering Department.

The single p.v.c. column in the centre is a 75 mm I.D. fixed bed of activated carbon used for final removal of organics ("polishing") from the ion exchange plant product water for the production of potable water.

Immediately to the left of each load column are 25 mm diameter stand-pipes which are connected to the diaphragm head positive displacement feed pump and to the liqiud inlet valve and thence to the base cone of the column. These stand-pipes are provided with overflows (back to their respective feed tanks) about 3 m above the top of each column. These serve to:

(a) release flow from the pump when the column inlet valve is closed during a resin pull-down sequence;
(b) provide some damping of the pulsating flow from the single head pump.

3.3 FEED PUMP

Figure 3.2 is a view of the feed pump. Each head has independently adjustable manual stroke control. No.1 head draws humus tank effluent from the day tank and delivers it to the cation load column via the stand-pipe, rotameter and inlet valve. No.2 head draws from the cation product water intermediate storage tank and delivers to the anion load column. No.3 head draws anion product water from the storage tank and delivers it to the sandfilter and chlorine contact tanks in sequence. Another diaphragm pump (not shown) delivered 0,6 kℓ/day of disinfected water to the carbon column from which the product water was again led into a final chlorination contact tank. Excess filtered and chlorinated water was discharged to waste as the carbon column used was designed to treat only a portion of the CCIX plant flow.

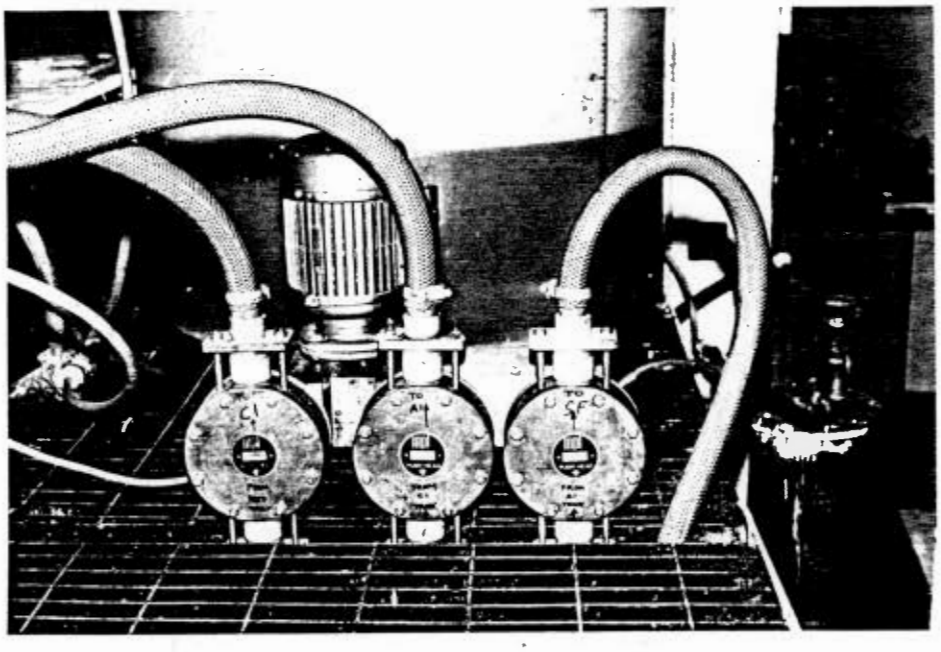

FIGURE 3,2 DIAPHRAGM PUMP FOR LOAD COLUMNS

3.4 ANION LOAD COLUMN DETAILS

Figure 3.3 is a closer view of the lower section of the anion load column. The 6 Omron timers in each box are for:

(a) primary cycle (seen at left of box): upflow; settle; pull-down.

(b) secondary cycle (at right of box): dewater catchpot; refluidize with regeneration waste; transport air.

Below the timer box is the resin pull-down controller box and alarm. This employs a conductive probe signalling a preset liquid level change in the top of the column which corresponds to a required down-flow of resin. Should the probe fail to operate (e.g. due to possible concurrent feeding of resin into the top of the column that is pulling down) the pull-down is stopped upon expiry of the pull-down timer. This timer then sets off an alarm which is not operative if the pull-down has already been stopped by the probe control. The valves used are of the air operated Saunders type. Each column

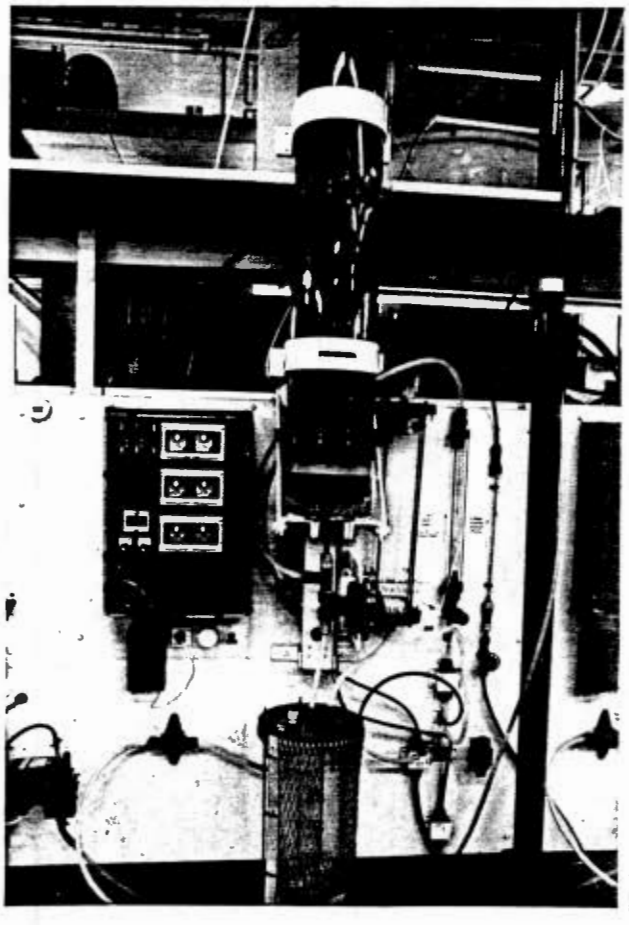

FIGURE 3,3 ANION LOAD COLUMN - LOWER SECTION

is provided with a rotameter for flow checking. However, flow rates are controlled by means of the stroke-adjustable metering pumps and the rotameters give a maximum and minimum indication of each pump head stroke. This was found to give a sensitive indication of any pump malfunctions.

Figure 3.4 shows the top of the anion load column with its hopper extension for receiving resin. This is on the second floor of the laboratory building. The outlet screen to collect any resin washed over the column outlet weir during resin inlet due to the sudden rush of air-driven flow

from the catchpot is seen to the left of the column. (On this small scale the typical commercial method of resin introduction from a SWECO screen could not be employed.)

The anion product tank is in the foreground and the cation product tank just behind it. Above the column is the air pressure release vessel into which the resin from the regeneration column catchpot is forced and from which the resin flows into the hopper by gravity.

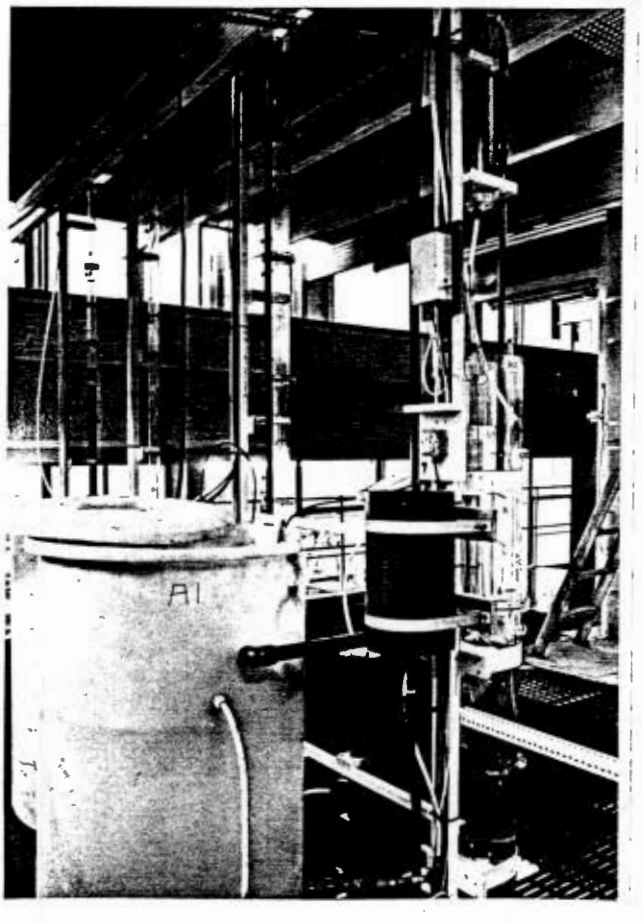

FIGURE 3,4 ANION LOAD COLUMN - TOP SECTION

3.5 ANION REGENERATION COLUMN DETAILS

Figure 3.5 is a view of the anion regeneration column. On the left is the simple timer box having only a primary cycle timer set. The resin transport is direct to the top of the load column as there is no need for replacing the water pulled down with the resin, as the liquid it will contact in the next column has already been used as the wash water in the regeneration column.

On the right is the metering pump for wash water injection into the base of the column, with its associated rotameter and stand-pipe (hidden behind the column). Each stage is provided with a sample tap near the top. These were used for measuring concentration profiles in the column.

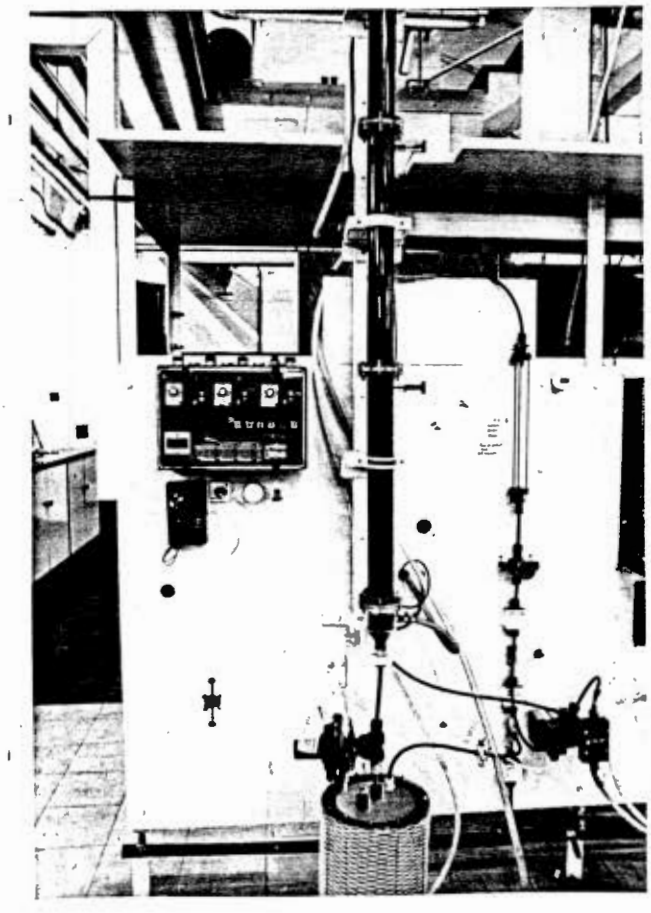

FIGURE 3,5 ANION REGENERATION COLUMN

3.6 SULPHURIC ACID RECYCLE SYSTEM

Figure 3.6 is a general view of the acid recycle system. On the right is the 50 mm diameter cation regeneration column. A 600 mm diameter upflow settler with a 1200 mm sidewall depth and 60° cone receives the overflow from the two-stage crystalliser stirred tanks through a central downcomer ending at the apex of the cone. This may be more clearly seen in Figure 3.7. Sludge is pumped from halfway down the cone of the settler into the first CSTR to provide the seed crystals to promote nucleation and precipitation of calcium sulphate from the supersaturated solution leaving the cation regeneration column. Make-up sulphuric acid is also added at this point.

The clarified solution leaving the settler is collected in a small catchpot from which it is pumped back into the column using a pair of diaphragm pumps. These are seen in the centre of the photograph. While the column is pulling down the level of this catchpot rises and any excess

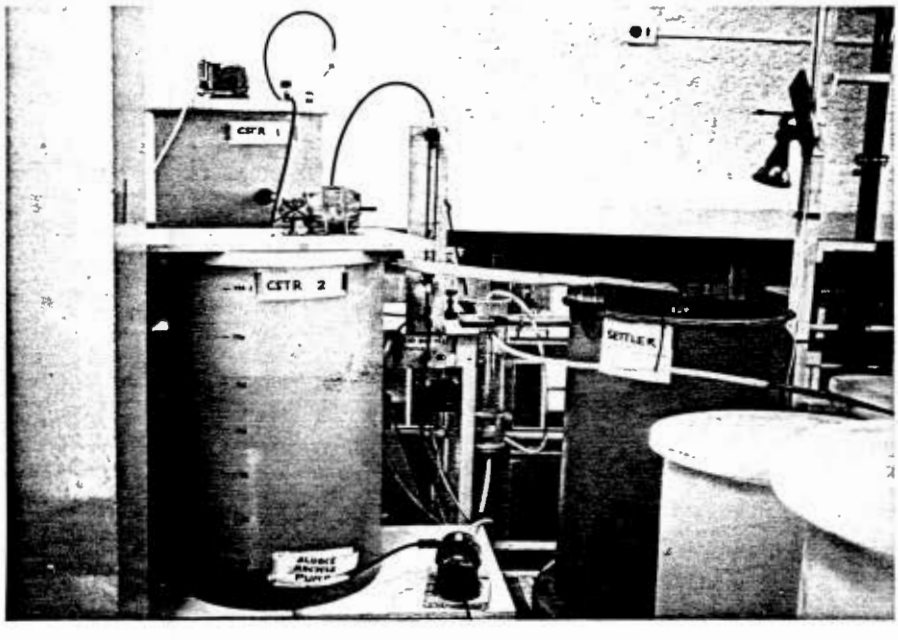

FIGURE 3,6 ACID RECYCLING EQUIPMENT

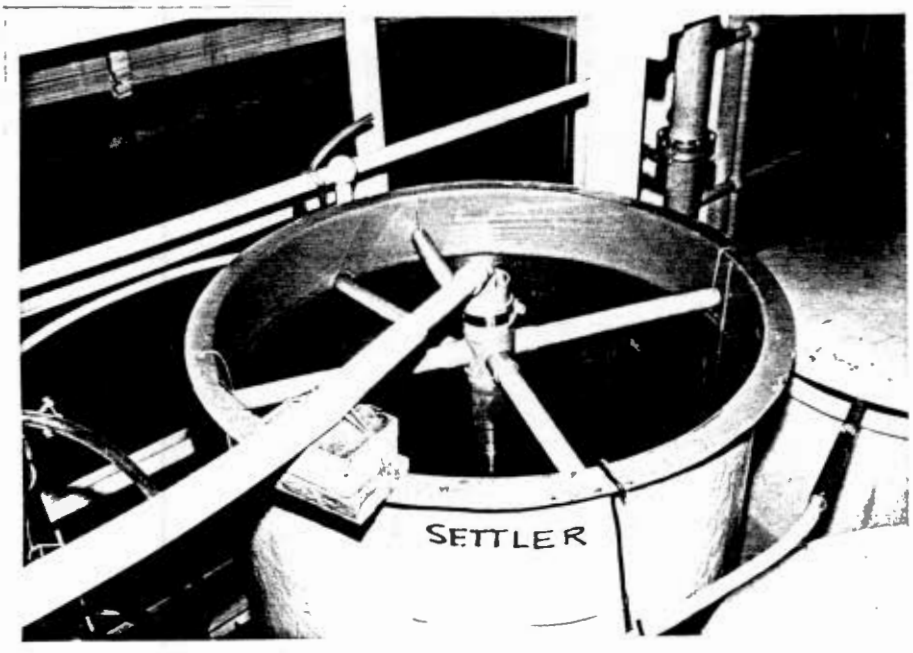

FIGURE 3,7 SETTLER FOR $CaSO_4$ SLURRY

solution overflows to waste thus displacing the volume equivalent to the wash water net upflow (±50 mℓ/min) during each column cycle. Figure 3.8 is a closer view of the catchpot and recycle pumps (900 mℓ/min).

3.7 RECIRCULATING BATCH ANION REGENERATOR

The batch regenerator system is shown in Figure 3.9. This was a new approach to contacting lime with resin. Its functioning is described in Chapter 4. The enlarged top section served to settle resin and prevent carryover to the outlet sieve. At the base a Saunders valve for pull-down of resin into the CCIX wash column hopper was controlled by an optical resin detector which stopped the pull-down as soon as the vessel was free of resin and prevented loss of the residual solution. The sensor could be adjusted to distinguish between a resin slurry and the turbid solution. Centrifugal

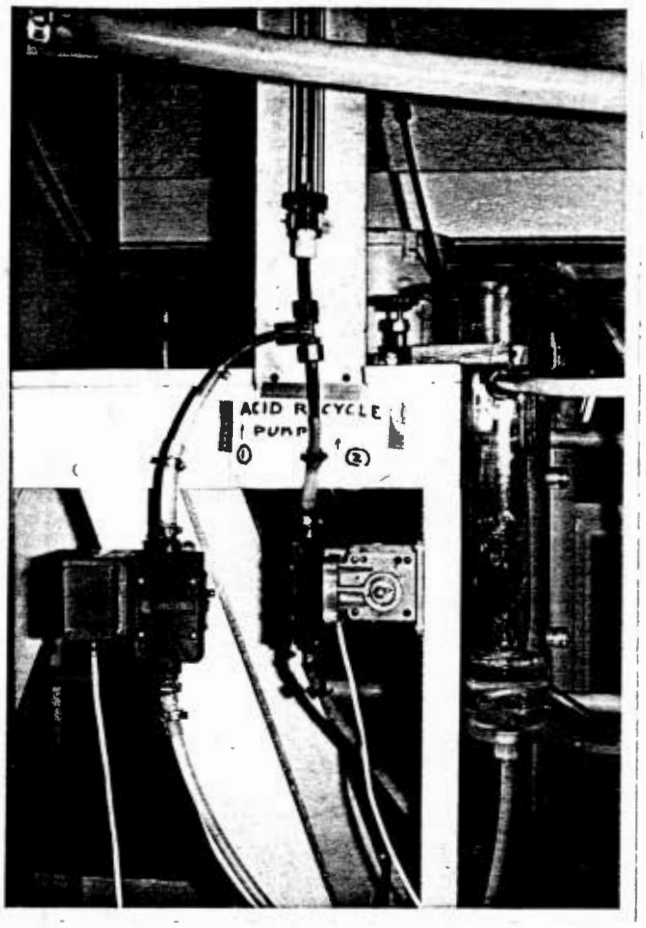

FIGURE 3,8 ACID RECYCLE PUMPS AND BALANCING VESSEL

pumps were used for recirculating the lime-dosed regenerating solution and the clarifying solution. For the latter the same sludge settler was used as for the acid recycle work. Its sidewall depth was reduced and thus also its liquid hold-up time. A relatively inefficient settler is adequate for the purpose required in this system.

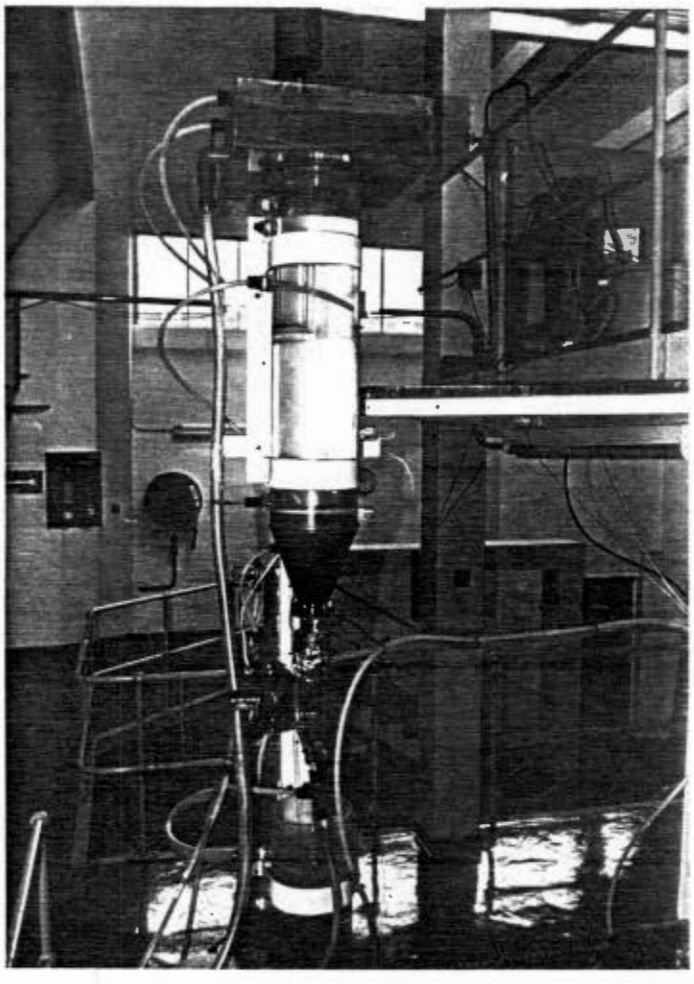

FIGURE 3,9 BATCH CONTACTOR FOR ANION REGENERATION

The details of the processes carried out in the equipment described above may be found in the flowsheets and descriptions in subsequent chapters.

CHAPTER 4

INVESTIGATION OF OPTIMUM OPERATING CONDITIONS FOR REGENERATION WITH SULPHURIC ACID AND LIME

4.1 INTRODUCTION

This chapter deals with the results of a series of experiments on the cation columns of the 6 kℓ/day capacity pilot plant. Since it is difficult to account for multicomponent equilibria and the different kinetics of the various species present in the effluents by means of a theoretical treatment, it was necessary to evaluate the effects of changing the sulphuric acid concentration, nominal R/L ratio and stage efficiency on the regeneration efficiency by experiments on the pilot plant. The effects on the regenerated resin composition (and hence on the loaded resin composition at steady state) with particular reference to the calcium ion fractions and the effective working capacity are discussed. The onset of scale formation with increasing acid concentration and higher R/L ratios and the significance of this effect are discussed.

Having established the optimum conditions for a four-column system attention was given to methods of reducing acid consumption by allowing higher concentrations and better regeneration to be obtained, by removing calcium using brine rinsing of the loaded resin prior to sulphuric acid regeneration. Following this, recycling of the sulphuric acid in the regeneration system is discussed.

The final section of the chapter deals with the use of lime in the anion regeneration column of the pilot plant. Results of modifications to the column and proposed methods of improving the operation are considered. The important problem of attaining maximum waste solution from a low solubility regenerant is discussed from a theoretical point of view. The significance of the results obtained is discussed.

4.2 CATION RESIN REGENERATION IN THE FOUR-COLUMN SYSTEM

4.2.1 Scope and approach

The sulphuric acid regeneration tests investigated the effects of (a) acid concentration, (b) stoichiometric ratio and (c) bed expansion on the efficiency and operability of the regeneration column. As these are the main parameters under the control of the designer or operator of a regeneration system, the comparison of the overall effect of these changes provides a basis for optimization of regeneration column performance. The important criterion is the consumption of sulphuric acid under any of these conditions to attain a desired extent of regeneration of the resin.

In the design of a plant the lowest cost of the water produced would be the optimization criterion and capital and other costs must then be taken into account as well.

The operating conditions are presented in Table 4.1. In all the tests a 50 mm I.D. column having 0,5 m deep stages was used. Eight stripping stages and 4 wash stages were used. The liquid flow rate and resin inventory and hence contact time per stage were constant for all the test conditions except for that in which bed expansion was increased from 35% to 60% by raising the flow rate from 425 mℓ/min to 840 mℓ/min. The liquid phase concentration was varied between 0,125 N and 1,0 N and the nominal R/L was tested at 0,8 and 0,5. Eight conditions were tested by carrying on operation for approximately one week under each condition to obtain steady state operation and collect reproducible data.

Liquid and resin samples were taken at four-hourly intervals and analysed on a daily routine. Resin compositions were obtained directly by analysis rather than relying on calculation from known liquid compositions and material balances. Resin compositions were measured in meq/mℓ of free settled resin. These results are contained in Appendix 2. From these the ion fractions of each ion were corrected for incomplete elution using separately determined factors and are presented in Table 4.2.

TABLE 4.1

CATION COLUMN OPERATING CONDITIONS FOR INVESTIGATION OF SULPHURIC ACID REGENERATION ON FOUR-COLUMN SYSTEM

	REGENERATION COLUMN							LOAD COLUMN		
RUN CODE NAME	CONC. N	R/L NOM.	ACID FEED (4N) mℓ/min	WASH FLOW mℓ/min	RESIN PER CYCLE mℓ	B.E %	UPFLOW TIME mins	FEED FLOW mℓ/min	RESIN PER CYCLE mℓ	UPFLOW TIME mins
A	0,125	0,8	12,6	424	794	35	29,4	1967	2677	92,1
1	0,15		29,0	813	684	60	11,0	4275	1634	29,1
C	0,50		41,3	393	795	35	9,0	(6571)	885	10,2
	1,00		65,0	371	794	35	5,3	4533	1544	12,3
D	0,125	0,5	13,3	417	795	35	44,6	1318	2541	147
4	0,15		29,9	813	684	60	17,1	2812	2125	57,4
F	0,50		45,3	389	795	35	13,1	4275	1634	29,1
	1,00		77,0	360	795	35	7,2	3816	1795	18,8

4.2.2 Resin composition and working capacity

The effective working capacity (defined in Section 2.5.2) of regenerated resin is the portion of the total capacity which is in the H^+ form. This is the capacity to load Na^+, Ca^{++} etc. From the ion-fraction data of Table 4.2 the effective working capacity for each operating condition has been extracted and presented in Table 4.3.

TABLE 4.2

RESIN COMPOSITIONS (ION-FRACTIONS)

(SULPHURIC ACID REGENERANT)

Nominal R/L	CONC	COLUMN	H^+	Na^{++}	Ca^{++}	Mg^{++}
0,8	0,125 N	load	0,00	0,10	0,54	0,37
		regen	0,25	0,04	0,47	0,20
	0,15 N	load	0,01	0,11	0,53	0,35
		regen	0,25	0,03	0,51	0,22
	0,50 N	load	0,03	0,15	0,44	0,34
		regen	0,37	0,07	0,37	0,15
	1,00 N	load	0,18	0,23	0,35	0,24
		regen	0,43	0,11	0,25	0,17
0,5	0,125 N	load	0,02	0,18	0,51	0,25
		regen	0,37	0,01	0,44	0,18
	0,15 N	load	0,00	0,15	0,53	0,32
		regen	0,30	0,03	0,50	0,17
	0,5 N	load	0,05	0,26	0,46	0,24
		regen	0,49	0,05	0,37	0,05
	1,00 N	load	0,21	0,24	0,36	0,20
		regen	0,52	0,06	0,31	0,10

TABLE 4.3

EFFECTIVE WORKING CAPACITY (meq H^+/mℓ resin)

(Calculated from Table 4.2 and total capacity = 1,6 meq/mℓ)

Nominal R/L		0,8	0,5
% EXCESS ACID (nominal)		25%	100%
CONCENTRATION	BED EXPANSION		
0,125 N	35%	0,46	0,53
0,15 N	60%	0,40	0,48
0,50 N	35%	0,59	0,78
1,00 N	35%	0,69	0,83

It can be seen that the use of a lower R/L (greater excess of acid over the stoichiometric requirement) results in an increase of the effective working capacity of the resin. The most significant increase is, however, due to increasing the concentration of the regenerant solution.

The improved working capacity is due mainly to the reduced fraction of calcium on the regenerated resin. These fractions are presented in Table 4.4. The ion-fractions of magnesium were also significantly lower. Because the

TABLE 4.4

ION-FRACTION OF CALCIUM ON REGENERATED RESIN

Nominal R/L		0,8	0,5
% EXCESS ACID (nominal)		25%	100%
CONCENTRATION	BED EXPANSION		
0,125 N	35%	0,47	0,44
0,15 N	60%	0,51	0,50
0,50 N	35%	0,37	0,37
1,00 N	35%	0,25	0,33

calcium and magnesium are both totally removed from the feedwater in all the operating conditions their reduced ion-fractions on the regenerated resin resulted in uptake of more sodium. Thus the sodium ion-fraction on both the regenerated resin and on the loaded resin showed an increase.

The concentration effect is ascribed to the resin being less selective towards all the cations and particularly Ca^{++} at higher concentrations. Hence regeneration is more easily accomplished. This is illustrated in Figure 4.1.

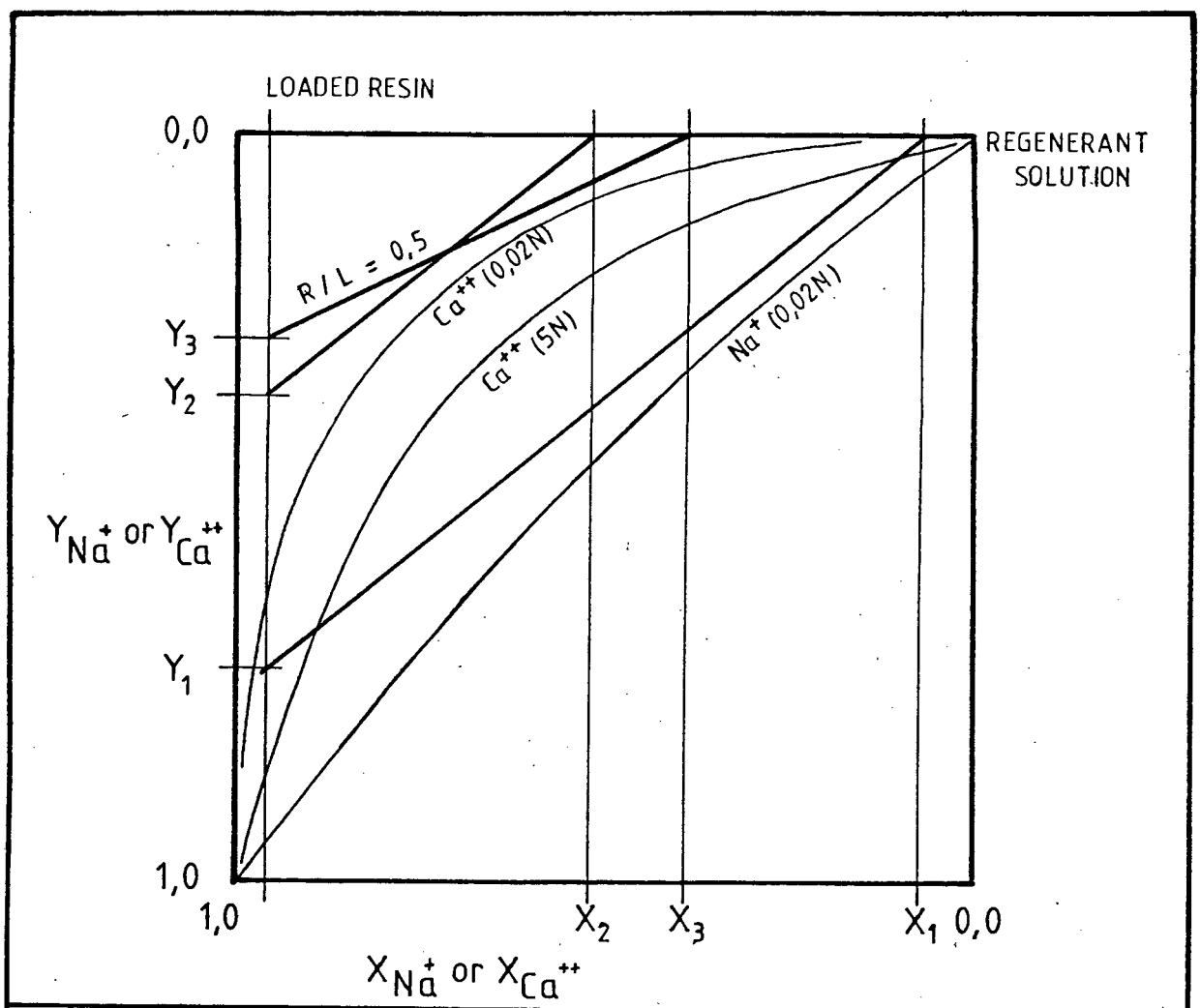

FIGURE 4,1 REGENERATED RESIN AND WASTE SOLUTION COMPOSITIONS (note reversed coordinates)

The effect is to increase the potential resin composition change in any particular stage. The improvement is achieved at the expense of using a greater net throughput of liquid to dilute the concentrations of the stripped ions while maintaining the H^+ ion concentration at a high value.

Figure 4.1 shows that, for Na^+ a lower resin ion-fraction (x_1) and higher liquid ion-fraction (y_1) is possible than in the case of Ca^{++} (x_2 and y_2), at a given R/L (= 0,8) due to the more favourable equilibrium conditions for Na^+. Similarly, changing the R/L to 0,5 would result in lower resin and liquid ion-fractions of Ca^{++} (x_3 and y_3).

4.2.3 Waste stream composition and acid consumption

The waste stream compositions measured in each of the tests are presented in Table 4.5 (complete data on liquid product compositions are presented in Appendix 2). The ion-fraction of H^+ remaining in the waste stream, considered

TABLE 4.5

WASTE STREAM COMPOSITIONS (CATIONS) FROM SULPHURIC ACID REGENERATION COLUMN - ION-FRACTIONS

(SULPHURIC ACID REGENERATION)

Nominal R/L		0,8				0,5			
	IONS	H^+	Na^+	Ca^{++}	Mg^{++}	H^+	Na^+	Ca^{++}	Mg^{++}
CONC.	B.E.								
0,125 N	35%	0,74	0,13	0,01	0,01	0,80	0,14	0,01	0,04
0,15 N	60%	0,65	0,22	0,02	0,09	0,79	0,08	0,04	0,09
0,50 N	35%	0,58	0,25	0,01	0,14	0,74	0,18	0,01	0,05
1,00 N	35%	0,66	0,21	0,02	0,05	0,73	0,17	0,03	0,06

in conjunction with the stoichiometric ratio and regenerant concentration, is an indication of the amount of acid actually utilized in exchanging cations on the resin. A clearer picture is obtained from comparing the amount of acid applied under the various conditions with the effective working capacity gained.

efficient way to use sulphuric acid is to use as high a nominal R/L as possible and to raise the regenerant concentration as far as possible. It should be noted that the use of high regenerant concentrations also allows short cycle times and smaller regeneration column diameters to be used for any given load column desalination duty. Effective working capacity is plotted against the nominal R/L in Figure 4.2 and against the effective R/L in Figure 4.3.

4.2.4 Effects on the load column performance

The composition of the feed water used in the tests is shown in Table 4.7. During the tests the content of magnesium in the feed water increased from 2,17 mg/ℓ to 3,17 mg/ℓ. The feed water typically contains 2,0 meq/ℓ Ca^{++} and 3,0 meq/ℓ Mg^{++} out of a total of 15 meq/ℓ. The composition of product water from the cation load column in each of the eight tests is given in Appendix 2. Table 4.8 shows the data in ion-fractions.

TABLE 4.7

FEED WATER COMPOSITION meq/ℓ

Nominal R/L	CONC.	Na^+	K^+	Ca^{++}	Mg^{++}	TOTAL	DATE
0,8	0,125 N	8,74	0,47	2,40	2,17	13,78	27/2 - 2/3/79
	0,15 N	9,37	0,53	2,80	2,40	15,10	17/2 - 15/2/79
	0,5 N	9,57	0,64	2,15	2,92	15,28	13/3 - 17/3/79
	1,0 N	9,10	0,51	2,30	3,10	15,01	19/3 - 25/4/79
0,5	0,125 N	8,52	0,36	2,20	2,17	13,25	22/2 - 26/2/79
	0,15 N	10,40	0,60	2,60	3,50	17,1	21/3 - 23/3/79
	0,5 N	9,74	0,56	2,56	2,42	15,3	3/3 - 7/3/79
	1,0 N	9,50	0,59	2,19	3,17	15,45	5/4 - 12/4/79
AVERAGE		9,37	0,53	2,4	2,73	15,03	

In each test, because of the resin's selectivity for calcium and magnesium over sodium, all of the calcium and magnesium is removed from the feed water in the load column while only a proportion of the sodium is removed depending on the effective working capacity remaining that is not occupied by Ca^{++} and Mg^{++}.

TABLE 4.8

LIQUID COMPOSITIONS - ION-FRACTIONS

Nominal R/L	CONC.	COLUMN	H^{+}	Na^{++}	Ca^{++}	Mg^{++}
0,8	0,125 N	load	0,49	0,50	0,00	0,00
		regen	0,75	0,13	0,01	0,01
	0,15 N	load	0,54	0,46	0,00	0,00
		regen	0,65	0,22	0,02	0,09
	0,5 N	load	0,71	0,29	0,00	0,00
		regen	0,59	0,25	0,01	0,14
	1,0 N	load	0,91	0,09	0,00	0,00
		regen	0,66	0,21	0,02	0,09
0,5	0,125 N	load	0,84	0,16	0,00	0,00
		regen	0,80	0,14	0,01	0,04
	0,15 N	load	0,51	0,49	0,00	0,00
		regen	0,75	0,08	0,04	0,09
	0,5 N	load	0,75	0,24	0,00	0,00
		regen	0,75	0,18	0,01	0,04
	1,0 N	load	0,58	0,02	0,00	0,00
		regen	0,73	0,17	0,03	0,06

Since under these circumstances the amount of Ca^{++} and Mg^{++} loaded onto the resin in the load column is the same in each run it is clear that any increase in effective working capacity would result in uptake of more

sodium from the feed water. Consequently the improved regeneration results in a shift of the calcium and magnesium ion-fractions of the loaded as well as the regenerated resins to lower values.

Thus the ion-fraction of sodium remaining in the load column product is greater when the ion-fractions of calcium and magnesium on the regenerated resin are greater (see Table 4.4).

The ion-fraction of H^+ appearing in the load column product is equivalent to the cations removed and is therefore directly related to the % desalination attained.

It was important to carry out the investigations using a typical wastewater to load the resin rather than any artificial feedwater containing only NaCl because the presence of divalent ions has a marked effect on the compositions of both loaded and regenerated resin even when present in low concentrations.

Experiments were carried out on the laboratory pilot plant even though a model exists for calculating the performance of CCIX columns because it is extremely difficult in a theoretical treatment to account for equilibria and kinetics in a multicomponent system of competing species. A second reason for using an experimental approach and for using a typical wastewater as feed is that under certain conditions the solubility of calcium sulphate may be exceeded in the regeneration column. This hazard limits the choice of acid concentration and R/L that can practically be used before precipitation of $CaSO_4$ on column surfaces and ancillaries precludes reliable operation. Tests using a typical calcium-containing wastewater afforded the opportunity to observe such effects and determine the limits for design of full scale equipment.

4.2.5 Formation of calcium sulphate scale

Under any given regeneration conditions the concentration of calcium which occurs in the waste stream is directly affected by the amount of calcium taken up by the resin from the feed water. This amount is controlled

by the concentration of calcium in the feedwater since all of the calcium is removed under most conditions. Thus the concentration of calcium in the feedwater would determine whether a given regeneration column operating condition were practically operable in terms of possible precipitation of calcium sulphate in the column.

Conditions found operable on a feedwater low in calcium would not necessarily be operable on a high calcium feed. The operability depends on whether precipitation of $CaSO_4$ occurs on column surfaces and ancillaries producing a hard scale which eventually sloughs off and produces flakes or clumps of resin-gypsum aggregates which block the inter-stage separator orifices thus preventing transport of resin to the stage below. Scaling is first noticeable in the hopper and top stages where the Ca^{++} concentration in the waste stream is highest.

Most of the waste solutions are supersaturated in $CaSO_4$. Table 4.9 gives solubility products. Literature (Perry[14]) values for solubility yield a saturation ion-product (in contact with $CaSO_4:2H_2O$) of $0,22 * 10^{-3}(mole/\ell)^2$ while ion-products up to 24 times as high have been measured in the four-column system and up to 50 times as great in the five-column system.

TABLE 4.9

ION-PRODUCTS OF $CaSO_4$ IN REGENERATION WASTE LIQUIDS

Nom.R/L	Conc.(N)	Sol.Prod.$CaSO_4$ in $(mole/\ell)^2*10^3$
4-column system, using sulphuric acid only		
0,8	0,125	0,044
	0,50	0,70
	1,00	4,0
0,5	0,125	0,02
	0,50	0,74
	1,00	5,3
5-column system, sulphuric acid recycle		
0,25	1,00	6,5 to 11,0

With an R/L = 0,5 the use of 1,0 N sulphuric acid resulted in troublesome scale formation on column surfaces and precipitate formation in the liquid near the top of the column. With R/L = 0,8 the use of 1,0 N H_2SO_4 for more than one or two days was impossible due to blocked stage separators. Precipitate forming on the resin particles could, however, be washed away with 5% HCl solution and resulted in no permanent damage to resin beads.

All other conditions of Table 4.1 were found to be entirely free of scaling and precipitation problems. A run at R/L = 0,65 and 0,75 N was also tested and found to be troublefree. The explanation for some supersaturated solutions not resulting in scaling is that the solutions tend to be metastable and nucleation does not occur unless vigorous agitation and seeding is applied. Only at higher supersaturation levels does the nucleation rate reach values which result in crystal formation within the retention time of the liquid in the column.

Nucleation lag of supersaturated $CaSO_4$ solutions

The results of bench scale experiments to study the rate of precipitation are reported in Appendix 3. A solution of sulphuric acid and calcium chloride can be highly supersaturated with no precipitation even with vigorous agitation for hours. A neutral solution of sodium sulphate and calcium chloride containing 0,5 eq/ℓ of $SO_4^{=}$ ions and 0,05 eq/ℓ of Ca^{++} ions took one hour to nucleate in spite of vigorous stirring on a magnetic stirrer and then took more than three hours to stabilize. In a repeat test but adding pulverised precipitate precipitation began immediately but 30 minutes elapsed before the system had stabilized. The ion-product in these tests was $6,25 * 10^{-3}(mole/\ell)^2$. In tests with an ion-product of $25 * 10^{-3}$ (no seeding) the nucleation time was 15 minutes and stabilization required about 1 hour. At an ion-product of $100 * 10^{-3}$ an immediate precipitation occurred. Thus the addition of solid phase and the degree of supersaturation both have a major effect on the stability of $CaSO_4$ solutions.

In the ion exchange column, nucleation appeared to be accelerated by the presence of resin particles particularly when a supersaturated solution was in contact with resin being transported from the load column catchpot to the regeneration column hopper. (Cation waste solution containing sulphuric acid was normally used for this transport step. The effect could be reduced by using feedwater to transport the resin.)

Kunin reports[10] that the metastability of supersaturated $CaSO_4$ solutions is the only reason for H_2SO_4 regeneration being successful in many fixed bed ion exchange plants. If the residence time of liquid in the regeneration column can be kept short enough the solution can be removed before nucleation occurs and precipitation in the column can be avoided even at high degrees of supersaturation. The observation was put to important use in the five-column system for recycling sulphuric acid described in Section 4.4.

The effect of stoichiometric ratio on scale formation. As a result of applying a larger quantity of regenerant solution (L) per unit of resin (R), reducing the R/L ratio results in dilution of the calcium concentration because the quantity of calcium taken up by the resin from the feedwater and released into the regenerant waste solution is unaltered. Reducing R/L from 0,8 to 0,5 means that the same amount of calcium is carried away in 0,8/0,5 = 1,6 times as much solution. For this reason a regeneration solution concentration which may be used at R/L = 0,5 without exceeding the saturation limit of $CaSO_4$ may result in precipitation at R/L greater than 0,5. It is important to note, however, that above R/L of about 0,8 the degree to which Ca^{++} can be concentrated further by raising the nominal R/L is limited because the regenerant concentration would then have to be reduced to avoid precipitation and this has an unfavourable effect on the economics of regeneration.

4.2.6 The effect of concentration of regenerant on scale formation

At a given R/L ratio increasing the acid concentration will have three important effects:

(a) Increased acid concentration implies the use of less wash water per unit of resin treated and therefore less dilution of the salts

removed from the resin. Thus for a given quantity of Ca^{++} loaded onto the resin in the load column the concentration of the $CaSO_4$ produced in the regenerant waste stream is increased in the same proportion as the acid concentration. This is depicted in Figure 4.4.

(b) The increased sulphate ion concentration tends to reduce the solubility of the $CaSO_4$ due to the common ion effect.

(c) The increased acid concentration results in faster regeneration kinetics as well as more favourable equilibrium. Therefore a greater change in the liquid phase concentration of $CaSO_4$ occurs in the top stages of the column. Thus the Ca concentration profile in the column is altered and supersaturation in localized areas is more likely to occur.

All of these effects tend to increase the rate of nucleation and promote precipitation of $CaSO_4$. Intermediate liquid samples withdrawn from the stages during operation under the following conditions indicate the effects mentioned:

REGENERANT CONC.	% CHANGE IN Ca CONC. IN THE TOP STAGE COMPARED TO AVERAGE CHANGE IN LOWER STAGES
0,125 N	100% (R/L = 0,5 in these tests)
0,15 N	255%
0,5 N	783%

Typical concentration profiles are presented in Figure 4.5.

With the increase in acid concentration and increased R/L both tending to increase the likelihood of precipitation occurring, it can be appreciated that the hazard can become serious at some critical operating concentration while even slightly below this level there may be no noticeable precipitation.

In general, it is concluded that for a typical feed water (such as Milnerton HTE) operation at BE = 35% is limited to R/L not greater than 0,8

at concentration of 0,5 N. Alternatively at R/L = 0,65 a concentration of 0,75 N should be entirely satisfactory.

4.2.7 Behaviour of cations other than calcium

The selectivity of the resin for different ions largely determines their relative removal from the feed water in the load column and from the resin in the regeneration column. The following values were measured:

TOTAL ION CONCENTRATION	5N	0,5N	0,25 N
$\alpha_{H^+}^{Na^+}$		1,5	
$\alpha_{H^+}^{Ca^{++}}$	4,7	6,2	7,3
$\alpha_{H^+}^{Mg^{++}}$		1,8	

(a) Magnesium. It is often supposed that because Mg is divalent it would have a similar α_H^{Mg} to α_H^{Ca}. The table shows that this is not the case, and α_H^{Mg} is in fact similar to α_H^{Na}. However, in the load column it was found that magnesium removal was complete (as for calcium) even when very low sodium removals were observed (see Table 4.8). The reason for this may be that α_H^{Mg} is greater at lower liquid compositions. (No selectivity measurements at low concentrations were attempted.) Examination of the regenerated resin compositions (Table 4.2) shows that the amount of magnesium remaining is lower than that of calcium but greater than sodium. The concentration profile for magnesium (Figure 4.5) shows that it is removed mainly in the lower stages, and tends to return to the resin phase in the middle stages at the point where Na and Ca liquid phase concentrations are increasing rapidly.

acid concentration that is important from the waste stream concentration point of view. Should a greater amount of salt be removed from the feedwater the cation waste stream volume would have to be increased in order to maintain this concentration. It is the calcium content in a typical feedwater and the resulting Ca concentration in the waste stream which limits the attainable water recovery. This effect is illustrated in Table 4.10. For 50% and 90% desalination of a 500 mg/ℓ TDS feed containing 100 mg/ℓ Ca the same amount of calcium is removed and the water recovery is unaltered at 87%, whereas for 50% desalination of feedwater of twice the calcium content the water recovery is reduced to 62%. The above restrictions due to calcium in the feed water are calculated on the basis of Ca solubility of 0,026 N or an ion-product for $CaSO_4$ of $3*10^{-3}(mole/\ell)^2$ in 0,5 N H_2SO_4.

If calcium were not present, higher waste concentrations could be attained and the water recovery considerably increased.

Possible use of feedwater as cation regeneration wash water to improve water recovery. The above discussion assumes the use of desalinated water as wash in the cation regeneration column. Although desalinated water is imperative in anion regeneration wash to avoid carryover of feed water constituents in the resin pore liquid to the final product of the anion load column, in the cation case a choice may be made between desalinated water and feed water in order to improve economy of operation since feed water is available at negligible cost.

A calculation based on 80% overall water recovery on a plant producing desalinated water at 30 c/kℓ shows that this unit cost would be reduced to 28,5 c/kℓ if feedwater wash were used on the cation regeneration column. This improved unit cost of water results from plant output being raised from 80% recovery to 85% recovery.

Neutralization of excess sulphuric acid in cation waste stream. The unused acid in the cation waste stream must be neutralized using limestone before discharge. At nominal R/L = 0,8 and conc. = 0,5 N (see Table 4.6), an effective working capacity of 0,59 meq/mℓ of resin is achieved for

TABLE 4.10

EFFECT OF CALCIUM IN FEED WATER ON CALCULATED WATER RECOVERY

CASE	ION	FEED		PRODUCT		REMOVED		% Desalination	Wash required as % of feed	Water recovery %
		mg/ℓ	meq/ℓ	mg/ℓ	meq/ℓ	mg/ℓ	meq/ℓ			
1	Na^+	900	35,1	500		400	17,4			
	Ca^{++}	100	5,0	0		100	5,0		19,2%	80,8%
	TOTAL	1000	44,1	500		500	22,4	50%	11,0%	
2	Na^+	AS				800	34,8			
	Ca^{++}	ABOVE				100	5		19,2%	80,8%
	TOTAL					900	39,8	90%	19,0%	
3	Na^+	1800	78,3	1000		800	34,8			
	Ca^{++}	200	10,0	0		200	10,0		38%	62%
	TOTAL	2000	88,3	1000		1000	44,8	50%	21%	

application of 2,0 meq(H_2SO_4)/mℓ resin resulting in wastage of 1,41 meq(H_2SO_4) /mℓ of resin. This working capacity will result in uptake of 0,59 meq of salt in the load column producing 0,59 meq of HCl which will require 0,59 meq of lime for anion regeneration.

In addition 1,41 meq of limestone (e.g. dolomitic flour) or other alkali will be consumed in neutralizing the wasted H_2SO_4 and the total cost for alkali will be roughly double the cost for the regenerant lime above. Also, neutralization will produce an additional 1,41 meq of $CaSO_4$ in the wastestream over the approximately 0,1 to 0,15 meq of $CaSO_4$ derived from the calcium removed from the feed water.

The modification proposed in Section 4.3 of using brine to remove calcium from the loaded resin reduces the acid wastage and thus also the cost of neutralization. Furthermore the modification proposed in Section 4.4 of recycling the sulphuric acid almost entirely eliminates sulphuric acid wastage and thus there is no extra cost for neutralization. In this case, however, the amount of $CaSO_4$ produced will be much lower being essentially equivalent to the salt removed in the cation load column.

4.2.9 Conclusions on use of sulphuric acid for cation resin regeneration in four-column system

The resin compositions attainable will allow desalination of the load column product water in excess of 90% to be attained.

The water recovery and maximum regenerant concentration which can be used is limited by the calcium content of the feed water. For a feed containing 2,0 meq/ℓ of calcium the regenerant concentration should be 0,5 N with a maximum 0,75 N under certain circumstances.

In designing a plant to treat a given feed water, calculation of the cation wash water required can be based upon the saturation concentration of calcium in the cation waste liquid (0,026 N). Higher concentrations are attainable but 0,026 N is a safe figure to use. The optimum acid concentration and R/L will then be determined by considering the effective working

capacities and effective R/L in Table 4.6 in conjunction with chemical and capital costs. At best the effective R/L with sulphuric acid will be about 0,29. In comparison with nitric acid where an R/L of 0,8 could be used giving a similar effective R/L, the four column sulphuric system will require about 0,8/0,25 = 2,8 times as much acid. However, since nitric acid costs about R19/kg-equivalent while sulphuric acid costs R4,20/kg-equivalent (or 4,5 times less) it may be clearly seen that sulphuric acid can result in important cost savings, in spite of its operating limitations.

However, chemical costs remain a major factor in the unit cost of water and their share increases when higher salinity water is to be treated and a search for still further cost reductions is justified.

The alternative flowsheets using sulphuric acid discussed in Sections 4.3 and 4.4 may be considered as a means of reducing the cost of desalination.

4.3 FIVE-COLUMN SYSTEM WITH BRINE RINSE TO REMOVE CALCIUM AND REDUCE SULPHURIC ACID WASTAGE

4.3.1 Alternative approaches to reducing sulphuric acid consumption

In order to reduce the consumption of sulphuric acid required to attain a given level of regeneration the following approaches may be considered:

(a) Attempt to operate the regeneration column using a higher concentration of sulphuric acid and thereby attain more favourable equilibrium, as discussed in Section 2.3.4. Ways of preventing precipitation of $CaSO_4$ inside the column would need to be sought. One suggestion is to feed a high concentration of finely ground gypsum crystals together with the regenerant in the expectation that any gypsum produced in the column will be precipitated on these nuclei and not on the column surfaces. This technique has been used for scale control on sea water evaporation desalting plants. Its effectiveness in a CCIX contactor would need to be tested and the problem of handling a slurry in the column would have to be considered. Because it is still possible for

supersaturation of $CaSO_4$ to exist even with seeding unless quite large amounts of seeding crystals are added, its effectiveness would depend on the slurry concentration used. Therefore this approach was not studied further at the stage of this work.

Another suggestion, to add an anti-precipitant such as poly-phosphates in threshold concentrations, would incur additional chemical costs and would add another component to the waste stream. The likelihood of this being effective has not been studied.

(b) A method of operation can be sought whereby unused sulphuric acid can be recovered and returned to the regeneration column. This would effectively eliminate wastage and achieve an effective R/L in the regeneration system close to 1,0 (i.e. only 1,0 equivalent of acid used per equivalent of salt removed from the load column feedwater). This approach is discussed in Section 4.4.

(c) A method can be sought to reduce the amount of calcium present on the resin feed to the regeneration column. This would have two important effects:

(i) less calcium would be present and its place would be taken by an ion which is more easily stripped than Ca^{++} resulting in a greater effective working capacity for a given acid consumption.

(ii) less $CaSO_4$ would be produced in the acid regeneration step permitting the use of a higher regenerant concentration. This would result in improved regeneration performance.

This method was tested and the results are discussed in Section 4.3.2 below.

4.3.2 Brine rinse to remove calcium from loaded resin

A suitable ion with which to replace Ca^{++} would need to be one having soluble sulphates, and available at low cost as a raw material or as a waste solution from a nearby source.

Two main possibilities can be considered: Na^{++} and Mg^{++}. The first could be obtained at reasonably low cost from sea water, a salt works or from some ground waters and possibly as an industrial waste solution. Mg^{++} is most easily obtained from sea water. Selectivity factors are $\alpha_H^{Ca} = 6,2$; $\alpha_H^{Mg} = 1,8$; $\alpha_H^{Na} = 1,5$ at 0,5 N. These indicate that a large number of stages would be needed to remove calcium.

It was thus decided to test the removal of Ca from the loaded cation resin using a solution made up from coarse salt containing mainly Na and only traces of Ca^{++} and Mg^{++} and to determine what quantity of salt would be needed to remove enough calcium from the loaded resin to achieve a satisfactory acid saving in the H_2SO_4 regeneration step. Further, the effect of Ca and Mg in the brine rinse solution was tested to evaluate the use of sea water. The flow sheet of the 5-column system with brine rinsing is shown in Figure 4.6

In order to carry out the tests on the pilot plant a previously tested four-column operating condition was chosen. The conditions of Run A (nominal R/L = 0,8 and acid concentration 0,125 N, see Table 4.1) were chosen since this gave one of the lowest effective resin working capacities and any improvements due to brine rinsing would be easily detectable. The operating conditions are given in Table 4.11. This condition was then set up and operated as before but with the inclusion of an intermediate column. This was fed initially only with tap water rinse to determine any effects this might have on the loaded resin composition. This run would thus serve as a better reference for comparison than the original Run A data.

Following this check a brine solution of 0,6 N $NaCl_2$ was introduced as feed to the intermediate column over 6 stages. Since wash water was still introduced in the bottom 6 stages the concentration in the column was reduced to 0,3 N. For this run the nominal brine R/L was 0,25.

The brine feed concentration was then reduced to 0,3 N and consequently the column concentration to 0,15 N and since all other conditions remained the same, the nominal R/L was thus increased to 0,5.

TABLE 4.11

OPERATING CONDITIONS FOR BRINE RINSE TESTS

(Load and regen. as for Run A in Table 4.1)

INTERMEDIATE COLUMN (Na^+/Ca^{++} exchange)									
BRINE RINSE		FEED COMPOSITION (N)			FLOWS		No.of Stages	Resin per cycle	UP TIME
R/L	CONC. (N)	Na^+	Ca^{++}	Mg^{++}	FEED mℓ/min	WASH mℓ/min		mℓ	mins.
RUN A REPEAT		Tapwater			250	250	-	795	30
0,25	0,30	0,61	-	-	"	"	6	"	"
0,50	0,15	0,30	- (NaCl)	-	"	"	6	"	"
0,25	0,30	0,459	0,020	0,106	"	"	6	"	"
0,25	0,30	"	" (Seawater)	"	"	"	8	"	"

An artificial sea water feed at 0,6 N was then used. This had the same proportions of Na, Ca and Mg as sea water:

Na^{+} 0,453 N
Ca^{++} 0,020 N
Mg^{++} 0,106 N

The nominal R/L was then again 0,25.

Finally the last condition was repeated with 8 brine rinse stages instead of 6 to check whether this would materially affect the Ca^{++}/Na^{+} column performance. This run was very short but served to confirm that the stages used were sufficient.

4.3.3 Brine rinse results

The resin compositions measured in these tests are presented in the form of ion-fractions in Table 4.12.

TABLE 4.12

BRINE RINSE RESIN COMPOSITIONS - ION-FRACTIONS

BRINE RINSE	COLUMN	H^{+}	Na^{+}	Ca^{++}	Mg^{++}
Run A repeat (tap water)	load	0,00	0,07	0,49	0,43
	int.	-	-	-	-
	regen.	0,36	0,00	0,45	0,19
0,25 0,30 (brine)	load	0,07	0,25	0,58	0,10
	int.	0,00	0,76	0,22	0,02
	regen.	0,73	0,07	0,17	0,02
0,50 0,15 (brine)	load	0,05	0,41	0,42	0,12
	int.	0,00	0,57	0,39	0,04
	regen.	0,59	0,05	0,31	0,05
0,25 0,30 (sea water)	load	0,00	0,34	0,35	0,31
	int.	0,00	0,42	0,27	0,30
	regen.	0,50	0,02	0,20	0,27
0,25 0,30 (sea water, 8 stages)	load	0,00	0,27	0,42	0,31
	int.	0,00	0,37	0,36	0,27
	regen.	0,49	0,01	0,28	0,23

Brine rinsing resulted in a marked change in the resin compositions. At brine R/L = 0,25 calcium ion fraction was reduced from 0,58 on the loaded resin to 0,22 on the intermediate resin and 0,17 on the regenerated resin. The latter figure may be compared with 0,45 when no brine was used. The use of brine at R/L = 0,25 was the most effective in reducing the ion fraction of calcium on regenerated resin and in increasing the fraction of H^+ on the regenerated resin and hence the working capacity. The effective working capacities under the various conditions tested are given in Table 4.13 in which the value obtained in the original Run A when no rinse was employed is also given for comparison.

TABLE 4.13

EFFECT OF BRINE RINSING

ON EFFECTIVE WORKING CAPACITY ($meqH^+/m\ell$ resin)

(Calculated from Table 4.9 and total capacity = 1,6 meq/mℓ)

(Operating condition for cation regeneration R/L = 0,8, conc. = 0,125 N)

Run A repeat (tap water rinse)	0,58
Brine rinse R/L = 0,25; 0,30 N	1,17
R/L = 0,50; 0,15 N	0,94
Sea water R/L = 0,25; 0,30 N	0,80
Sea water - 8 stages	0,78

Increasing the brine R/L to 0,5 and simultaneously reducing the concentration to 0,15 N reduced the effective working capacity. The different calcium ion-fractions are given in Table 4.14. The reduced brine R/L was clearly less effective in replacing calcium with sodium.

rinsing the magnesium content was almost unaltered. In the regeneration column, of course, magnesium is not as easily stripped as sodium and therefore the effective working capacity was not as high with seawater rinsing as with pure NaCl brine rinsing.

4.3.5 Improved load column performance

The improved working capacities attained during the tests necessitated raising the flow rate of feed to the load column by 20% from 1967 mℓ/min to 2360 mℓ/min in order to ensure that the resin was fully loaded. At the same time the composition of the product from the load column improved. Table 4.15 shows the ion-fraction of H^+ in the load column product liquid. It can be seen that the use of brine rinse resulted in upgrading of the performance from 68% desalination to over 90% desalination in addition to the increased load column throughput.

TABLE 4.15

EFFECT OF BRINE RINSE

ON ION-FRACTION H^+ IN LOAD COLUMN PRODUCT

Run A repeat (tapwater rinse)	0,68
Brine rinse R/L = 0,25; 0,30 N	0,93
R/L = 0,50; 0,15 N	0,94
Seawater R/L = 0,25; 0,30 N	0,94
Seawater, 8 stages	0,94

As described in Chapter 2 the improved working capacity results in less acid being required to remove a given amount of salt from the feedwater in the load column. Accordingly Table 4.16 gives the acid consumption ratio and effective R/L for the brine rinse conditions. The effective R/L with both brine at R/L = 0,25 (0,53) and seawater at R/L = 0,25 (0,47) are well above the best attained with acid only (0,34), (see Table 4.6, R/L = 0,8; 1,0N).

TABLE 4.16

EFFECT OF BRINE RINSE ON
ACID CONSOMPTION AND EFFECTIVE R/L

REGEN. R/L	0,8				
REGEN.CONC.(N)	0,125				
BRINE R/L	Run A	Run A	0,25	0,5	0,25
BRINE COMPOSITION	Original	Repeat	NaCl	NaCl	Sea
BRINE CONC.	None	Tapwater	0,30	0,15	0,30
ACID APPLIED meq/mℓ resin	2,00	2,00	2,00	2,00	2,00
WORKING CAPACITY "	0,46	0,58	1,17	0,94	0,80
ACID WASTED	1,54	1,42	0,83	1,06	1,20
ACID APPLIED/CAP. GAINED	4,35	3,45	1,71	2,13	2,50
EFFECTIVE R/L	0,23	0,29	0,59	0,47	0,40

4.3.6 Effect on waste stream concentration

Because calcium is partly removed by the brine rinse less calcium sulphate will be produced in the regenerant wastestream. Consequently, it would be possible to operate the regeneration with higher acid concentrations without $CaSO_4$ precipitation becoming limiting. Thus further acid savings (not evaluated in the tests discussed here) should be possible. Furthermore, brine rinsing will be of particular benefit when treating a feedwater with a high calcium content where the $CaSO_4$ scale limitation would otherwise be more severe and the relative advantages of the technique would be much greater than with the feedwater used here. The limiting concentrations for each situation can be calculated from the resin ion-fractions in a similar way to that done in Section 4.2.8.

Wash water requirements. While all the tests carried out on the laboratory pilot plant used wash water in the intermediate column to dilute the brine in the column this was done only for more convenient operation.

This in itself will result in wastage of acid. However, it is possible to consider what will occur if the ion stripped from the resin produces a relatively insoluble sulphate. The concentration of the ion will then be limited by precipitation of the sulphate at some point in the system and if the acid (H^+) concentration is considerably higher than this it can be seen that the H^+ ion fraction will remain high. In fact it would be possible to set whatever H^+ ion-fraction was desired merely by increasing the total solution concentration.

In order to apply this principle it would be necessary to

(a) equip the acid regeneration column with an external means of precipitating the $CaSO_4$ from the supersaturated waste solutions which are encountered, separating it, and then returning the sulphuric acid solution which remains (now saturated, only, in $CaSO_4$) back to the stripping section of the column.

(b) ensure that the only cation present on the feed resin to this recycle regeneration system was one with a low solubility sulphate. Calcium is a suitable cation. The presence on the feed resin of appreciable quantities of any other cations having soluble sulphates would result in an accumulation of these in the recycle solution, ultimately degrading the essential high ion-fraction of H^+. Therefore it is necessary to include an intermediate column in which all other cations present on the product resin from the load column can be displaced by calcium. To do this it is necessary to feed the intermediate column with a solution containing a very high ion-fraction of calcium and virtually no other cation. The quantity needed is a stoichiometric excess over the cations to be stripped.

In the lime regeneration column the wash solution produced contains $CaCl_2$. The quantity produced is stoichiometrically equivalent to the amount of cations loaded onto the cation resin. Since 80% of these are not calcium there is fortunately more than a stoichiometric equivalence of Ca in the anion waste stream to the

ions to be displaced from the loaded cation resin. The use of this waste stream is a suitable means of providing the needed calcium ions for conversion of the loaded cation resin to the calcium form.

(c) In order to recycle as much as possible of the sulphuric acid after $CaSO_4$ precipitation it is necessary to avoid addition of large quantities of wash water and to add the make-up sulphuric acid at as high a concentration as possible. Each of these is possible. The wash water upflow rate can be set to very low values, just sufficient to exceed the average downflow rate of water with resin pulled down thus producing a very small, but sufficient, net upflow of wash water while still maintaining stable fluidization. The limitations of this technique depend on the regenerant concentration being used and were discussed in Section 2.5. The same can be done in the intermediate column to avoid incurring unnecessary additional wash water consumption. The net upflow of regeneration wash flow determines the calcium sulphate slurry concentration to be disposed of from the settler. This and the sulphuric acid concentration in the recycle solution determines the quantity of acid wasted in the $CaSO_4$ slurry.

The supersaturated calcium sulphate solution leaving the regeneration column must be stabilised so that the recycled solution will not precipitate further $CaSO_4$ in the recycle pumps and pipe work or in the stripping section of the column. Similarly the concentration of $CaSO_4$ particles remaining in the recycled solution must be low enough to prevent blockages in the system.

Consequently, a crystallizer and a suitable separation step are required. The requirements for a crystaller are:

(i) to provide mechanical agitation and thus to create the nucleation needed for precipitation to occur.
(ii) to provide enough retention time for complete precipitation.

Finally the process will be aided if the supersaturated solutions produced in the column are of such a nature that nucleation does not easily occur under conditions existing in the column but can be made to occur outside the column by mechanical agitation or similar means.

Fortunately it has been shown by laboratory tests (see section 4.2.6), that quite high concentrations of Ca and SO_4 can be maintained without precipitation even in the presence of vigorous agitation if no seed crystals are present.

4.4.2 Pilot plant acid recycle flowsheet

A five-column system as shown in the flowsheet of Figure 4.8 was set up on the pilot plant. Based on the considerations discussed in Section 4.4.1 two stirred tank crystallizers in series (total retention time 2 hours: ½ hour + 1½ hours) were employed for crystallizing duty. An upflow sludge-blanket type of settling tank was built for removal of fine crystals. The solids contact and additional retention time (±3,0 hours) of this unit ensured that the settled solution was completely stabilized. The base of the settler was conical to allow concentration of the $CaSO_4$ collected and provide for intermittent slurry discharge with minimal liquid loss.

The first crystallizer received recycled solids from the settler for nucleation seed. The purpose of the second crystallizer was to counteract any short circuiting in the first unit. The maximum crystal yield would thus be attained ensuring that complete stabilization of the solution had occurred before it entered the settler. Any tendency to scale formation would be likely to cause cementation of crystals in the settler which could lead to desludging difficulties.

In order to test the operation the same regeneration column operating conditions and load column conditions were chosen as for the brine rinse tests. The acid concentration was allowed to rise steadily in the recycle system by constant acid addition until an adequate H^+ ion fraction was attained. Care was taken not to exceed 1,0 N the concentration at which

precipitation inside the column could occur due to too high a supersaturation level of $CaSO_4$ (i.e. too much Ca being removed from the resin for the recycle flow rate being used). The recycle flow rate used was 900 mℓ/min which can be compared to a total flow of 450 mℓ/min in the acid only condition. Thus about twice as much $CaSO_4$ could be carried out of the column at the same safe and entirely operable $CaSO_4$ concentration as attained in the acid-only operation (1,0 N maximum). However, with supersaturation effects mentioned earlier it might be possible to handle an even greater $CaSO_4$ load.

Since bed expansion was greater at 900 mℓ/min the resin pulled down was only 400 mℓ/cycle and consequently the cycle time was reduced to 15 minutes in order to maintain the same average resin flow rate.

4.4.3 Acid recycle results

The concentration of sulphuric acid was gradually raised and it was found that at 1,0 N very similar performance of the resin regeneration was obtained as originally found with straight acid regeneration at that concentration. Precipitation inside the column did not occur except on 3 occasions in the top (hopper) section. This was due to transporting the resin from the intermediate column in 1,0 N acid solution. Normally resin is transported in the original solution pulled down with it and dewatered after transport but this was not convenient on the pilot plant. The result was that calcium sulphate formed in the stagnant catchpot and reach scale-forming concentrations. Scale formation and precipitation was not observed in any stages below the hopper.

The remainder of the recycle system functioned extremely well and considering that only about three weeks of initial operation provided little time for operators to become familiar with the rather complex flow sheet, entirely manually controlled, the three stoppages that occurred are not significant.

In conclusion, the method works very satisfactorily and no problems should be encountered in operating a large scale plant provided due care is

taken to avoid conditions where resin/acid mixtures are stagnant. When the plant had to be stopped for about 2 hours as a result of a pump failure, the acid in the regeneration column was simply flushed out to avoid possible trouble due to stagnation in the column. The steady state run reported here was continued over a week with 3 stops of between 30 minutes to 90 minutes to repair a leaking pump and remove gypsum from the hopper as described above.

4.4.4 Resin composition and acid consumption

The resin composition and liquid composition for the steady state run are presented in Table 4.17. The removal of sodium from an ion-fraction of 0,23 on the loaded resin to 0,02 on the intermediate resin and the corresponding increase of the calcium ion-fraction from 0,47 to 0,82 shows clearly the role of the Ca^{++}/Na^{+} exchange in replacing the exchangeable ions by Ca^{++}. It is also to be noted that the magnesium on the loaded resin is reduced from 0,21 to 0,16 but is not significantly reduced in the regeneration column. This shows that most of the magnesium removed from the feed water by the resin is rejected in the intermediate column, being replaced by calcium on the resin.

After regeneration the calcium ion-fraction is reduced to 0,51. Although this calcium ion-fraction is high, because the sodium on the resin was so effectively reduced, a satisfactory effective working capacity of 0,54 meq/mℓ resin was attained and the H^{+} ion-fraction in the load column product liquid shows that the feed was 80% desalinated.

The most significant factor, however, is the ratio of acid applied to working capacity gained. The only losses of sulphuric acid which could occur were with the calcium sulphate slurry and net solution overflow from the column. The latter balances the input of water from make-up sulphuric acid and small net upflow of wash water. (Concentrated sulphuric acid could be applied since it is diluted in the recycle stream.) The calculated loss of acid amounted to 8% of the sulphuric acid applied. Thus the acid application ratio, ideally 1,0 meq/meq is degraded to 1,08/1,0 = 1,08 and the effective R/L is thus 0,92.

TABLE 4.17

SULPHURIC ACID RECYCLE:

RESIN AND LIQUID COMPOSITIONS

	H^+	Na^+	Ca^{++}	Mg^{++}
RESIN (ion-fractions)				
load	0,09	0,23	0,47	0,21
intermediate	0,01	0,02	0,82	0,16
regen.	0,34	0,01	0,51	0,15
LIQUID (ion-fractions)				
	H^+	Na^+	Ca^{++}	Mg^{++}
load	0,80	0,20	0	0
intermediate	0,07	0,76	0,07	0,10
regen.	0,92	0,01	0,04	0,04

4.4.5 Conclusions on the use of the five-column system for sulphuric acid recycle

The technique was found to function extremely well. Operation was straight-forward but because of limitations in the size and design of the relatively small pilot plant and lack of automatic controls for the acid recycle section some difficulties were experienced. Nevertheless it was demonstrated that such a process will function well on a larger scale.

The design of column diameters, crystallizers and settlers for this process cannot, however, be undertaken from the results of this demonstration. Development work on a larger scale is required. Because of the extremely important acid savings this development is considered essential.

4.4.6 Improved acid recycle system using $CaSO_4$ seeding

With the above in mind a very short test was carried out to evaluate the feasibility of eliminating the crystallizers by causing the crystallization to occur within the column. Thus $CaSO_4$ crystals were injected just

above the acid injection point in the regeneration column. Calcium form resin was fed into the column. It was found that enough slurry could be injected, without any adverse fluidization effects on column operating problems, completely to prevent scale formation even when the acid concentration was raised to 2,0 N. This technique is thus a combination of the external acid recycle system originally tested and of the seeding proposal discussed in Section 4.3.1. The results serve to offset the reservations regarding its potential expressed there. The use of a batch contactor can also be considered when seeding is applied in this way.

It is thus recommended that future work on acid recycling should employ the in-column seeding technique. It eliminates the need for the high recirculation flow rates and the crystallizers and allows a smaller and less efficient settler to be employed. It thus has a major capital cost advantage over the external seeding method.

4.5 REGENERATION OF WEAK ANION RESIN USING LIME

4.5.1 Introduction

When lime is used in the CCIX regeneration column its low solubility of 1,85 g/ℓ or 0,05 N implies that it should be injected as a slurry in order to attain the waste solution concentration at which it is desired to operate the process. The waste solution is thus formed by the gradual dissolution of lime solids and consists mainly of $CaCl_2$ formed from the HCl molecules being stripped from the loaded resin. The reactions are as follows:

Anion load

$$R{\equiv}N + HCl \rightleftharpoons R{\equiv}NH^+ + Cl^-$$

$$R{\equiv}NH^+ + Cl^- \longrightarrow R{\equiv}NHCl$$

Anion Regeneration

$$2R{\equiv}NHCl + Ca(OH)_2 \longrightarrow 2R{\equiv}N + CaCl_2 + 2H_2O$$

Sulphates, and other anions present on the loaded resin, form the corresponding calcium salts.

Because a stoichiometric quantity of lime is used and there is no increase in efficiency to be gained from applying an excess of solid lime, only enough lime is added to maintain the pH of the regenerant solution above 12,0. Thus only a trace of free lime is present in the spent regenerant solution leaving the top of the regeneration column. However, even if lime is injected at numerous points in the regeneration section it must be injected and distributed as a slurry.

As with any other regenerants (such as ammonium hydroxide) the final waste solution concentration is inversely proportional to the average flow of wash water up the column. Reducing the wash water flow rate will increase the lime slurry concentration within the column and thus the waste solution concentration. In the CCIX column the net wash water upflow rate can be made very small while still attaining efficient desorption of electrolytes from the resin pores. Thus the spent wash water leaving the wash section and entering the regeneration section can be made to attain high concentrations. This concentration is then increased after addition of and dissolution of the lime as the liquid moves up the column through the regeneration section.

4.5.1.1 Adverse effects of lime solids. There are a number of important effects which make the use of lime at high concentrations difficult:

(1) Even if the lime is injected at distributed points the lime solids interfere with fluidization of the resin and the inventory of resin in each stage is reduced due to the presence of the lime solids. This reduces the amount of resin that can be transferred in each cycle thus reducing the resin-handling throughput of the regeneration column. Consequently larger equipment is needed. For example, the column diameter may need to be increased compared to that required if ammonia were the regenerant.

(2) In order to entrain the lime solids (and flocculated precipitates of calcium salts of the humic acids stripped from the resin) a certain minimum superficial liquid velocity and bed expansion must

be maintained both in the wash section and the regeneration section. The velocity must be great enough to wash all the lime solids from the fluidized beds near the lime injection point during the upflow period. If this is not achieved the lime solids remaining will be drawn down with the resin during the following pull-down. The regenerated resin leaving the column would then contain lime which would contaminate the anion product water leaving the top of the anion load column.

Resin density and particle size largely affect the required wash velocity, and the column diameter then determines the quantity of wash water that must be used. Therefore increasing column diameter to increase the resin throughput as suggested in (1) above carries the penalty of lower water recovery in the anion section of the process and lowers the waste solution concentration of the regeneration column. At a given wash water velocity more time may be provided for lime to disengage by increasing the upflow time. This would, however, reduce the resin handling capacity of the column and would also increase the wash water consumption. A minimum upflow time may, however, be expected to exist below which it is impossible to attain adequate lime solids disengagement even at very high wash water velocities.

(3) An obvious way to raise the waste solution concentration is to recycle it around the upper regeneration stages. Kinetic tests showed that this was acceptable although higher waste solution concentrations slightly retarded the regeneration kinetics. This implies that longer contact times would be needed when the waste solution concentration is increased if the stage efficiency is to be maintained. Alternatively more contact stages would be needed. In view of the minimum liquid velocities and the effect of column diameter on water recovery, longer contact times can only be obtained by increasing the column height. Since there is a maximum practical height it is apparent that the pursuit of maximum

attainable waste solution concentrations must concentrate on
(a) maintaining a high stage efficiency in the CCIX column and
(b) on developing a new contacting system where the resin inventory of the contactor would not be affected adversely by high lime solids concentrations. (Refer to Section 4.5.6.)

(4) While the inorganic salt concentration of the regenerant waste solution (mainly $CaCl_2$) is increased the organic sludge concentration also increases. Experience has shown that the floc becomes tougher and reforms more readily after any breakage due to agitation or increased liquid velocities. As the waste concentration is raised to about 0,2 N the problem in (2) becomes predominantly one of preventing pull-down of the organic sludge rather than of the lime itself.

(5) Finally, wall effects and particle bridging at the start of an upflow cycle, due to packing of resin and lime solids after the settle period, make stable operation difficult in a small diameter column. Originally a 50 mm I.D. anion regeneration column was used on the pilot plant. By increasing the diameter and reducing the settle period to avoid tight packing it was possible to obtain perfectly stable operation:
(a) higher lime slurry concentrations could be employed, and
(b) the minimum wash velocity mentioned in (2) could be reduced.
Column diameters must, however, be increased in proportion because increasing only the anion regeneration column diameter will incur greater wash water consumption without a corresponding increase in load column product throughput.

The use of higher density resins could assist in counteracting all of the detrimental effects of lime solids and would thus allow greater waste solution concentrations to be obtained. Suggestions have also been made regarding use of

(a) finely milled special grades of lime.
(b) floc dispersants such as sodium silicate in trace amount.

(c) indirect use of lime to regenerate a recirculated primary solution of NH_4OH thus avoiding handling of lime in the column itself. However, use of lime rather than ammonia to regenerate the resin has a major advantage. Difficulty in rinsing the last traces of NH_4^+ ions from the weak anion resin pores in the presence of adsorbed organics leads to carryover of about 20 mg/ℓ of NH_4^+ into the anion load column product water. With lime this is replaced by Ca^{++} ions which have no adverse effect on normal uses of the product water whereas residual NH_4^+ makes subsequent chlorination expensive.

(d) Additives such as sodium and magnesium salts or sucrose to increase the solubility of lime. These methods have not been studied in this work.

4.5.1.2 Importance of attaining high anion waste solution concentrations.

On wastewaters such as Milnerton (TDS ±750 mg/ℓ) fairly high concentration factors are readily attained in the anion system regenerated with lime. Treating more saline water of TDS up to 2500 mg/ℓ (e.g. Walvis Bay ±2200 mg/ℓ) is perfectly feasible with ion exchange using lime regeneration but the concentration factor needs to be increased in proportion to the feed salinity and degree of desalination required in order to maintain high water recovery. The following comparative figures illustrate the concentrating performance that must be aimed for:

	Milnerton	Hypothetical Case
Feedwater TDS mg/ℓ	±750	±2500
Feedwater concentration eq/ℓ	0,015	0,05
Anion waste concentration eq/ℓ readily attained with lime	0,2	0,2
Concentration factor (based on 100% desalination)	13,3	4
Water recovery in anion section	92,5%	75%
Desired anion waste concentration eq/ℓ	-	0,5-0,75

While the water recovery on a 0,015 N feedwater is acceptable it is too low on a 0,05 N feed. To increase it would require a greater lime concentration to be handled in the regenerator. Such a requirement would arise in treatment of some domestic wastes (such as Walvis Bay) and in many industrial effluents. The refinements and developments discussed in (a) to (d) above would need to be considered only for such saline waters if water recovery is the primary concern. However, greater concentration ratios remain of interest in any application because of the incentive to reduce the volumes and costs involved in brine disposal. Even when water recovery is already high enough that no incentive for high concentration factors remains on this account they would still improve the economics of potential chemical recovery from the waste brines.

Any improvements which can be made in the ability of ion exchange systems to handle concentrated solutions and/or solids in suspension will also benefit various applications of ion exchange in chemical processing. For example, an ion exchange route to producing Na_2CO_3 from limestone and NaCl waste brine solutions is a technically feasible adjunct to any large desalting plant. Economics of such a process would depend largely on the concentration of the available NaCl waste stream from the desalting plant and on efficient lime regeneration equipment.

4.5.1.3 Scope of experimental investigations using lime regeneration.

This section discusses work carried out on various aspects of using lime. It is shown that, with suitable design, it is possible to attain anion waste concentrations of 0,2 N and to achieve excellent column operating stability when injecting lime directly into the column. Results with a liquid recirculating batch regenerator (see Section 4.5.7) in which loaded resin was treated before introducing it into the CCIX column indicated that the waste solution concentration can be increased to about 0,5 N. This system included a settler in the recirculation circuit which controlled accumulation of suspended solids, thus avoiding fludization problems.

Although there is no theoretical reason why greater concentrations cannot be attained in this batch/CCIX combination (see Section 4.5.7), practical limitations of the small scale of equipment used in the pilot plant resulted in difficulty in demonstrating higher concentrations. Control of a number of vessels in series and the additional sequencing of operations must be done automatically to be successful to obtain stable operation over long periods and this was not available on a small scale. The configuration of ion exchange contactor and how it is used determines the efficiency of an ion exchange concentrating process. The concentrating capability of ion exchange processes is determined ultimately by the properties of the ion exchange materials used - capacity, pore volume, density, etc. The last section (4.5.7) of this chapter examines this question and provides the motivation for a search for improvements in this area. The study of liquid ion exchangers and of ion exchange membranes are considered.

Overall objectives of experiments with lime

The various effects and alternatives discussed in (1) to (5) of Section 4.5.1 were systematically investigated. The first task was to ascertain the maximum amount of lime that could be handled in a CCIX column with the simplest plant configuration, i.e. injecting it directly into one stage of the existing regeneration column. Improvements in operating stability and regeneration performance could then be sought through systematic equipment and process modifications and development.

4.5.2 Results of earlier preliminary tests using lime in the 50 mm I.D. pilot plant column

Possible methods of using lime

There are three basic methods of applying lime in a small pilot plant CCIX column. The basic requirement is to be able to meter the quantity injected or to control the average rate of injection in some way.

(1) Injection of enough lime for the entire upflow cycle into the lowermost regeneration stage during a metered interval at the start of an upflow cycle. This depends upon there being adequate upflow

time for the lime to distribute upwards and be completely eliminated from the region near the injection point before the next resin pull-down. The large plug of lime introduced in this method will displace resin from the injection stage and during the upflow cycle all the stage resin inventories must become restabilized before the next pull-down. It can be seen that this method would be rather inefficient.

(2) Lime can be pumped continuously throughout the upflow cycle and can be distributed into one or more stages (or even into multiple points in these stages). A metering pump can be used having an adjustable delivery. This method allows the correct amount of lime to be added with the lowest possible lime solids concentration or accumulation at any given point in the column. Reliable metering of the small flow of lime slurry (±30 mℓ/min of 2½% slurry) is, however, a problem on a small pilot plant, but it is suitable for larger installation.

(3) By withdrawing liquid from the top of a stage and recirculating it, with addition of make-up lime, into the bottom of the stage the upflow velocity and bed expansion can be increased to facilitate lime/resin disengagement without increasing the net upflow rate of wash water or solution in the stage or column. In this method a fully mixed liquid flow would be approached in each stage. Similar effects might be achieved by agitation of the stage contents but mechanical agitation is likely to increase resin attrition and losses and is best avoided. Liquid recirculation requires an enlarged cross-section at the top of each recirculating stage to attain liquid/solid separation to allow liquid to be withdrawn. Alternatively, liquid may be recirculated over the entire regeneration section. This would be simple but would lose some of the advantages of multistage countercurrent contact. A fraction of the spent regenerant can be indirectly recycled by using it to make up the lime slurry for injection.

Early test results

Originally method (1), above, was used on the 50 mm I.D. column with similar cycle times as for ammonia regeneration[7]. This served to demonstrate that lime was an effective regenerant and that waste concentrations were not as great as attained with ammonia. Results are presented in Table 4.18. Batch kinetic tests showed that the rate of regeneration with lime was much slower than with NH_4OH and that presence of $CaCl_2$ retarded the rate. Figure 4.9 compares the kinetic curves for 0,5 N NH_4OH, 0,05 N $Ca(OH)_2$ (solubility limit) and $Ca(OH)_2$ in 0,5 N $CaCl_2$ solution. (The latter two curves are taken from Figure 2.7.)

Although the retarding effect of the $CaCl_2$ produced in solution is significant at 0,5 N concentration, it can be compensated for by providing slightly larger contact times through larger equipment. The lower regeneration rate with lime does not detract greatly from the overall advantage gained from the much lower running costs with the cheaper lime as regenerant even though larger equipment than needed for ammonia is indicated.

Table 4.18 shows that regeneration and desalination performance was adequate in these tests. However, column operation was troublesome due to blockages and unstable resin inventories. Better control was needed and in all future work method (2) with a metering pump was used for lime injection. Initially one injection point was used with 6 wash stages below it and 6 regeneration stages above it. Following this the effects of using 9 wash stages and 3 regeneration stages and, finally, of splitting up the lime over the top 6 stages of the column were tested.

Practical features of later experimental work.

For the tests described here lime was made up in an agitated tank as a 2,5% suspension. Premier grade high calcium hydrated lime was used. This was pumped using a piston head metering pump capable of delivering between 10 and 130 mℓ/min of the suspension. In larger scale operation 10% slurries can be metered using diaphragm heads. Trouble with this lime feeding system occurred if resin particles entered the slurry tank or if the pump was switched

TABLE 4.18

PRELIMINARY RESULTS USING LIME
IN 50 mm I.D. REGENERATION COLUMN

FEED WATER ANALYSIS (MILNERTON HTE)

Run No.	CONCENTRATIONS (mg/ℓ)								
	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+	Cl^-	NO_3-N	$SO_4^=$	COD
1	224	23	22	31	7	335	14	125	95
2	235	23	32	32	5	344	13	89	89
3	218	21	32	31	<5	327	14	140	87
4	217	21	36	32	<5	352	13	106	130

PRODUCT WATER ANALYSIS

Run No.	CONCENTRATIONS (mg/ℓ)							
	Na^+	K^+	Ca^{++}	NH_4^-	Cl^-	NO_3-N	$SO_4^=$	COD
1	15	2	20	<5	51	13	<5	32
2	17	3	16	5	29	7	<5	35
3	7	2	31	<5	27	8	<5	52
4	12	3	26	5	27	3	<5	55

DESALINATION PERFORMANCE

RUN NO.	PRODUCT FLOW ℓ/d	AVE FEED TDIS mg/ℓ	NO.OF REGEN. STAGES ANION	$CaCl_2$ RECYCLE	DESALIN-ATION %	WATER RECOVERY %	FEED COD mg/ℓ	PROD COD mg/ℓ	WASTE CONC. CATION mg/ℓ	WASTE CONC. ANION mg/ℓ
1	4838	820	4	No	85	84	95	32	10 700	10 900
2	4685	820	4	No	91	82	85	35	11 200	9 500
3	5024	820	4	Yes	85	88	87	52	18 800	14 500
4	5024	820	6	Yes	81	88	130	55	16 300	12 500
(5)	4650	1250	4	-	88	92	89	20	23 300*	145 450†

Runs 3 & 4 used recirculation of CaCl in the lime slurry make-up. Run (5) is with 5-column ammonia-nitric system for comparison.

* Brine waste † Ammonium nitrate byproduct

the "gap" propagates downward on each successive cycle. The nozzle caps on the bottom stage separator also aid in preventing gaps. Because the commercial resin consists of a distribution of bead sizes there is a tendency for smaller beads to be found at the top of any stage and larger ones at its base. There is also a marked size segregation up the column (smaller at the top).

For a given liquid flow rate this means that the bed expansion will be greater and the stage resin inventory smaller in the higher stages. In a column operated with a soluble regenerant solution density will exert a further effect. When a lime slurry is present the bed expansion is very much increased particularly where the lime is still undissolved, i.e. in the lime feed stage or the one just below it where there tends to be some accumulation of lime.

Measurement of individual stage bed expansions on 50 mm I.D. column

In order to determine the correct quantity of resin to pull down under the various possible operating conditions and to find those conditions which would optimize this amount and maximise the resin-handling capacity of the regeneration column, measurements were made of the settled resin bed height in each stage. From these readings the individual stage bed expansions were calculated.

These measurements were made for the following operating conditions:

(a) without addition of lime and without pulling down resin in order to determine limiting conditions which might occur with long upflow times;

(b) without lime but after 18 cycles to observe any mixing effects;

(c) with lime injected at stage no.7;

(d) lime injected at stage no.10;

(e) with $CaCl_2$ solution recycle over the regeneration section;

(f) at different wash flow rates, upflow times and with excess free lime solids. (These tests were done mainly to check the effect of free lime on removal of organic material, $CaSO_4$ precipitation or related effects on the regeneration performance.)

(g) A test was also run with ammonia to obtain comparative data.

Table 4.19 gives a summary of the operating conditions tested while Table 4.20 gives the measured bed expansion data. Other tables (4.21, 4.22 and 4.23) give product and waste liquid plus resin compositions.

Discussion of results of bed expansion tests

(a) Segregation of particle sizes:

The effect of wash flow rate and the resin particle size distribution on the bed expansions are both clearly seen from the tests done without cycling, i.e. without pulling down resin. At 100 and 200 mℓ/min wash flow the top stages contained the least resin and the effect of flow rate was more marked on the lower stages. At 300 and 400 mℓ/min there was a marked disturbance at the "feed" stage where a distributor fitting was installed but the top stages are still considered limiting.

(b) Effect of mixing due to cycling on the size segregation:

Cycling of the column might be expected to reduce the size segregation effect since a mixed batch of resin from the load column is dumped into the top of the regeneration column. However, even at a high flow rate 400 mℓ/min and high average bed expansions (50-90%) and short cycle times all of which would be expected to encourage mixing there was still a marked size segregation. These results are a confirmation that resin is transported in plug flow from one stage to the one below it and "ordering" is maintained during the upflow cycle. Provided liquid distribution is even and there are no currents, mixing of the resin phase does not occur during upflow. In a fluidized bed, however, finer particles must move to the top of the bed. Thus any axial mixing occurring in the resin plug during passage through the stage separator during pull-down is effectively "un-mixed" due to this effect. Clearly this takes place within a time period shorter than the 10 minute upflow time used in these tests.

(c) Operation with 6 wash and 6 regeneration stages and effect of wash flow rate:

The column was then put into operation with lime injected at stage no.7 counting from below, i.e. with 6 wash and 6 regeneration stages. The lime feed slurry concentration was 7,5% solids and it was injected at 25 mℓ/min

TABLE 4.19

50 mm I.D. COLUMN OPERATING CONDITIONS FOR INVESTIGATION OF LIME REGENERATION

RUN SERIES IDENTIFICATION	WASH FLOW mℓ/min	LIME/SLURRY CONC. %	LIME/SLURRY FEED FLOW mℓ/min	UPFLOW TIME mins	NUMBER OF REGEN. STAGES	RESIN TRANSFERRED EACH CYCLE m	ANION LOAD COLUMN LIQUID FLOW RATE mℓ/min
1	400	7,5	25	10	6	290	2200
2	100	2,5	35	30	6	600	1900
3	150	2,5	30	30	6	500	2000
4	150	2,5	30	30	3	410	2000
5 (Excess lime)	150	2,5	30 to 60	30	3	410	1800
6 (Excess lime)	150	2,5	50	30	3	410	1920
7	100	2,5 in $CaCl_2$	40	30	3	610	1900
8	100	2,5 in water	40	30	3	610	1900
9	100	Ammonia	-	15	3	710	4000

(Note: Additional runs to experiment with wash flow and cycle times were done between Run 1 and 2. See Table 4.15.)

TABLE 4.20

% BED EXPANSION IN INDIVIDUAL STAGES OF 50 mm I.D. ANION REGENERATION COLUMN WITH ZEROLIT MPH (AGED)

DATE 1979	WASH FLOW (mℓ/min)	LIME SLURRY (%)	FEED FLOW (mℓ/min)	LIME IN COLUMN (Nom.) %	UPFLOW TIME (mins)	1 BOTTOM	2	3	4	5	6	7 REGEN FEED STAGE	8	9	10 ALT FEED	11	12 TOP	RESIN VOLUME IN LIMITING STAGE (mℓ)
TESTS DONE WITHOUT CYCLING THE REGENERATION COLUMN - NO LIME INJECTED																		
17/4	100	-	-	-	-	0	9	12	13	16	18	64	28	37	49	63	73	810
	200	-	-	-	-	12	24	24	30	33	35	71	35	44	53	58	73	810
	300	-	-	-	-	16	39	44	46	51	60	131	73	82	82	112	108	662
	400	-	-	-	-	27	63	73	76	86	93	181	89	108	126	154	136	554
MEASURED AFTER 18 CYCLES OF REGENERATION COLUMN - NO LIME INJECTED																		
	300	-	-	-	-	18	37	43	44	44	51	107	53	63	63	68	93	
	400	-	-	-	10	53	79	86	89	89	79	151	82	93	89	76	68	

into a wash water upflow rate of 400 mℓ/min giving a nominal lime slurry concentration of 0,44% (4,4 g/ℓ or 0,12 N) in the lime feed stage. The upflow time was 10 minutes. This concentration of lime proved to be troublesome resulting in depletion of resin in some stages. Frequent manual pulsing was needed to maintain the stages full of resin. It was even necessary to stop the lime feed for some hours to regain stable inventories. From this experience it was clear that lime could not be distributed and disengaged with such a short upflow period and it thus accumulated. The bed expansion values presented in Table 4.20 are for steady operation and do not reflect directly the observed unstability. Only 290 mℓ of resin could safely be transferred each cycle giving an average resin rate of 23,2 mℓ/min. (Total cycle time ±12,5 minutes.)

Consequently the upflow time was extended to 30 minutes and the lime injection rate reduced correspondingly by diluting the feed slurry to 2,5%. (The feed pump delivery was unreliable below about 20 mℓ/min.) A major improvement in stability was noted and the bed expansion data was more evenly spread. It proved possible to pull down slightly more resin, 320 mℓ/cycle. However, the average resin rate dropped to only 10 mℓ/min (because of longer cycle time) and the nominal lime concentration to 0,14% (0,038 N). This is in fact below the solubility of lime 0,05 N.

In order to attempt to raise the waste concentration the effect of gradually reducing the wash flow rate to 100 mℓ/min was tested. Table 4.20 shows that at 100 mℓ/min the nominal lime slurry concentration in the feed stage was 0,42% or almost that in the first test at 10 minutes upflow. All the bed expansions were much lower and the disturbance at the lime feed stage was hardly noticeable. This test run showed the benefits gained from extending the cycle time. The bed expansion data for the four wash flow rates show that there is a marked sensitivity of the fluidization properties to higher flow rates at a point between 100 and 200 mℓ/min. (In the 200 mℓ/min test excess lime was being added to observe any major effects and the bed expansions are in fact higher in some stages than at 300 mℓ/min. This was followed up in bench tests of fluidization at different lime strengths. See Section 4.5.5.

At 100 mℓ/min wash flow rate it was possible to transfer 600 mℓ of resin per cycle giving a resin rate of 18,5 mℓ/min. For comparison Table 4.19 gives the conditions typically attainable with ammonia: 710 mℓ/cycle at ±15 minutes upflow or 40,6 mℓ/min (17,5 minutes total cycle time), and 57 mℓ/min at a 10 minute upflow time.

Clearly, then, although a reasonable waste solution concentration of about 0,12 N was being attained the resin handling capability of the 50 mm diameter column was severely reduced. This is reflected also in the anion load column liquid flow rate of about 2000 mℓ/min compared to 4000 mℓ/min and above with ammonia. (Load column flow was adjusted to maintain complete conversion at each regeneration condition tested as a measure of the working capacity of the cycling resin. In some of the later runs this did lead to difficulties in ensuring complete loading of the resin fed to the regeneration column. Table 4.22 gives measured resin compositions.)

Table 4.21 presents the analyses of the anion waste solution. These serve as very approximate values only (except for Cl^-) because of large and variable errors in the analyses due to the suspended solids and organics present in the solutions analysed. Thus more Ca was measured in some cases than was added to the system.

The anion load column product water analysis is given in Table 4.23. Bearing in mind the experimental nature of these test runs, the data show that regenerated resin composition was adequate to provide good conversion and COD removal in the anion load column.

Although a wash flow of 100 mℓ/min resulted in very stable column operation it was found that lime solids still tended to move downwards from the feed stage. Although most of the lime disengaged upwards near the feed stage (bed expansion ±60%) small amounts, not large enough to give noticeable physical problems, remained and were pulled down. In the lower stages (lower bed expansion) liquid velocities were apparently too low to cause disengagement. The result was that the traces of lime moved out with the resin to

TABLE 4.21

ANION WASTE STREAM COMPOSITION (mg/ℓ)

LIME REGENERATION OF Z-MPH

RUN NO.	WASH RATE	Ca^{++}	Cl^{-}	$SO_4^{=}$	NO_3^{-}	COD	pH	LIME ADDED meq/ℓ	Ca^{++} DISSOLVED meq/ℓ
1	400	2012	2165	693	505	397	11,4	119	100
2	100	4051	3767	2174	505	620	11,5	106	203
3	150	2328	2388	883	232	403	11,4	113	116
4	150 (3 regen.stages)	2162	1388	1088	232	315	12,2	113	108
5	150 (Excess lime)	2060	1477			213	12,7	113 to 194	101
6	150	2322	2231			306	12,6	143	123
7	100 ($CaCl_2$ recycle)	2734	4239			133	12,5	194	137
8	100	1975	2741			148	12,4	194	99
9	100 (Ammonia)	0	12407			(3360)⁺	10,0	0	0

(⁺COD due to ammonia)

TABLE 4.22

ANION RESIN COMPOSITION (meq/mℓ)

LIME REGENERATION OF Z-MPH

RUN	COLUMN	Cl^-	$SO_4^=$	NO_3^-	COD (mg/mℓ)	TOTAL INORGANIC	FREE BASE	TOTAL INORGANIC +FREE BASE
1	load	-	-	-	-	-	0,04	-
	regen	-	-	-	-	-	1,15	-
2	load	0,57	0,27	0,31	6,1	1,24	0,08	1,32
	regen	0,01	0,03	0,07	1,4	0,11	1,35	1,46
3	load	0,60	0,19	0,25	4,0	1,04	0,06	1,12
	regen	0,02	0,03	0,04	1,0	0,09	1,22	1,31
4 3 regen stages	load	0,50	0,27	0,23	4,4	1,00	0,16	1,16
	regen	0,05	0,01	0,06	1,5	0,13	1,21	1,34
5 Excess lime	load	0,51	0,22	0,14	3,8	0,87	0,07	0,94
	regen	0,06	0,01	0,03	0,9	0,10	1,14	1,24
6 Excess lime	load	0,56	0,16	0,11	3,7	0,83	0,15	0,98
	regen	0,05	0,00	0,05	0,8	0,11	1,19	1,30
7 ($CaCl_2$ recycle	load	0,55	0,12	0,12	3,0	0,79	0,38	1,17
	regen	0,06	0,01	0,05	0,7	0,12	1,17	1,29
8	load	0,44	0,14	0,06	2,1	0,63	0,60	1,23
	regen	0,07	0,01	0,02	0,5	0,10	1,21	1,31
9 (Ammonia)	load	0,51	0,09	0,03	2,9	0,63	1,10	1,73
	regen	0,06	0,0	0,02	0,5	0,08	1,45	1,53

TABLE 4.23

ANION LOAD COLUMN PRODUCT ANALYSIS (mg/ℓ)

LIME REGENERATION OF Z-MPH

RUN NO.	WASH RATE	FEED		ANION PRODUCT							% REMOVAL OF COD
		COD	Cl^-	Na	Ca	Cl^-	$SO_4^=$	NO_3^-N	COD	pH	
1	400	58	338	31	14	14	2,5	-	22	7,4	62
2	100	70	392	87	15	129	2,0	5	37	7,0	47
3	150	85	382	90	6,3	130	0	3,6	41	5,6	52
4	150 (3 regen stages)	85	383	76	11	185	0	2,6	41,1	4,0	52 (avg. 53)
5	150 (Excess lime)	73	370	8,3	20	36	3,3	-	20	6,6	73
6	150 (Excess lime)	70	376	12,6	21	65	0	1,2	24	4,7	66
7	100 ($CaCl_2$ recycle)	33	403	6,8	50	59	5	5	10	7,5	70
8	100	31	459	10,0	50	25	6	5	9,4	7,6	70 (Avg. 70)
9	100 (Ammonia)	108	350	1,0	0	5,5	0	1,8	19	7,9	

the top of the load column. This was observed to occur suddenly over a period of 5-10 cycles even after as many as 50 cycles without the effect appearing. Once it appeared the only remedy was to stop the lime feed or raise the wash flow for a few hours. The lime solids carryover resulted in contamination of the anion product water. It appeared therefore that a certain minimum bed expansion (about 50 to 60%) was needed. Consequently the wash flow was raised again to 150 mℓ/min in the 50 mm I.D. column. The effect was thought to be likely to be more marked in the narrow column than it would be in a large one due to wall effects causing uneven fluidization and liquid flow distribution in the lower wash stages at the low prevailing bed expansion. A larger column was later constructed and it was confirmed that lower flow rates and bed expansions could be used without this effect See Section 4.5.4.

Tests at 150 mℓ/min were carried out and it was found that 500 mℓ/cycle of resin could be transferred. No detailed bed expansion measurements were made. The lime migration problem was not observed with this wash flow rate.

(d) Operation with 3 regeneration and 9 wash stages:

As a possible alternative remedy to the lime migration problem and to shorten the path of lime movement lime was injected at stage no.10. Thus the stages below this point would have greater bed expansions than otherwise which would be expected to assist in removing the last traces of lime before it reached the lower wash stages. The presence of some lime in these stages say from no.3 to no.9, would keep the pH high so that they would still effectively be regeneration stages. In effect, moving the lime feed point further up resulted in concentrating the lime where it was needed most and avoiding high lime solids where there was no need for it.

With this system the bed expansion in the top stages was much higher, as expected. This did not, however, have a detrimental effect on stability and it was still possible to transfer 450 mℓ/cycle of resin. This implies that in some of the topmost stages more than the stage inventory of resin was being pulled down. However, due to the proximity to the hopper and the

pulsing of the lime feed pump the affected stages refilled rapidly so that in the long term depletion of the stages was not observed.

At this stage a set of reciprocating diaphragm pumps was installed on the columns to aid in accurate wash flow rate control. The additional pulsing effect made it unnecessary for manual pulsing by the operator and contributed further to easy operation.

Effect of excess lime solids

The optimum way to operate the 50 mm column was now considered to have been found. It was now of interest to determine the maximum lime solids concentration that could be used and also to observe any effects on regeneration performance. It was found possible to operate with as much as 0,71% lime solids (nominal) in the feed stage (no.10). The only improvement noted was in COD removal in the load column. The extra lime may have promoted precipitation of calcium-organic salts thus promoting removal of the organics from the resin by maintaining lower solution concentrations. This was not confirmed, however.

Volume of resin transferred each cycle had to be reduced from 450 mℓ to 410 mℓ/cycle. These tests showed that up to 100% excess lime could be handled by the column if required. It would only be possible to put this to use if the resin equivalent rate could be increased in proportion. This would require a higher capacity resin to be employed. This would achieve a greater waste solution concentration.

Comparison test with water only

A test was done without lime but injecting water at the lime injection point. From the bed expansion data it can be seen that there is little scope for further improving the operation of the 50 mm diameter column with the Zerolit MPH resin using lime. The effect of lime solids has been reduced to very close to the disturbance found with water injection. The following conditions were thus adopted for all future work on this column:

concentration of flocculated organic sludge was observed. Floc became tougher and reformed more rapidly above resin/liquid interfaces where shearing effects of interstitial flow were reduced. The reformed sludge became denser than the resin and completely displaced resin from some of the stages. No amount of pulsation was of any use and the sludge had to be drained off. Increasing the wash flow rate had little effect except if prolonged which defeated the objective of the experiment.

Thus the situation became sludge concentration limited rather than lime solids concentration limited. Clearly, further improvements could now be sought only with a heavier density resin or with a new type of recirculating regenerator avoiding solids in the CCIX column. Since the heavier density resin considered (SENBRIX) was not available at the time, this could not be tested on the pilot plant.

Conclusions

From the experience gained with the 100 mm column it was concluded that at 400 mℓ/min wash flow rate, upflow time of 30 minutes and 1800 mℓ/cycle resin transfer (55 mℓ/min average) a concentration of 0,2 N could be obtained in the waste solution. If it were possible to reduce the cycle time in yet larger, more stable columns one might postulate a concentration up to 0,4 N being attained. If no organics were present this could well be exceeded. Using a higher density resin could result in even higher concentrations being attainable.

4.5.5 Bench-scale fluidization tests to predict effect of lime solids concentration and heavy resins

Purpose of tests

In order to predict the fluidization behaviour of high density resins in the presence of lime and to observe the effect of narrow size distributions on the bed expansion, tests were carried out in a 25 mm I.D., 1000 mm deep column into which liquid was introduced using a metering pump. Used Zerolit MPH (weighted through uptake of organics during use), new MPH and new SENBRIX higher density resin were compared. Bed expansion was measured at various

flow rates in tapwater and up to 1% lime solids (equivalent to 0,27 N solution). The results are presented in Table 4.24. The technique used was to adjust the metering pump to give a specified bed expansion value and then to record the flow rate. For a given bed expansion the required superficial velocity for each resin may be determined from the table.

(1) In tapwater the new SENBRIX requires 2,8 times greater flow than new MPH for 10% bed expansion and 2,35 times for 100% bed expansion.

(2) As much as 30% of the commerically supplied resins are discarded when a 20/40 mesh screening is carried out. Most of the discard consists of fines. Consequently it would be expected that a 20/40 cut would have a lower bed expansion than the resin as supplied. Consideration could then be given to screening the resin before installation in a CCIX plant or specifying a larger size distribution. This would allow higher superficial velocities to be used, aiding lime disengagement. Table 4.24 does not include tests on screened used MPH but does show that "aged" resin can tolerate much higher velocities than the new, screened, MPH resin.

(3) There was little difference between the freebase (FB) form and the HCl form of the weak anion resins at low bed expansions but the HCl form of the SENBRIX could tolerate 29,2 cm/min compared to 26,4 cm/min for the free-base form for 100% expansion in tapwater. There was no significant difference between the two forms for the used MPH resin (Any effects present may have been masked due to the wider range of particle size distributions. Swelling behaviour of organically loaded resins may be different to that of new resins. No work was carried out to study this but it is recommended that such effects be included in any comparison of resin properties in future.)

(4) The fluidization properties of the higher density SENBRIX weak anion resin are intermediate between the Zerolit MPH weak anion resin and the Zerolit 625 strong cation resin used in the pilot plant.

TABLE 4.24

FLUIDIZATION TESTS IN 25 mm I.D. COLUMN - SUPERFICIAL VELOCITIES, cm/min

BED EXPANSION			10%	20%	40%	60%	75%	100%	150%	200%	300%
RESIN	FORM	LIQUID									
Z-MPH	Used in Columns Free base form	Tapwater	2,8	-	8,9	-	-	20,6	-	32,2	35,6
		0,25% lime	3,55	5,22	7,69	8,88	9,07	14,0			
		Repeat	3,35	4,93	7,3	9,47	11,05	14,0	18,74		
		0,5% lime	3,45	5,03	7,69	10,05	11,14	14,6	19,3		
		1,0% lime	1,58	2,56	3,55	4,24	4,73	6,02	7,89	9,86	
	HCl	Tapwater	2,56	4,24	7,3	10,8	13,4	17,2	24	33	
Z-MPH	New screened 20/40 FB form	Tapwater	1,22	2,24	4,18	5,8	7,74	11,2	15,9	20,2	
SENBRIX	New screened 20/40 FB form	Tapwater	3,45	5,13	11,83	16,5	18,3	26,4	34,6	43,2	55,6
		0,25% lime	3,45	6,5	10,45	15,45	19,5	90% 22,9			
		0,5% lime	2,96	5,52	9,57	14,4	17,9	90% 21,7			
		1,0% lime	2,86	4,73	8,68	13,0	16,7	90% 20,1			
	HCl	Tapwater	3,55	5,71	12,8	19,9	23,5	100% 29,2	37,7		
Z 625	H^+	Tapwater	6,9	10,8	19,9	31,2	36,7	47,3	64,1	76,5	

(5) Taking the data for MPH resin at 40% bed expansion, up to 0,5% lime solids made little difference to the superficial velocity but at 1% lime solids the velocity was reduced to half that in the lower lime concentrations and in tapwater.

By comparison the SENBRIX resin showed a far lower sensitivity to lime solids concentration. Taking the data for 100% expansion MPH was sensitive to lime even at 0,25% solids while SENBRIX tolerated from 0,25% to 1,0% lime solids equally well.

In order to relate the data measured in the 25 mm I.D. bench column to values expected in the feed stage in a CCIX column, Table 4.25 shows a comparison of superficial velocities in some of the pilot plant test conditions and the bed expansion measured in the feed stage of the 50 mm I.D. CCIX column as a ratio of that predicted from the bench column for similar nominal lime solids concentrations. (Bed expansions were predicted by interpolation in Table 4.24 for the nominal lime concentration of the CCIX feed stage.)

The bed expansion in the CCIX column was greater than predicted by a factor of 1,5 for feed stage no.7 and by a factor of 2,0 for feed stage no. 10. The differences are due to (a) the actual lime solids concentration in the feed stage being greater than the nominal concentration due to accumulation of lime solids, and (b) the resin particle size being smaller in stage no.10 than in stage no.7.

Conclusions

The data and results allow a reasonably good guess to be made that under similar conditions the improvement noted with SENBRIX heavy density resin in the bench column will be reflected in the CCIX column. In the CCIX column more than 0,7% lime solids (nominal) resulted in operating difficulties and this coincided with the increased bed expansion sensitivity at greater than 0,5% in the bench column with MPH resin. Thus it should be possible to achieve greater than 1% solids (nominal) in the CCIX column when using SENBRIX resin on the basis of the bench column results. The bench column

tests should be repeated on commercially supplied SENBRIX resin (or any other selected for use with lime) with a wider range of lime solids concentrations to determine the point of expected CCIX column operating problems. This would eliminate a lot of experimentation on the CCIX column to find limiting and optimum operating conditions.

The effect of organic sludge concentration was not tested in these experiments. However, increased resin density and the corresponding ability to use greater liquid superficial velocities may be expected to result in similar operating advantages with respect to organic sludge solids as with lime solids.

4.5.6 Experiments with a single stage lime regenerator with liquid recirculation.

Concept of an alternative contactor

As pointed out in Section 4.5.1.1 (3) and in Section 4.5.1.3 an alternative method of using lime is to use a contactor system in which the resin inventory would not be affected adversely by high lime solids concentrations, such as a recirculating batch regenerator. Thus the solution flow rate can be increased in order to wash lime and flocculated organic sludge out of the resin without increasing the wash water flow rate in the CCIX wash stages. The increased bed expansion resulting from the higher flow rates used could be accommodated by providing a deeper vessel than that typically used in the CCIX columns (0,5-1,0 m). Thus the bed expansion need not be limited to the same extent as in the CCIX column. The unit may be designed to process a large enough batch to achieve the required resin throughput even when long contact times (retention times) are necessary. Thus retarded kinetics due to increased solution concentrations (see Figure 4.9) may be compensated for by increasing the contact time as required, within practical limits. Using this contactor for lime regeneration and the CCIX column for resin washing has the potential to attain greater waste concentrations than is possible with the use of lime in the CCIX column on its own.

Because sufficient high density SENBRIX resin was not available it was not possible to develop the use of lime in the CCIX column any further. Therefore further efforts were directed at the batch contactor concept and a unit was constructed and linked to the pilot plant, using the original 50 mm I.D. CCIX anion regeneration column as a wash column only.

Alternative stirred stage contactor concept

An alternative approach which was considered was to use low shear agitators in a series of completely mixed stages in the CCIX column (see Figure 4.10). The agitators would be used to break up organic sludge and promote lime dissolution without the use of high liquid velocities. Each stage would separately receive a controlled lime feed. This method was not tried since it was felt that resin attrition rates would be too great. The batch regenerator would achieve the required improvement without this risk and would be simpler.

Recirculating solution, batch regenerator

Referring to Figure 4.11 the solution leaving the fluidized resin bed passed through an enlarged cross-section, in which resin particles were retained. During the regeneration this solution entered a small intermediate storage tank from which it was recirculated, after lime addition. After about 1,5 hours, when the resin batch was near equilibrium conversion lime injection was stopped. Recirculation was then continued for about 0,5 hour in order to use up the remaining free lime. The liquid overflow was then diverted to the settling tank the clarified solution being again recycled via another small tank and pump. During this period (± 30 minutes) organic sludge was disengaged from the resin batch and removed in the settler. Upflow was then stopped, the resin allowed to settle and then pulled down into the CCIX column hopper. The entire cycle was synchronized with the anion load column cycle. The cycle time of the latter is normally more than 2 hours and can be extended considerably to accommodate long batch regenerator times. For very long batch times intermediate resin storage might be required and can be readily provided. Spent wash water from the CCIX column was introduced into the regenerator recycle solution the excess of which was discharged at a high concentration as an overflow from one of the small storage tanks.

Results of batch regenerator tests

During continuous operation the concentration of the recirculating solution steadily increased reaching 0,2 N in some runs. However, due to the temporary nature and small scale of the equipment adequate flow balancing and control of liquid flows were not provided. Continued operation thus depended entirely on the operator and tapwater was frequently added to make up liquid levels after solution had overflowed and been lost to the drains. Consequently maximum concentrations and a steady state were never achieved. The work did prove, however, that it was possible to remove effectively lime and organic solids from the resin batch before transferring it to the CCIX column for washing thus allowing: (a) lower wash water flows to be used, and (b) greater column resin throughput. Both of these result automatically in greater waste solution concentration.

Although the batch regenerator would not provide complete resin regeneration even with the relatively favourable equilibrium, pore solution drawn with the resin into the CCIX column has $Ca(OH)_2$ in solution, sufficient to continue regeneration in the top stages of that unit. Since most of the organics have been removed, some lime can still be added to the top of the CCIX column to aid in complete regeneration without incurring a serious sludge problem. Alternatively a series of batch regenerators could be employed. The number used would be determined by a compromise between capital cost and regeneration efficiency.

Predicted wash water flow and water recovery

Very low flow rates can be used in the CCIX wash column if lime and sludge interferences are absent. The following example shows that at 100 mℓ/min in the 50 mm I.D. column it should be possible to attain 0,5 N waste concentration:

Anion load column feed concentration	0,015 N
Flow in load column	4,70 mℓ/min
Desalination duty for 80% salt removal	50 meq/min
Resin flow at 1,5 meq/mℓ resin capacity	33,3 mℓ/min

Wash water flow = waste solution flow	100 mℓ/min
Waste concentration	0,5 meq/mℓ = 0,5 N
Water recovery	97,6%

Wash flow rates equivalent to 25 mℓ/min net upflow on the 50 mm I.D. column are feasible on larger diameter units where wall effects and particle bridging are absent. Thus 2 N waste solutions should be attainable in a correctly designed system. This would allow the treatment of 0,1 N feed waters with a water recovery of 96%. When dealing with higher feedwater concentrations water recovery will drop.

Limitations of pilot plant testing

The recirculating regenerator system described above is relatively complex compared to a simple NIM-CCIX column. It involves additional pumps, control valves and vessels. It is rather difficult to maintain the control on a very small pilot plant and certain difficulties are experienced which make it impossible to carry the testing to the extremes mentioned above. The reason for these examples being important also does not relate to the treatment of the relatively low salinity wastewater with which this project is primarily concerned.

However, a number of applications of the CCIX technology developed in this project have been examined and studied on bench and pilot scale to evaluate potential snags. These involve higher salinity solutions than are normally regarded as being within the range, economically speaking, of ion exchange. But with the availability of an efficient technique of using lime, a relatively cheap regenerant, CCIX can provide a good answer to effluent problems provided a high water recovery can be attained.

4.5.7 Practical maximum anion waste solution concentration

The regeneration and spent wash solution concentrations which can be attained are limited by practical considerations: (a) physical operating limitations of the resin-liquid contactor, e.g. the CCIX wash column, and (b) concentration effects on the exchange processes taking place inside the ion exchanger and in the bulk solution (e.g. suppression of $Ca(OH)_2$ solubility).

Solution concentrations greater than about 3 N have been found to cause Zerolit MPH to float. Thus in a CCIX wash column resin will settle in the bottom stages but float in the top stages. The SENBRIX high density resin could tolerate higher concentrations. Specially designed contactors could be used to overcome this problem but would have other limitations. Very high electrolyte concentrations in the pore liquid may result in precipitation or other solution phase effects. It seems quite reasonable to consider all the ions on the fixed sites of a weak anion exchanger becoming concentrated in the pore liquid. Thus a 1,5 meq/mℓ capacity resin with a pore liquid volume of 0,35 mℓ/mℓ would have a pore solution concentration of 4,3 N. Taking the sorption ratio of 2,5 (Figure 2.4) the external solution concentration in equilibrium would then be 10,7 N. Regenerant concentrations as high as this are not likely to be encountered but there does not seem to be any theoretical reason why they should not be feasible to use. Consequently there is no reason why 2 N solutions cannot be attained apart from density and solubility effects in the solutions themselves. Such concentrations have been used with the strong cation resin.

The use of liquid ion exchangers could overcome the solution density problem. Normally used in a hydrocarbon carrier, they are lighter than the solution under all conceivable solution concentrations. Other problems will appear such as mutual solubility of the phases and stable emulsion formation which will be affected by solution concentration. Their success in water treatment for organic removal[16] and in recovery of metals and strong mineral acids (such as aluminium and sulphuric)[17], show that they have potential use in place of solid ion exchangers. Application of liquid ion exchangers in the presence of lime suspensions is an interesting prospect since a mechanically agitated liquid phase contactor is involved. Processes involving precipitates such as $Fe_2(OH)_6$ in the treatment of acid mine drainage waters are also of interest.

From the above discussion it is clear that there is scope for further study of (a) better solid ion exchangers - higher density and capacity, and (b) liquid ion exchangers.

4.5.8 Conclusions

Before a final assessment of this new contactor configuration can be made it is necessary to develop it further. This will require larger equipment which can, however, be designed on the basis of the flowsheet tested in this work. Because of the cyclic operations and the need to link three units (load column, regenerator and wash column) careful attention must be given to the inclusion of effective and reliable control methods.

The economic viability of this batch/CCIX process depends on the effectiveness of lime regeneration in higher solution concentration backgrounds and on the efficiency of the CCIX column for desorbing the electrolytes from the regenerated resin pores. Higher waste concentrations imply greater wash column operating loads and the countercurrent operation becomes of utmost importance. Although there are limitations, the potential exists to produce high anion waste solution concentrations with lime as the regenerant. The CCIX column can be used alone for low wastewater salinity and will give good water recoveries. The batch regenerator/CCIX combination should be considered for higher salinity wastewaters. These include acidic paper bleach plant and mine drainage effluents (around 0,05 N) and acid tailings solutions of up to 0,45 N.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 INTRODUCTION

The investigations reported in Chapter 4 have led to the conclusion that sulphuric acid and lime are effective regenerants for the CCIX desalination process. This chapter discusses the costs of CCIX treatment of a typical wastewater and points out the advantages of the improved five-column flowsheets.

The importance of developing the acid recycling system and the batch system of lime regeneration is discussed. Recommendations are made for continuation of the study of ion exchange processes and materials and of the potential applications of the CCIX process. The process has been developed to the stage where a larger scale plant can be designed and it is now important to make use of the technology by proceeding to the construction of a larger unit on which current applications can be demonstrated and new applications can be tested.

5.2 COST OF CCIX DESALINATION

5.2.1 Capital cost

Two licencees for the construction of the patented NIM-CIX column equipment supplied capital cost estimates for a 10 000 kℓ/day plant[15]. The estimates (R4,8 million and R4,3 million) were based on a specification for a demonstration plant which would have included numerous additional and special features. They were thus considered to be realistic and somewhat conservative. To remain on the conservative side a figure of R5 million was adopted for basing capital charges. With the cost of the resin inventory this figure becomes R6,5 million. The capital cost is depreciated over a period of 20 years giving a charge of R0,10/kℓ of water treated.

5.2.2 Operating costs for four-column system

The main cost is for regenerant chemicals. The prices of these commodities are dependent upon the transportation distance. Prices in Cape Town are relatively high because of the distance from limeworks which can supply high calcium lime and the inadequate capacity of local sulphuric acid plants necessitating railage of extra supplies. The following prices were established after consultation with Cape Lime and AECI.

Sulphuric acid 98%	R 83-00 per ton
	= R 4-15/kg eq
Lime (high calcium)	R 59-00 per ton
	= R 2-27/kg eq

These may be compared with the prices of the alternative regenerants:

Nitric acid 50%	R150 per ton
	= R 18-87/kg eq
Ammonia (anhydrous NH_3)	R500 per ton
	= R 8-50/kg eq

The following data is relevant to removal of 500 mg/ℓ TDIS from typical wastewaters such as Milnerton HTE or Cape Flats using a four-column CCIX system.

Cation exchange duty	86 kg eq/day
H_2SO_4 consumption factor	3,4 eq acid/eq of working capacity
Acid consumption	292 kg eq/day
Acid cost	R1212/day
or	12,1 c/kℓ treated

Anion exchange duty	86 kg eq/day
Lime consumption factor	1,0 eq acid/eq of working capacity
Lime consumption	86 kg eq/day
Lime cost	R195/day
or	2,0 c/kℓ treated

Rock salt	R 25-00 per ton
	= R 1-45/kg eq
Seawater from a seawell (all costs included)	R 0-03/kℓ of seawater

The additional capital charge for the intermediate (fifth) CCIX column is estimated at 1 c/kℓ. The acid consumption factors are now:

With salt rinse	1,7 eq acid/eq working capacity
With seawater rinse	2,5 eq acid/eq working capacity

From these figures the total chemical cost can be calculated. The comparative data is presented in Table 5.1.

TABLE 5.1

COMPARISON OF CHEMICAL AND CAPITAL COSTS FOR ALTERNATIVE CATION REGENERATION SYSTEMS

OPERATING SYSTEM	ACID CONS. FACTOR	ACID COST	BRINE COST	ADDED CAPITAL CHARGE	LIME NEUT.	LIME REGEN.	TOTAL
4-column	3,4	12,1	-	-	3,1	2,0	17,2
5-column							
salt rinse	1,7	6,1	7,4	1,0	0,9	2,0	17,4
seawater rinse	2,5	8,9	0,3	1,0	1,9	2,0	14,1
acid recycle	1,08	3,9	-	2,0	0,1	2,0	8,0

Clearly, unless salt is available at very much lower cost salt rinse is of no benefit. When the plant is situated near the coast there is a significant saving. A suitable source of brine may well arise at an inland plant where the ion exchange waste solutions must be evaporated in pans. Precipitation of calcium salts can then render the brine suitable for re-use in the intermediate column.

5.2.4 Operating costs with the acid recycle system

The simplified acid recycle system using $CaSO_4$ seeding offers capital cost advantages over the earlier method because it eliminates the stirred tank crystallizers and avoids high liquid flow rates resulting in a smaller column and settler. In addition, the separating performance required of the settler is not as great since solids must in fact be present in the recycled solution. An additional capital allowance for crystallizers and settlers of 3,0 c/kℓ would be considered, compared with 1,0 c/kℓ for the settler alone.

Table 5.1 shows that the acid recycle system can save nearly 10 c/kℓ treated on chemical costs. In addition the water recovery would increase to approximately 92% bringing the total unit cost of product water down to 34,5 c/kℓ (31,7÷0,92). This overall saving of 13,6 c/kℓ (or nearly 30%) is a compelling reason to use the acid recycle system.

The most important factor to bear in mind is the calcium content of the water being treated. Increased calcium content makes it more difficult to use sulphuric acid efficiently in the four-column system and the water recovery and acid consumption factors will be poorer. In these cases even greater savings will be evident with the five-column acid recycle system.

5.3 CONCLUSIONS: SUITABILITY OF SULPHURIC ACID AND LIME AS REGENERANTS

The use of sulphuric acid in a four-column system has been studied in detail to establish optimum operating conditions and sufficient pilot plant experience has been obtained to enable evaluation and process design to be undertaken for any proposed application.

Two alternative five-column systems with brine rinsing of the cation resin have been studied which may provide cost savings in certain locations where either the cost of sulphuric acid is very high due to transportation costs, or brine or seawater can be obtained at relatively low cost.

The alternative of acid recycle with calcium sulphate precipitation has been successfully demonstrated on the pilot plant and shown to provide a major overall cost saving. At the present stage a preliminary design for this flowsheet can be produced. However, longer term testing is necessary to obtain complete design information. The application, locality, feedwater composition and acid cost at the site will determine the choice of these alternatives. The acid recycle system will show cost advantages under almost all circumstances.

The use of lime in a CCIX regeneration column introduces physical limitations which result in low waste solution concentrations and low water recovery. Even so lime is an economical regenerant for desalination of secondary effluent and brackish water. Improved methods of lime contacting in the batch system are expected to extend the use of lime to applications in which water recovery with the CCIX column alone would be uneconomically low.

In general, the CCIX process can offer the potential of high water recovery, use of very cheap regenerants, can attain high waste solution concentrations and allows potentially useful, high purity, high concentration by-products to be formed. The ability to handle solids and precipitates opens up a wide range of applications including industrial water treatment and chemical processing. The CCIX process has been demonstrated to achieve reclamation and desalination of secondary effluents at reasonable cost, in one step, using sulphuric acid and lime as the regenerants.

5.4 RECOMMENDATIONS

5.4.1 Applications

A number of potential applications for desalination and reclamation of municipal wastewater were mentioned in Chapter 1. Brackish borehole or surface waters, especially those containing high calcium hardness, are also applications for which the CCIX process is seen as an available technology. Industrial effluents are generally of higher salinity and require higher waste solution concentrations to be produced by the CCIX process. The work

this objective. However, ion exchange processes including liquid ion exchange used in the metallurgical industry can be adapted and developed for this purpose. The continued study of ion exchange processes and materials will lead to these developments and is strongly recommended.

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APPENDIX 1

(a) Drinking water standards

(b) Results of potability tests

TABLE 1

PHYSICAL CHEMICAL AND AESTHETIC QUALITY CRITERIA FOR POTABLE WATER

Constituents	WHO		USPHS	SABS	USSR
	International (1971)	European (1970)	(1962)	(1971)	(1970)
pH	7,0-8,5	N.S.	N.S.	6-9	N.S.
TDS	500	N.S.	500	500	N.S.
MBAS	0,2	0,2	0,5	0,5	0,5
NH_3-N	N.S.	0,05	N.S.	N.S.	2
Fe (total)	0,1	0,1	0,3	0,3	0,5
Ca	75	N.S.	N.S.	N.S.	N.S.
Mg	30-150	30-125	N.S.	100	N.S.
Total hardness ($CaCO_3$)	100	100-500	N.S.	20-200	N.S.
Cl^-	200	200	250	250	N.S.
$SO_4^=$	200	250	250	250	N.S.
Mn	0,05	0,05	0,05	0,1	N.S.
Al	N.S.	N.S.	N.S.	N.S.	500

N.S. = Not specified

TABLE 2

HEALTH STANDARDS FOR POTABLE WATER QUALITY (CHEMICALS AND MACRO-POLLUTANTS IN $\mu g/\ell$

Constituent	WHO		USPHS	SABS	USSR
	International (1971)	European (1970)	(1962)	(1971)	(1970)
Arsenic	50	50	10	50	50
Barium	N.S.	1 000	1 000	N.S.	4 000
Beryllium	N.S.	N.S.	N.S.	N.S.	0,2
Cadmium	10	10	10	50	10
Chrome (hexavalent)	N.S.	50	50	50	100
Cobalt	N.S.	N.S.	N.S.	N.S.	1 000
Copper	50	50	1 000	1 000	100
Cyanide	50	50	10	10	100
Extractables (CCE)	N.S.	200-500	200	N.S.	N.S.
Hydrogen sulphide	N.S.	50	N.S.	N.S.	0
Lead	100	100	50	50	100
Mercury (total)	1	N.S.	N.S.	N.S.	5*
Nickel	N.S.	N.S.	N.S.	N.S.	100
Phenolic compounds	1	1	1	1	1
Selenium	10	10	10	N.S.	1*
Strontium	N.S.	N.S.	N.S.	N.S.	2 000
Zinc	5 000	5 000	5 000	5 000	1 000
Silver	N.S.	N.S.	50	N.S.	N.S.
Nitrate (NO_3) mg/ℓ	45	<50	45	10 as N	10 as N
Fluoride mg/ℓ	0,6-1,7	0,7-1,7	0,6-1,7	1,0-1,5	1,5

N.S. = Not specified
* = for organic compounds
* = as $SeO_3^=$

DRINKWATER STANDAARDE

(Department of Water Affairs, South West Africa)

1. TOKSIESE CHEMIESE BESTANDDELE:

	MAKS. TOELAATBARE KONSENTRASIE
Lood (as Pb)	0.10 mg/liter p.p.m.
Arseen (as As)	0.20 " "
Selenium (as Se)	0.10 " "
Chroom (heksavalent Cr)	0.05 " "
Cadmium (as Cd)	0.05 " "
Sianide (as CN)	0.20 " "
Barium (as Ba)	1.00 " "
Silwer (as Ag)	0.05 " "

2. NIE-TOKSIESE CHEMIESE BESTANDDELE:

	GROEP A	GROEP B	GROEP C	GROEP D
pH	7.0 - 8.5	7.0 - 8.5	6.5 - 9.2	5.6 - 9.2
Totale Opgeloste vasstestowwe (180°C)	1500	2000	3000	6000
Sulfaat (SO_4)	250	500	20	110
Nitraat (as N)	20	20	20x	
Fluoried (F)	1.5	2.0	2.0	6.0
Natrium (Na)	-	-	-	2000
Calsium ($CaCO_3$)	-	-	-	2500
Magnesium ($CaCO_3$)	200	600	-	2057
Chloried (Cl)	-	-	-	3000
Yster (Fe)	0.3	1.0	1.0	-
Mangaan (Mn)	0.1	0.5	0.5	
Koper (Cu)	1.0	1.5	1.5	
Sink (Zn)	5.0	15.0	15.0	

x slegs vir babas onder 1 jaar

Groep A: Dorpe met bevolking van meer as 10,000 mense.

Groep B: Dorpe met minder as 10,000 inwoners, publieke ruskampe en vakansie-oorde en klein gemeenskappe wat deur die Staat van drinkwater voorsien word.

Groep C: Waar die bron deur 'n beperkte aantal mense gebruik word soos op plase en poste waar slegs enkele persone van die water afhanklik is.

Groep D: Veesuiping.

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THE USE OF ION EXCHANGE COLUMNS IN WATER RECLAMATION STUDIES

RESULTS AND DISCUSSION OF CHEMICAL ANALYSES DONE ON SAMPLES SENT BY THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF CAPE TOWN

by

J F J van Rensburg

PRETORIA
SEPTEMBER 1981

INTRODUCTION

Table 1 summarises the terms and abbreviations used in the secton on organic micropollutants. The normal tables used in the laboratory are in Afrikaans. Table 1 should therefore be consulted for the English equivalents.

VOLATILE HALOGENATED HYDROCARBONS AND THEIR PRECURSOR SUBSTANCES (Table 2)

The VHH potential (VGK-P) of the feed water (Z53) is obviously extremely high, indicating high concentrations of precursor compounds. The cation exchange process succeeds in removing 60 to 70 % of these compounds (Z54). No further significant removal is observed, until after the active carbon process (Z57). This reduction brings the concentration levels of these substances down to a level (below 400 to 600 for VGK-P), where normal chlorination disinfection is unlikely to produce VHH-T concentrations above the limit of 100 µg/ℓ. This is well demonstrated by the results for the final product Z58. Any VHH's formed by chlorination of the sand filter product (Z56) is also easily removed by active carbon absorption.

ORGANIC POLLUTION INDICES AND THE REMOVAL OF ORGANIC MICROPOLLUTANTS OTHER THAN VHH's (Table 3)

The general organic micropollutants (OBI-VID in Table 3 are found at high concentrations in the feed water (>20 µg/ℓ)). Anion exchange (Z55) removes 50 %+ of these compounds with a final removal by carbon filtration.

Due to the low concentrations of the chlorinated hydrocarbons/pesticides in the feed water (<1 µg/ℓ) (OBI-EVD) no significant removal of these compounds could be obtained.

Phenolic compounds (OBI-PHEN). A significant reduction of the phenolic compounds is obtained by cation exchange (Z54 - Z53). This effect is not reflected by the PHENOL determination.

The significant decrease in OBI-PHEN by anion exchange is small compared to the almost complete removal of PHENOL. Final reduction of OBI-PHEN is again by the active carbon filtration.

Why cation exchange has an effect on OBI-PHEN is not clear. The anion exchange removal of PHENOL would be expected. Why the effect on OBI-PHEN is not so large is probably due to the fact that the gaschromatographic method used for OBI-PHEN determines a group of compounds which, although phenolic in character, is dissimilar from the group determined as PHENOL by the Auto-Analyser system.

The group parameters UV_{40}^{275} and TOK (English TOC), show little or no removal by cation exchange (which is at variance with VGK-P). The significant lowering of both UV_{40}^{275} and TOC by anion exchange, corresponds with the change in PHENOL, but not with the effect on the pollution indices and VGK-P.

Both the anion and cation exchangers play an important (but not a clearly understood one) in the removal of organic material from the water. The active carbon step remains a very necessary one. The presence of the ion exchangers will obviously prolong the life of the active carbon considerably.

CHEMICAL DETERMINANDS (Table 4)

Although these results were not requested, they were determined to obtain an overall picture of the water reclamation process. Together with the suggested limits for a domestic water supply, these results present a completely acceptable final water.

PRETORIA

JvR/ER
1981-09-21

TABLE 1. List of abbreviations used in the determination of organic micropollutants

English	Afrikaans	Meaning
Abs_{40}^{275}	the same	Absorbance of sample measured at 275 nm wavelength in a cell with path length 40 mm
GC/MS	the same	Gaschromatography coupled with mass spectrometry
OPI	OBI	Organic pollution index, indicated by A/B-C-D(-E), where A is the total concentration (µg/ℓ), B the number of compounds with concentrations >10 µg/ℓ, C the number of compounds 1-10 µg/ℓ, D the number of compounds 0,1-1 µg/ℓ and E the number of compounds 0,01-0,1 µg/ℓ
-DPHEN	the same	- determined by gaschromatography, specific for chlorinated phenols
-FID	-VID	- determined by gaschromatrography with flame ionisation detection for organic substances in general
-GEN	-ALG	- the same as -FID
-ECD	-EVD	- determined by gaschromatography and electron capture detection, specific for chlorinated hydrocarbons/pesticides
-NP	the same	- determined by gaschromatrography, specific for nitrogen and phosphorus containing organic compounds
THM	the same	Trihalomethanes (chloroform, bromoform, bromodichloromethane, dibromochloromethane)
TOC	TOK	Total organic carbon (in practice DOC - dissolved organic carbon - is meant)
UV	the same	Ultraviolet (- light)
UV_{40}^{274}	the same	See Abs_{40}^{275}
VHH	VGK	Volatile halogenated hydrocarbons (including the trihalomethanes)
-S	-M	Concentrations at time of sampling
-P	the same	Potential values, determined by chlorination to 75-100 mg/ℓ chlorine and allowing reaction to take place for 48 h before determination of VHH
-T	the same	Terminal values, determined by allowing at least 48 h at 25 °C between sampling and determination.

REC. LIMIT — FEED — CATION PRODUCT — ANION — SAND FILTER — CARBON PRODUCT — FINAL WATER AFTER CHLORINATION

INSENDER .....

RESULTATE VAN CHEMIESE ANALISE

VERS .....

DATUM IN 1981/03/11 DATUM UIT .....

			Recommended / Risk limit							
		Monsternommer		Z53	Z54	Z55	Z56	Z57	Z58	
		Lab. nommer								
		Troebelheid	1/5	10	4	3	1	1	1	
		Kleur	10/20	118	71	25	16	7	10	
		pH	7-8,5/6-9,5	6,9	2,2	5,9	6,2	5,9	6,1	
		Elektriese geleiding (mS/m)	70/200	133	377	19	25	25	26	
mg dm^{-3}		Natrium (Na)	200/400	220	26	24	34	40	40	
		Kalium (K)	200/400	22	2	2	2	2	2	
		Kalsium (Ca)	150/200	33	<1	8	9	11	14	
		Magnesium (Mg)	70/100	24	<1	<1	1	1	<1	
		Kjeldahl-stikstof (N)		1,8	1,7	0,8	0,7	0,9	0,8	
		Ammoniak-stikstof (N)	0,1/2	0,2	<0,2	←	<0,2	→		
		Nitraat+Nitriet-Stikstof (N)	0,6/10	18,0	17,2	1,8	1,8	0,9	1,9	
		Nitriet-stikstof (N)		←		<0,1		→		
		Silika (Si)								
		Sulfaat (SO_4^{2-})	200/300	110	70	<5	5	5	7	
		Totale fosfaat (P)		13,5	12,0	2,1	2,7	3,2	7,7	
		Ortho-fosfaat (P)		11,5	10,5	2,1	2,6	4,8	7,2	
		Chloried (Cl^-)	250/600	275	235	48	58	60	60	
		Totale alkaliniteit ($CaCO_3$)		42	<5	<5	<5	<5	<5	
		Chemiese suurstofbehoefte (CSB)		53	43	16	11	10	10	
µg dm^{-3}		Metileenblou Aktiewe Stowwe (LAS)	200/600	1335	1250	320	330	230	330	?
		Aluminium (Al)	150/500	←	(460)?		<100	→		
		Boor (B)	500/2000	390	390	380	350	450	470	?
		Fenol	1/5	8	4	←		<1	→	
		Fluoried	1000/1500	170	170	130	115	110	110	
		Sianied	200/300	<50	→					
		Bromied	1000/2000	1250	930	350	220	220	240	
		Kobalt	250/500	<25	←				→	
		Arseen (Anorg.)	100/300	<5	←				→	
		Selenium (")	20/50	<5	→					
		Kwik	5/10	<1	→	→	→	1	1	
µg dm^{-3}		Kadmium (Cd)	10/20	7	<5	6	7	14	19	?
		Chroom (Cr)	100/200	<25	→					
		Koper (Cu)	500/1000	<25	<25	<25	105?	<25	300?	
		Yster (Fe)	1000/1000	90	35	35	215	430	<25	?
		Mangaan (Mn)	30/100	30	<25	35	40	<25	<25	
		Lood (Pb)	50/100	35	35	40	<25	<25	<25	
		Sink (Zn)	1000/5000	620	<25	<25	→			
		Anorganiese stikstof (N)	250/500	<25	→		→	60	<25	
		Organiese-koolstof (C)	1/5	11,4	10,2	3,2	2,7	0,7	0,8	

OPMERKINGS : .....

.....

4. The final product.

At the plant a sample (40 ℓ) was passed through a XAD-4 column (length : 90 mm; diam. 13 mm). At the NIWR the column was washed with 60 ml of distilled water and the adsorbed material eluted with 60 ml of acetone containing 10 % water. The eluate was concentrated to 3½ ml in a rotary vacuum evaporator. Ames tests were done with the *Salmonella Syphimunium* strain TA98 - with as well as without rat liver enzymes - in triplicate using 0,2 ml of the extract per plate. TA98 was used because the mutagens so far detected in South African waters could be detected with this strain.

RESULTS AND DISCUSSION

TABLE 1: Mutation Ratio of Samples from Plant *

Sample	With liver enzymes	Without liver enzymes
Feed	2,8	1,0
Between sandfiltration and 1st chlorination	16	17
After 1st chlorination	14	25
Final product	1,3	1,3

* Mutation ratio = MR = $\frac{\text{Average number of mutations on test plate}}{\text{Average number of mutations on control plate}}$

When MR>2, mutagenicity has been detected.

As the low (1,3) MR of the final product could mean either no mutagenicity or toxicity, Ames tests were done on dilutions (with acetone/10 % water) of the final product (with liver enzymes).

TABLE 2: Mutation ratio of final product

Relative concentration	M R
100 %	1,2
50 %	1,1
25 %	0,7

Table 2 shows no increase in the M R with dilution, ie. no toxic effects were present and the final product contained no amounts of mutagens detectable with our method. Only strain TA78 was used and as this strain can only detect frame shift mutagens, more samples will have to be collected in order to establish the presence of other types of mutagens with other strains.

REMARK : The increase in mutagenicity of water after treatment with ion-exchanges and chlorine has been mentioned in the literature and has been noticed by us before, respectively.

APPENDIX 2

Tables of data on liquid and resin compositions.

RESIN COMPOSITIONS (meq/mℓ of resin) FROM ANALYSIS

(SULPHURIC ACID REGENERATION)

R/L	CONC.	COLUMN	H^+	Na^+	Ca^{++}	Mg^{++}	TOTAL
0,8	0,125N	loaded	0,00	0,15	0,67	0,53	1,35
		regen.	0,50	0,05	0,53	0,26	1,34
			0,50	0,10	0,14	0,27	
	0,15N	loaded	0,03	0,20	0,76	0,58	1,57
		regen.	0,48	0,05	0,65	0,32	1,50
			0,45	0,15	0,11	0,26	
	0,50N	loaded	0,06	0,30	0,56	0,51	1,43
		regen.	0,68	0,10	0,45	0,27	1,50
			0,62	0,20	0,11	0,24	
	1,00N	loaded	0,33	0,34	0,41	0,33	1,41
		regen.	0,70	0,15	0,31	0,21	1,37
			0,37	0,19	0,10	0,12	
0,5	0,125N	loaded	0,04	0,24	0,56	0,36	1,20
		regen.	0,56	0,01	0,44	0,21	1,22
			0,52	0,23	0,12	0,25	
	0,15N	loaded	0,00	0,26	0,72	0,49	1,47
		regen.	0,53	0,05	0,58	0,22	1,38
			0,53	0,21	0,14	0,27	
	0,50N	loaded	0,08	0,37	0,52	0,31	1,28
		regen.	0,76	0,07	0,38	0,11	1,32
			0,68	0,30	0,14	0,20	
	1,00N	loaded	0,36	0,35	0,41	0,26	1,38
		regen.	0,86	0,08	0,34	0,13	1,45
			0,50	0,27	0,07	0,13	

APPENDIX 3

Bench scale tests to study the rate of precipitation of calcium sulphate.

BENCH SCALE TESTS TO STUDY RATE OF PRECIPITATION OF $CaSO_4$

Suitable solutions of $CaCl_2$ and Na_2SO_4 were prepared and mixed in equal proportions to obtain different starting ion-products of $CaSO_4$. CP or AR grade reagents were used to make up solutions. The solutions were agitated in a 500 mℓ glass beaker on a magnetic stirrer using a 25 mm x 5 mm stirrer bar at approximately 500 r.p.m.. The total solution volume was 300 mℓ.

The progress of the precipitation was followed by periodically withdrawing a 20 mℓ sample of the mixture and reading the turbidity on a Hach 2100A turbidimeter (nephelometer).

The results obtained with various initial concentrations where the Ca concentration was kept at 1/10 of the SO_4 concentration in all the tests (i.e. at a similar ratio of Ca/SO_4 as typically occurs in sulphuric acid regeneration of the cation resin), are given in Table A3.1.

TABLE A3.1

$CaSO_4$ NUCLEATION TESTS

Test No.	Starting Conc. of each ion in mixture		Starting ion product	Measured ion product at end of test	Time to reach almost constant turbidity
	SO_4 mole/ℓ	Ca mole/ℓ	$(mole/ℓ)^2$	$(mole/ℓ)^2$	hrs
1	1,0	0,1	$100*10^{-3}$	$18*10^{-3}$	immediate
2	0,5	0,05	$25*10^{-3}$	$6,9*10^{-3}$	0,25
3	0,57	0,029	$16,6*10^{-3}$	-	1,0
4	0,25	0,025	$6,25*10^{-3}$	$2,4*10^{-3}$	3,0
5	ditto seeded with old crystals		"		3,0
6	ditto seeded with pulverised crystals		"		1,0

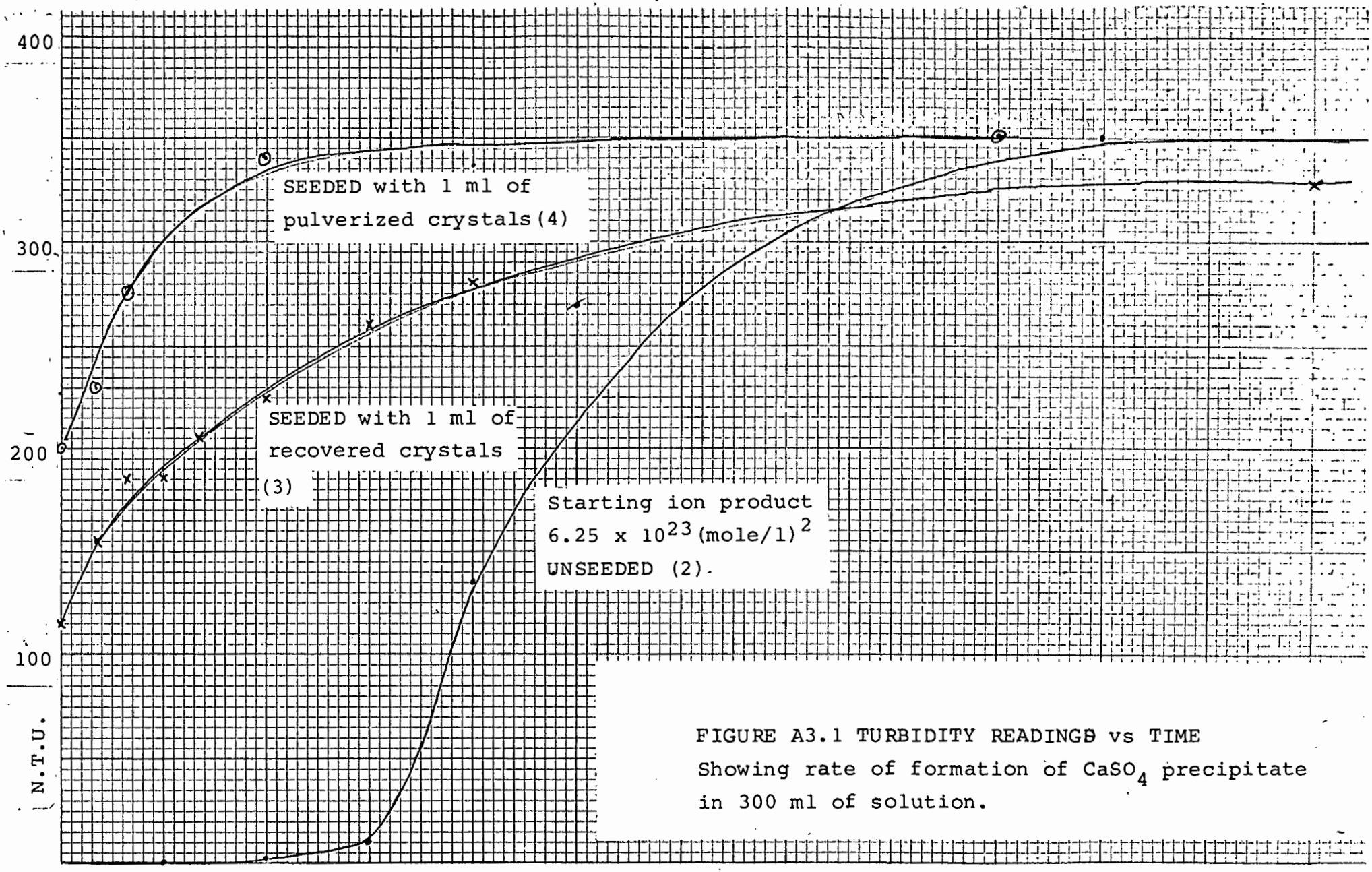
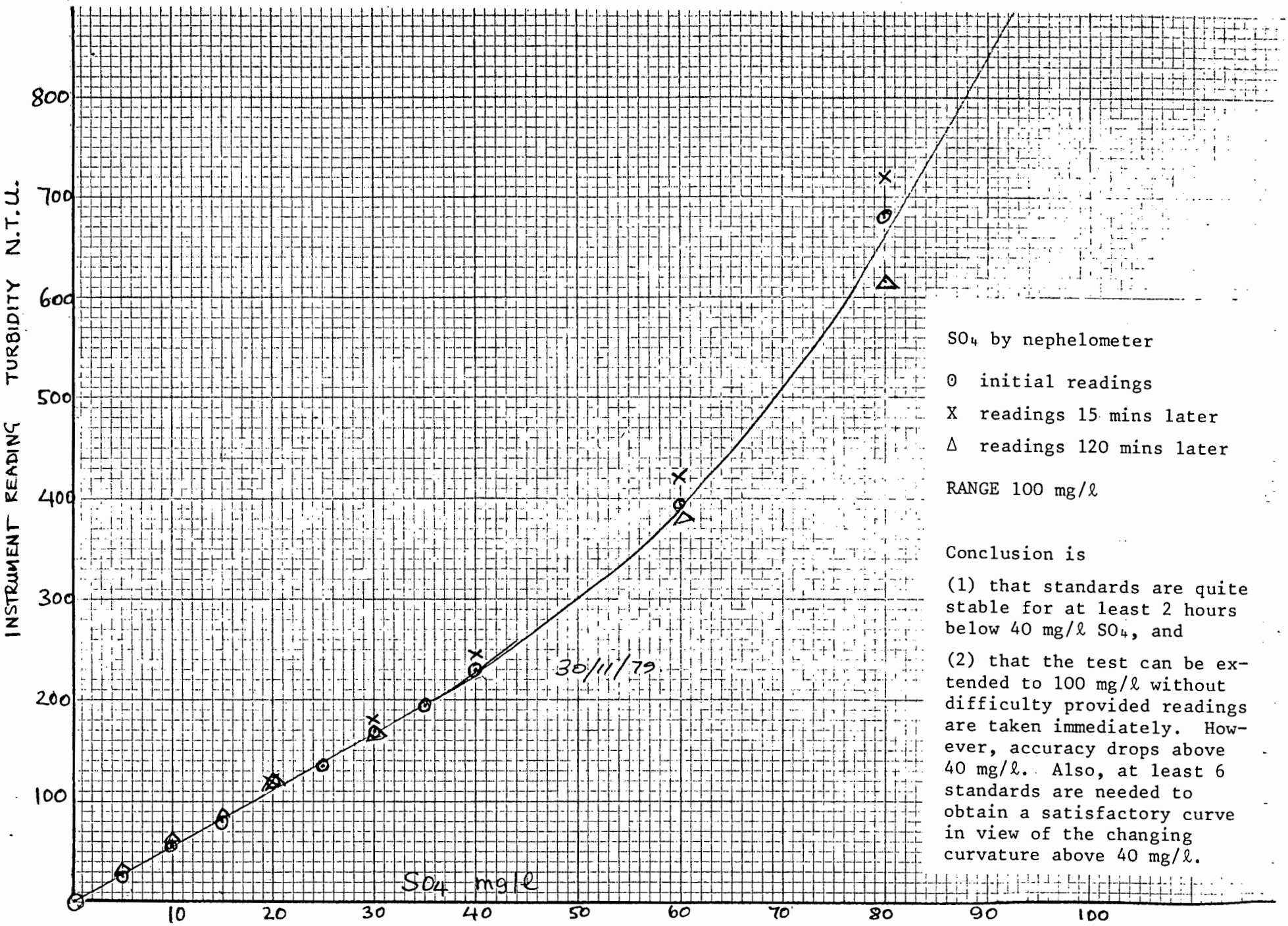


FIGURE A3.1 TURBIDITY READINGS vs TIME
Showing rate of formation of $CaSO_4$ precipitate in 300 ml of solution.


INSTRUMENT READING TURBIDITY N.T.U.
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
90
100
SO4 mg/l
30/11/79.
SO4 by nephelometer
0 initial readings
X readings 15 mins later
Δ readings 120 mins later
RANGE 100 mg/ℓ
Conclusion is
(1) that standards are quite stable for at least 2 hours below 40 mg/ℓ SO4, and
(2) that the test can be extended to 100 mg/ℓ without difficulty provided readings are taken immediately. However, accuracy drops above 40 mg/ℓ. Also, at least 6 standards are needed to obtain a satisfactory curve in view of the changing curvature above 40 mg/ℓ.

APPENDIX 4

(a) Resin bed expansion data

(b) Resin manufacturers data sheets

Technical Publication
Ref. 25-6-9

Zerolit 625 925 cation exchange resins

DESCRIPTION

Zerolit 625 & Zerolit 925 These strongly acidic, unifunctional, cation exchange resins contain suphonic acid active groups. They are based on crosslinked polystyrene and have a macroporous structure. This combined with their comparatively high degree of crosslinking, gives the resins exceptional stability both chemically and physically. They are supplied as moist beads in the hydrogen form, or in the sodium form when required for softening.

Zerolit 625 A close graded material recommended for use in conditions where the resin is subjected to high levels of osmotic and mechanical stress. For example, in the ion exchange treatment of certain process liquors, in high flow rate de-ionising such as condensate polishing and in continuous ion exchange plants.

Zerolit 925 A standard grade material for water softening and de-ionising under conventional flow conditions. It is also recommended for effluent treatment such as plating swill water recovery when the fluid to be treated may contain oxidising agents or an unusually high level of free chlorine.

SOFTENING

Zerolit 625 or 925 can be operated in the sodium cycle using conventional regeneration with sodium chloride. Zerolit 925 is the recommended macroporous cation exchanger for this purpose, but Zerolit 625 may be used for high flow rate operation.

DE-IONISING

Information is given in this publication for the operation of Zerolit 625 or 925 in the hydrogen cycle, using a mineral acid as the regenerant.

Two-stage de-ionising In a de-ionising pair, Zerolit 625 or 925 can be used as the cation exchanger in the first column with a Zerolit macroporous anion exchanger in the second column. Dependent upon the quality of treated liquid required, the weak base Zerolit MPH or the strong base Zerolit MPF or MPN anion exchange resins may be used.

Mixed bed de-ionising Zerolit 625 may be used as the cation exchange resin in mixed bed de-ionising. When used with Zerolit MPF strong base anion exchanger the highest possible treated water quality can be achieved. The combination of Zerolit 625 and MPF is ideally suitable for high flow rate applications such as condensate polishing.

Treatment of process liquors The macroporous resins Zerolit 625 and 925 are recommended for the treatment of process liquors when oxidising or other chemical reactions may cause decomposition or degradation of conventional gel resins.

Continuous ion exchange The resin transfer conditions and feed water flow rates pertaining to continuous ion exchange systems subject the resins to higher physical stresses than is common with most conventional ion exchange systems. Zerolit 625, because of its excellent osmotic and mechanical strength is particularly suitable for use in continuous ion exchange plants.

CHARACTERISTICS

PHYSICAL

Physical form:	Moist beads
Weight/volume ratio:	840 kg as supplied will occupy 1 m^3 in a unit after exhausting, backwashing and draining.
Wet screen grading:	(Zerolit 625) 0.50 to 1.2 mm (−14+30 B.S. Sieve) (Zerolit 925) 0.35 to 1.2 mm (−14+44 B.S. Sieve)
Uniformity coefficient:	≃ 1.4
Osmotic strength:	Excellent
Mechanical strength:	Excellent
Pressure loss:	(Zerolit 625) see Fig.22 Zerolit Publication Ref. 25 (Zerolit 925) see Fig.21 Zerolit Publication Ref. 25
Bed expansion:	See Fig. 23 Zerolit Publication Ref. 25
Maximum flow rate:	100 $m^3/h.m^2$

CHEMICAL

Maximum operating temperature:	120°C(H^+ cycle) 140°C (Na^+ cycle)
pH stability range:	0 – 14
Resistance to oxidising agents:	Excellent
Resistance to chlorine:	Dependent on the temperature of the feed water. Free chlorine must not exceed the values shown in the table. Any excess of these amounts can be eliminated by sodium sulphite dosing.

Temperature °C	Free Chlorine g/m^2
< 15	2.0
15 – 30	1.0
> 30	Nil

Resistance to reducing agents:	Excellent
Resistance to organic solvents:	Excellent
Total ion exchange capacity:	≃ 90 $kgCaCO_3/m^3$ (1.8 kg equiv/m^3) by volume
Regenerants:	HCl, HNO_3 or H_2SO_4 (H^+ cycle) NaCl (Na^+ cycle)

Zerolit 625
925

OPERATING CAPACITY

The operating capacity of Zerolit 625 and 925 is generally proportional to that of Zerolit 225 under the same conditions of operation, and reference should be made to Zerolit Technical Publication Ref. 25 in conjunction with the following notes:—

Softening When operated in the sodium cycle, the exchange capacity of Zerolit 625 or 925 is determined by: the quantity of salt employed, the total hardness and sodium content of the liquid being treated, and the volumetric flow rate through the bed of resin.

De-ionising The capacity of Zerolit 625 or 925 when operating in the hydrogen cycle is dependent upon the type and quantity of acid employed. Capacity is also affected by the composition of the water or solution being treated, and the flow rate.

Regeneration level At low regeneration levels, the operating capacity of Zerolit 625 is obtained by calculating the capacity of Zerolit 225 under the same conditions and multiplying by a factor of 0.85. At maximum regeneration levels, the capacity obtained for Zerolit 225 should be multiplied by a factor of 0.75. The capacity at intermediate regeneration levels is then obtained on a proportional basis.

The operating capacity of Zerolit 925 is obtained in a similar manner to that for Zerolit 625. Using the capacity derived from the data for Zerolit 225, multiply by a factor of 0.9 at low regeneration levels and by a factor of 0.8 at maximum regeneration levels. At intermediate levels the capacity is obtained on a proportional basis.

Sulphuric acid When H_2SO_4 is used as the regenerant it is possible for calcium sulphate to be precipitated during the regeneration stage, particularly if the water is high in Ca^{++}. Precipitation can be avoided by appropriate choice of acid concentration and flow rate — see Technical Publication Ref. 25.

TREATED WATER QUALITY

As a general rule, leakage data will be the same for both Zerolit 625 or 925 and Zerolit 225 at the same operating capacity rather than the same regeneration level.

Zerolit Limited
632-652 London Road
Isleworth
Middlesex
England
TW74EZ

telephone 01 568 3161/7
telex 8811096
cables Zerolit Hounslow
Reg No 774065

Zerolit

Portals Water Treatment

SHIPPING SPECIFICATION

Weight: 840 kg/m^3

Packing: The resin is supplied in polyethylene – lined woven polypropylene bags.

Volume	0.05m^3
Nett weight	≃42 kg
Gross weight	≃43.5 kg

In addition - for export - special packing can be arranged.

Capacity data are based on the results of laboratory testing. The achievement of these results depends on the efficiency of plant design and the operating techniques employed. It will therefore be appreciated that no guarantee in respect of plant performance can be given.

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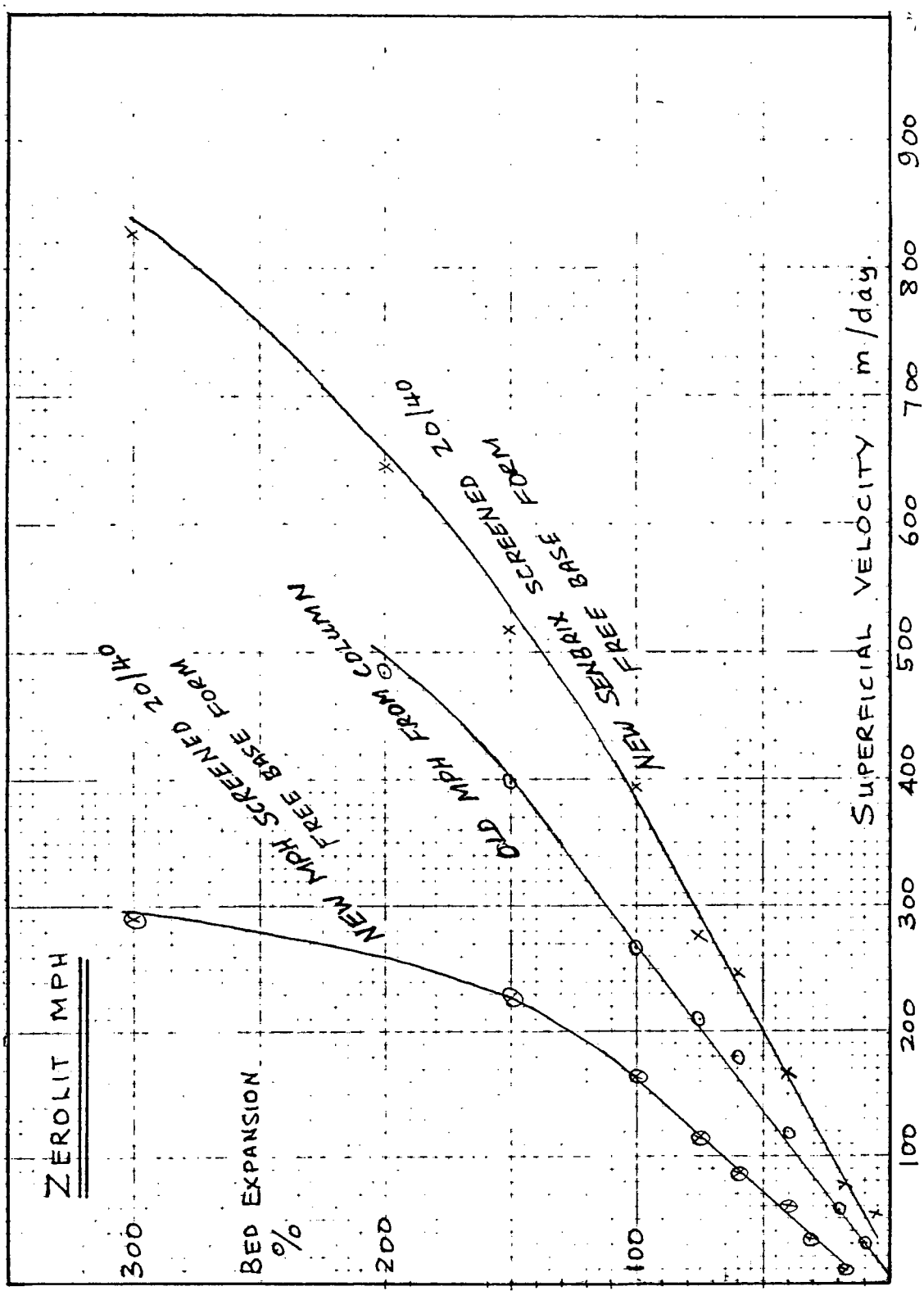
Printed in Great Britain


ZEROLIT MPH
BED EXPANSION %
SUPERFICIAL VELOCITY m/day.
100
200
300
400
500
600
700
800
900
NEW MPH SCREENED 20/40
NEW MPH FREE BASE FOAM
OLD MPH FROM COLUMN
NEW FREE SPARAX BASE FOAM
OLD SCREENED FOAM 20/40

Technical Publication
Ref. MP-H

Zerolit MPH anion exchange resin

DESCRIPTION

Zerolit MPH

A weak base anion exchange resin in bead form, containing tertiary and some quaternary ammonium groups. It is based on crosslinked polystyrene, and has a macroporous structure which gives excellent mechanical strength and exceptional resistance to osmotic shock.

Zerolit MPH has a high capacity for, and has excellent resistance to poisoning by, the natural organic matter present in some surface waters.

Operation of this anion exchange resin can be effected at a high regeneration efficiency. The reaction rate is fast, and the resin has an essentially constant capacity at operating cycle times longer than 12 hours. It is thus eminently suitable for use in automatically controlled water treatment plants.

APPLICATIONS

Two-stage de-ionising

Zerolit MPH is recommended for use in two-stage de-ionising by ion exchange when silica removal is not required. It is particularly suitable for use where the resin may be subjected to high levels of osmotic and mechanical stress as, for example, in high flow rate de-ionising, in continuous ion exchange treatment plants, and in the treatment of certain process liquors.

An inherent quality of this resin is its capacity for taking up natural organic matter from the water being treated. As this organic matter is readily removed by the sodium hydroxide used for regeneration, fouling of the resin is avoided, provided adequate regenerant is used.

When used as the anion exchanger in a two-stage de-ionising plant preceding a mixed bed unit, Zerolit MPH affords protection against fouling of the strong base anion exchanger in the latter unit. At the same time, it assists in the production of a treated water with a low residual of organic matter and hence an extremely low final conductivity.

De-ionising two-stage

CHARACTERISTICS

PHYSICAL

Physical form:	Moist beads
Weight/volume ratio:	715 kg as supplied, will occupy 1 m^3 in a unit after exhausting, backwashing and draining.
Wet screen grading:	0.35 to 1.2mm (−14+44 B.S. Sieve)
Uniformity coefficient:	$\simeq$ 1.4
Osmotic strength:	Excellent
Mechanical strength:	Excellent
Bed expansion:	See Fig. 3
Pressure loss:	See Fig. 4
Volume change:	Free base → Cl^-/SO_4 = form +20% approx.

CHEMICAL

Ionic form (as supplied):	Cl^-
Maximum operating temperature:	Free base form 80°C Cl^- and other forms 100°C
pH stability range:	0—14
Resistance to reducing agents:	Excellent
Resistance to oxidising agents:	Excellent
Total ion exchange capacity:	$\triangleq$ 80kg $CaCO_3/m^3$ (resin in free base form) $\triangleq$ 1.6 kg equiv/m^3 (resin in Cl^- form)
Regenerants:	NaOH Na_2CO_3 NH_3
Operating Capacities:	See Figs. 1a—c, 2a—c

Zerolit MPH

TYPICAL OPERATING DATA (co-flow regeneration)

TWO-STAGE DE-IONISING

Bed-depth:	0.75 – 1.8m
Rising space:	Allow 50% of maximum bed depth. (i.e. when the resin is in the exhausted form)
Typical flow rate:	Up to $100m^3/h.m^2$
Volume change:	Expansion of Zerolit MPH during the treatment (exhaustion) cycle increases the bed depth by approximately 20%
Pressure loss:	See Fig. 4 – note: the overal pressure loss will increase during the treatment (exhaustion) cycle by about 20%, corresponding to the resin volume change.
Backwash:	At a rate to give 30–40% bed expansion, see Fig.3
Regenerant:	5% w/v solutions of NaOH, Na_2CO_3 or NH_3 The data contained in this publication have been obtained with NaOH equivalent to 150% of the operating capacity. Should the OA*: EMA ratio lie between 0.008 and 0.016, the recommended amount of regenerant may be reduced to the equivalent of 140% of the operating capacity. If the feed water is virtually free from organic matter the regeneration level may be reduced to the equivalent of 120–130% of the operating capacity. When Na_2CO_3 is used as the regenerant for Zerolit MPH, the operating capacity (see Figs.1a and 2a) should be reduced by 15%. If NH_3 is used for regeneration the operating capacity (see Figs. 1a and 2 a) should be reduced by 10%.
Regenerant injection:	Inject in not less than 30 minutes.
Rinse volume:	$5m^3/m^3$
Rinse flow rate:	$10m^3/h.m^3$

* Oxygen absorbed by 4h.27°C method.
To convert to 4h.27°C values multiply:
Kubel values by 0.3
30 min.100°C values by 0.5

OPERATING CAPACITY

Two-stage de-ionising

The operating exchange capacity of Zerolit MPH when used as the anion exchanger in a two-stage de-ionising system is determined by the following factors:—

a. The treatment flow rate (exhaustion time for the resin).
b. The composition of the water to be treated — specifically, the concentration of mineral acid anions (EMA), the Cl^-:$SO_4^=$ ratio and the CO_2 content.

Regeneration

Zerolit MPH may be regenerated with NaOH, Na_2CO_3 or NH_3. Recommended quantities of each regenerant are given under OPERATING DATA.

Effect of EMA

Figs. 1a and 2a show the relationship between exchange capacity and the EMA of the feed water.

Effect of Exhaustion Time

Figs. 1b (factor f_1) and 2b (factor f_3) show the relationship between operating exchange capacity of Zerolit MPH and exhaustion time.

Effect of Carbon Dioxide

Fig. 1c (factor f_2) shows the effect of CO_2 on the sulphate capacity of Zerolit MPH. Fig. 2c (factor f_4) shows the effect of CO_2 on chloride capacity at various EMA values. When the CO_2 content is above 100g/m³ no correction factor need be applied. It is recommended that where a degasser is used to remove CO_2 it should be downstream of the anion exchange unit.

Effect of Cl^-:$SO_4^=$ ratio

The capacity of Zerolit MPH (Figs. 1a and 2a) depends upon the ratio of Cl^-:$SO_4^=$ in the water to be treated. The operating exchange capacity is the sum of the fractions of the sulphate capacity and the chloride capacity (Fig. 1a multiplied by factors f_1, f_2 and Fig. 2a multiplied by factors f_3, f_4). See example, page 5.

ABBREVIATIONS

Data givne in this publication are expressed in terms of calcium carbonate($CaCO_3$). The following abbreviations also have been used:—

EMA	Equivalent Mineral Acidity
OA	Oxygen Absorbed
ppm(g/m³)	Parts per million
$CaCO_3$	Calcium Carbonate
Cl^-	Chloride
CO_2	Carbon Dioxide
Na_2CO_3	Sodium Carbonate
NaOH	Sodium Hydroxide
NH_3	Ammonia
$SO_4^=$	Sulphate

EQUIVALENTS

1 μmho/cm	=	1 μS/cm = 1 reciprocal megohm/cm
1 mg NaOH/l	≃	5 μmhos/cm at 20°C
1 mg NaCl/l	≃	2.4 μmhos/cm at 20°C

Zeolit MPH

EXAMPLES (use of graphs)

Water to be treated has the following analysis expressed as $gCaCO_3/m^3$:–

$SO_4^=$	(sulphate)	75	alkalinity	47
Cl^-	(chloride)	50	free CO_2	8
EMA		125	Total CO_2	55

thus:–

$SO_4^=$ fraction = $\frac{75}{125}$

Cl^- fraction = $\frac{50}{125}$

An exhaustion time of 7h is required.

Capacity due to sulphate

$SO_4^=$ fraction x $SO_4^=$ capacity (Fig. 1a) x exhaustion time factor f_1 (Fig. 1b) x CO_2 factor f_2 (Fig. 1c)

$= \frac{75}{125} \times 64 \times 0.97 \times 0.98 = 36.5 kg\ CaCO_3/m^3$ resin

Capacity due to chloride

Cl^- fraction x Cl^- capacity (Fig. 2a) x exhaustion time factor f_3 (Fig. 2b) x CO_2 factor f_4 (Fig. 2c)

$= \frac{50}{125} \times 57 \times 0.92 \times 0.80 = 16.8 kgCaCO_3/m^3$ resin

Total operating capacity

Capacity due to sulphate + capacity due to chloride
= 36.5 + 16.8 = 53.3kg $CaCO_3/m^3$ resin

Regenerant

150% of total operating capacity (see page 3) converted to NaOH

$= 53.3 \times \frac{150}{100} \times \frac{40}{50} = 64 kg\ NaOH/m^3$ resin

corresponding to:

84.8kg Na_2CO_3/m^3 resin or, 27.2kg NH_3/m^3 resin

When Na_2CO_3 or NH_3 is used as the regenerant, the operating capacity should be adjusted – see page 3.

De-ionising two-stage

Fig. 1a Operating Exchange Capacity (free base form resin) — Sulphate

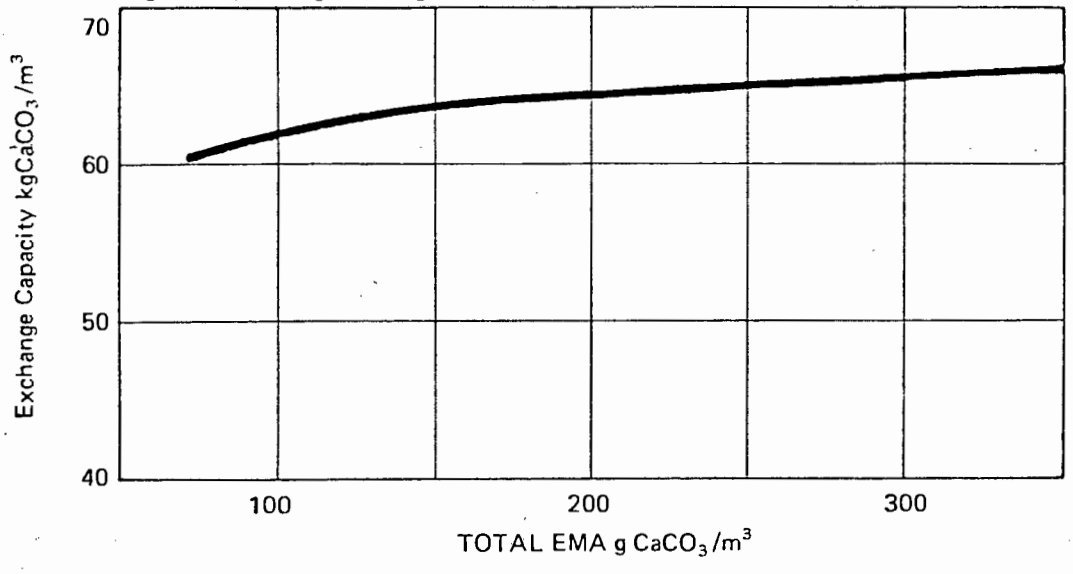


Fig. 1b Exhaustion Time Factor f_1 — Sulphate

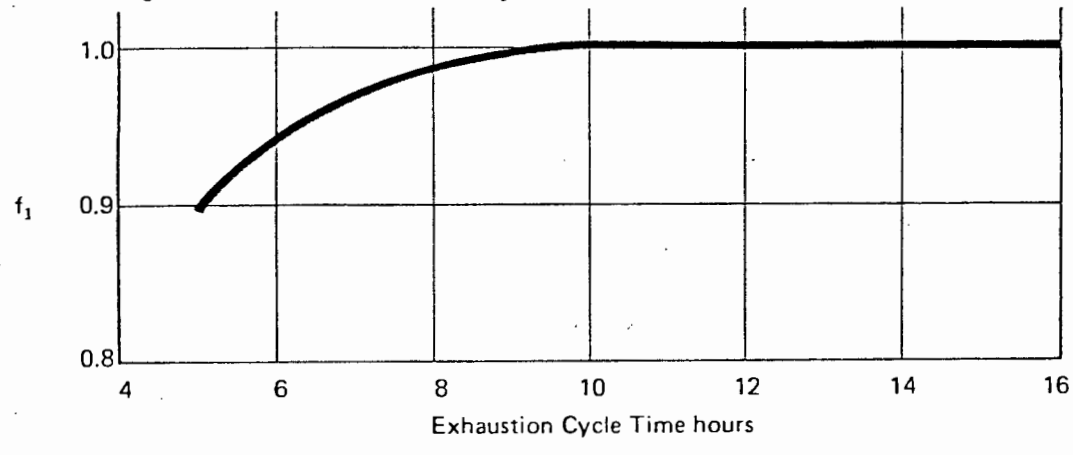
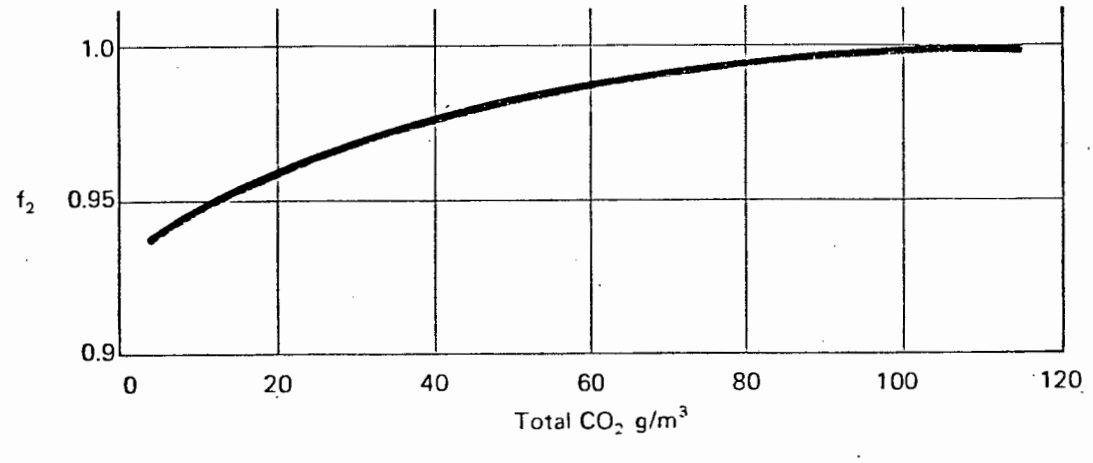


Fig. 1c CO_2 Factor f_2 — Sulphate



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OPERATING EXCHANGE CAPACITY. SODIUM HYDROXIDE (co-flow regeneration)

Fig. 2a Operating Exchange Capacity (free base form resin) – Chloride

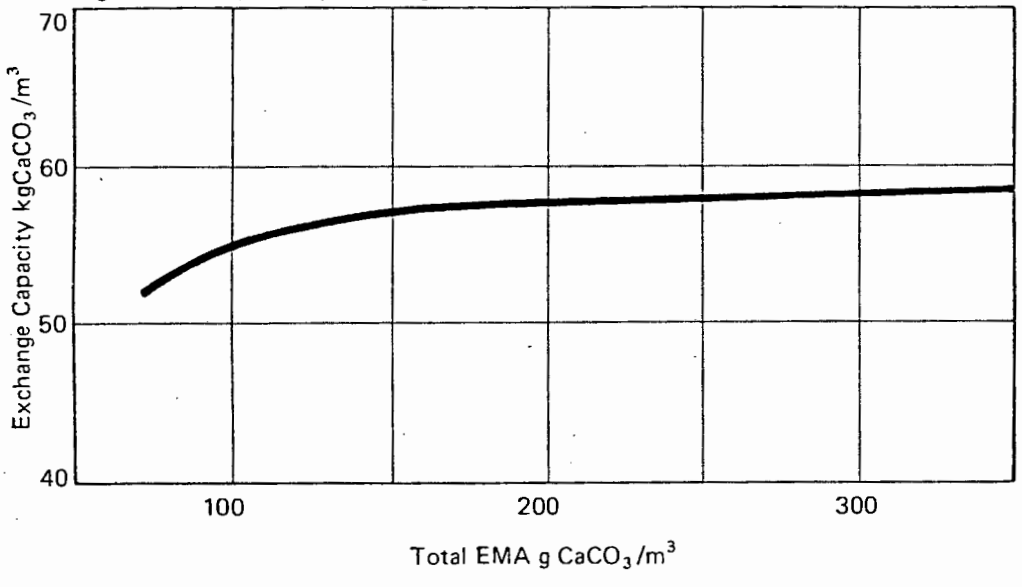

Fig. 2b Exhaustion Time Factor f_3 – Chloride

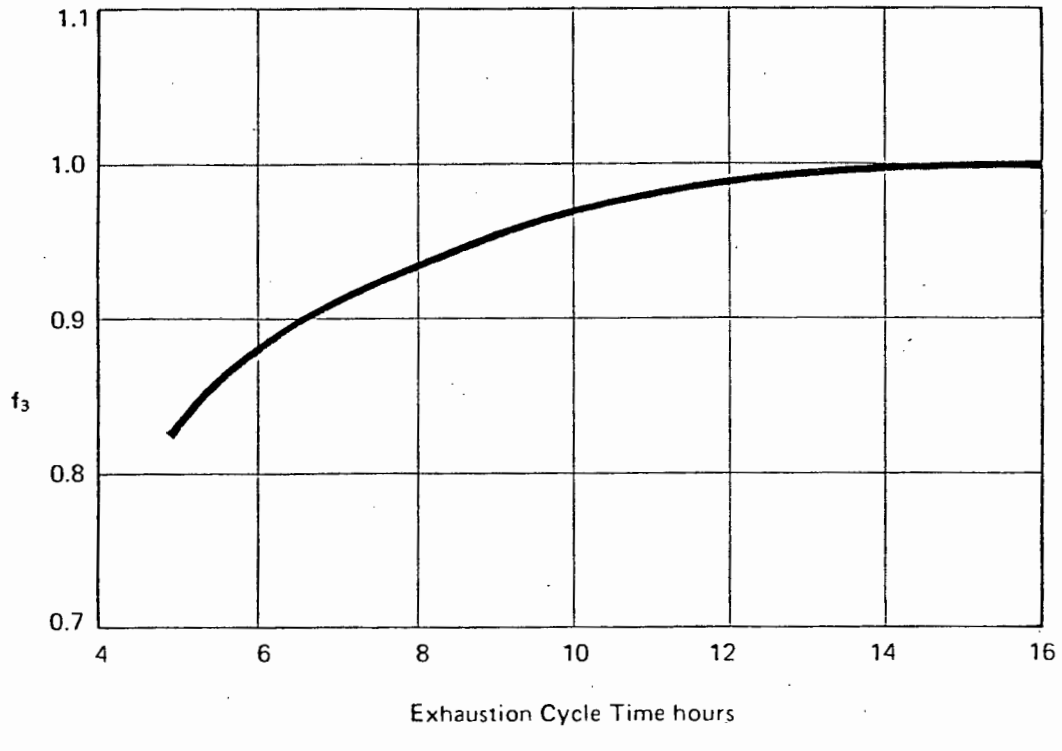

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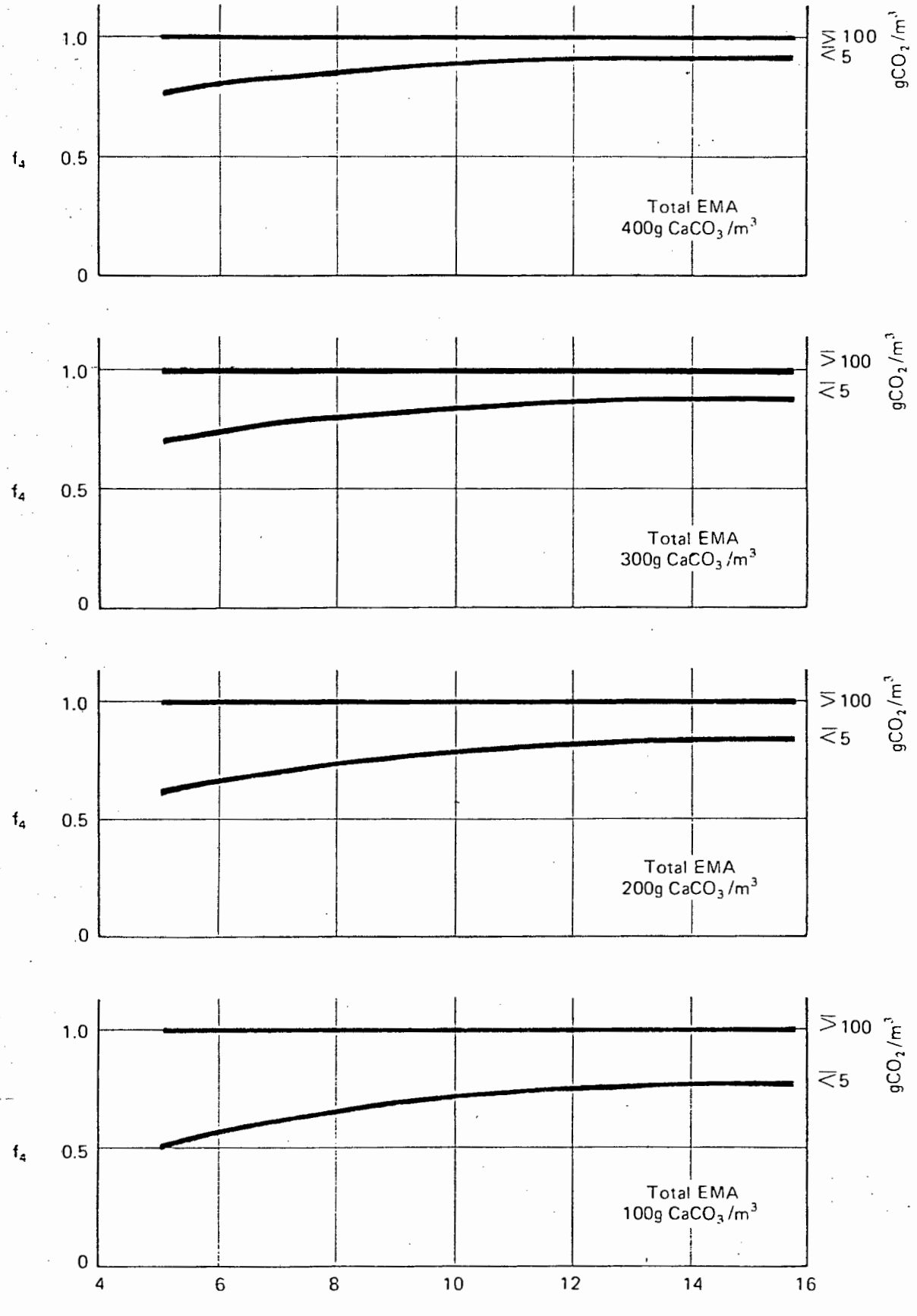
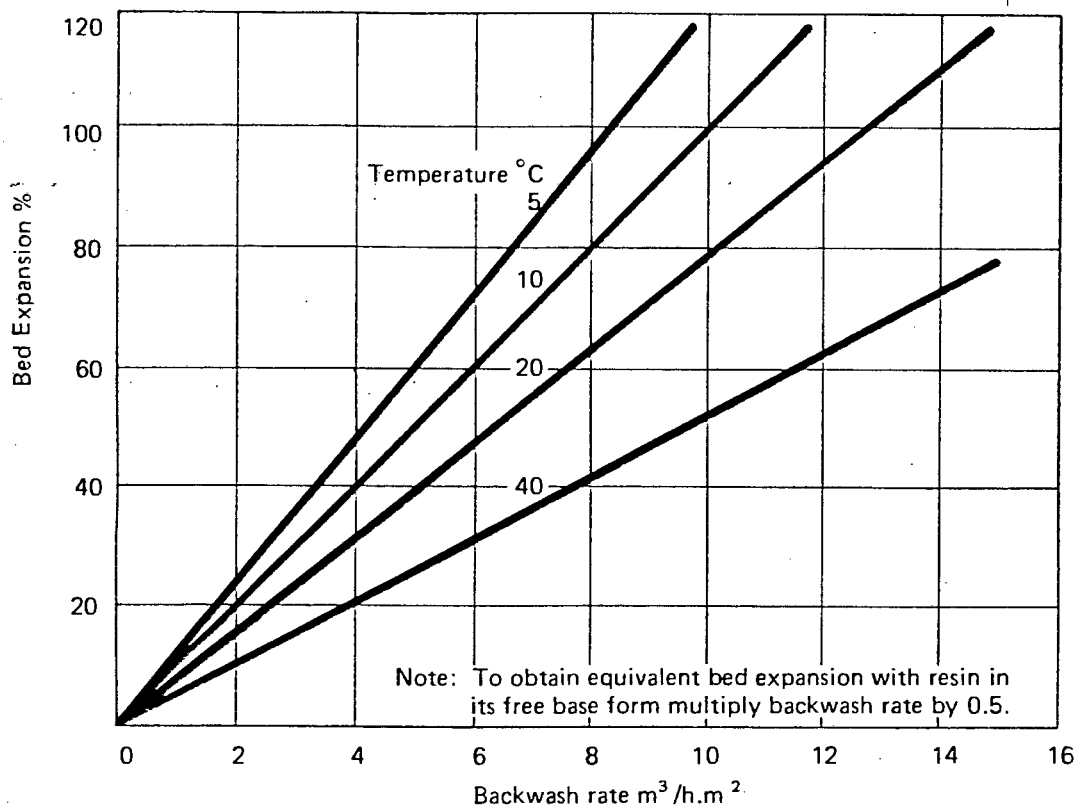
Fig. 2c CO_2 Factor f_4 – Chloride



Physical characteristics

BED EXPANSION

Fig. 3 Bed Expansion (exhausted form resin)



PRESSURE LOSS

Fig. 4 Pressure Loss