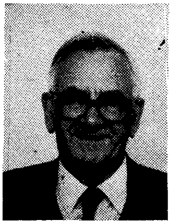
THE TREATMENT OF UNDERGROUND MINE WATERS FOR THE REMOVAL OF CALCIUM AND SULPHATES BY A GYP-CIX PROCESS



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THE TREATMENT OF UNDERGROUND MINE WATERS FOR THE REMOVAL OF CALCIUM AND SULPHATES BY A GYP-CIX PROCESS

ABSTRACT

The paper will describe the developments of a novel ion exchange resin process suitable for the desalination of large volumes of mine waters with a TDS of up to 6500 mg/l approximately which is also high in calcium and sulphate, to meet effluent discharge specifications. Typically acid mine water or acidic effluents that have been neutralised with lime for anti-pollution measures are high in calcium sulphate and therefore present a problem for desalination.

The GYP-CIX process consists of a two stage operation. The first is the removal of cations in a multi stage continuous loading train, using cation exchange resin. The second operation is the removal of anions, again in a multi stage continuous loading train using anion exchange resin. The novelty of the process lies in the use of cheap reagents such as sulphuric acid and lime for regeneration of the ion exchange resins in a seeded batch regenerator. In both cases the waste produced is a brine slurry containing precipitated calcium sulphate ($CaSO_4$).

The process was successfully piloted to treat 24 m^3 of underground mine water per day continuously. A cost estimate for a full scale plant compares well with other desalination processes. The GYP-CIX Process finds its niche in the treatment of scaling effluents and could be considered for several different applications where other processes are limited due to the scaling aspect.

KEYWORDS

Desalination, Removal of Calcium and Sulphates, Ion Exchange Resin, Gypsum Waste, Regeneration with Sulphuric Acid and Lime, Desalination Market.

1. INTRODUCTION

The treatment of acid rock drainage or acid mine drainage by lime neutralisation is a recognised anti-pollution measure.

Acid rock drainage refers to the acidification of water in the environment, caused by the oxidation of sulphide minerals to the soluble metal ions and sulphates. The exposure of sulphide containing rocks to air and water, usually assisted by bacterial action, is most commonly the cause of this phenomena.

The reaction of the lime with the acids present during neutralisation results in precipitation of metal hydroxides as well as gypsum, where there are sulphates present. The precipitate is concentrated in a settler or thickener and discharged as a thick sludge for disposal. The clarified supernatant solution is now free of excess acidity and at neutral pH, however a saturated solution of calcium sulphate results.

The solubility of gypsum in water is 2,25 g/l, which translates to 520 mg/l of Calcium and 1250 mg/l of Sulphate. The levels of these ions are seldom at the saturation value however, due to the low reaction rate of crystal formation. Supersaturated solutions of calcium sulphate have been known to exist for several days, before stabilising at equilibrium concentrations.

Saturated or supersaturated solutions of calcium sulphate are characterised by their scaling potential. The gypsum will precipitate on pipe and equipment walls, resulting in a hard layer of scale that is extremely difficult to remove. This effect will invariably preclude the further use of the neutralised water in any process or equipment as maintenance costs due to cleaning are high.

The disposal of this high salinity saturated effluent to the environment also presents a problem. Although of low toxicity, it can contribute a high annual salt load into the environment, which increases the salinity and therefore pollutes the natural water courses.

This situation has prompted the development of a process designed to remove the residual calcium sulphate from saturated solutions so that the water can be reused. This process, known as GYP-CIX, uses ion exchange resins to remove the offending ions. The resins are regenerated in a novel way using lime and sulphuric acid, whereby gypsum is precipitated in the regeneration stage and is the only waste from the process.

The paper will show that the GYP-CIX process has been successfully developed and can be used in an economic and cost effective way to remove the scaling elements so that the water can be re-used. Desalination of scaling effluents which was not available in the past, is now a possibility.

2. THE GYP-CIX PROCESS FOR LOW COST TREATMENT

The conventional ion exchange process for the purification of waters and the normal requirements for expensive reagents such as NaOH and HCℓ for resin regeneration, as well as the undesirable production of concentrated soluble waste products, is well known.

The use of alternative chemicals such as sulphuric acid and lime would present the lowest cost method for regeneration. However, these chemicals have been precluded in the past for the practical problems involved in their use, because of their potential for fouling the resin with $CaSO_4$, eventually destroying the resin and reducing the useful life of the resin to the extent that the resin replacement would become too expensive.

The use of the low cost chemicals mentioned above, the production of gypsum in the saturated regeneration solution and making use of the unique properties of the expended fluidised bed of resin to be regenerated, has resulted in the process being successfully chemically engineered. The break through achieved is the prevention of the resin fouling. It has been extensively tested in long run tests to prove fouling does not occur and is the subject of the patented process.

Furthermore the 'planned' production of gypsum during regeneration allows the discharge of a slurry as the waste product, thereby reducing disposal problems. With a high water recovery and hence, a low volume of waste to be disposed, zero run-off aspirations are attainable.

To evaluate the process a pilot plant with a capacity of 24 m3/day was commissioned and has been operated successfully on acid mine waters from underground for almost three years to test the long cycle affects on the process. A flow diagram of the pilot plant is given in Figure 1.

3. THE PILOT PLANT (Figure 1)

3.1 Feed Water

The feed water to the pilot plant consists of acid mine water from a producing mine pumped from underground, which has been limed and clarified. The feed water has the following typical salt concentration:-

TABLE 1
Feed Water Concentrations

Ca	180 mg/l
Mg	50 mg/l
Na	50 mg/l
SO_4	700 mg/l
Cl	40 mg/l
pH	6 - 8
TSS	25 NTU
Cond	145 mS/m
TDS	1100 mg/l

3.2 Resin Loading

The feed water is pumped to the cation loading section, where it gravitates through six upflow fluidised bed contact stages. The strong acid resin is airlifted between stages counter-current to the water flow.

The decationised and decarbonated water is then pumped to the anion loading section which contains six fluidised stages of weak base resin. The mechanical operation of this section is the same as for the cation loading section

The continuous counter-current technique used for cation and anion loading is well known, commercially proven, cost effective and very suitable for the treatment of large volumes of water.

The resulting product water is at a neutral pH, low in Calcium and Sulphate and other heavy metal ions and is non scaling and meets effluent discharge specifications.

3.3 Regeneration of Loaded Resins

The novel of the GYP-CIX process is in the resin regeneration technique and the planned production of gypsum as a solid waste product.

3.3.1 Cation Regeneration

The fully loaded cation resin is airlifted out of the loading section into a batch regenerator, where it is contact with a 10% H_2SO_4 solution, seeded with gypsum crystals.

The solubility of $CaSO_4$ is low and as soon as the solubility limit is reached $CaSO_4$ will precipitate as gypsum. The precipitation of gypsum is enhanced by adding gypsum crystals as seeds to act as precipitation nuclei to avoid the formation of supersaturated solutions.

3.3.2 Anion Regeneration

The regeneration of the loaded anion resin is achieved with lime. To overcome the low solubility of lime a 2% lime slurry is used, which is again seeded with gypsum crystals.

The anion regeneration also produces gypsum which is removed from solution by settling and finally discharged as a solid waste.

The continuous removal of gypsum from solution in both the anion and cation sections in a settler, allows the clarified solution to be reused for subsequent regenerations which further minimises reagent consumption.

4. RESULTS OF PILOT PLANT OPERATION

4.1 Resin

4.1.1 Resin Fouling

Irreversible resin fouling by iron, silica, and organics would add substantially to the operating cost and limit the desalination performance of such a process.

After the equivalent of one year of continuous operation, no detrimental signs of resin fouling have been detected.

4.1.2 $CaSO_4$ Scaling of Resin Bead

Electromicrographic examination of the resin beads show no presence of $CaSO_4$ either on the surface or inside the beads after 500 cycles of loading and regeneration.

4.1.3 Resin Capacity

The total capacity (Figs. 2a & 2b) as well as the loading kinetics (Figs. 3a & 3b) were tested at regular intervals and no drop in performance was noted.

The working capacity of the strong acid cation resin was typically 55% and for the weak base anion resin 85% of the total capacity respectively. These values are typical for continuous ion exchange processes.

4.1.4 Resin Loss/Breakage

On average the rate of resin loss due to breakage of beads was about 10% per annum for the macroporous styrenic cation resin and approximately 5% p.a. for the acrylic anion resin.

The higher loss for the cation resin was as expected due to the bead having less resistance to attrition. This resin loss is normal and well within the limits for counter-current ion exchange applications.

4.2 Plant Performance

4.2.1 Product Water

The typical plant product water analysis is given in Table 2. In addition to the low levels of Calcium and Sulphate, a significant reduction in radioactive elements such as Radium and Uranium was achieved. Residual metal values, such as Iron and Manganese were also removed to low levels in the plant.

TABLE 2

Produce Water Concentrations

Ca	20 mg/l
Mg	10 mg/l
Na	10 mg/l
SO_4	100 mg/l
C1	20 mg/l
pH	7 - 8
TSS	25 NTU
Cond	20 mS/m
TDS	150 mg/l

4.2.2 Water Recovery

The plant achieved an average water recovery in excess of 90%.

5. ADVANTAGES OF THE GYP-CIX PROCESS

Some of the advantages of the process are listed below:

i) The process uses cheap, locally available chemicals.

ii) The plant requires no pretreatment in the way of feed filtration, chlorination or pH adjustment.

iii) The required degree of partial desalination can be controlled if required.

iv) Slurry waste stream enables easy disposal of a solid and inert waste.

v) Resin replacement is low being between 5 and 10 % per annum.

vi) Removal of salts and heavy metal ions is effected to within effluent specifications.

vii) High water recoveries are possible.

viii) Radioactive elements are removed to low levels in the process.

xi) The process can be fully automated and does not require highly skilled labour.

x) Metals that do not precipitate or residual valves after liming are removed to comply with drinking water standards.

xi) The process is relatively low technology and the plant consists primarily of non-pressurised vessels, pumps, valves and common instrumentation.

The process is particularly suited to the desalination of scaling effluents, such as those occurring when effluents are limed. Neutralisation of effluents with lime is a common practice, which although ridding one of many dissolved metals usually leaves an effluent saturated in calcium sulphate that is highly scaling in nature and cannot be reused.

6.0 THE ECONOMICS OF DESALINATION

Desalination processes can be compared in terms of various economic factors which will dictate which is the most economical process for any particular application.

6.1 Desalination Capability

The first question that must be asked when considering a new application is which of the available technologies are suited to the problem. In particular it must be considered whether the process can produce the required product water quality and what pretreatment of the feed will be required.

Different processes will be more or less suitable depending on the salt content (concentration of salts to be removed) and the type of salts present. The reliability of the process in terms of maintenance required and anticipated down time must also be considered.

6.2 Water Recovery

A desalination process will produce a concentrated waste stream and a purified product water. The percentage of the feed that is recovered as a recyclable product is known as the water recovery and provides an important indicator of the efficiency of the process.

Conversely, the higher the water recovery, the smaller the volume and the more concentrated the waste stream that is produced. This is also an important consideration as facilities must be provided for the further concentration disposal or storage of this waste. Naturally, the smaller this waste stream, the smaller and less expensive will be the facilities required to handle it. A solid waste has particular advantages in this respect as it can be easily contained on a waste dump, whereas a brine stream will require further concentration to attain a zero run off status.

6.3 Operating Cost

The operating cost of the process will ultimately be a critical factor in the decision as to whether to proceed with a desalination plant or not. If product water can be recovered for reuse at a lower cost than that of fresh make-up water, then an important advantage can be achieved.

The operating cost of a desalination process can be broken down as follows:

- Chemicals: Any chemicals that are consumed in the process
- Consumables: Any items of equipment or inventory that require regular replacement over the operating life of the plant
- Power: The average cost of the electrical power required to run the process
- Labour: The annual cost of labour to operate the plant
- Maintenance: The estimated annual cost of maintenance of the plant

The above running costs should all be expressed as a cost per m^3 of product water by summing the annual costs and dividing by the quantity of product water recovered in a year. The individual costs can then be summed and an overall treatment cost per m^3 of product water can be estimated.

6.4 Capital Cost

The capital cost of the plant can be estimated using recognised cost estimating procedures. Allowance must be made for plant hardware, erection of the plant, an initial inventory of consumables, engineering fees and contingency. (ie: total installed cost).

The capital costs of the plant can be amortised over the lifetime of the plant to arrive at a figure for the annual cost of the plant capital. This figure can then be added to the plant operating cost. Where the product water is reusable or saleable, the plant can usually be written off over a longer period of time, say 15 years. In other situations and particularly mining applications, the write off against special tax concessions usually require a short capital depreciation period.

7.0 WATER RECOVERY OF THE GYP-CIX PROCESS

The water recovery of a process is crucial to the efficiency of that process. A water recovery of above 70% is essential in inland areas and above 80% is desirable.

The water recovery of the GYP-CIX process shows a inverse linear relationship with the TDS of the water to be treated. The higher the TDS the more the water recovery drops off until at a TDS of 4000 mg/l, the limit of 70% water recovery is reach, as shown in Fig. 4.

8.0 OPERATING COST OF THE GYP-CIX PROCESS

The operating cost of the GYP-CIX process is largely dependant on the cost of chemicals used in the regeneration of the resin. This comprises approximately 50% of the operating cost and is in turn dependant largely on the TDS of the feed water. Normally, no pretreatment of the feed is required such as softening or adjustment of the plugging index which results in a large cost saving being possible. The balance of the operating costs is made up of fixed overheads such as labour and maintenance. This trend is reflected in the graph in Fig.5 which shows a linear dependence of the operating cost on the TDS of the feed water.

9.0 CAPITAL COST OF THE GYP-CIX PROCESS

The capital costs of the GYP-CIX process shows a significant saving in unit capital cost over the range of plant sizes studied. This is because the equipment consists primarily of tanks, pumps and valves, which when scaled up do not increase proportionately with size.

10.0 GYP-CIX MARKET NICHE

The range of effluents to be desalinated can be characterised by their TDS (Total Dissolved Solids) and calcium content. The graph in Fig.6 shows the range of waters to be desalinated and the different areas of the market. This graph was compiled from the previous graphs given for water recovery and operating costs, excluding capital costs.

The sloping line indicates the division where the water recovery of GYP-CIX is greater than that of membrane processes, above and to the left of this line. The vertical line indicates the cut-off, where GYP-CIX running cost is lower than membrane processes to the left of this line. These lines enable the range of effluents to be treated to be broken down into 4 distinct market areas which are discussed as follows.

Area 1

This areas is suitable for GYP-CIX, where TDS levels are in the range suitable for resins and the calcium levels are easily handled. This is the niche for GYP-CIX, extending significantly the range of existing water desalination technology. GYP-CIX is cheaper in capital and operating costs and has a higher water recovery.

Area 2

This is the range where calcium makes only a modest contribution to TDS, the predominant salts usually being sodium (as sodium chloride) or magnesium. GYP-CIX is still cheaper in capital and operating cost but membrane processes have a higher water recovery due to the low calcium content.

Area 3

This area is most suited to membranes, due to the high salt loads, usually sodium chloride. It is a small niche market usually for brackish water of low calcium content, and extends to the application for which R.O. has been most useful, notably the desalination of sea water for drinking purposes. The water recovery of membrane processes drops off dramatically as the TDS increases, from the recovery of about 80% at the lower TDS range to a recovery of 35% at the TDS of sea water.

Area 4

This range involves a high TDS, with calcium making a significant contribution and as is typified by a boiler or cooling tower blowdown with scaling tendencies. It is therefore not suitable for membrane processes as very low water recovery would result. The high salt load also restricts the use of the GYP-CIX process in this application.

It has however been found from our research in both fields of R.O. and ion exchange that a combination of the two technologies, known as GYP-SOFT would be capable of a very satisfactory solution. A recovery in the range 80 to 90% can be achieved and with further brine concentration of the small residual volume, a zero runoff concept is attainable.

11.0 CONCLUSION

The GYP-CIX process has been successfully piloted and is capable of economically desalting large volumes of hard and scale forming acid mine water.

The use of counter-current fluidised resin bed loading stages allows the feed of an unclarified water.

Regeneration of the loaded resins is accomplished efficiently and with the cheapest possible regenerants, namely sulphuric acid and lime, instead of the more costly hydrochloric acid and caustic soda.

It also results in the generation of a slurry waste product in the form of gypsum, which significantly eases final effluent disposal problems and the cost thereof.

The GYP-CIX process is favourably competitive with other desalination processes in terms of operating and capital costs. The water recovery in the case of effluents high in calcium sulphate is very good which enables the recovery of large quantities of water for recycle.

The range of effluents can be characterised by the TDS and calcium content of the feed. The desalination market can be divided into different niche areas where one or more technology can be considered technically feasible and economically attractive.

A market niche has been identified for the new GYP-CIX technology where the process is capable of achieving a high water recovery at a low cost for scaling waters. The capabilities of the GYP-CIX process extend beyond this market niche into areas where the bulk removal of salts is desired and other desalination processes fail due to fouling or are too costly.

This development has, therefore, significantly extended the range of existing desalination technologies to include the troublesome scaling effluents, even when a high TDS background exists.

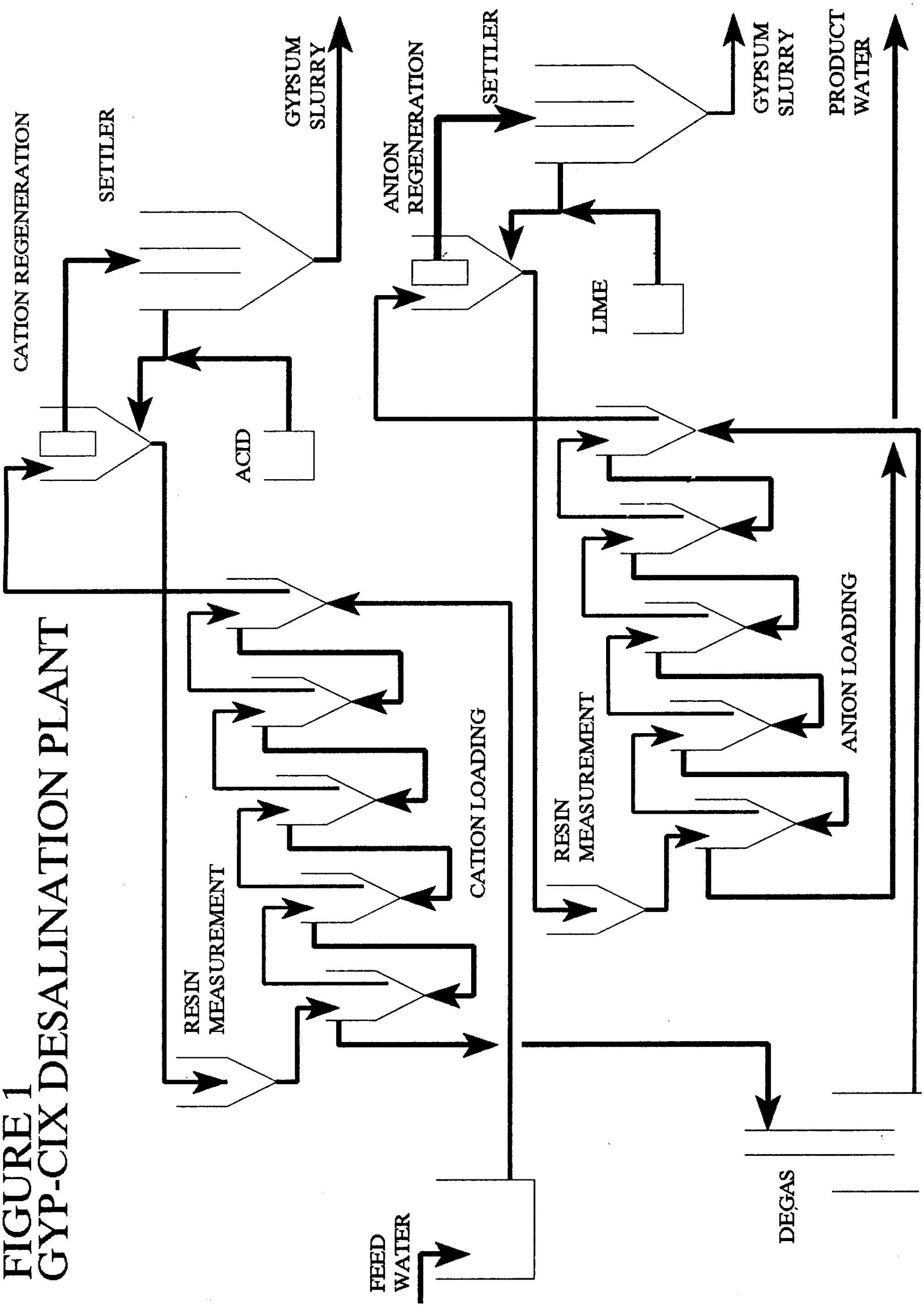


FIGURE 1
GYP-CIX DESALINATION PLANT

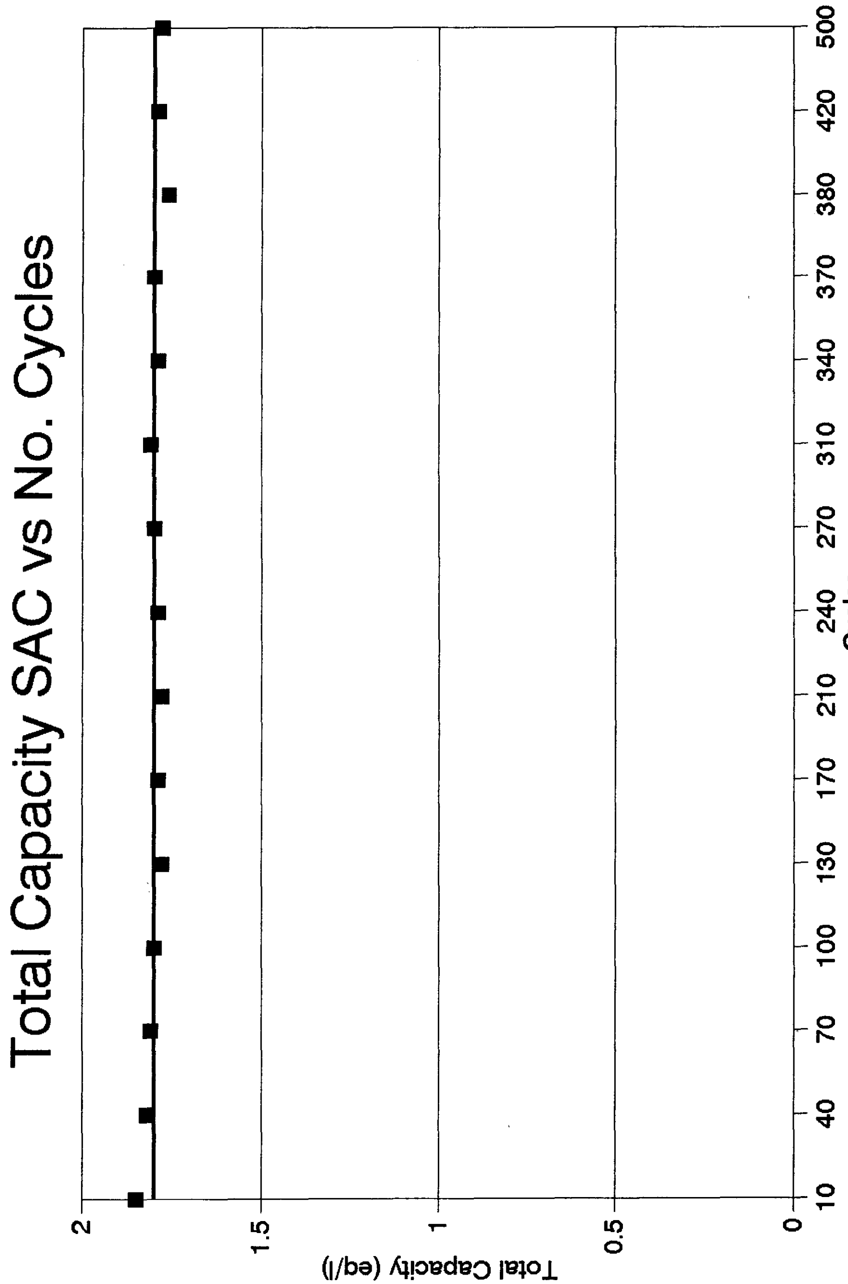

Total Capacity SAC vs No. Cycles
Total Capacity (eq/l)
2
1.5
1
0.5
0
Cycles
10
40
70
100
130
170
210
240
270
310
340
370
380
420
500

FIGURE 2a

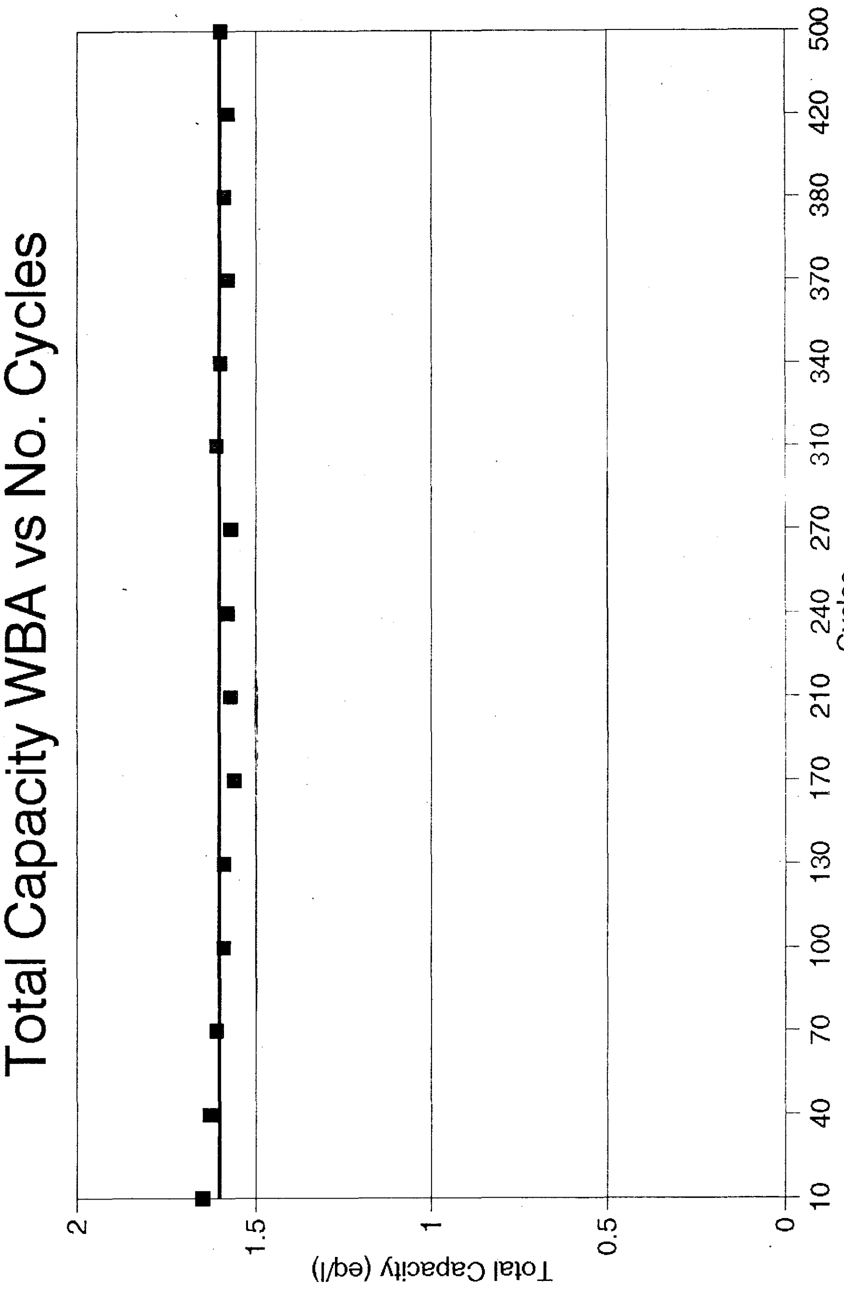
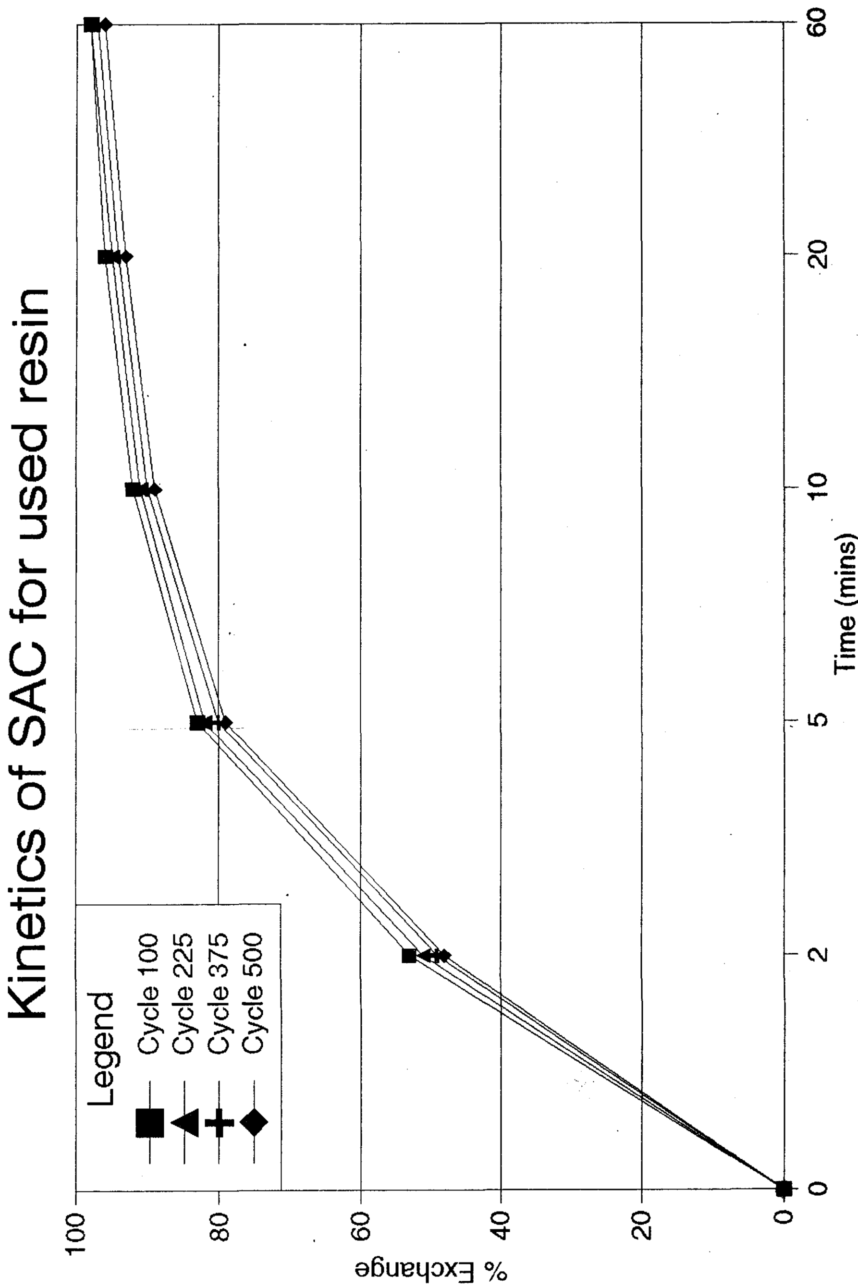

Total Capacity WBA vs No. Cycles
Total Capacity (eq/l)
2
1.5
1
0.5
0
Cycles
10
40
70
100
130
170
210
240
270
310
340
370
380
420
500

FIGURE 2b



Kinetics of SAC for used resin
Legend
Cycle 100
Cycle 225
Cycle 375
Cycle 500
% Exchange
100
80
60
40
20
0
Time (mins)
0
2
5
10
20
60

FIGURE 3a

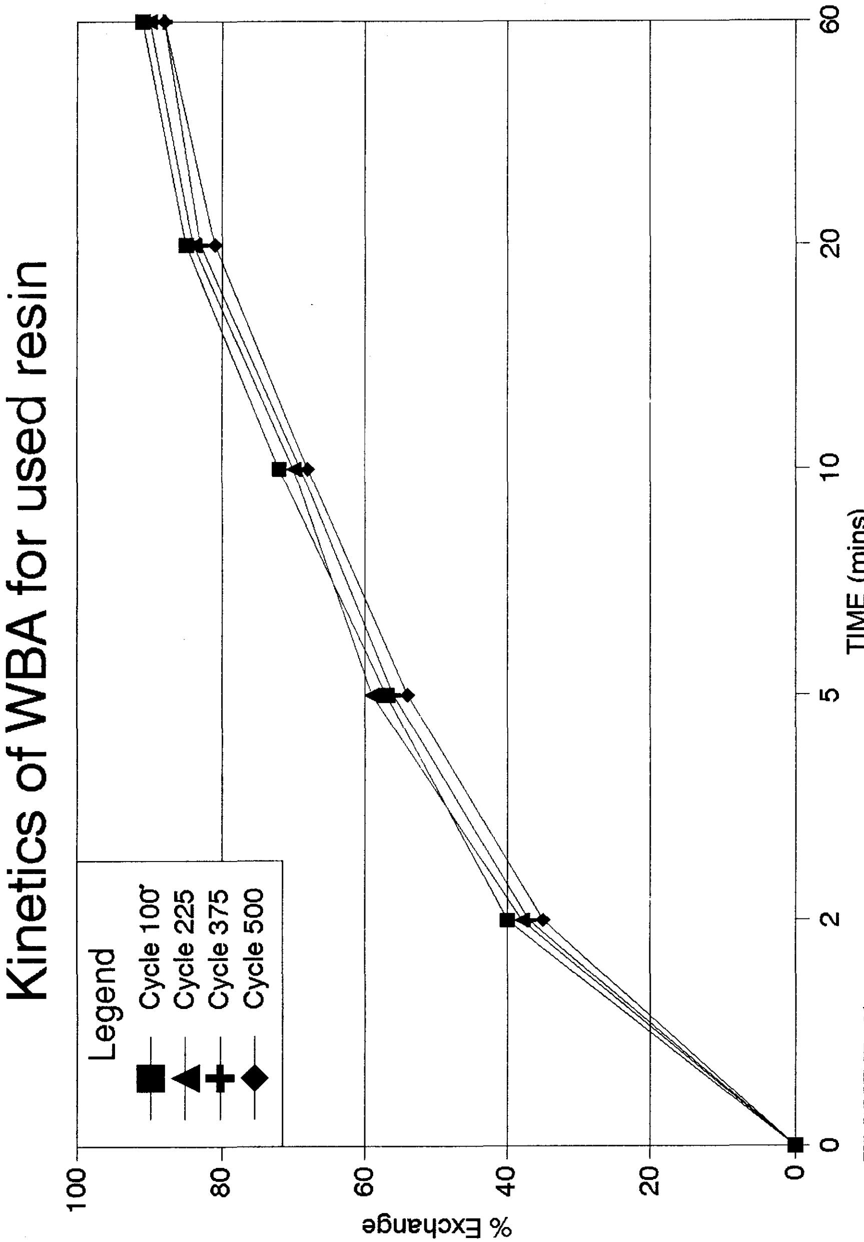

Kinetics of WBA for used resin
Legend
Cycle 100
Cycle 225
Cycle 375
Cycle 500
% Exchange
0
20
40
60
80
100
TIME (mins)
0
2
5
10
20
60

FIGURE 3b

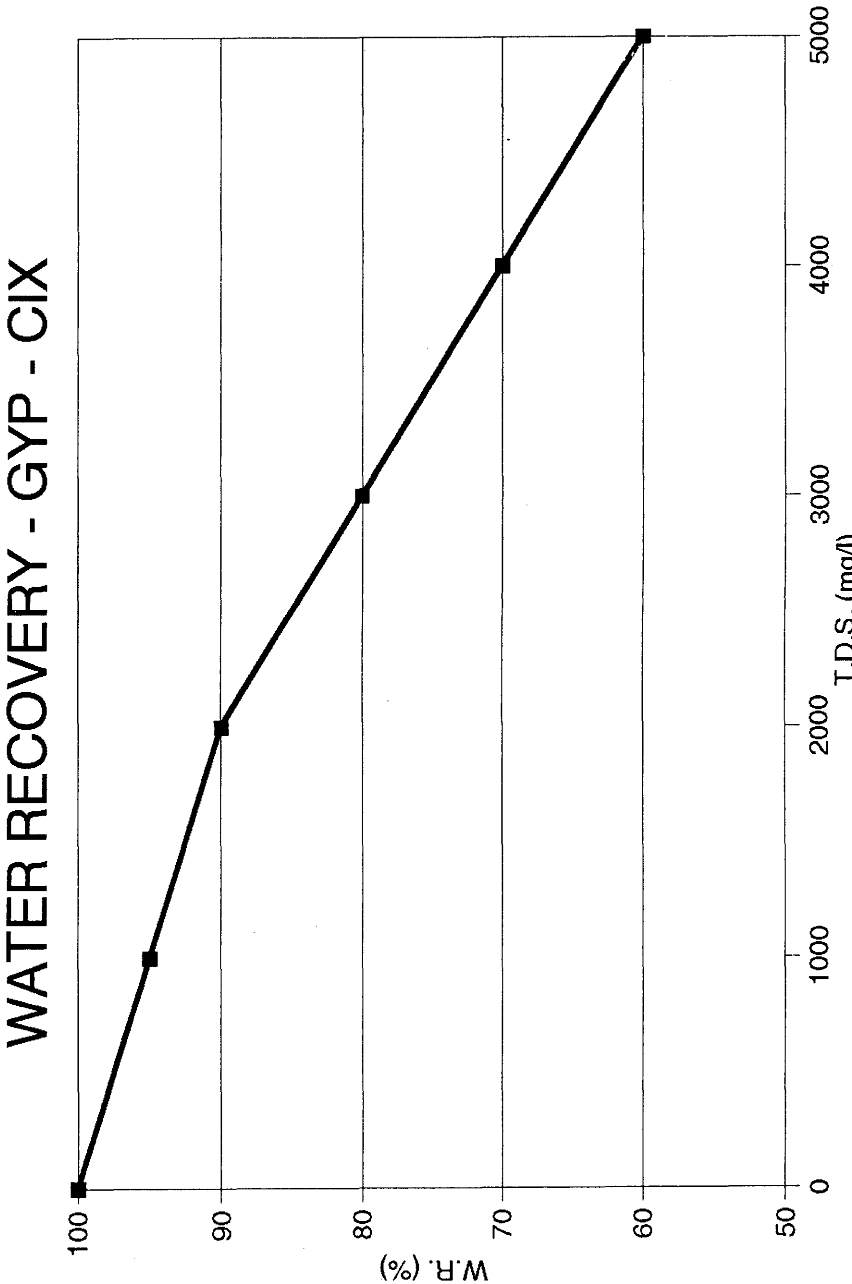

WATER RECOVERY - GYP - CIX
W.R. (%)
100
90
80
70
60
50
T.D.S. (mg/l)
0
1000
2000
3000
4000
5000

FIGURE 4

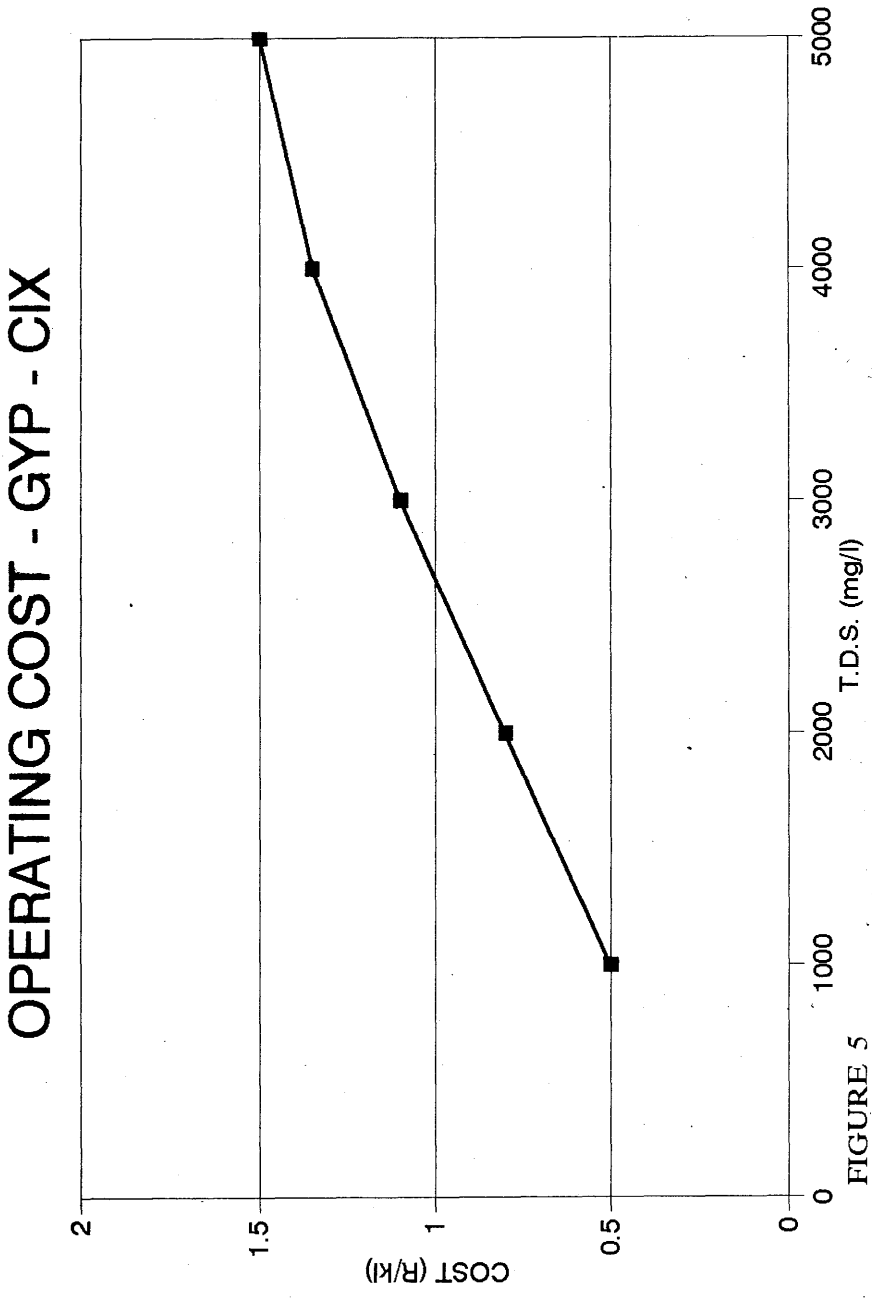

OPERATING COST - GYP - CIX
COST (R/kl)
0
0.5
1
1.5
2
T.D.S. (mg/l)
0
1000
2000
3000
4000
5000

FIGURE 5

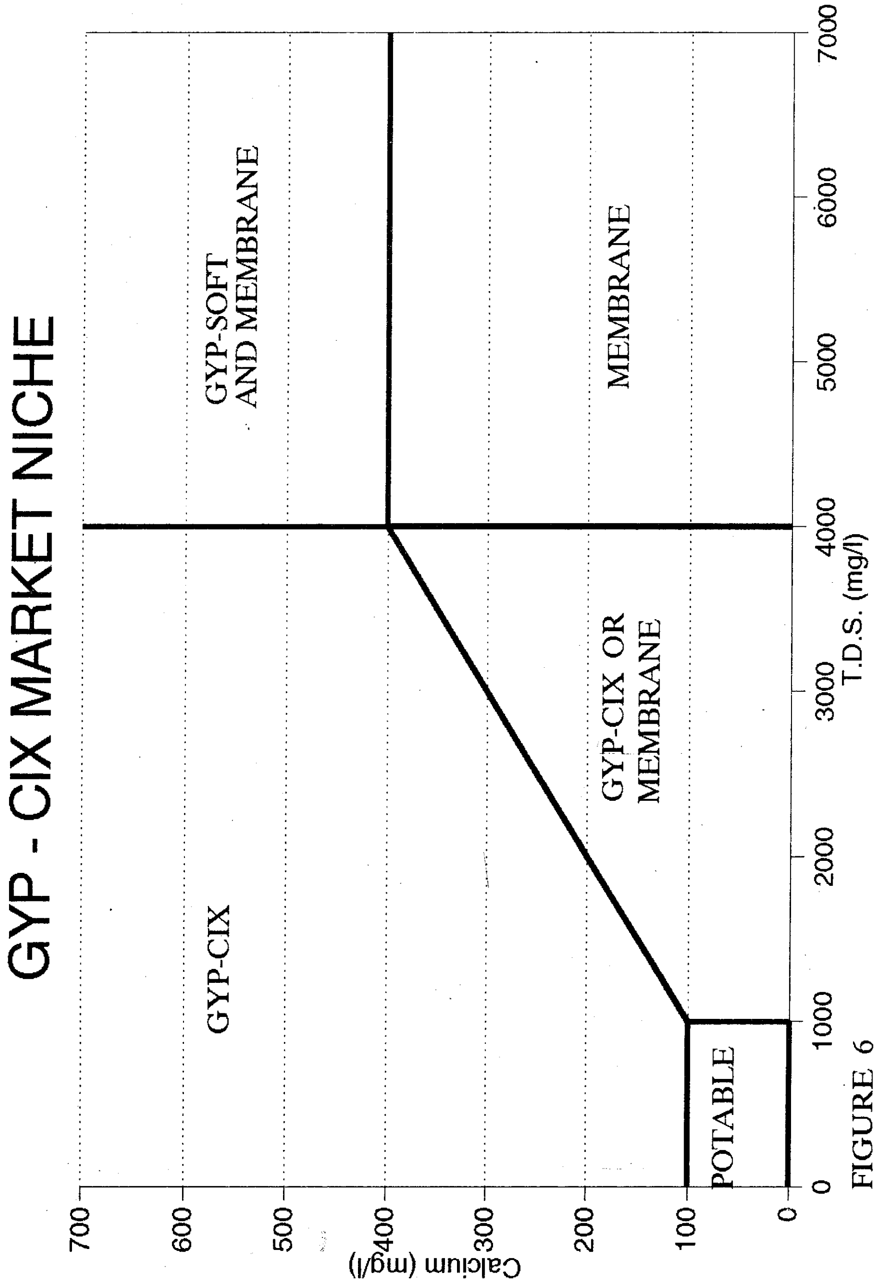

GYP - CIX MARKET NICHE
GYP-SOFT
AND MEMBRANE
MEMBRANE
GYP-CIX
GYP-CIX OR
MEMBRANE
POTABLE
Calcium (mg/l)
0
100
200
300
400
500
600
700
T.D.S. (mg/l)
0
1000
2000
3000
4000
5000
6000
7000

FIGURE 6