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(54) Title: PROCESS FOR MANUFACTURE OF CARBOXYLIC ACID SALTS

(57) Abstract: The invention relates to a process for manufacture of carboxylic acid salts in the form of alkali metal or alkaline-earth metal carboxylates of 1 to 3 carbon atoms. The continuous manufacturing process comprises: 1) passing carboxylate salt of a starting cation through one or several ion exchange beds containing solid cation exchanger charged with an alkali metal or alkaline-earth metal cation,2) collecting a product solution containing alkali metal or alkaline-earth metal carboxylate eluted from the one or several ion exchange beds in step 1,3) simultaneously with step 1, regenerating one or several ion exchange beds containing solid cation exchanger charged with the starting cation by passing a regenerating solution containing a salt formed by an anion and the alkali metal or alkaline-earth metal cation through the one or several ion exchange beds,4) collecting an effluent solution containing the starting cation and the anion eluted from the one or several ion exchange beds in step 3, and 5) shifting the inlet and outlet points of the solutions in the same direction to other ion exchange beds.

Process for manufacture of carboxylic acid salts

The invention relates to a process for manufacture of carboxylic acid salts.

At the present, for example potassium formate is normally manufactured as a neutralization reaction between formic acid and potassium hydroxide, wherein formic acid must always be available. Also a direct synthesis between CO and KOH is a possible manufacturing technique for obtaining potassium formate directly (Encyclopedia of Chemical Technology, 3rd ed., vol. 18, p. 938). This latter reaction requires the application of a high temperature and pressure, and a bit difficult raw material because of its toxicity, carbon monoxide.

It is characteristic of all these methods that the raw material is potassium hydroxide, and when potassium formate is manufactured in a neutralization reaction, formic acid must always be used as a source of formate anion. Potassium hydroxide and formic acid are relatively expensive sources of potassium and formate, respectively.

Sodium formate is obtained as a side product of pentaerythritol. Pentaerythritol is manufactured in a reaction between formaldehyde and acetaldehyde by using sodium hydroxide as a catalyst. A side product of this process is dilute sodium formate which can be further converted to formic acid with sulphuric acid.

In connection with this process, also electrodialytic manufacture of potassium formate from K_2SO_4 and HCOONa has been developed. An electrodialytic process with a concentrated sodium formate solution and a potassium sulphate solution as starting materials is described in international publication WO 96/01250. The electrodialytic manufacturing process starting from said materials requires various types of selective membranes. Furthermore, the electrodialytic device also requires much maintenance for securing its faultless operation, *e.g.* to prevent clogging of the membranes. Electrodialytic processes require also a lot of energy.

Swiss patent 439249, to which corresponds British patent 1033030, discloses a method for manufacturing inorganic and organic salts. Table 1 and example 5 of the patent present the conversion of formic acid into sodium formate with a weak-base anion exchanger in liquid form by mixing an aqueous solution of formic acid and sodium chloride with the weak-base anion exchanger dissolved in an organic phase. The manufacturing method requires the dissolving of the anion exchanger in a suitable organic solvent which is insoluble in water, mixing of the substances and separating the water phase for separating the final product.

Methods for manufacturing calcium formate, in turn, are disclosed in US patent 2,913,318 and DE application publication 4126730. The methods are based on reactions between calcium hydroxide and carbon monoxide and between calcium hydroxide and formaldehyde, respectively. The former method requires a pressure reactor, and the latter requires handling of formaldehyde.

It is an aim of the invention to eliminate the above-mentioned drawbacks and to present a simpler manufacturing method which is suitable for industrial use and in which it is possible to start from a suitable formate solution or formic acid, *i.e.* in principle from any substance containing the formate anion, and to obtain an alkali metal or alkaline-earth metal formate as a final product.

A simple way of manufacturing alkali metal or alkaline-earth metal formate is further disclosed by WO 00/18717. The principle is in anion exchange with solid ion exchangers between metal chloride and sodium formate.

A general drawback of ion exchange processes is that a lot of waste streams are produced and a lot of water is required during the regeneration steps of the resin. The manufacture by ion exchange is a batch process.

It is therefore an object of the present invention to present the process where a desired alkali metal or alkaline-earth metal carboxylate of 1 to

3 carbon atoms in the chain (salt of formic acid, acetic acid or propionic acid) can be obtained continuously with a good conversion using ion exchange. For achieving this object, the process according to the invention is mainly characterized by the features set forth in the characterizing portion of claim 1.

The conversion of the carboxylate salt to a desired salt, where the anionic part (formate, acetate or propionate) remains the same takes place in a cation exchanger using a series of columns packed with cation exchanger resin. The production step where the original cation of the raw material salt is exchanged for the alkali metal or alkaline-earth metal cation of the produced salt takes place in one section of the series of columns, and this production section is moved using the principle of simulated moving bed, the remaining sections consisting of a regeneration step and intermediate washing steps.

The amount of the raw material stream can be determined on the basis of the amount of the desired cations in the cation exchanger bed after regeneration step and the selectivities of the cations to cation exchanger. Similarly the amount of renegerating solution stream can be determined on the basis of the amount of starting cations in the cation exchanger bed after production step and the selectivities of the cations to cation exchanger.

In the following, the invention will be described in more detail with reference to the appended drawings which illustrate the steps of the cation exchange process and its alternatives. In the drawings,

Fig. 1 shows the general principle of the process as a simplified diagram,
Fig. 2 shows the process according to a first embodiment,
Fig. 3 shows the process according to a second embodiment,
Fig. 4a shows a process according to a third embodiment,
Fig. 4b is a diagram explaining the third embodiment,
Fig. 5 shows equilibrium curves of some cation exchange resins,
Fig. 6 shows the process with some aftertreatment operations, and

Figs. 7 to 20 illustrate the variation of ions throughout the whole manufacture line in various examples.

The purpose is to manufacture alkali metal or alkaline-earth metal salt of a carboxylic acid continuously with a high conversion and with a high purity. In the process, four steps are proceeding simultaneously in different beds. In the production step, the raw material carboxylate having a starting cation is passed as a solution through one or several beds. The starting cation in the solution replaces the desired alkali metal or alkaline-earth metal cation of the ion exchanger in a cation exchange process, and the alkali metal or alkaline-earth metal cation is entrained in the solution and the starting cation remains in the resin. In the first washing step, one or several beds through which the raw material solution has been passed in the previous production step are washed with water to remove the water-soluble ions that are not fixed in the bed. In the regeneration step one or several beds that have been washed in the washing step are charged with the desired cation of the end product by passing a salt of that cation (in which the anionic part can be any anion except the carboxylate anion of the product, preferably an inorganic anion, especially chloride) as a solution through said one or several beds, during which step said cation replaces the starting cation of the cation exchanger in a cation exchange process. In the second washing step, one or several charged beds are washed with water to remove the water-soluble ions not fixed in the bed in the previous step.

All the steps go on simultaneously so that one or several beds are always allocated to the production step. The beds are changed using a predetermined sequence so that the cation exchange resin moves virtually countercurrently to the streams of solutions and wash liquids passed through the beds, by a principle known as simulated moving bed (SMB).

Figure 1 shows schematically the process of the present invention, using aqueous sodium formate solution as an example for the raw material stream (sodium ion being the starting cation) and aqueous potassium formate solution as an example for the product stream

(potassium being the desired cation of the produced salt of carboxylic acid). In this case, the basic carboxylic acid whose different salts exist in different aqueous streams is formic acid, but the method is well applicable to salts of acetic acid and propionic acid as well.

The section of one or several beds where the production step takes place is on the right hand side of the figure, and the section where the regeneration step takes place is on the left hand side of the figure. The sections representing the washing steps between the production step and the regeneration step are on the upper and lower side of the figure. It should be noted that the figure is a diagram intended only to illustrate the principle of simulated moving bed where the inlet and outlet points of various solutions are changed periodically and in a synchronized manner so that the resin can be thought to move countercurrently to the streams of the raw material solution and regeneration solution. The washing steps can include the recovery of extra wash water (not shown in fig. 1 or fig. 2) by collecting part of the wash waters for reuse.

Figure 2 shows a process diagram which corresponds more to the real situation. The ion exchange plant consists of several columns (in this case, 20 columns), each packed with cation exchanger resin. Columns are preferably vertical columns placed in an array next to each other. The cation exchanger resin is of the same type in each of the columns. Further, there is a source of raw material solution (such as a tank), the source of regenerating solution (such as a tank), and the source of wash water (such as a tank). A stream from each of the sources can be coupled to the inlet point of any of the columns. The outlet point of any column can be coupled to any of the two collecting lines for the product stream and regeneration eluate salt stream, respectively (and to the wash water collecting and recirculation tanks to be used as a wash water later). The outlet point of any column can also be selectively coupled to an inlet of any column. The collecting line for the product stream leads to the aftertrretment, such as concentration, and the collecting line for the regeneration eluate salt stream leads to the treatment of effluent.

For the sake of illustration, the columns are numbered consecutively. In the situation shown by Fig. 2, columns no. 4 to 9 are in the production step in a serial connection to each other (sodium formate solution fed in and potassium formate solution, the product stream, taken out). Column no. 10 will be filled with potassium formate solution and wash water (which is in the column because of the previous switch) is pushed to the next column 11. Columns no. 11,12 and 13 are in the washing step (wash water can be collected from the outlet of column 12), column no. 14 will be filled with wash water, and regeneration salt solution (which is in the column because of previous switch) is pushed to the next column 15. Columns no. 15 to 19 are in the regeneration step in a serial connection to each other (KCl fed in and the regeneration eluate salt solution, NaCl solution taken out), column no. 20 will be filled with regeneration eluate salt solution, and wash water (which is in the column because of previous switch) is pushed to the column 1, columns no. 1 to 3 are in the washing step, column no. 3 will be filled with wash water and production salt solution, which is in the column because of previous switch, is pushed to the next column 4. The whole process can of course done noncontinuously or stepwise during the switchtime.

In Fig. 2, it is also seen that water discharged from the column 20 is recirculated to the inlet of the washing step to form a part of its inlet stream. The product stream, potassium formate solution eluted from the production step (columns no. 4 to 9) and sodium chloride solution eluted from the regeneration step (columns no. 15 to 19) are led to the collecting lines of their own and can be collected and treated separately.

The inlet and outlet points of each step is moved in the direction shown by arrow, that is, in the direction of increasing column numbers while the columns and beds remain stationary. The act of moving the points by one column is termed "shift" and the phase between two consecutive shifts is termed "switch" or "switchtime" in this application. The principle can be illustrated also so that the feeds and outlets remain stationary and at the end of each switchtime each column takes one step backwards i.e. column 2 comes, "shifts", to the place of

column 1, column 3 to the place of column 2 etc. and column 1 comes to the place of column 20. The shifting of the inlet and outlet points of each stream takes place preferably simultaneously by one column at a time so that the same configuration is preserved. The new location of each stream after the inlet and outlet points are shifted by one column is denoted by broken lines in Fig. 2. Stepwise shifting of the inlet and outlet points in one direction will cause the resin to move counter-currently to the product streams according to the diagram of Fig. 1.

To make the ion exchange effective, the ion exchange resin bed in the column should have minimum dead volume to avoid extra mixing of solutions. Flow in the columns can be arranged from top to bottom or vice versa. The only energy needed in the process is for pumping the liquid streams from tanks to the columns and through the columns. Some energy is required for keeping the liquid streams at a desired temperature.

In principle, the process can take place in an array of four columns, each column for one step. However, for the process to be more flexible, its is preferable that the number of columns is more than four so that at least one of the regeneration step or production step or both can take place in two or more columns connected in series. In view of flexible continuous mananufacture the number of columns is preferably 10 or more. The cation exchanger beds in the different columns are preferably of equal volume so that the active cation exchanger volume can be adjusted by the number of beds (columns) that are allocated for each step in the SMB process.

Resin utilization can be improved and the potassium loss in regeneration step eluate can be lowered in two ways, which will be described in the examples later.

In the production step, a side stream is taken out from a column in the middle of the production step columns (for example where the molar ratio of the two cations in the solution is 40/60–60/40), as is illustrated by Fig. 3. This results in a better resin utilization, that is, for a given resin amount, a larger product output is obtained. The potassium salt

consumption can be lowered at the same time, because the regeneration step outlet solution (eluate) contains lowered amounts of potassium salt. The amount of the side stream can be for example about half of the total production step stream, for example 40–60 % by volume. In the end of the production step, after the point where the sidestream is taken out, the resin liquid ratio is increased correspondingly.

The words "end" and "beginning", as far as the location of columns within a step is concerned, denote the location with respect to the direction of liquid flow through the successive columns connected in series.

Another possibility is to take part of columns in the middle of the production step, for example one or several columns where about half of the resin is converted to sodium form (for example where the molar ratio of the two cations in the solution is 40/60 – 60/40), out of the serial connection and to subject them to washing. This alternative is illustrated by Fig. 4a. The washing water pushes the sodium formate/ potassium formate mixture out of the column to an intermediate tank and to the serial connection of the rest of the production step columns, that is, back to the production. In this alternative, the resin liquid ratio is increased in the end of the production step because the flow of resin in the SMB system is increased compared with the beginning of the production step. The column taken out and filled with washing water is next connected to the regeneration step, in the middle of the serially connected regeneration step columns so that the regeneration solution is partly directed through this column and pushes water out of it. The connection point in the regeneration step is chosen so that the proportion of potassium of the total cations in the resin of the column to be connected matches the corresponding proportion in the columns of the regeneration step at the connection point. Consequently, if in the column taken out from the production step, about half of the resin is converted to sodium form, the point of connection to the regeneration step is where about half of the resin has been converted back to potassium form (for example somewhere in the range between the molar ratios of 40/60 and 60/40 if the disconnection point was chodsen

correspondingly). After the column has been filled with the regenerating solution, it can be placed in the series of the regeneration step columns.

According to Fig. 4a, every *n*th shift is a shift where the so-called "small rotation" occurs, that is, a column is disconnected from the serial connection of the production step and connected parallel to it, a column that was connected parallel to the regeneration step is added to the serial connection of the regeneration step, and it is replaced by a new column moved from the series of columns connected parallel to the production step. In Fig. 4a, in the shift occurring between the switches 0 and 1, column no. 8 is disconnected from the serial connection of the production step and connected in parallel with the production step to the point from where it was disconnected (between columns no. 7 and 9) and in series with column no. 30 that is moved one column backwards with respect to the flow of water and placed to the place of column no. 29, which in turn is connected in parallel with the regeneration step to the place of column no. 31 which in turn is connected in series with the columns of the renegeration step, to the point where it was connected in parallel with them (between columns no. 22 and 23). The shifts between said *n*th shifts are the shifts of the so-called "large rotation", that is, the usual shifts of each inlet and outlet points (including the points of parallel coupling) by one column. In Fig. 4a, each 3rd shift is the shift of small rotation (between switches 0 and 1 on one hand and 3 and 4 on the other hand), whereas the remaining shifts are those of large rotation. When a shift of "small rotation" is made, the number of serially connected columns in each step is kept constant despite losing or gaining one column by shifting the inlet and outlet points by one column between the production step and regeneration step. Thus, the outlet point of the production step and the inlet point of the regeneration step is moved one column forward in a shift of “small rotation”.

It should be noted that the columns need not be physically moved in the embodiment of Fig. 4a either, because the columns can be disconnected from and connected back to the series of columns by coupling the outlet and intlet points of the stationary columns in a

suitable way with each other and with possible other process parts, such as tanks.

Figure 4b illustrates the increase of the resin liquid ratio in the end part of the process step and in the forepart of the regeneration step. In course of several switches, when a long term average is taken, the resin flow countercurrently to the liquid is 1,5 times greater in the end part of the production step and in the forepart of the refgeneration step, because one column is taken every third time from the middle of the producttion step to the middle of the production step. In the example of Fig. 4b it is assumed that the average amount of sodium formate (NaFo) and potassium chloride (KCl) fed is 1 equivalent/switch and the amount of resin in each column is 1 equivalent.

In this context, resin liquid ratio means the ratio of the equivalents of resin to the equivalents of cations in the solution in the SMB system during several switches.

Any cation exchange resin, both weak and strong, can be used in the process. The requirement for the resin is that it has a certain selectivity for cations to be changed which allows for the exchange in both directions, i.e. the exchange of a first cation in the resin for a second cation in the solution and the exchange of the second cation in the resin for the first cation in the solution, depending on the concentrations of the first cation and the second cation in the solutions to be processed.

The process parameters can be chosen according to the desired result, such as output, purity of product (proportion of the starting cation in the product stream for example) etc. The temperature of the ion exchange operations (both that of the production step and regeneration step) can be between 0 - 110°C, preferably in the range between 40 and 70°C. The raw material solution introduced to the production step is at a sufficiently high concentration so that the product can be collected at high concentration, minimizing the need of e.g. evaporation to reduce the water amount in product.

Weak resins, strong resins, and mixtures of a weak resin and strong resin can be used. A preferred weak cation exchange resin is of the type where the active groups are carboxylic acid groups (R-COOH). A preferred strong cation exchange resin is of the type where the active groups are sulphonic groups ($R-SO_3H$). An example of the former is Purolite C104 and of the latter Purolite C160. Both resins are macroporous, but with different matrixes. Purolite C160 has a polystyrene matrix and Purolite C104 a polyacrylic acid matrix. Both resins are crosslinked with divinylbenzene (DVB). A person skilled in ion exchange can evaluate the best resin for the purpose of ion exchange process case by case.

The role of the resin can be best exemplified by Fig. 5 showing the K/Na equilibrium curves for Purolite C104, for Purolite C160 and for a mixture of both resins in a ratio 1:1. In the figure when solution to be handled is on the left side of equilibrium line tends to give potassium cations to the resin and taking sodium cations (regeneration) and when solution is on the right side it tends to give sodium cations to the resin and taking potassium cations (production). Purolite C160 prefers K to Na, because the equilibrium curve is below the diagonal. This means that in the practice the resin is optimal for the regeneration step with potassium when potassium carboxylate is to be manufactured starting from sodium carboxylate, and regeneration takes place easily (less columns are needed). The situation is contrary in the production step, where more columns will be needed and it is more difficult to achieve the high purity and high conversion for both outlets. On the other hand, because Purolite C104 prefers Na to K (equilibrium curve above the diagonal), it is optimal for the production step at the expense of regeneration step, where more columns would be needed.

A good compromise is the mixture of both resins, whose equilibrium curve is close to the diagonal according to Fig. 5. This means that the process is well balanced and no excessive number of columns is needed for either step and high purity and conversion can be achieved. A resin having a molar proportion equilibrium curve whose maximum deviation from the diagonal in the direction of the solution axis is less

than 10% for the pair of cations concerned (starting cation and the cation of the product) is advantageous for this purpose.

Fig. 6 shows a process flow diagram of a plant where the purpose is to manufacture potassium formate. The diagram includes also the optional treatment of the wastewater and the recovery of a byproduct, sodium chloride therefrom (NaCl is contained in the eluate of the regeneration step). The sodium chloride is a natural constituent of sea water and therefore not hazardous as such if it is discharged to sea, but if the local regulations require, the wastewater can be handled by evaporation and crystallization. The optional aftertreatment step includes the separation of KCl, which also is contained in the wastewater in small amounts, from the NaCl/KCl mixture by known separation methods, for example based on different solubilities. The products of the wastewater treatment are water for the recycling, NaCl in solid form, and KCl in solid form, which can be recycled to the ion exchange plant and dissolved for the regeneration step. By crystallizing and recycling KCl the plant can be operated with almost no loss of potassium.

Figure 6 also shows how the optional sidestream eluate, a mixture of potassium and sodium formates, can be treated to separate sodium formate form potassium formate and to recycle it to the production step. This sidestream production is described in examples.

A process where an alkali metal or alkaline-earth metal formate is formed from sodium formate as raw material is one preferred embodiment of the invention, because sodium formate is well available as a byproduct from some industrial processes. Potassium formate is presented as one desired end product. Also other formates having an alkali metal or alkaline-earth metal cation other than sodium can be formed by ion exchange in an analogical manner.

The invention is not limited to formates but it can be applied to acetates and propionates of alkali metals or alkaline-earth metals as well. In this case the production takes place analogically, starting from an acetate or propionate that has a cation other than the alkali metal ion or

alkaline-earth metal ion of the end product. By alkali metal ion or alkaline-earth metal ion is meant any monovalent or divalent metal ion with which an ion exchanger can be charged and which can be eluted from the ion exchanger after it has been exchanged for another cation. Potassium can be mentioned as one example of alkali metal ion. An example of a possible alkaline-earth metal ion of the end product is calcium.

The invention will be described in the following examples, which do not restrict the scope of the invention.

Example 1. KFo production with strong cation exchanger

The test was made in smb-pilot system which consists of 20 ion exchange columns, wherein bed height was 1.5 m and diameter was 0.1 m. The columns were packed with a macroporous strong acid cation-exchange resin, Purolite C160.

The switch time of smb-unit was 330 s and the number of switches was 80. During one switch 1.5 l sodium formate (concentration 9.6 mol/l, average flow rate 0.27 l/min and temperature 50 °C) and 7.1 l potassium chloride (concentration 3.9 mol/l, sodium content 2.5 mole-%, average flow rate 1.3 l/min and temperature 20°C) was fed to the smb-unit. In addition to that water was fed for washing.

Figure 2 illustrates the column configuration. Sodium formate was fed to the column 4 and potassium chloride to the column 15. The production outlet was from column 9 and regeneration outlet was from column 19.

Figure 7 illustrates the percentage of counter ions in each column and Figure 8 illustrates concentration profiles in solution. The profiles are calculated with simulation model. The results are presented in Table 1. The production during one switch was 13.5 mole potassium formate, which sodium content was 9 mole-%. The regeneration product content was 51 mole-% sodium chloride and 49 mole-% potassium chloride.

Example 2. KFo production with strong cation exchanger and side stream

It was noticed that by taking side stream out from the production side the resin utilization can be improved and potassium content of the regeneration outlet (=potassium loss) can be reduced without diminishing the product quality.

The switch time was 330 s and the number of switches was 80. During one switch 3.7 l sodium formate (concentration 9.6 mol/l, average flow rate 0.67 l/min and temperature 50 °C) and 7.0 l potassium chloride (concentration 3.9 mol/l, sodium content 2.5 mole-%, flow rate 1.3 l/min and temperature 20°C) was fed to the smb-unit. In addition to that water was fed for washing.

Figure 3 illustrates the column configuration. Sodium formate was fed to the column 2 and potassium chloride to the column 14. The production outlet was from column 9 and side stream outlet was from column 5 and regeneration outlet was from column 19.

Figure 9 and 10 illustrate the resin and solution profiles. The difference of resin utilization can be seen comparing Figures 7 and 9. The production during one switch was 14.3 mole potassium formate (sodium content 9 mole-%). The side stream product was 12.5 mole potassium formate (sodium content 51 mole-%, which can be reduced by after treatment to 25 mole-%). The regeneration product content was 82 mole-% sodium chloride and 18 mole-% potassium chloride.

The sidestream taken out contains thus sodium formate and potassium formate. This mixture can be a final product. The salts can also be separated by crystallization, whereby sodium formate crystals are separated and recycled as raw material for the production step. The other product is potassium formate solution having a lowered sodium formate content.

Example 3. KFo production with strong cation exchanger and variable resin liquid ratio

Smb-unit can be run so, that resin liquid ratio is higher in the middle of system (the end part of the production section and the forepart of the regeneration section) than elsewhere in the system. This can be arranged by switching columns as shown in Figure 4a. Figure 4a illustrates a configuration where resin liquid ratio is 1.5 times higher in the middle of the smb-unit. With this system same benefits as in side stream system (mentioned in Example 2) can be achieved without taking a separate side stream.

In the simulation model the situation can be imitated by taking out liquid from the production section and feeding liquid to the regeneration section. The simulation run described below differs from the actual arrangement of Fig. 4 in that respect.

In the simulation run the number of columns was 24. The switch time was 330 s and the number of switches was 96. During one switch 3.4 l sodium formate (concentration 9.1 mol/l, average flow rate 0.62 l/min and temperature 50 °C) and 7.3 l potassium chloride (concentration 4.1 mol/l, sodium content 2.5 mole-%, average flow rate 1.3 l/min and temperature 20°C) was fed to the smb-unit. In addition to that water was fed for washing.

Sodium formate was fed to the column 2 and potassium chloride to the column 16. The production outlet was from column 11 and regeneration outlet was from column 23.

Figure 11 and 12 illustrate the resin and solution profiles. The production during one switch was 26.1 mole potassium formate (sodium content 14 mole-%). The regeneration product content was 81 mole-% sodium chloride and 19 mole-% potassium chloride.

Example 4. KFo production with weak cation exchanger

The test was made in pilot as described in Example 1. A macroporous weak-acid cation exchange resin, Purolite C104E, was used.

The switch time of smb unit was 430 s and the number of switches was 80. During one switch 1.8 l sodium formate (concentration 9.6 mol/l, average flow rate 0.25 l/min and temperature 50 °C) and 12.7 l potassium chloride (concentration 4.0 mol/l, sodium content 2.5 mole-%, average flow rate 1.8 l/min and temperature 20°C) was fed to the smb-unit. In addition to that water was fed for washing.

The column configuration was same as in example 1.

Figure 13 and 14 illustrate the resin and solution profiles. The production during one switch was 18.0 mol potassium formate (sodium content 5 mole-%). The regeneration product content was 41 mole-% sodium chloride and 59 mole-% potassium chloride.

Example 5. KFo production with mixture of strong and weak cation exchanger

The test was made in pilot as described in example 1. A 1:1 mixture of weak-acid cation exchange resin, Purolite C104E, and strong acid cation-exchange resin, Purolite C160 was used.

The switch time of smb unit was 430 s. The number of switch was 80. During one switch 2.7 l sodium formate (concentration 9.6 mol/l, average flow rate 0.38 l/min and temperature 50 °C) and 8.3 l potassium chloride (concentration 4.0 mol/l, sodium content 2.5 mole-%, average flow rate 1.2 l/min and temperature 20°C) was fed to the smb-unit. In addition to that water was fed for washing.

The column configuration was same as in example 1.

This experiment was made only in pilot, not with model, so the profiles are not presented. The production during one switch was 25.5 mol

potassium formate (sodium content 17 mole-%). The regeneration product content was 66 mole-% sodium chloride and 34 mole-% potassium chloride.

Example 6. Potassium propionate production with strong cation exchanger

When sodium propionate is used instead of sodium formate, potassium propionate can be produced.

The switch time was 330 s. The number of switches was 80. During one switch 3.2 l sodium propionate (concentration 6.0 mol/l, average flow rate 0.58 l/min and temperature 50 °C) and 7.0 l potassium chloride (concentration 3.9 mol/l, sodium content 2.5 mole-%, average flow rate 1.3 l/min and temperature 20°C) was fed to the smb-unit. In addition to that water was fed for washing.

Sodium propionate was fed to the column 2 and potassium chloride to the column 14. The production outlet was from column 9 and regeneration outlet was from column 19.

Figure 15 and 16 illustrate the resin and solution profiles. The product during one switch was 19.1 mol potassium propionate (sodium content 11 mole-%). The regeneration product content was sodium chloride 66 mole-% and potassium chloride 34 mole-%.

Example 7. Magnesium formate production with strong cation exchanger

When magnesium chloride is used instead of potassium chloride, magnesium formate can be produced.

The switch time was 330 s. The number of switch was 80. During one switch 6.5 l sodium formate (concentration 4.0 mol/l, average flow rate 1.2 l/min and temperature 50 °C) and 14.6 l magnesium chloride (concentration 1.0 mol/l, average flow rate 2.7 l/min and temperature

20°C) was fed to the smb-unit. In addition to that water was fed for washing.

Sodium formate was fed to the column 2 and magnesium chloride to the column 7. The production outlet was from column 9 and regeneration outlet was from column 19.

Figure 17 and 18 illustrate the resin and solution profiles. The product during one switch was 14.1 mol magnesium formate (sodium content 15 mole-%). The regeneration product content was sodium chloride 90 mole-% and magnesium chloride 10 mole-%.

Example 8. KFo production with strong cation exchanger from potassium sulphate

The salts with another anion as chloride can also be used as a raw material. When potassium sulphate is used instead of potassium chloride and the regeneration outlet is sodium sulphate.

The switch time was 330 s and the number of switches was 80. During one switch 2.0 l sodium formate (concentration 9.1 mol/l, average flow rate 0.36 l/min and temperature 50 °C) and 10.8 l potassium sulphate (concentration 1.2 mol/l, sodium content 2.5 mole-%, average flow rate 2.0 l/min and temperature 80°C) was fed to the smb-unit. In addition to that water was fed for washing.

Sodium formate was fed to the column 2 and potassium sulphate to the column 13. The production outlet was from column 8 and regeneration outlet was from column 19.

Figure 19 and 20 illustrate the resin and solution profiles. The product during one switch was 18.0 mol potassium formate (sodium content 8 mole-%). The regeneration product content was sodium sulphate 70 mole-% and potassium sulphate 30 mole-%.

The data of various examples is summarized in the table at the end of the description.

				Switch time	NaFo feed	KCl feed	KFo product
Example	Variable	Status	Resin	s	mol/switch	mol/switch	mol/switch
1		pilot	C160 (strong)	330	14,4	27,7	13,5
2	Side stream	model	C160 (strong)	330	35,5	27,3	14,3 (12,1)
3	Resin liquid ratio	model	C160 (strong)	330	30,9	28,2	26,1
4	Resin	pilot	C104 (weak)	430	17,3	50,8	17,9
5	Resin	pilot	mixture*	430	25,9	33,2	25,5
6	K-propionate	model	C160 (strong)	330	19,2**	27,3	19,1**
7	Mg-formate	model	C160 (strong)	330	26,0	14,6****	14,1
8	K2SO4 as raw material	model	C160 (strong)	330	18,2	13,0***	18,0
		*	Mixture is 50 % C160 and 50 % C104				
		**	Propionate instead of formate				
		***	Sulphate instead of chloride				
		****	Magnesium instead of Potassium				

				Na content in product	Regeneration outlet	K content in regen. outlet	Resin utilisation
Example	Variable	Status	Resin	mol-%	mol/switch	mol-%	%
1		pilot	C160 (strong)	9	27,2	49	46
2	Side stream	model	C160 (strong)	9 (25)	27,5	18	83
3	Resin liquid ratio	model	C160 (strong)	14	35,6	19	85
4	Resin	pilot	C104 (weak)	5	50,3	59	68
5	Resin	pilot	mixture*	17	30,9	34	74
6	K-propionate	model	C160 (strong)	11	27,3	34	66
7	Mg-formate	model	C160 (strong)	15	26,5	10****	92
8	K2SO4 as raw material	model	C160 (strong)	8	12,9	30	65
		*	Mixture is 50 % C160 and 50 % C104				
		**	Propionate instead of formate				
		***	Sulphate instead of chloride				
		****	Magnesium instead of Potassium				

Claims:

1. Process for manufacture of carboxylic acid salts in the form of alkali metal or alkaline-earth metal carboxylates of 1 to 3 carbon atoms, **characterized** in that it comprises the following steps of a continuous manufacturing process:

1) passing a raw material solution containing a carboxylate salt of a starting cation through one or several ion exchange beds containing solid cation exchanger charged with an alkali metal or alkaline-earth metal cation, to replace the starting cation in the solution by the alkali metal or alkaline-earth metal cation in an ion exchange with the cation exchanger,
2) collecting a product solution containing alkali metal or alkaline-earth metal carboxylate eluted from the one or several ion exchange beds in step 1,
3) simultaneously with step 1, regenerating one or several ion exchange beds containing solid cation exchanger charged with the starting cation by passing a regenerating solution containing a salt formed by an anion and the alkali metal or alkaline-earth metal cation through the one or several ion exchange beds, to replace the alkali metal or alkaline-earth metal cation in the solution by the starting cation and to charge the cation exchanger with the alkali metal or alkaline-earth metal cation in an ion exchange with the cation exchanger
4) collecting an effluent solution containing the starting cation and the anion eluted from the one or several ion exchange beds in step 3, and
5) shifting the inlet point of the raw material solution, the outlet point of the product solution, the inlet point of the regenerating solution and the outlet point of the effluent solution in the same direction to other ion exchange beds.

2. Process according to claim 1, **characterized** in that it comprises additionally the following steps:

6) simultaneously with all steps 1 to 4, passing wash liquid through one or several ion exchange beds through which the raw material solution has been passed, to wash the one or several beds for step 3, and/or

7) simultaneously with all steps 1 to 4, passing wash liquid through one or several ion exchange beds through which the regenerating solution has been passed, to wash the one or several beds for step 1, and

8) shifting the inlet points of the wash liquid in same direction as the inlet points in step 5.

3. Process according to claim 2, **characterized** in that the salt contained in the wash liquid passed through the one or several beds in step 7 is recirculated to step 3 for use in the regeneration.

4. Process according to claim 2 or 3, **characterized** in that the carboxylate salt of the starting cation contained in the wash liquid passed through the one or several beds in step 6 is recirculated to step 1 for use in the production.

5. Process according to any of the preceding claims, **characterized** in that in step 1, production step, the resin liquid ratio is increased in part of the production step, preferably in the end of the production step beds.

6. Process according to claim 5, **characterized** in that part of the solution is taken out before the last bed of the production step as a product solution in a side stream.

7. Process according to claim 5, **characterized** in that the resin liquid ratio is increased in the production step by disconnecting one or several beds from the series of beds of the production step and connecting them in the middle of the regeneration step.

8. Process according to claim 6 or 7, **characterized** in that the side stream is taken from a bed or the disconnected bed is a bed where the molar ratio of the starting cation and the alkali metal or alkaline earth metal cation is 40/60–60/40 in the solution.

9. Process according to any of the preceding claims, **characterized** in that in step 1 and/or step 3, the temperature is between 0–110°C, preferably in the range between 40 and 70°C.

10. Process according to any of the preceding claims, **characterized** in that it is conducted by using more than four columns each containing an ion exchange bed.

11. Process according to claim 10, **characterized** in that it is conducted by using at least ten columns each containing an ion exchange bed.

12. Process according to any of the preceding claims, **characterized** in that the cation exchanger is a resin having a molar proportion equilibrium curve whose maximum deviation from the diagonal in the direction of the solution axis is less than 10% for the pair of cations concerned (starting cation and the cation of the product).

13. Process according to any of the preceding claims, **characterized** in that the carboxylate contained in the raw material solution is formate.

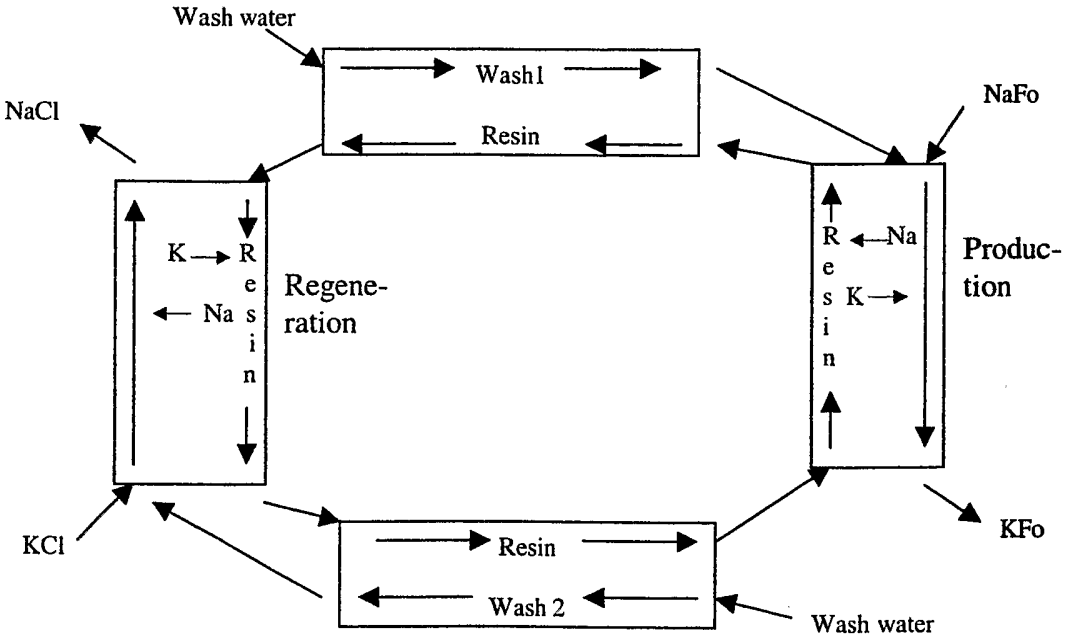
14. Process according to claim 13, **characterized** in that the starting cation is sodium.

15. Process according to claim 13 or 14, **characterized** in that the alkali metal or alkaline-earth metal cation is selected from the group consisting of potassium and magnesium.

16. Process according to claim 14, **characterized** in that the anion contained in the regenerating solution is chloride or sulphate.

17. Process according to claim 16, **characterized** in that the starting cation is sodium, the anion contained in the regenerating solution is chloride, and the sodium chloride contained in the effluent solution collected in step 4 is crystallized.

Figure 1


Wash water
Wash1
Resin
NaCl
NaFo
K
Resin
Na
Regene-
ration
R
Na
Resin
K
Produc-
tion
KCl
Resin
Wash 2
KFo
Wash water

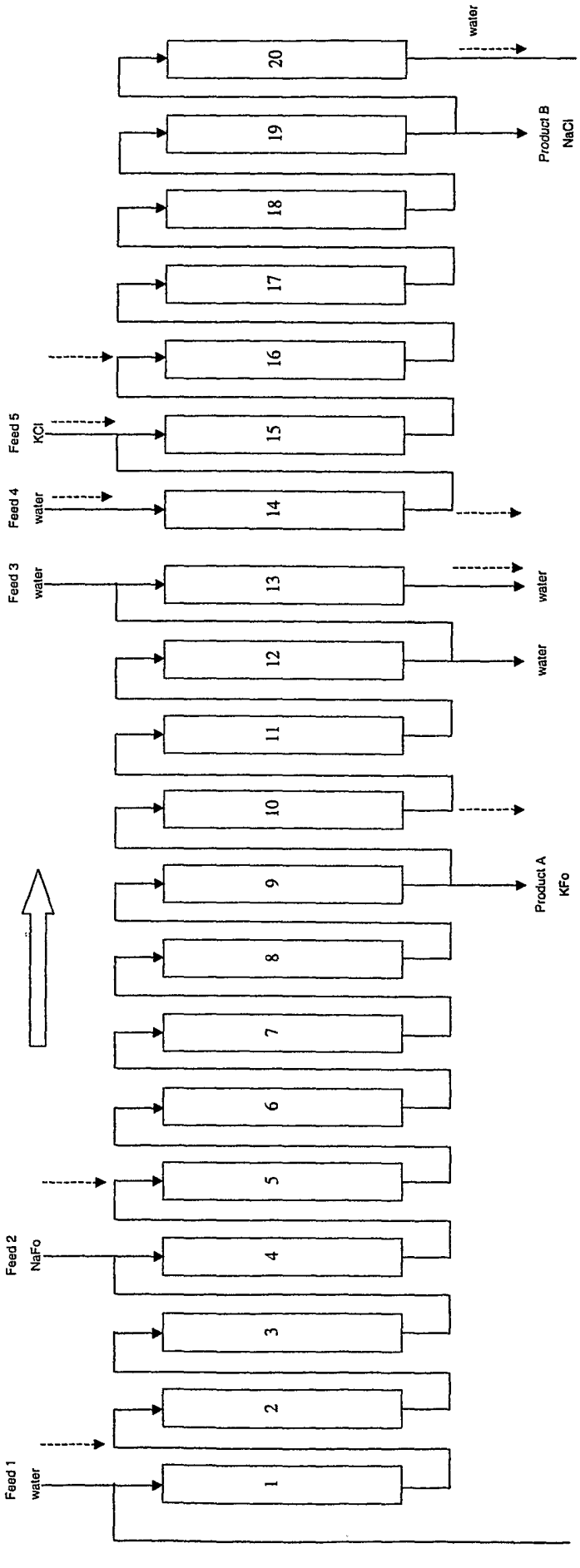

Feed 1
water
Feed 2
NaFo
Feed 3
water
Feed 4
water
Feed 5
KCl
Product A
KFo
Product B
NaCl
water
water
water
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

Figure 2

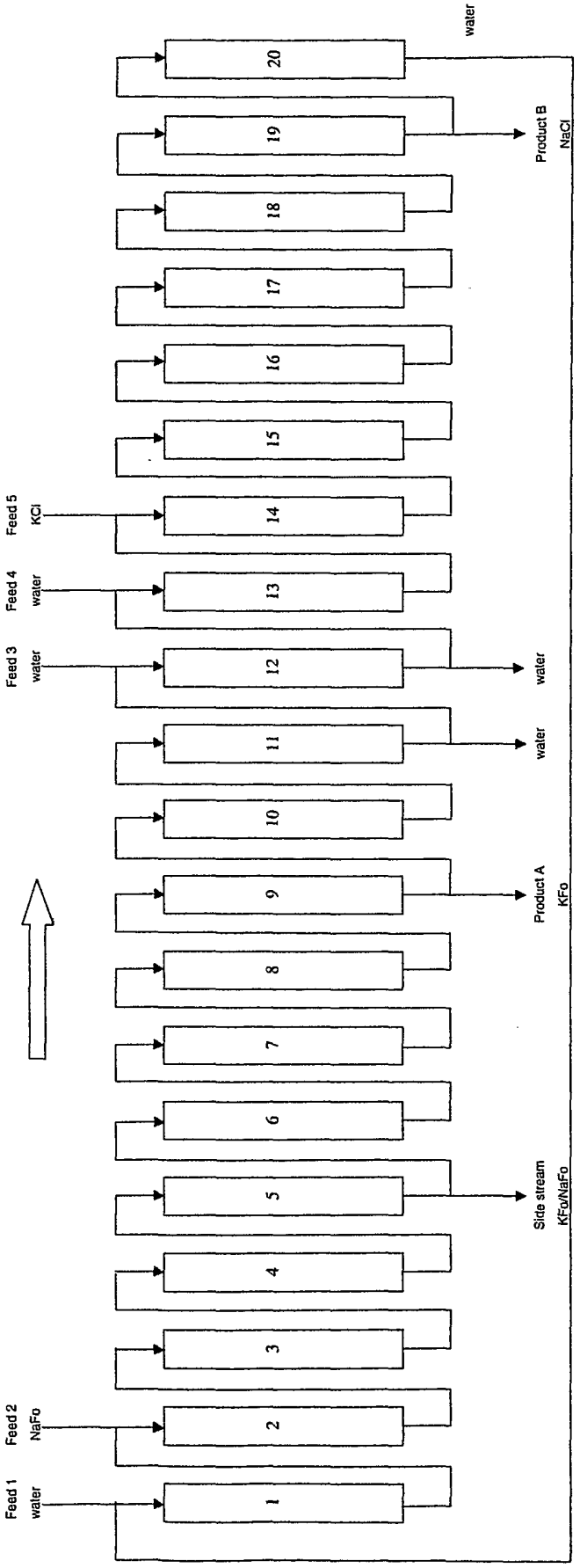

Feed 1
water
Feed 2
NaFo
Feed 3
water
Feed 4
water
Feed 5
KCl
water
Product B
NaCl
Product A
KFo
water
water
Slide stream
KFo/NaFo
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20

Fig. 3

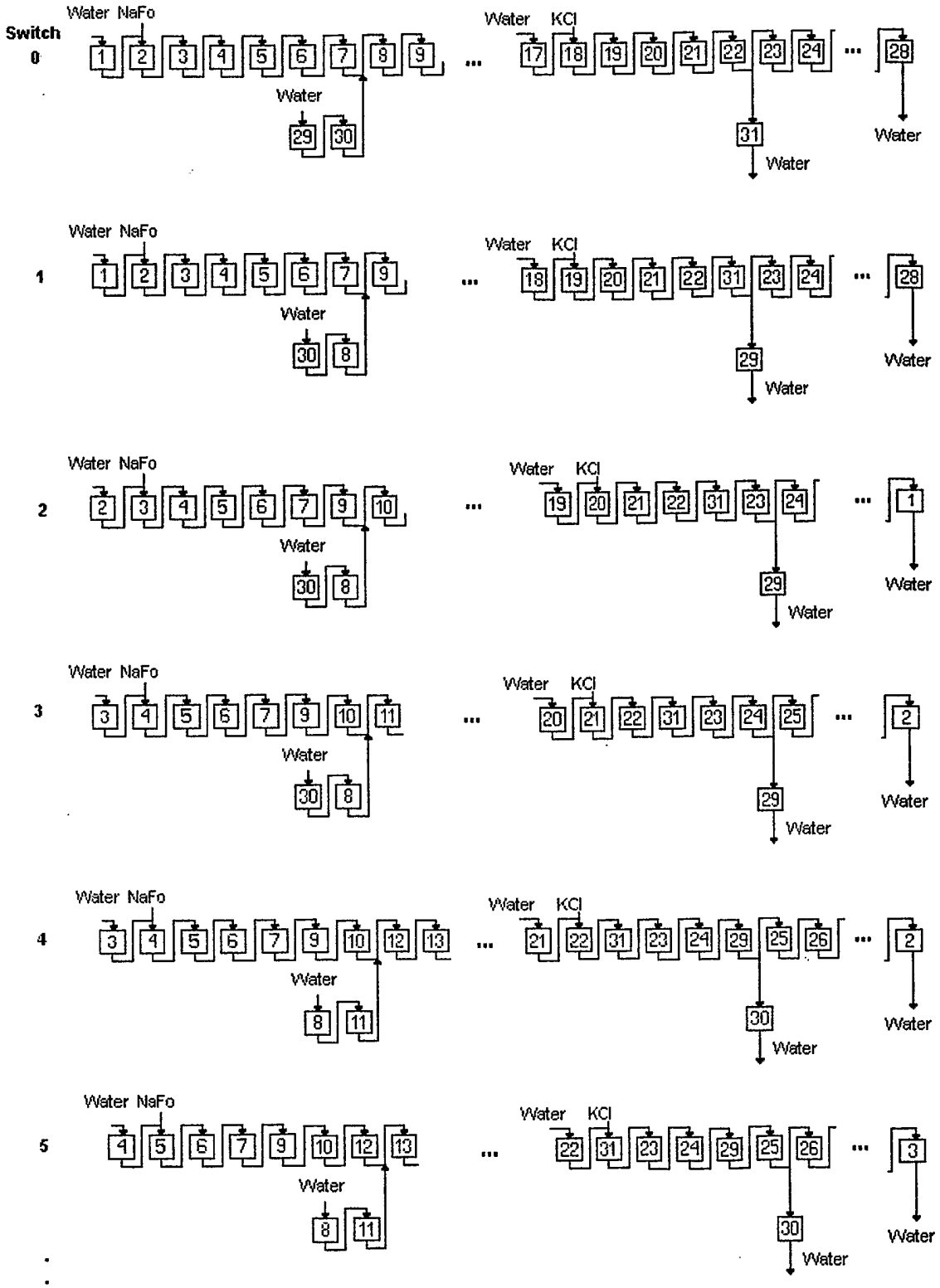


Figure 4a

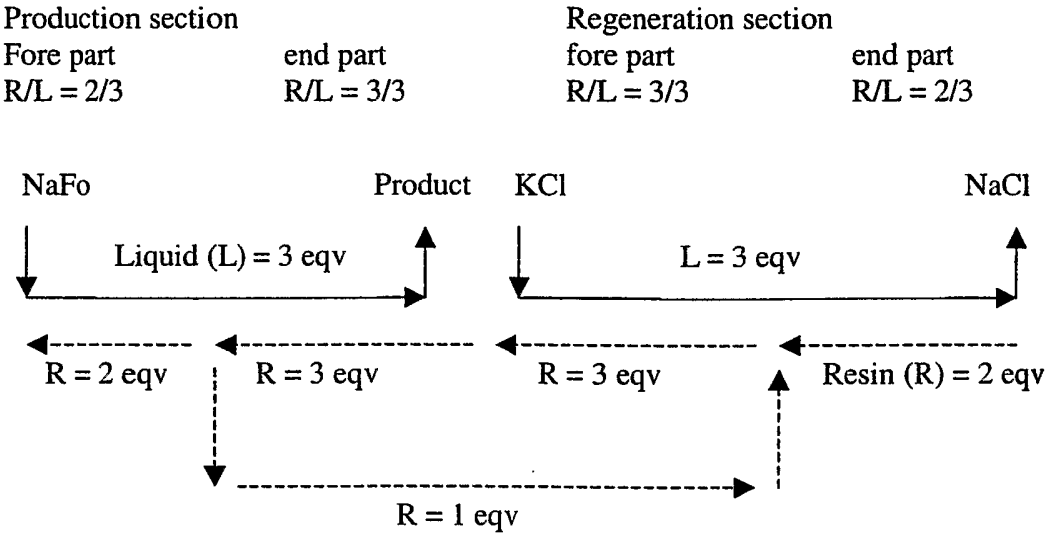

Production section
Fore part
R/L = 2/3
end part
R/L = 3/3
Regeneration section
fore part
R/L = 3/3
end part
R/L = 2/3
NaFo
Product
KCl
NaCl
Liquid (L) = 3 eqv
L = 3 eqv
R = 2 eqv
R = 3 eqv
R = 3 eqv
Resin (R) = 2 eqv
R = 1 eqv

Fig. 4b

Figure 5.

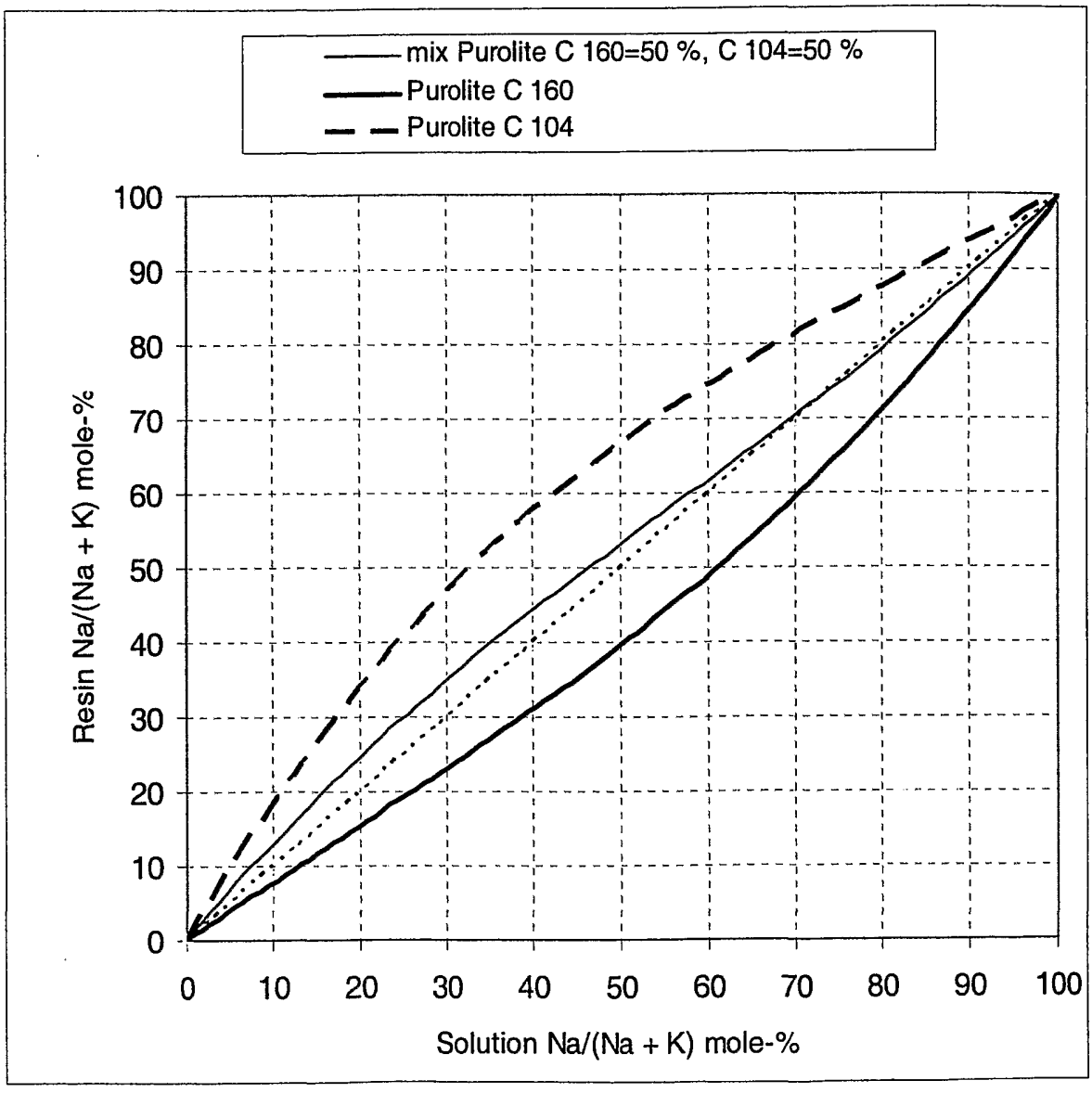
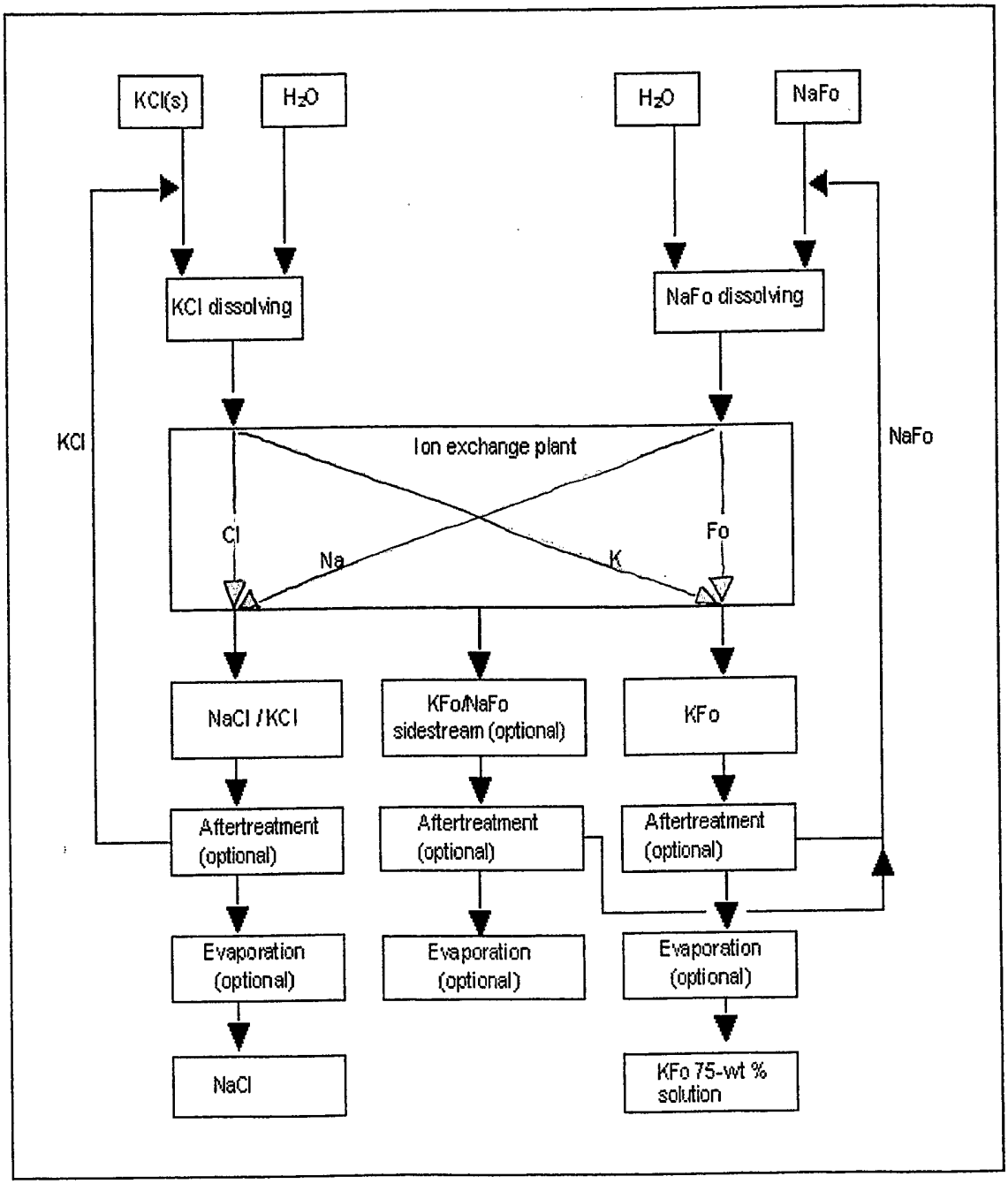

mix Purolite C 160=50 %, C 104=50 %
Purolite C 160
Purolite C 104
Resin Na/(Na + K) mole-%
Solution Na/(Na + K) mole-%
0
10
20
30
40
50
60
70
80
90
100

Figure 6.


KCl(s)
H2O
H2O
NaFo
KCl dissolving
NaFo dissolving
KCl
Ion exchange plant
NaFo
Cl
Na
K
Fo
NaCl / KCl
KFo/NaFo sidestream (optional)
KFo
Aftertreatment (optional)
Aftertreatment (optional)
Aftertreatment (optional)
Evaporation (optional)
Evaporation (optional)
Evaporation (optional)
NaCl
KFo 75-wt % solution

(Example 1)

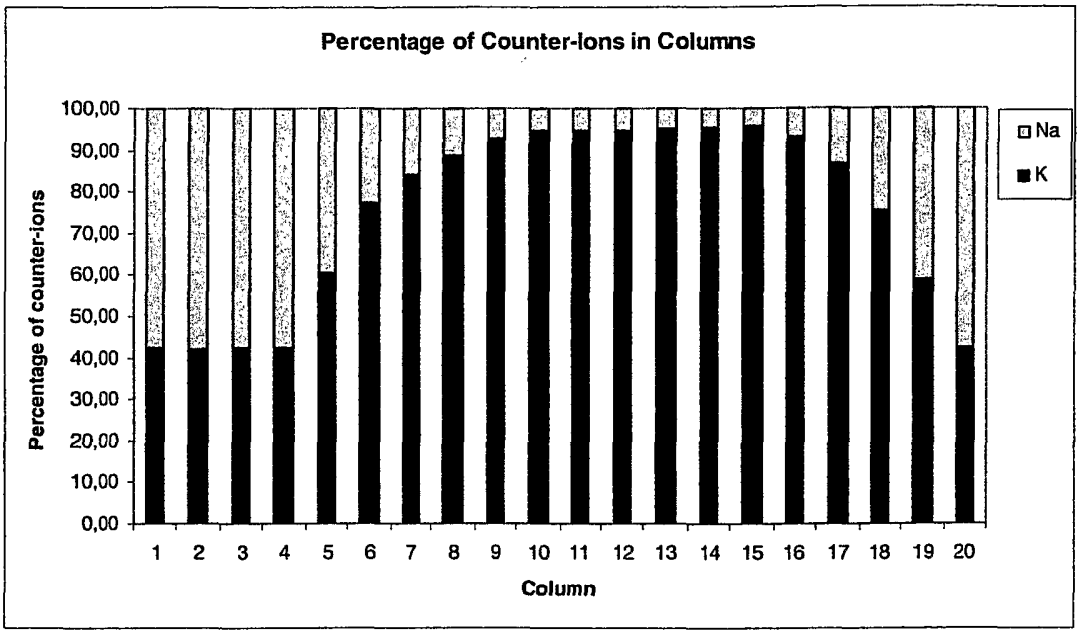


Figure7.

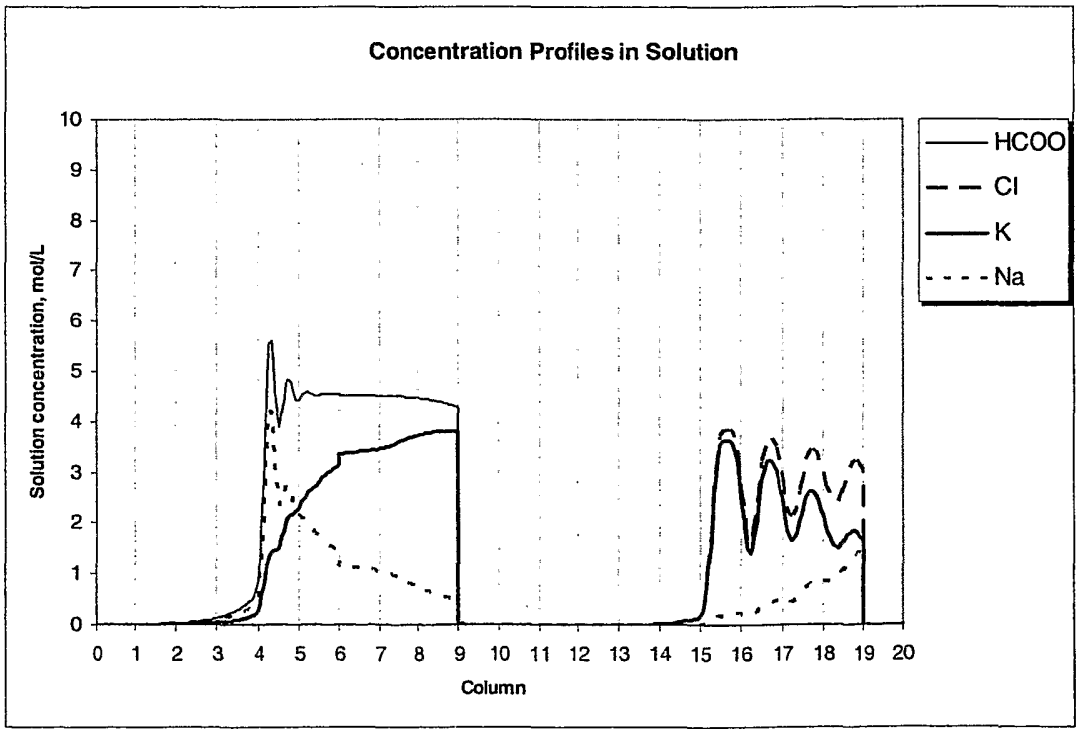


Figure 8.

Example 2.

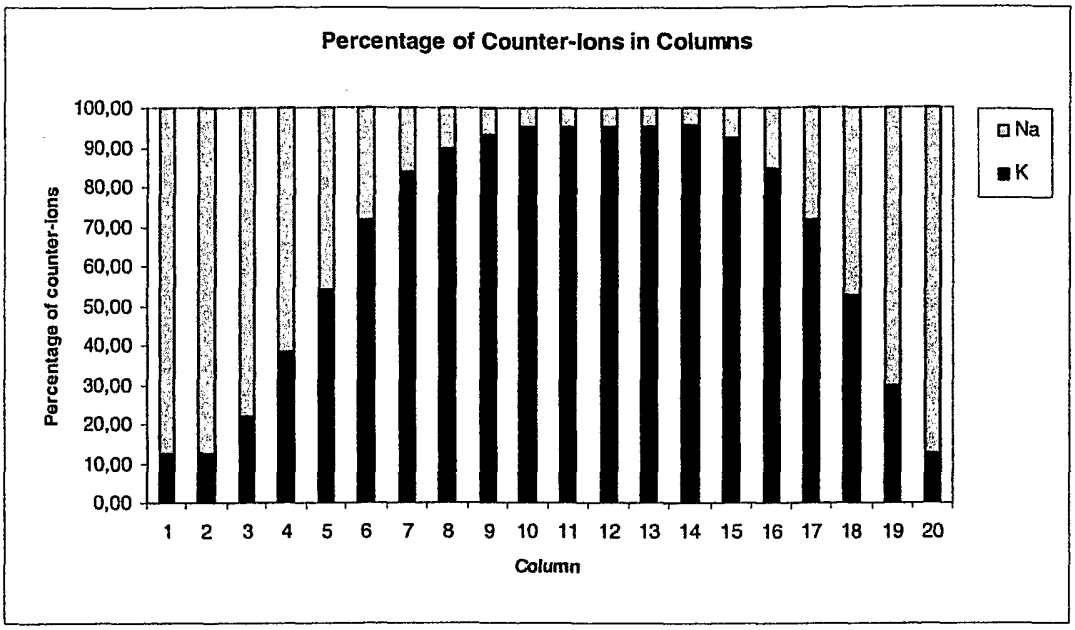


Figure 9.

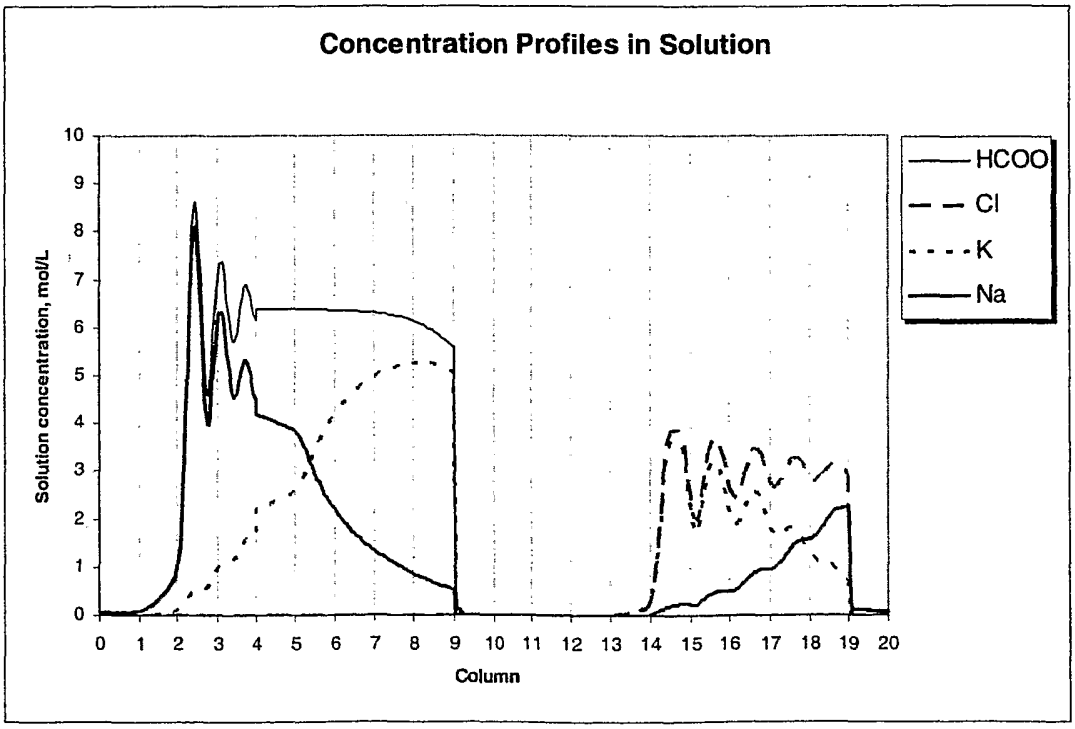


Figure 10.

Example 3

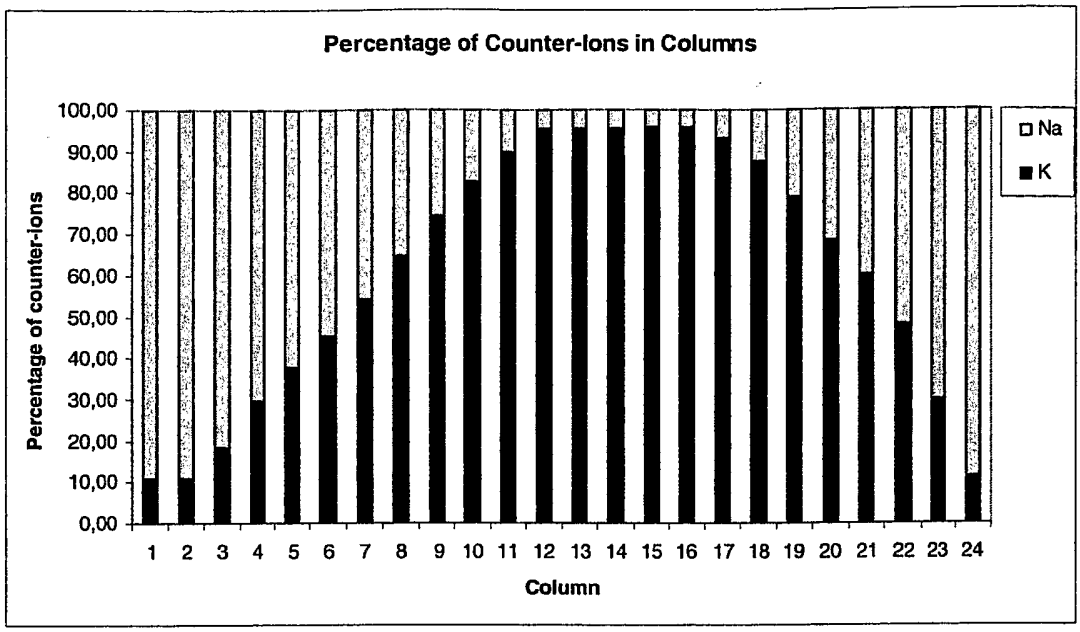


Figure 11.

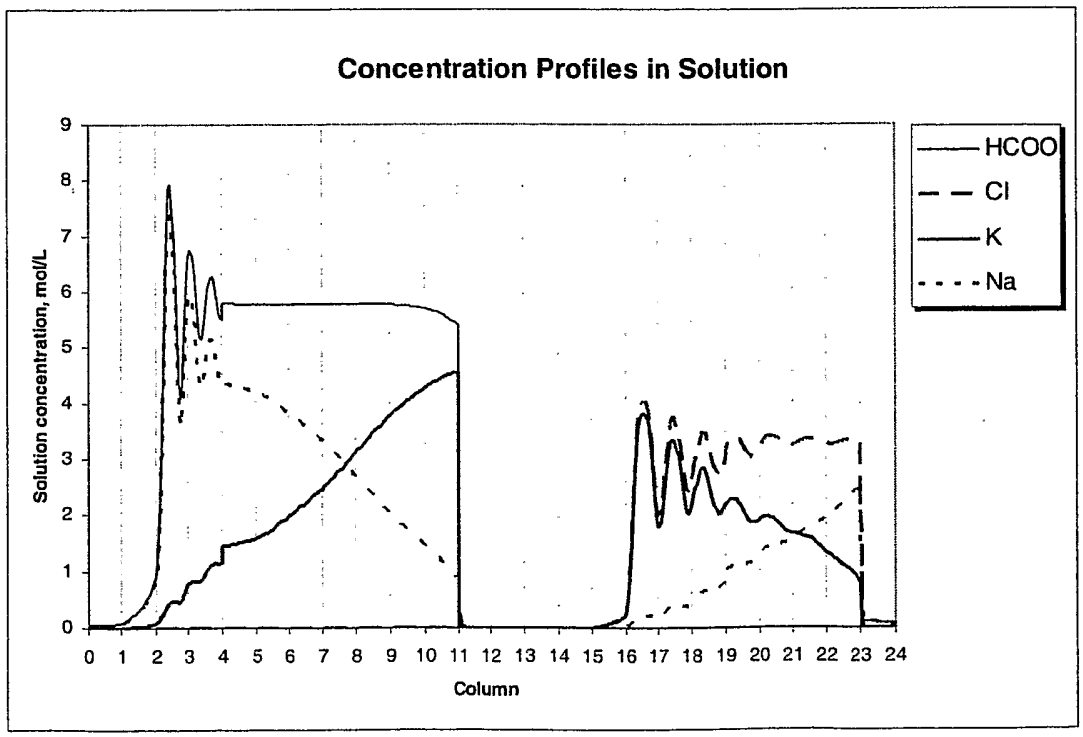


Figure 12.

Example 4

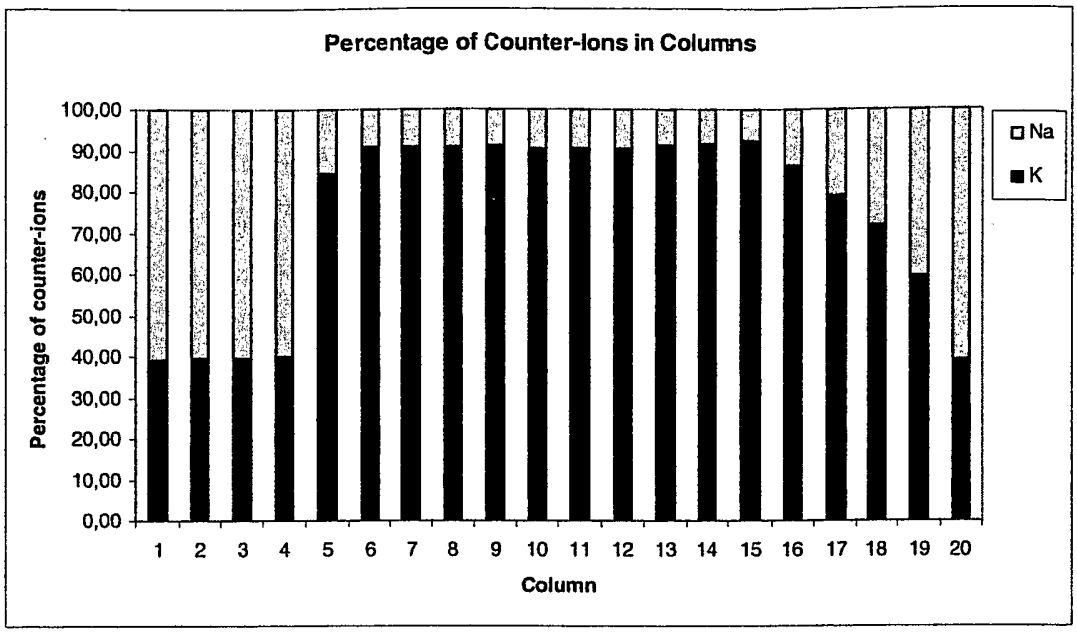


Figure 13.

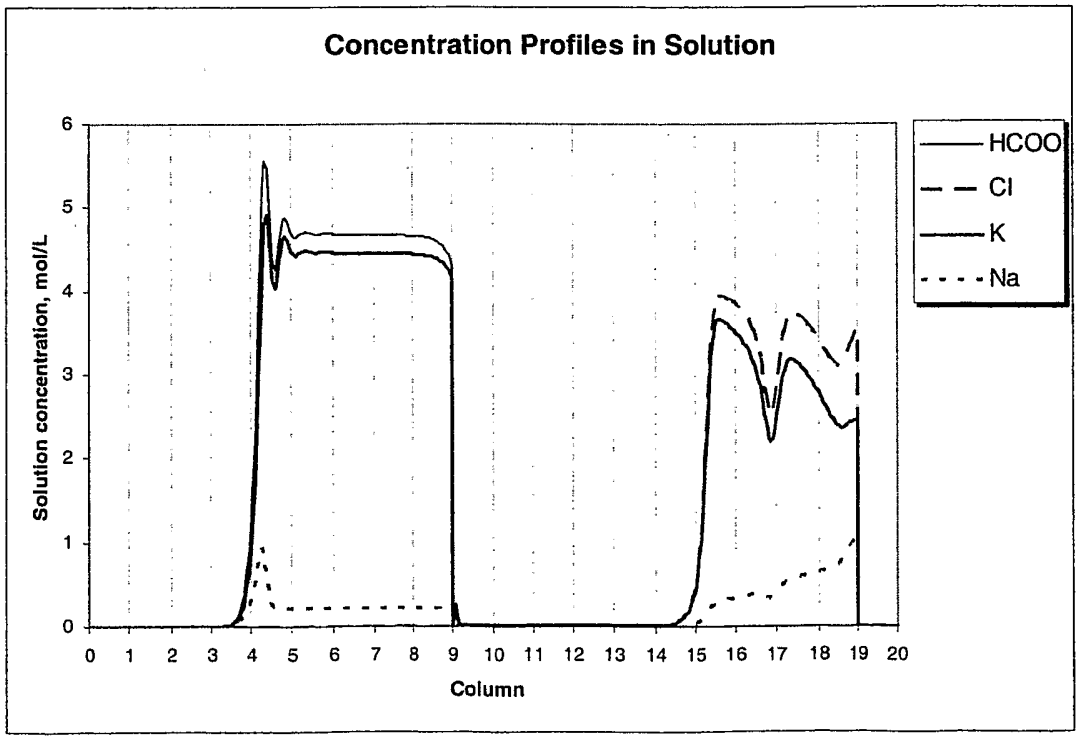


Figure 14.

Example 6

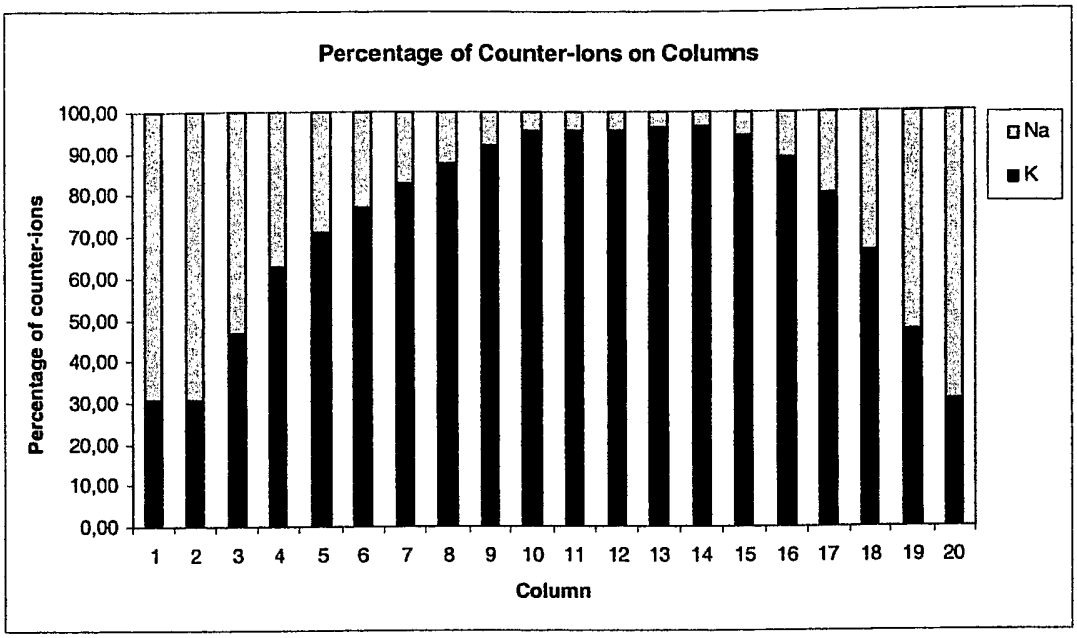


Figure 15.

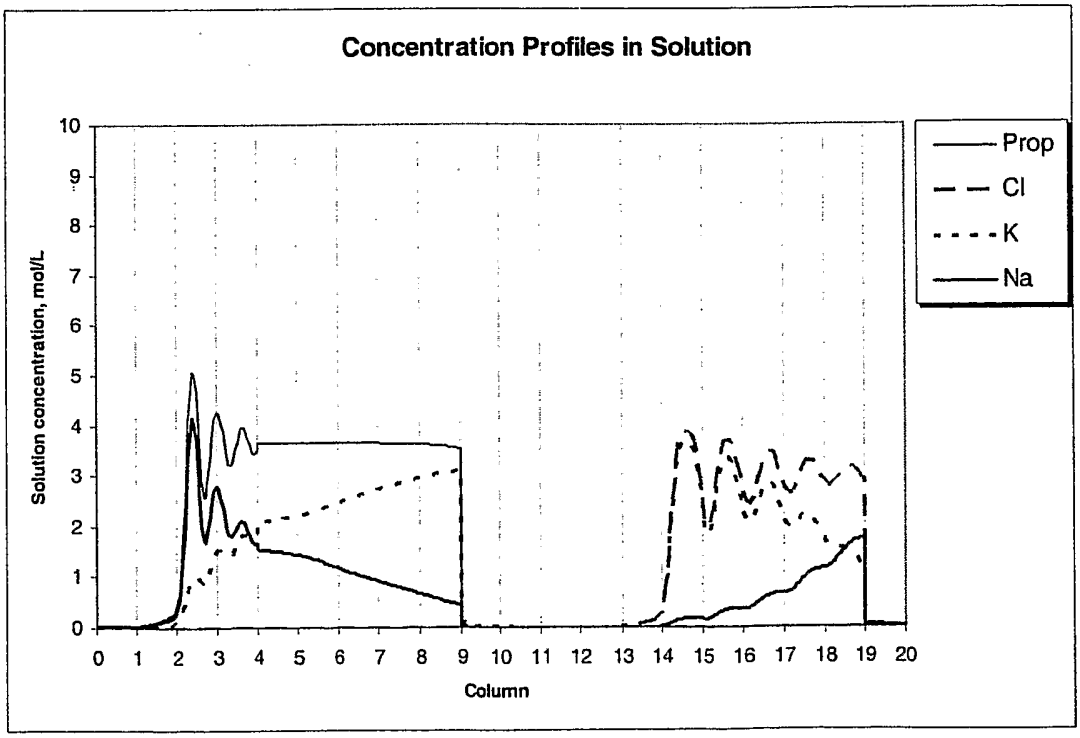


Figure 16.

Example 7

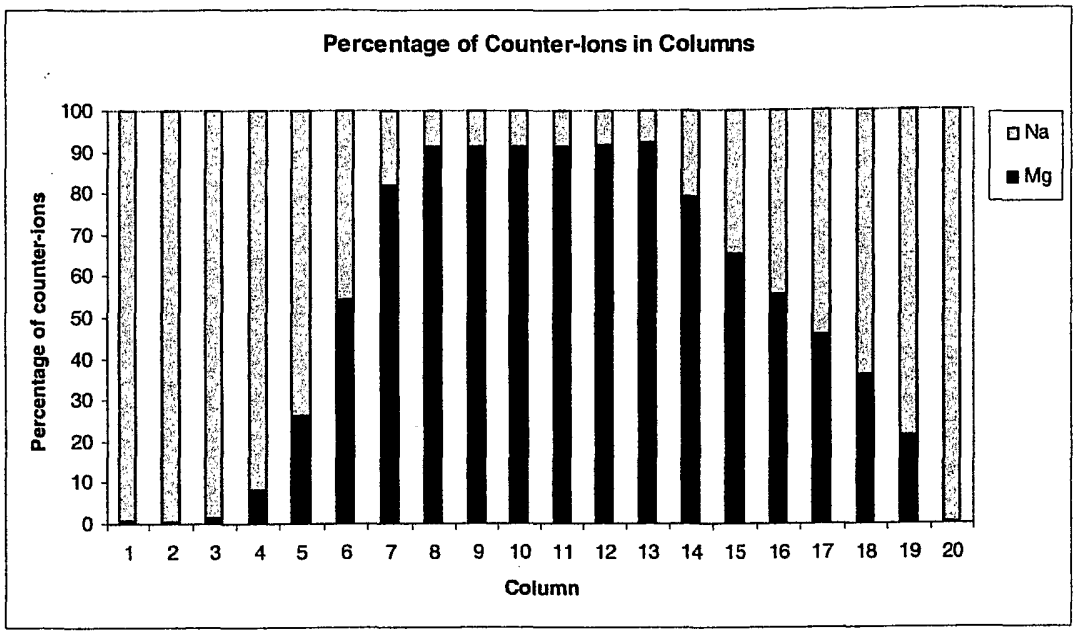


Figure 17.

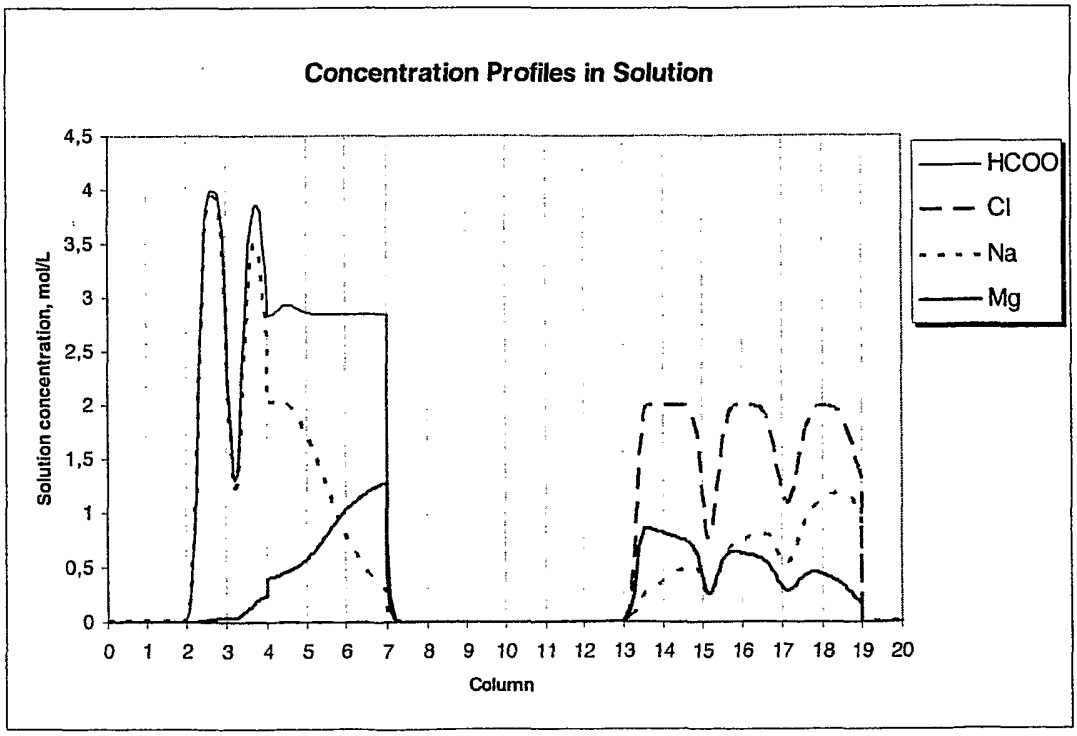


Figure 18.

Example 8

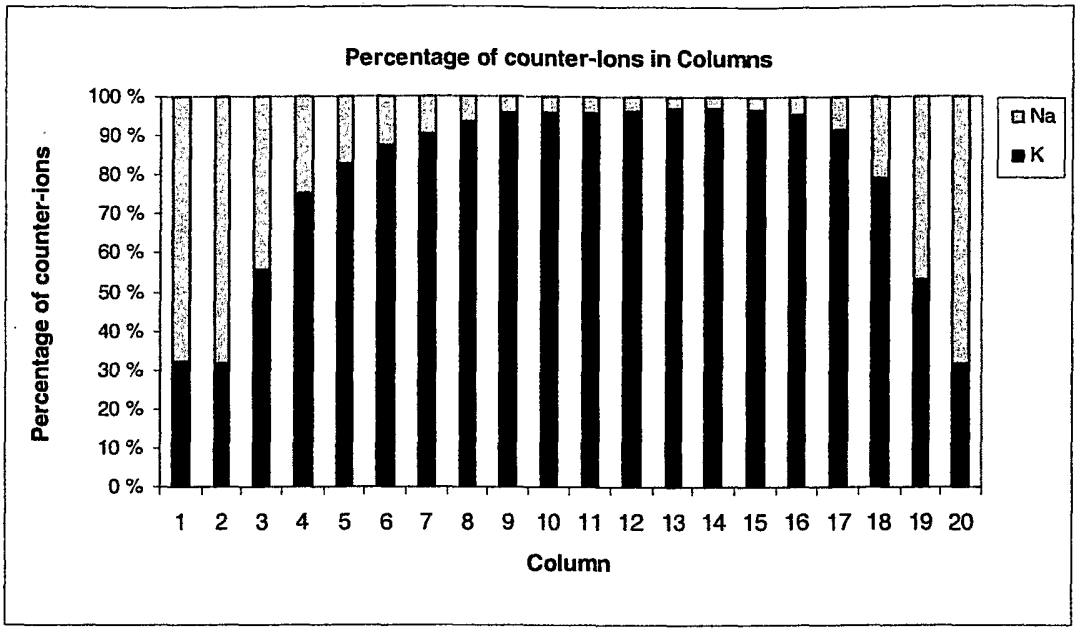


Figure 19.

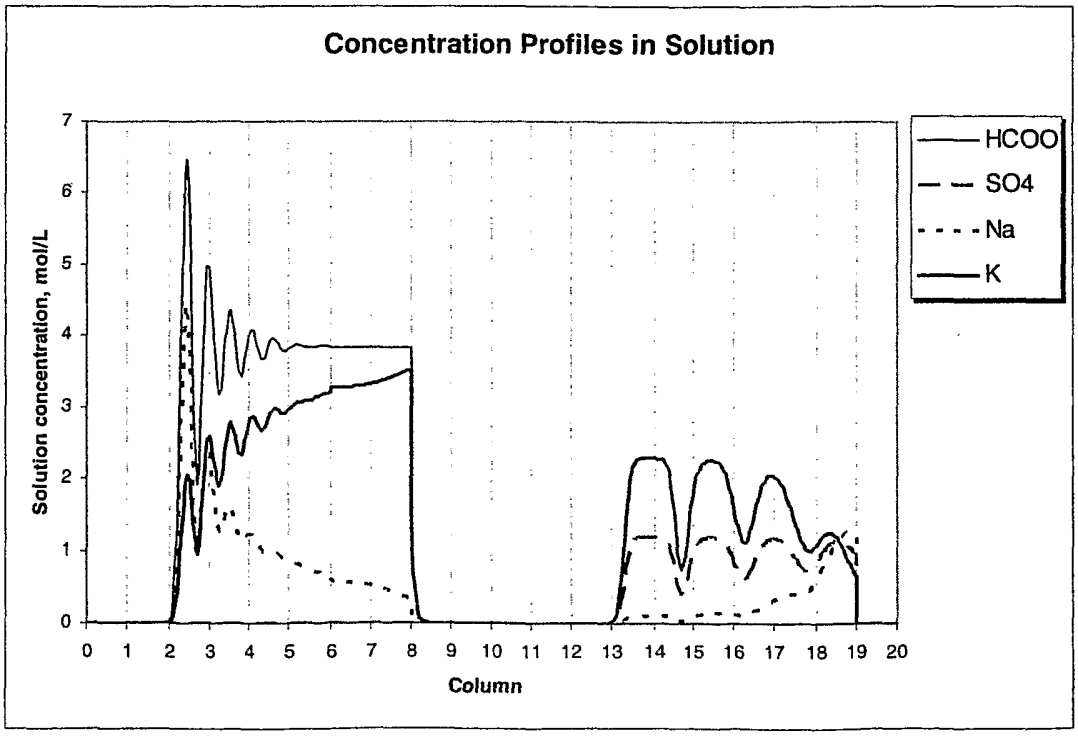


Figure 20.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/FI 03/00611

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C51/41 C07C53/06 C07C53/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 18717 A (KEMIRA CHEMICALS OY ;PAATERO ERKKI (FI); LAHTINEN MARKO (FI); SAAR) 6 April 2000 (2000-04-06) the whole document ---	1-17
A	WO 97 13580 A (YISSUM RES DEV CO ;GODWIN EDGAR JAMES (GB); EYAL AHARON MEIR (IL)) 17 April 1997 (1997-04-17) the whole document ---	1-17
A	DE 38 08 633 A (NALON QUIMICA SA ;FERTILIZANTES EMPRESA NAC (ES)) 6 October 1988 (1988-10-06) the whole document ---	1-17
A	US 2 751 280 A (WILLEM HASSELDER) 19 June 1956 (1956-06-19) the whole document -----	1-17

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 November 2003	19. 12. 2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	EVA JOHANSSON /EÖ

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/FI 03/00611

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