

The Softening of Potable Water in Western Europe

B.G. Wienk

Akzo Zout Chemie, Hengelo, The Netherlands

ABSTRACT

Clients and producers of (potable) water are increasingly unsatisfied with the traditional "natural" quality of this product which is used on an ever increasing scale, but which is becoming more and more scarce. Softening of the water improves this quality considerably for a large number of applications. At this moment partly or complete softening of (drinking) water is in the center of interest in Europe.

The use of sodium chloride as a regenerating agent in the technically important ion exchange softening process caused the European Committee for the Study of Salt to set up a "Commission of special salts for water softeners". On behalf of this commission, which will lead the discussion on water softening in general and the use of salt in the main softening process in particular in Western Europe, a number of important data are discussed in this paper.

The following subjects will be reviewed: complete or partly softening, salt consumption, environmental aspects of softening, central softening versus home softening and the attitude of the authorities in Western Europe versus water softening.

INTRODUCTION

In the early 1970's the consumption of salt for the regeneration of ion exchangers for water softening in the household sector in the USA was said to be more than 3,000,000 tons yearly. A figure which must have shown a gradual increase in the meantime, in view of the growth of 10–15% annually, then expected. More than 7 million home softeners (100% ion exchange) and 1,000 central softening installations (~ 40% ion exchange, ~ 60% chemical precipitation) are producing 20 million m³ of softened water daily¹.

Now, in 1978, no signs of such a development can be noticed in Western Europe at all. A rough estimate shows that the salt consumption for water softening in the household sector is in the order of magnitude of 100,000 tons a year. A slow beginning of growth is observed at intervals. This is a reason for the various commercial and ideal interest groups to start with and contribute to the promotion of responsibility against the opposition to water softening. This contribution needs to outline the actual situation and to try to indicate how the development in Western Europe might be twenty years from now.

For people involved in "salt" the question is whether the application of regeneration salt for water softening for

domestic use is a great promise for the salt producers in the near future, or not. That is, are the sales in this sector in Western Europe to be 5,000,000 tons of salt in 1999 or still 100,000 tons a year?

Water consumption and water quality. For a population of 350,000,000 people, Western Europe produced 45 milliard m³ of water in 1975. When prosperity increases, water consumption will do so too. It is expected that the consumption per capita will have risen to 700 liters a day (exclusive of cooling water) in the year 2000. Now the consumption is approximately 350 l a day. As a result of the growth of population and an increasing consumption per capita, the production will have to be brought up to 110 milliard m³ a year (growth of 4%/year) between 1975 and 2000 (Fig. 1).

Water for home use (inclusive of the retail industry, hospitals etc.) is almost exclusively produced and supplied by public water works. These, to an ever increasing extent, will be compelled to make use of (often strongly polluted) surface water. Now, mainly underground water is used. A good picture of the expected shifts in origin and the use of water is outlined in Figure 2, where the situation in the Netherlands is visualized. This picture can be considered representative for Western Europe within wide limits. Be-

side a shift from underground water to surface water it is striking that industry is more and more switching over to water supplied by the public water works.

Qualitatively the drinking water in Western Europe is generally very good. An exception, however, to this is the hardness. Only 10% of the water is unmistakably soft (hardness ≤ 2 mval Ca per liter), 40% of the drinking water has a hardness of 2–5 mval Ca/l and 50% of the water is hard to very hard (≥ 5 mval Ca/l)². It is justified to expect

that, with a view to the hardness of the available raw material, there will sooner be a worsening rather than an improvement of the actual situation.

Softening of potable water or not? About half the water used in households is heated (especially in washing apparatus). In this heating equipment the disadvantages of hard water with regard to soft water are manifest. Incrustations and chokings up by lime scale require a higher energy consumption and considerably more wear and maintenance of equipment. Soft water saves soap and washing agents. The content of phosphate (which is unfriendly to the environment) in washing agents can be drastically reduced when using soft water. Finally there are the aesthetic advantages to the use of soft water, e.g. the prevention of lime soap formation in baths, the feeling of "softness" of the water on the skin and the soft touch and whiteness of textiles washed in soft water. It appears that a family can save DM 40. = annually (DM value 1971), when the hardness of the tap water amounts to 2 mval of Ca instead of 7 mval of Ca per liter³.

But objections also are made against the use of soft or softened water. The most important are that 1) Soft water is

| Water consumption in W. Europe | | |
|--------------------------------|---|--|
| | 1975 | 2000 |
| population | 350 million | 420 million |
| total consumption | 45.10 ⁹ m ³ /year | 110.10 ⁹ m ³ /year |
| per head, per day | ~350 l. | ~700 l. |

Figure 1. Water consumption in Western Europe.

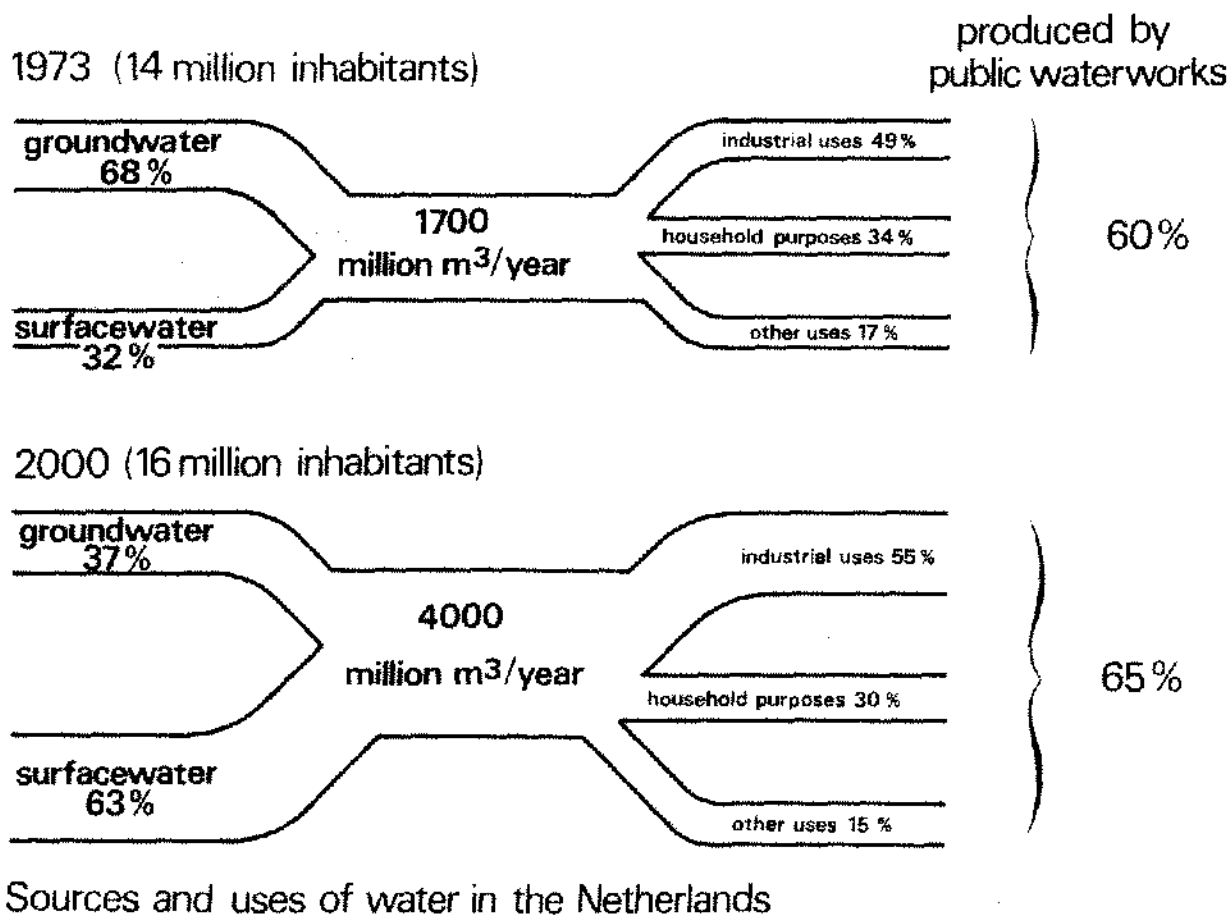


Figure 2. Sources and uses of water in the Netherlands.

more corrosive for concrete and metals than hard water, 2) Because of a lacking protective CaCO_3 layer on the (metal) tubes, soft water may contain a higher content of heavy metals, which may have medical consequences, 3) A connection could exist between the hardness of water and the prevention of heart diseases (lack of calcium and/or magnesium could be the cause of heart diseases), 4) Softening processes increase the sodium content of the water which could lead to problems for sodium-poor diets, 5) Softening processes burden the environment because of the chloride purge, and 6) When applying (organic) ion exchanger resins, the possibility of bacteriological contamination of water is not to be excluded. The main objections, to a great extent, are met by partial softening of water to 1–2 mval of Ca per liter, whereas the advantages will be maintained almost completely.

As a conclusion it can be said that an increasing need for soft or softened water exists especially for all occurring washing treatments in Western Europe. The objections against soft water, especially against soft consumptive water, can be met to a great extent.

METHODS OF HARDNESS CORRECTION

The most important methods available for hardness correction are the following.

Chemical precipitation. By means of addition of NaOH or $\text{Ca}(\text{OH})_2$ the pH of the water is increased in such a way that present Mg is precipitated as $\text{Mg}(\text{OH})_2$ and HCO_3^- is converted into CO_3^{2-} , by which also Ca is precipitated. Besides, additional Na_2CO_3 is added in order to precipitate the excess of calcium as calcium carbonate. The method is only fit for large scale application ($> 4000 \text{ m}^3$ water/day); the installation requires much space. The process is insensitive to the quality of the rough water (suspending components, iron) and gives water with a minimum hardness of 0.8 mval Ca/l, at a very low price.

Ion exchange. The Ca and Mg ions causing the hardness in the water are exchanged for Na ions through an ion exchange resin. The resin has to be regenerated. This takes place in a separate process step by means of a NaCl solution. This replaces the Ca and Mg in the resin for sodium again. The salt solution is purged after use as a rule. The process is simple and extremely fit for application on a small to very small scale ($<< 1 \text{ m}^3/\text{h}$), and requires (also for higher capacities) little space and hardly any supervision and maintenance. The water to be treated should be clear. The treated water has completely been softened. The costs per m^3 for large installations are low (DM 0.10–DM 0.15/ m^3 water). For very small installations, with limited use (home softeners), the cost will strongly rise (to $> \text{DM } 1./\text{m}^3$ water).

Reverse osmosis. In this process the water to be softened is passed through a membrane permeable for water. It is

separated into one part softened water (pressed through the membrane) and one part water containing more Ca and Mg (not pressed through the membrane). The process is relatively complicated, especially also because pollution and consequently clogging up of the membrane should be prevented by prefiltration and decarbonization with acid. The method is fit for the deionization of brackish water. The costs are high and prohibitive for large scale application. In Figure 3 the processes mentioned are compared with each other.

Water softening location. Softening occurs centrally, on a large scale by the public water works and privately, on a small scale. Private softening is done through an installation between the public pipe system and the service connection (home softening); or at the point of use, built in into equipment as a rule (dishwashers, boilers). The advantages of central softening are low costs per m^3 and a good check of the water quality. It is a disadvantage that all water is softened, at least as long as no second (very expensive) public pipe line system exists. Home softening also has this disadvantage. The possibility of a separate system for soft water next to one for "normal" hard water can be realized more simply and cheaper here, especially in new constructions. It is also important that people can make their own choice with home softening. Finally for the "point of use" softening there are the high costs per m^3 of water versus the advantage of the selective use of softened water.

ACTUAL SITUATION IN WESTERN EUROPE

In view of the big differences in water consumption, water quality and prosperity level within Western Europe and also in view of the attitude of authorities in the various countries very general remarks only can be made on the subject.

Hardness correction of drinking water made its appearance in Western Europe about 10–15 years ago when the first dishwashers appeared on the market to some extent. It stands to reason that the manufacturers built an (ion-exchanger) softening into their machines (lime scale on glass and dishes made this necessary). The expectation that manufacturers of washing machines/boilers etc. would follow this example on a large scale, did not come true. The philosophy still is that the consumer is not (yet) willing to pay more for the machine (with softener) as long as additional phosphate dosing through washing agents compensates for the disadvantages of hard water.

Apart from this the softening equipment industry did not succeed, until now, in realizing a large breakthrough of home softeners. This has happened on a limited scale in England, Switzerland and Belgium. There is a distinct progression in the use of softened water in the retail industry (laundries), public institutions (hospitals, homes) and in housing blocks. This softening takes almost completely

Comparison Softening Processes

| | chemical softening | ion-exchange | reverse osmosis ^{★★} |
|--|--|---|--|
| chemicals | NaOH or Ca(OH) ₂ Na ₂ CO ₃ | NaCl | HCl (+ energy ~1.5 kWh/m ³) |
| process control | simple (lye treatment) complicated (lime + ash) | simple (small units) complicated (large units) | complicated |
| pretreatment raw material | none | filtering | filtering |
| min. hardness reachable | .8 mval Ca | 0 mval Ca | .5 mval Ca |
| size of process unit | only large units | all sizes | medium/large units |
| disposal (per m ³ treated) | ~ 250 g. Ca + Mg salts as sludge or solids | ~ 500 g. chlorides (Na, Ca, Mg) | ~ 300 l. water with 3x impurity level intake |
| influence on treated water | 60-100 g. Na/m ³ | 100-120 g. Na/m ³ | none |
| costs [★] (DM/m ³ water) | | | |
| very small units | -- | .75 - 1.80 | -- |
| medium size units | -- | .35 - .90 | .9 - 1.8 |
| large units | .06 - .10 | .10 - .15 | ~.20 |

★ for hardness correction of 5 mval

★★ can be used for brackish water

Figure 3. Comparison of softening processes.

place via ion exchange. Momentarily, softening takes place through reverse osmosis on a very modest scale and mainly in clinics and hospitals in order to prevent any semblance of possible contamination through bacterial growth on ion exchanger resin.

After the 1973 energy crisis, public authorities became concerned about water softening. On the one hand because they are responsible (or feel so) for the quality of drinking water used, and on the other hand because of the growing interest in the waste of energy and washing agents and because of environmental protection reasons (phosphate). Of course they are considering central softening.

In Belgium, Great Britain and in the Netherlands central softening has started on a small scale. For large installations the choice of a chemical hardness correction is obvious (see Table 1). Since the development of the so-called Spiractor process, during which the CaCO₃ precipitate will be available in the form of hard, marble grains, the chance that, like in the USA, a considerable part of the central softening will take place through ion exchange is very small.

The conclusion that Western Europe is at the beginning of a large development in water softening seems to be justified. In this development there are great interests for the salt producers.

REGENERATION SALT

For capacities up to thousand cubic meters of water per day there is only one simple and paying process. It is softening via ion exchange. The resin used should be regenerated with a solution of a salt with a univalent cation. For this only NaCl is qualified as a matter of fact. This is because 1) NH₄⁺ + K⁺ are undesirable in the softened water, 2) Cl⁻ doesn't form precipitates with Ca⁺⁺ and Mg⁺⁺, 3) NaCl is chemically almost inactive and doesn't attack the resin, 4) NaCl doesn't give problems during a misoperation, 5) NaCl only gives minimum environmental problems, and 6) NaCl is available in a good quality and at a low price.

During softening, Ca and Mg are replaced by Na in equivalent quantities. So, per 1 liter of treated water 5 mval (Ca + Mg) are changed for 5 mval of Na during a reduction of hardness by 5 mval Ca/l. The softened water then contains $5 \times 23 = 115$ mg of sodium per liter more.

During the regeneration of the resin with a NaCl solution the Ca and Mg caught on the resin are replaced by Na. Ca and Mg pass on to the regeneration solution. This is drained as a rule. The regeneration efficiency is considerably lower than 100%. High efficiencies on salt ($\geq 60\%$) are obtained when a low effective resin capacity and full use of this

Utilization of sodium chloride when generating ion-exchangers

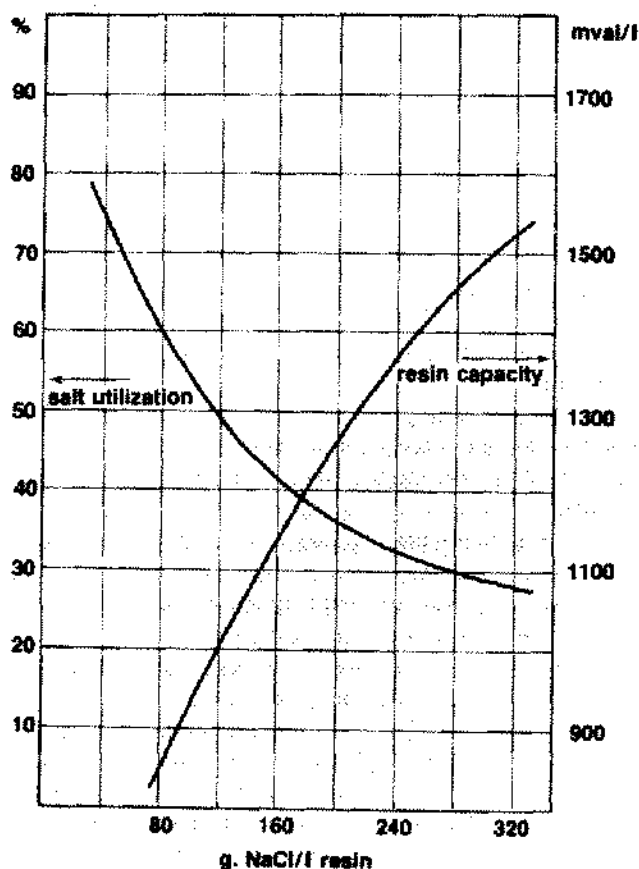


Figure 4. Utilization of sodium chloride when generating ion-exchangers.

capacity are accepted (see Fig. 4). In small installations often very low efficiencies on NaCl are accepted. Small resin volumes and consequently high effective resin capacities and very frequent regeneration (e.g. after each wash) are the causes for low efficiencies ($\leq 20\%$!).

Hardness correction being 5 mval Ca/liter, the quantity of regeneration salt needed is 0.5 kg/m³ water with 60% efficiency and 1.5 kg/m³ water with 20% efficiency!

In the West-European households approximately 15 milliard m³ of water a year is used now. In 2000 this quantity will rise to 35 milliards m³. This means a potential market of some millions tons of salt per year, even with a relatively modest percentage of softening through ion exchange! These quantities of salt and the generally very low salt efficiencies now realized during regeneration of the resin, resulted in the argument against ion exchange, which is often heard, as if serious damage would be inflicted upon the environment.

The used NaCl indeed is getting into the waste water (Cl⁻ through draining of the regeneration liquid, Na⁺

through the water treated and through the regeneration liquid purge). Is it harmful in the quantities produced there? Harmful in the waste water purifications, in the surface water, in the drinking water?

An example is given for comparison. Suppose an overall water consumption of 500 liters per head per day and household consumption of 30% of the overall consumption. If there is a hardness correction of 4 mval Ca per liter for 20% of the household water consumption, and a regeneration efficiency on salt of 50%. Then the following parameters are evident. The treated water will contain 100 mg of sodium per liter extra. The waste water of the location will contain 11 mg of sodium and 18 mg of chloride extra. As a result of dilution with other (surface) water (rainfall) in densely populated areas such as the Paris area, the German Ruhr and the Western part of the Netherlands a sodium increase of approximately 4 mg and a chloride increase of about 7 mg per liter will be found. In thinly populated areas the level for sodium will rise by less than 2 mg and for chloride by less than 3 mg per liter. Natural water contains approximately 25 mg of sodium and approximately 5 mg of chloride per liter. Rhine water contains approximately 150 mg of chloride per liter.

The presumed harmfulness of these sodium and chloride quantities in the water is minimal; consider the following data. Sodium chloride itself (in small quantities) is not poisonous. The threshold value for the taste lies at approximately 150 mg of chloride per liter. The threshold value for damage to certain sensitive horticultural vegetation lies between 100 and 150 mg chloride per liter. A detrimental influence of NaCl on forms of life in water (inclusive of sludge fermentation) begins at concentrations of 5 g sodium chloride per liter. An increase of sodium in consumption water by 100 mg per liter may give problems for sodium-poor diets. But the increase of the sodium content in (recycled) surface water is low with regard to the natural content of sodium in water.

These data led to the conclusion that in general the environmental impact caused by the amount of salt used for regeneration of resins for water softening is of little importance and will stay so in future.

The authorities and drinking water (softening). More than 95 percent of all water supplied for household purposes in Western Europe is produced and distributed by Public Water Works. In all West-European countries this water should meet a number of quality demands. Demands are made with regard to the chemical composition (impurities), physical nature (clearness, conductivity) and microbiological (bacteriological) factors (number per volume). The demands are not uniform and more or less differ by country.

Also the location in the water distribution system where the demands apply is different. In Belgium and Denmark e.g. they apply, when leaving the water works; in Great

Britain, Switzerland and Germany they apply on the connection of the private system to the public pipe work. In France and in Spain on each water drain.

The authorities are fairly general finally responsible for the quality of water. But also here we see that there is no uniformity again. In some countries the local authorities, in others the regional authorities, but in most countries the federal authorities bear the responsibility. A first step towards equal demands for drinking water for whole (Western) Europe has been made by the WHO (World Health Organization). In 1970 the 2nd edition of "European Standards for Drinking Water" appeared at the WHO⁵. A second step to uniformity, in a somewhat different direction, has been taken recently by the European Economic Community. An EEC commission worked out a proposal for generally applying demands, to be made to water for household purposes (Nr. C 214/2, published in the "Official Journal of the European Communities" of 18-9-1975) (lit. 4). Both "Standards" are *not* identical. Finally a "proposal" for demands to be made to all chemicals to be used in water treatment installations has recently been published by an EEC commission⁶. These demands in fact are derivatives to the demands for drinking water.

What is the opinion of the authorities about water softening? A uniform answer to this, applying to the whole of Western Europe cannot be given. It is, however, striking that in those countries where softening in relatively small unities becomes popular (in Germany, Scandinavia and the Netherlands) resistance of the authorities against this softening is growing. This is comprehensible when it is realized that they *are or feel* themselves responsible for the quality of the water *from the tap*. An intermediate treatment which *cannot* be checked or checked only with great difficulty (the case for softening) might be harmful to the quality of the water (e.g. from heavy metals, bacteriological infection). An additional fact is that the governments care for the environment.

So the authorities are against rather than *for* softening. Especially when this happens in the home softener. They are defending themselves against home softening by 1) forbidding home softening (through ion exchange) (e.g. in Denmark); 2) making demands on the installation of softening equipment (e.g. in Germany, Great Britain, the Netherlands and Switzerland); 3) promoting central softening (less unfriendly to the environment, quality of the water can be supervised, cheap but unfit for selective use); and 4) making quality demands as to the drinking water, which makes softening impossible.

Although the last has not yet occurred, it is good to point out the "Maximum Admissible Concentration" for sodium of 100 mg/l (= 4 mva liter sodium ion/l) in the EEC proposal for drinking water (partly reproduced in Figure 5). When an associated country does not use the present possibility to determine a higher *Exceptional* Maximum Admis-

| component | units | guide level | maximum admissible concentration | minimum required concentration |
|----------------|-----------|-------------|----------------------------------|--------------------------------|
| total hardness | mvalCa/l. | 7 | — | — |
| magnesium | mval/l | 2.5 | 4.2 | — |
| calcium | mval/l | 5 | — | — |
| sodium | mval/l | ≤ 1 | 4.3* | — |
| potassium | mval/l | ≤ 25 | — | — |
| chloride | mval/l | — | 5.6* | — |

* recourse to "exceptional maximum admissible concentration" is possible for the E.E.C. Member States.

Figure 5. The EEC proposal for the quality of water for human consumption.

sible Concentration for sodium, then softening with more than 4 mval Ca/liter through ion exchange has become impossible!

Moreover, minimum required concentrations of respectively 0.5 mval and 0.4 mval per liter are required in the EEC proposal for calcium and magnesium. With this, total softening has also become impossible.

A task for the salt industry. A development with regard to water softening for household use has set in. There exists an increasing interest for the use of (partly) softened water, especially obtained through small (home or point of use) installations. The system is ion exchange with regeneration through NaCl solution. Does this mean that the salt industry can quietly wait for, what is coming, i.e. a "big boom" in regeneration salt? No, certainly not.

Softening of drinking water in general and that through ion exchange in particular is a vexed question at this moment. The objective weighing of *pro's* and *con's* is difficult or impossible. There is a need for data and experiences with which prejudices can be obviated. Apart from this, also the last word on ion exchange and the equipment needed has not yet been spoken.

There is a task here for the industry and also for the producers of regeneration salt. This task should involve 1) Collecting and providing of all relevant data from literature and practice as to production and use of soft water, and 2) Development of methods and advising for *salt waste* gradually changing to *salt consumption*. This item needs some elucidation. The salt efficiency during the regeneration of resin is now very low on an average ($\approx 30\%$). The smaller the equipment, the worse is the efficiency. Considerable improvements in salt efficiency may be expected from the following measures: a) application of a larger volume of resin per water output given. b) Application of up-flow regeneration instead of downflow. c) Development of less selective resin grades (which will release the Ca and Mg more easily when regenerating), and d) Development of a cheap system indicating when the resin has been satu-

rated to Ca and Mg and has to be regenerated. 3) Promoting of the use of "point of use" softening equipment. 4) Promoting of the construction of a second distribution system for softened water to heating equipment (washing machines, boilers, etc.) in houses, blocks of houses, institutes etc. 5) Investigations into the extent to which it is possible to realize a central regeneration (by the salt producer!) of ion exchanger resin out of small-scale equipment (use interchangeable cartridges).

Opposite to the costs of the transport of the interchangeable cartridges are the following advantages: the resin capacity is completely used, the resin can be disinfected excellently and environmental load by means of the regeneration salt is out of the question.

Especially the actions summarized under 1 lend themselves to a central approach. During their annual General Assembly (1976) the European Committee for the Study of Salt decided to set up a Commission of Special Salts for Water Softening (Chairman: Mr. A.F. van Kooten, Akzo Zout Chemie, Hengelo, the Netherlands). In this commission the West-European countries represented are: Belgium, France, Great Britain, Italy, The Netherlands, Austria, Spain, The Federal Republic of Germany, Switzerland and Denmark. The main task of the commission is the collection, inventory and supply of all information with regard to water softening. Apart from this, the commission will take initiatives for investigation which is considered to be necessary.

AQUA EUROPA, the (Western) European Water Conditioning Association (67, Rue de Saint Jean, CH-1201, Geneva) is wider in its scope and has objectives in all regions of water treatment. The activities of one of its working parties i.e. ion exchange techniques overlaps those of the CEES commission. In view of the large differences between the West European countries in the approach to water softening, it is recommended that local action be taken. It stands to reason that close cooperation of the salt producers should be sought between producers of softening equipment, National Associations in the "water field", institutes and the local authorities.

REFERENCES

1. Dickinson, W. 1972. The Salt Industry to 1980. In A.H. Coogan (ed.). Fourth Symposium on Salt, Northern Ohio Geological Society, Cleveland, Ohio. 1:7-11.
2. Carlotti, R. 1977. Ned. Chem. Ind. 12:2.
3. Rapport van de Commissie Centrale Ontharding. 1971. Keuring Instituut voor Waterleiding Artikelen Rijswijk, The Netherlands. Nov. 1971.
4. Official Journal of the European Communities. 1975. No. C214/8, Sept. 18, 1975.
5. European Standards for Drinking Water. 1970. World Health Organization, 2nd Edition. Geneva.
6. Report of Bureau-commission 13. 1977. Water Services needs of reagents and additives for the treatment of drinking water. March, 1977.