An Evaluation of Water Softening

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*University of Central Florida*

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AN EVALUATION OF WATER SOFTENING

BY

JAMES BURR ATON
B.S.M.E., Oklahoma State University, 1969

RESEARCH REPORT

Submitted in partial fulfillment of the requirement for the degree of Master of Science in Engineering in the Graduate Studies Program of Florida Technological University, 1973

Orlando, Florida
ABSTRACT

AN EVALUATION OF WATER SOFTENING

By

JAMES BURR ATON

B.S.M.E., Oklahoma State University, 1969

Dynamic modeling is proposed in this paper as a method of developing a computer model to simulate a water softening treatment unit. Information on water softening economics and ion exchange are examined.

The development of a dynamic model is oriented toward uniform effluent water quality and operational flexibility. Several methods are presented to determine the reaction rate used in the completely mixed flow reactor's dynamic model. Based on preliminary data the proposed dynamic model would calculate removal rate similar to those found in an existing plant.

John Paul Hartman, P.E.
Director, Research report
ACKNOWLEDGMENTS

I would like to thank my committee, Dr. T. C. Edwards, Professor J. P. Hartman, Dr. M. P. Wanielista, and Dr. Y. A. Yousef, for their kind attention and scholarly advice. Certainly, my typist, Mrs. Donna Wood, deserves my gratitude and praise.
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<td>II-5</td>
<td>28</td>
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<td>III-1</td>
<td>43</td>
</tr>
<tr>
<td>III-2</td>
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</tr>
</tbody>
</table>
INTRODUCTION

There are several reasons for softening of water. Among these are the aesthetic value of good water, soap consumption, and the elimination of scale from hot water pipes and boilers.

The process of water softening is a many faceted problem. There are several independent parameters controlling the process. Dynamic modeling and systems information analysis is proposed here as a method of developing a computer model to simulate a water softening treatment unit. It is believed by the author that development and implementation of this technique will lead to economics in the lime-soda ash softening process. With stochastic influent quality, dynamic modeling of treatment facilities will help insure a uniform output of water quality and add flexibility to plant operations (Wanielista, 1971).

The objective of this research report is to lay down the foundation for the development and evaluation of the appropriate dynamic model as applied to the combination mixing basin and upflow clarifier used in precipitation water softening. In support of this objective and to provide understanding of the water softening field, do the following:

1. Provide background and economic justification for water softening
2. Examine the kinetics of two processes for the removal of hardness from water
3. Find theoretical or empirical data or approaches by which the results of the simulation technique may be evaluated.
I. BACKGROUND

Two things can be said about water without contradiction. Water is the basic fluid of life and without an adequate supply of good water economic development will not proceed. The objective of water treatment is to meet this need. The goal of municipal water treatment plants is to provide water that is potable, chemically and biologically stable, appetizing and reasonably priced. It is important that these goals be met so that the consumer will not turn to some other source of water which is unsafe.

In many parts of the country with the growing consumption per capita and growing population it is increasingly difficult to find a raw water supply of sufficient quantity and quality to meet the public demand. These communities have been forced to turn to water supplies which are unfit for consumption in their native form or were previously considered unfit for treatment. Many of these new sources are ground and surface waters either high in color and turbidity, bad tasting, or hard and staining. Water of high hardness requires softening and sanitizing to render it fit for consumption.

The requirements for a public water supply are that it:

1. Shall contain no organisms which cause disease.
2. Be sparkling clear and colorless.
3. Be good tasting, free from odors, and preferably cool.
4. Be reasonably soft.
5. Be neither scale-forming nor corrosive.
6. Be free from objectionable gas, such as hydrogen sulfide, and objectionable minerals, such as iron and manganese.

(Riehl, 1962)

Two through six of the above list of requirements indicate the need for chemical treatment or softening of water. Softening reduces the soap and detergent consumption and removes the staining characteristics of water making it more suitable for use in laundry and personal hygiene. Softening can, by removal of fixed dissolved solids, reduce the accumulation of scale in hot water pipes, water heaters, boilers and other appliances. Softened water is more acceptable to food processing and industrial cooling water requirements. Water high in magnesium and sulfates have laxative properties. High levels of sodium ion concentration may be troublesome to people on low salt diets.

WATER QUALITY STANDARDS

Standards for water quality have been established by the U.S. Department of Health, Education, and Welfare for water used on common carriers. The 1962 standards are approved by the American Water Works Association, The American Public Health Association, and the Water Pollution Control Federation, and are used by most state, county, city, and community governments as the criteria for potable water. The intent of these standards is that a water source consistently meet the standards review below or be treated so that it does.

To meet the bacteriological quality, a water must contain no more than one coliform organism in 100 ml of tap water. Defined in the standard is the testing frequency. Typical minimum number of monthly
tests or samples are prescribed as follows:

<table>
<thead>
<tr>
<th>Population served (in thousands)</th>
<th>1-2</th>
<th>10</th>
<th>50</th>
<th>100</th>
<th>900</th>
<th>2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples per month</td>
<td>2</td>
<td>12</td>
<td>50</td>
<td>95</td>
<td>300</td>
<td>400</td>
</tr>
</tbody>
</table>

In addition the supplies to a community should be examined once a week at representative points in the system for color, odor, and taste. The maximum acceptable values are 5 units of turbidity, 15 units of color, and a threshold odor number of 3. Also defined in the standards are tests which must be made twice a year for chemical characteristics and maximum concentration for certain toxic materials. The allowable level of radioactive material in water supplies is defined in the standards.

ECONOMIC JUSTIFICATION FOR SOFTENING

The softening of water for other than aesthetic reason must be justified on an economic basis. A comprehensive report (Aultman, 1955) shows that municipal treatment is the most economical means of softening water. The report compared the cost of soap and detergent softening of water in the home to the cost of municipal softening. The test involved a family of five and was supervised by Purdue University. The family was given new linens, underwear, and a tea kettle at the beginning of each six week period. These items were then compared to determine the effect of a) 380 ppm hard water, soap, b) 380 ppm hard water, syndets detergents, c) zero hardness water, soap, and d) zero hardness water, syndets detergents. Records were kept of the cost and amounts of detergent used. The conclusions of the test were:

1. The detergents do not perform quite as well in hard water - this situation becomes worse as the hardness increases.
2. Hardness ions interfere and cause some of the dirt to be redeposited in the fabric.

3. A greater amount of synthetic detergent is needed in hard water.

4. In soft water a 0.15% concentration (of syndets) would clean while in 21 grain hardness, probably 0.3% concentration would be required.

It may be assumed that softening fairly hard water would save the average family 1/3 to 1/2 carton of detergent (20-22 oz. size) per week.

To bring the cost data to 1970 dollars the ratio of the consumers' retail index was used (World Almanac, 1971). Soft water could save $48.00 per year for a family of five for syndets detergents and $74.38 per year for soap exclusively. Assuming present day usage of predominately detergents this means a $9.76 savings per person per year in zero hardness water. The $9.76 savings reduces to $7.56 for 100 ppm hardness water. It was calculated (Aultman, 1955) that the municipal plant could produce water of 100 ppm hardness for a treatment cost of $1.83 per person per year. The net savings per person per year for municipally softened water versus detergent softened water is $5.53 per person per year. "Thus for each $1 spent at the plant $4 is saved in the home" (Riehl, 1962). This is a great benefit to the underprivileged who can not afford to soften their own water anyway except by detergents. Softening also helps reduce the amount of detergents that are difficult to degrade; thus, the amounts of pollution being dumped into our natural waters are decreased. Aultman also indicated the following additional benefits resulting in savings due to softened water.

1. A 25% savings is realized on fuel for heating soft water by the elimination of deposits of scale which retards heat flow.
2. An 18% savings is obtained on repairing, cleaning, and replacing plumbing that is caked.

3. Fabrics show 25% less wear and tear in soft water.

4. Food cooked in soft water retains its natural color and appearance, and its digestive properties.

5. In making tea and coffee, 50% less leaves and grounds are used in soft than in hard water.

6. Soft water provides for better skin care, and eliminates the need for expensive bubble bath preparations. There is no bathtub ring.

Another method of water softening is the home softener or ion exchange column. Based on prices and usage information obtained from the Culligan Water Conditioning of Orange County, Inc. and Montgomery Ward Mail Order Catalog, and estimate of home water softening cost was obtained. These calculations are given in Appendix A. The calculations were made by reducing 380 ppm hardness to 100 ppm hardness in order to compare with the municipal softening costs. The capital and operating cost of a softener maintained to produce 100 ppm of soft water over a 10 year service life period is $12.03 per person per year. The rental of a Culligan softening tank, installed and maintained by the company cost $43.60 per person per year. When compared to the $1.83 per person per year for municipal softening the advantage is readily seen.

Softening has the following advantages from the plant operation standpoint. When the softening of surface waters accompanies the removal of turbidity and color, the added precipitates due to softening accelerate the sedimentation process. When magnesium is precipitated as magnesium hydroxide, the gelatinous precipitate acts as a coagulant aid. Softening also reduces the load on the filters and lengthens the period between backwash, thus reducing the costs associated with the filtration (Richl, 1962).
WATER SUPPLIES

Raw water supplies are generally to two types: surface water or ground water. Surface water is generally turbid, colored, high in organisms and organic material and medium to low in mineralization or hardness. The degree of mineralization changes with the seasons, low stream flow being the most mineralized.

These surface waters are generally treated with aluminum and iron sulfates as coagulant aids to remove turbidity and color by flocculation and sedimentation. Surface waters are sometimes bad tasting and have an unpleasant odor. This is primarily due to the organic material, either alive or dead, in the water. Surface waters are often polluted from man-made sources. In spite of these drawbacks, surface waters are the ones most used by large cities. For example, in Ohio, in 1961, there were 538 public water supplies serving approximately 7 million people (1960 census). Of these public supplies 80% were well supplies, but the 20% which were surface water supplies served 72% of the people (Riehl, 1962).

Ground waters are generally low in turbidity, color, organic matter, and organisms, but are more highly mineralized than surface waters. Ground water comes from infiltrated rain. Rainwater as it falls upon the earth is incapable of dissolving the tremendous amounts of solids found in ground waters. The rain water absorbs CO₂ from bacteria in the top soil forming carbonic acid (H₂CO₃). As the rain water infiltrates into the earth, it is this acid which dissolves calcium and magnesium salts to produce hardness in ground water as indicated in Figure I-1.
Ground waters are usually limited in quantity but are adequate to serve many small communities. Ground water sources are usually less expensive to develop because they do not require the acquisition and maintenance of a water shed and impounding dam. However, treatment may be complicated by having wells of different mineralization.

In many locations water softening is a fact of life. It is required to meet the public demand for good water. There are several processes by which water can be softened such as: reverse osmosis, electrodialysis, ion exchange and lime-soda ash precipitation. At present the membrane processes of reverse osmosis and electrodialysis...
are too expensive except where high concentration of dissolved solids must be removed because of limited choice of supply. Ion exchange has widespread use but is limited by cost to smaller applications. Lime-soda ash process is the least expensive when applied to municipal treatment and has the following advantages (Riehl, 1962):

1. Disinfection
2. Removal of organic material and bacteria
3. Eliminates worry about well contamination
4. Simultaneous removal of iron and manganese with hardness
5. Aids coagulation and flocculation of turbid water
6. Controls turbidity and aids filtration

There are more than 600 lime-soda ash installations in the United States and several in Florida. Because of the frequency of its use and the advantages listed above, the detailed evaluation of the lime-soda ash process is warranted.
II. THE ION EXCHANGE AND LIME-SODA ASH WATER SOFTENING PROCESSES

DEFINITION OF HARDNESS

To the consumer hard water is water that requires large amounts of soap to form a lather. With hard water, scale is formed in appliances, hot water pipes and boilers. This condition is brought about by concentrations of dissolved divalent metallic cations and the anions they associate with in natural waters. When water is heated some of these mineral compounds decrease in solubility and precipitate out in pipes and boilers forming scale. In addition, the divalent ions combine with soaps and to a lesser extent detergents, to form precipitates. The precipitates are partly the cause of bath tube rings and make cleaning and washing clothes more difficult. The divalent metallic cations causing water hardness are shown in Table II-1.

TABLE II-1

PRINCIPAL CATIONS CAUSING HARDNESS IN WATER AND THE MAJOR ANIONS ASSOCIATED WITH THEM

<table>
<thead>
<tr>
<th>Cations Causing Hardness</th>
<th>Associated Anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>Ca^{++}</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg^{++}</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr^{++}</td>
</tr>
<tr>
<td>Ferrous iron</td>
<td>Fe^{++}</td>
</tr>
<tr>
<td>Manganous ion</td>
<td>Mn^{++}</td>
</tr>
</tbody>
</table>

(Sawyer, 1967)
Hardness in water is measured in mg/l as calcium carbonate (CaCO₃). One milligram per liter (mg/l) is equivalent to one part per million (ppm). The concentration of each ion in mg/l is converted to mg/l as CaCO₃ by using the following example calculation:

\[
\text{Hardness (mg/l as CaCO}_3\text{)} = \frac{\text{eq.wt. of CaCO}_3}{\text{eq.wt. of M}^{++}} \times \text{M}^{++} \text{ (in mg/l)}
\]

where: \( M^{++} \) represents any divalent cation

(Sawyer, 1967)

Thus the hardness of a water is the total concentration of all the divalent cations expressed as CaCO₃.

Water is classified as to its relative hardness as follows:

- **Soft**: 0 - 75 mg/l as CaCO₃
- **Moderately Hard**: 75 - 150 mg/l as CaCO₃
- **Hard**: 150 - 300 mg/l as CaCO₃
- **Very Hard**: above 300 mg/l as CaCO₃

When a water is hard or excessively hard, the hardness should be removed to provide a good water for general consumption. Of the three processes named in the first chapter, only two types will be discussed: ion exchange and lime-soda ash. The third type of softening by membrane processes is not discussed because of insufficient development to justify its use in large scale production.

**ION EXCHANGE SOFTENING PROCESS**

The softening of water by the ion exchange or zeolite process is well-developed. There are several companies which have ready-to-install equipment on the market. Softening by the ion exchange process involves passing the hard water through the exchange media where the
unwanted divalent cation is absorbed and the water is softened. When the exchanger media is saturated with hardness ions, it is regenerated with a salt (NaCl) solution.

A number of natural materials have ion exchange ability including soils, humus, cellulose, wool, protein, activated carbon, coal, lignin, metallic oxides, and living cells such as algae and bacteria. Reviews of ancient Greek literature indicate the use of clays and minerals for demineralizing drinking water. In 1876 Lembury demonstrated reversible ion exchange reactions in transforming the mineral leucite ($K_2OAl_2O_3 \cdot 4SiO_2$) to analcime ($Na_2OAl_2O_3 \cdot 4SiO_2$) and back (Weber, 1972). The original application of zeolites to softening is credited to Gans, a German chemist who called the process permulis (Riehl, 1962). In 1935, a modern resin exchanger was discovered by I. B. A. Adams and E. L. Holmes. The media was crushed, phenolic phonograph records (Weber, 1972).

The zeolite is natural river sand commonly called green sand. These are natural aluminosilicates ($Al_2O_3 \cdot 4SiO_2$) and exchange sodium ($Na^+$) for calcium ($Ca^{++}$). A synthetic zeolite can be made by drying mixed solutions of sodium silicate ($Na_2SiO_3$) and sodium aluminate ($Na_2Al_2O_3$). These are then crushed to the desired size. All zeolites operate on the sodium cycle and are regenerated with salt solution (Fair, 1968).

At the present, synthetic ion exchange resins are the most frequently used exchange material. Depending on the choice of resin these resins can exchange anions or cations. Synthetic resins have the capability to exchange on a selective basis. Some resins can be regenerated on more than one ion cycle. In softening resins, two types
predominate: methacrylic acid crosslinked with divinly benzene and sulfonated styrene with divinly benzene crosslinking. The preparation of the second kind is shown in Figure II-1.

![Chemical structure and reaction diagram]

Sulfonated styrene is preferred because of its strongly acidic exchange characteristics. This resin can operate in the hydrogen cycle as well as the sodium cycle which allows it to be used in demineralization. However, since sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) is the regenerant, demineralization is too expensive for public works.

The simple stoichiometric reaction of the exchange can be written:

\[ A^{n+} + n(R^-)B^+ \xrightarrow{\text{(Solution)}} nB^+ + (R^-)_nA^{n+} \text{ (II-1)} \]
However, this is not quite true since ion exchange is a sorption phenomenon rather than a reaction. However, it does provide a good analytical model. $A^{n+}$ is a multivalent ion, $B^+$ is a monovalent ion and $R$ represents the resin.

Synthetic resin demonstrates a distinct selectivity in the rate of sorption of ions. If several ions are present in the same concentration, one may be removed much faster than the rest. This affinity for different ions by the resin can be expressed in a series. A typical example is:

1. $\text{Li}^{++} < \text{H}^+ < \text{Na}^+ < K^+ = \text{NH}_4^+ < \text{Rb}^+ < \text{Ag}^+$
2. $\text{Mg}^{++} = \text{Zn}^{++} < \text{Cu}^{++} < \text{Co}^{++} < \text{Ca}^{++} < \text{Sr}^{++} < \text{Ba}^{++}$

(Fair, 1968)

This characteristic of resins is quantified by the selectivity coefficient, $K_B^A$.

$$K_B^A = \frac{[B^+]^n (X_{RnA}) (f_{RnA})}{[A^{n+}] (X_{RB})^n (f_{RB})^n}$$

(II-2)

Where: [ ] = denotes molar concentration

$X$ = equivalent ionic fractions

$f$ = activity coefficients

Table II-1 presents the selectivity coefficient for polystyrene base resin (Weber, 1972). The activity coefficient ($f$) is a factor which converts molar concentration to a value which expresses quantitatively the true mass action effect.

Another quantitative approach to selectivity is the selectivity quotient. This term is neither numerically or thermodynamically constant but varies with the relative concentration of the different phases. The selectivity quotient $Q_s$ is defined by:
<table>
<thead>
<tr>
<th>Replaceable Ion</th>
<th>4%</th>
<th>8%</th>
<th>16%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Monovalent cations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>1.00</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>H</td>
<td>1.32</td>
<td>1.27</td>
<td>1.47</td>
</tr>
<tr>
<td>Na</td>
<td>1.58</td>
<td>1.98</td>
<td>2.37</td>
</tr>
<tr>
<td>K</td>
<td>2.27</td>
<td>2.90</td>
<td>4.50</td>
</tr>
<tr>
<td>Rb</td>
<td>2.46</td>
<td>3.16</td>
<td>4.62</td>
</tr>
<tr>
<td>Cs</td>
<td>2.67</td>
<td>3.25</td>
<td>4.66</td>
</tr>
<tr>
<td>Ag</td>
<td>4.73</td>
<td>8.51</td>
<td>22.9</td>
</tr>
<tr>
<td>Tl</td>
<td>6.71</td>
<td>12.4</td>
<td>28.5</td>
</tr>
<tr>
<td><strong>Divalent cations</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>2.95</td>
<td>3.29</td>
<td>3.51</td>
</tr>
<tr>
<td>Ca</td>
<td>4.15</td>
<td>5.16</td>
<td>7.27</td>
</tr>
<tr>
<td>Sr</td>
<td>4.70</td>
<td>6.51</td>
<td>10.1</td>
</tr>
<tr>
<td>Ba</td>
<td>7.47</td>
<td>11.5</td>
<td>20.8</td>
</tr>
<tr>
<td>Pb</td>
<td>6.56</td>
<td>9.91</td>
<td>18.0</td>
</tr>
<tr>
<td><strong>Monovalent anions (2% c.l.)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>0.80</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td></td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>1.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>2.7</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>9.0</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>NO₃</td>
<td></td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>SCN</td>
<td>6.0</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>ClO₃</td>
<td>9.0</td>
<td>10.0</td>
<td></td>
</tr>
</tbody>
</table>

Data are for polystyrene base resins, sulfonic acid cation exchanger, and type 2 quarternary base anion exchanger. Data of Bonner and Smith (J. Phys. Chem., 61, 326) for cation exchanges; Gregor, Belle, and Marcus (J. Amer. Chem. Soc., 77, 2731) for anion exchanges.

A value greater than 1 indicates preferential absorption of ion named against the reference ion (Li for cations, Cl for anions).


(Weber, 1972)
\[
Q_s = \frac{[R A_n^+] [B^+]}{[R B] [A_n^+]} = \frac{\text{(Moles } A_n^+ / \text{gm resin}) \text{(Moles } B^+ / \text{ml solution})}{\text{(Moles } B^+ / \text{gm resin}) \text{(Moles } A_n^+ / \text{ml solution})}
\]

If \( Q_s = 1 \), the resin shows no selectivity. For \( Q_s > 1 \), the resin has a preference for \( A_n^+ \) and if \( Q_s < 1 \), it has a preference for \( B^+ \). The larger the value of \( Q_s \) the shorter the length of ion exchange column required (Weber, 1972).

From the above discussions, the distribution of two ions of different valence between the solution and resin is strongly dependent on solution concentrations. In hetero-ionic exchange, the resin increasingly prefers the divalent ion to the monovalent ion with decreasing concentrations in the solution. The equilibrium position can be characterized graphically by the exchange isotherm of Figure II-2. For no selectivity, the line is the diagonal of the graph. The curves above the diagonal show preference for \( Ca^{++} \) and curves below the diagonal show preference for \( Na^+ \) (Fair, 1968).

The quality of operation of an ion exchange column is represented by the breakthrough curve. This curve is obtained for each installation and shows the capacity and quality of the column. Figure II-3 shows this type of curve and a schematic of an exchange column or bed. The flatter the line the better the efficiency of the column. The degree of tailing in the breakthrough curve gives an indication of channeling of flow or fouling of the exchange material. The point at which the ion being removed appears in the effluent is called the breakthrough point. It indicates the end of an exchange cycle and calls for the regeneration of the column (Fair, 1968).

A typical ion exchange softener installation usually consists of one or more units similar to mechanical filters with zeolite or syn-
Exchange isotherms for the reaction $\text{Ca}^{++} + 2 \text{[Na}^+\text{R}^-\text{]}^+ \rightarrow \text{[Ca}^{++}\text{R}_2^-=\text{]} + 2\text{Na}^+$. In dilute solutions the exchanger shows a strong preference for $\text{Ca}^{++}$ over $\text{Na}^+$. This selectivity decreases with increasing ion concentration. The 45° line represents the isotherm for an exchanger with no selectivity. The exchanger can be regenerated with concentrated salt solutions.

(Fair, 1968)

The change in design, in design, is accounting for the difference in density of the exchange media and sand and the greater depth 24 to 70 inches, of the exchange media. The range of feed ratio for exchangers range over the values from 4 gal/sq ft/min. to 8 gal/sq ft/min. These rates are somewhat higher than for rapid sand filters which range from 2 to 5 gal/sq ft/min. The units may be closed pressure units of up-flow or down-flow design or be the open gravity feed type. Pressure units are usually used in smaller installations while open gravity flow units are used in large plants.
Figure II-3 Columnar operation of an ion exchanger. (Fair, 1968)

Down-flow units have the advantage of acting as a filter to remove any final turbidity, although this may have a detrimental effect on the exchanger efficiency. A schematic of an ion exchanger softener is shown in Figure II-4.

General piping requirements are as follows:

1. Hard water inlet
2. Soft water outlet
3. Salt-solution inlet for regeneration
Filter or Pretreatment for Iron and Manganese Removal

375 ppm Hardness

Flow Control

375 ppm Hardness

Backwash Brine To Disposal

Ion Exchange Resin Bed

20 Percent Bypass For Desired Hardness

0 ppm Hardness

Rinse Water To Disposal

Effluent 75 ppm Hardness

Salt Dissolver or Natural Brine Chlorinator

Water or Brine

Figure II-4 Schematic of an ion-exchanger softener
4. Combination salt-solution, rinse, and backwash water outlet

5. Wash water or backwash inlet usually used to backwash when exchanger is used as filter

6. Controls for flow rates

7. Sampling cocks on soft water outlet, wash water outlet and salt solution inlet

8. Typical under drainage system or support for exchange media

Three important economic considerations in ion exchange softening design are the availability and cost of salt, problems of brine disposal and the amount of iron in the water. Iron when in its trivalent state is easily oxidized to form an iron oxide colloidal suspension. This suspension can clog the pores of the exchange media and gradually reduce its effectiveness to zero. Thus iron-bearing water must be pretreated to remove the trivalent iron, thus increasing the operating and physical costs of the softening facility (Riehl, 1962).

The cost of salt varies from place to place. If natural brine waters are available their concentration should be considered in the cost analysis because they are generally not as effective as prepared solutions. Sea water may be used but must be disinfected first. The disposal of the wasted brine is a difficult problem. If disposed of in a surface water, sufficient dilution must occur to avoid polluting the water and killing marine life. The brine can also be disposed of by deep well injection but care must be taken not to pollute fresh water aquifers.
THE LIME-SODA ASH PROCESS

In the lime-soda ash softening process, unwanted hardness ions are removed by precipitation rather than by substitution as in the ion exchange softening process. The process has several advantages, such as disinfection, reduction in dissolved solids, and simultaneous removal of iron and manganese with hardness.

Cavendish of England is credited with discovering softening by lime in 1766. He added lime to natural water and deposited the carbonates of calcium \((\text{CaCO}_3)\) and magnesium \((\text{MgCO}_3)\). Dr. Thomas Clark of Aberdeen, Scotland built the first large scale plant in 1841. In 1856, Dr. Porter, of London, suggested the use of soda ash to remove non-carbonate hardness.

The first municipal water softening plant in the United States was built in Oberlin, Ohio and there are presently over 600 municipal plants in the United States using lime or lime-soda ash softening (Riehl, 1962).

Softening by the lime-soda ash process removes the divalent alkyline earth cation by precipitation. The major contributors to hardness in natural waters are calcium \((\text{Ca}^{++})\) and magnesium \((\text{Mg}^{++})\). For this reason the lime-soda ash process is based on their precipitation.

Calcium associates itself with the various anions listed in Table II-1. Calcium has a hypothetical affinity for each of the different anions. Listed in decreasing order of affinity, calcium forms these compounds, calcium bicarbonate \((\text{Ca(HCO}_3)_2)\), calcium sulfate \((\text{CaSO}_4)\), calcium chloride \((\text{CaCl}_2)\), calcium nitrate \((\text{Ca(NO}_3)_2)\), and
calcium silicate \((\text{CaSiO}_3)\) (Riehl, 1962). Depending on the individual water supply some or all of these may be present. Compounds containing the bicarbonate \((\text{HCO}_3^-)\) and the carbonate \((\text{CO}_3^{2-})\) radical are classed as carbonate hardness. Sulfate \((\text{SO}_4^{2-})\), chloride \((\text{Cl}^-)\), nitrate \((\text{NO}_3^-)\), and silicate \((\text{SiO}_3^{2-})\) are classed as non-carbonate hardness. Carbonate hardness is removed by calcium hydroxide \((\text{Ca(OH)}_2)\), hydrated lime. Sufficient calcium hydroxide is added to raise the pH to 10.8 (Sawyer, 1968). This converts the bicarbonate form to the carbonate form simultaneously exceeding the solubility of calcium carbonate and precipitating it from solution. This is described by the following equation:

\[
\text{pH 10.8} \\
\text{Ca(HCO}_3\text{)}_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O} \quad \text{(II-3)}
\]

However 17 mg/l as \(\text{CaCO}_3\) will remain in solution due to the slight solubility of \(\text{CaCO}_3\).

The non-carbonate hardness of calcium is removed by precipitating it with sodium carbonate, \((\text{Na}_2\text{CO}_3)\), soda ash. The following reactions describe the precipitation of calcium non-carbonate hardness.

\[
\text{CaSO}_4 + 2\text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}_2\text{SO}_4 \quad \text{(II-4)}
\]
\[
\text{CaCl}_2 + 2\text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl} \quad \text{(II-5)}
\]
\[
\text{Ca(NO}_3\text{)}_2 + 2\text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaNO}_3 \quad \text{(II-6)}
\]
\[
\text{CaSiO}_3 + 2\text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}_2\text{SiO}_3 \quad \text{(II-7)}
\]

Magnesium is the second most abundant hardness-causing cation. Like calcium, it has different hypothetical affinity for the different anions in Table A-1. In order of decreasing affinity, magnesium forms the following compounds such as: magnesium bicarbonate \((\text{Mg(HCO}_3\text{)}_2)\), magnesium sulfate \((\text{MgSO}_4)\), magnesium chloride \((\text{MgCl}_2)\), magnesium nitrate
(Mg(NO₃)₂), magnesium silicate (MgSiO₃) (Riehl, 1962). Magnesium hardness is removed by precipitation as magnesium hydroxide (Mg(OH)₂) at an optimum pH of 10.8 (Sawyer, 1967). Calcium hydroxide is used to raise the pH and provide the hydroxyl ions, (OH⁻).

The removal of magnesium hardness is described by these equations:

\[
\begin{align*}
\text{Mg(HCO}_3\text{)}_2 + 2\text{Ca(OH)}_2 & \rightarrow \text{Mg(OH)}_2 + 2\text{CaCO}_3 + 2\text{H}_2\text{O} \quad (\text{II}-8) \\
\text{MgSO}_4 + \text{Ca(OH)}_2 & \rightarrow \text{Mg(OH)}_2 + \text{CaSO}_4 \quad (\text{II}-9) \\
\text{MgCl}_2 + \text{Ca(OH)}_2 & \rightarrow \text{Mg(OH)}_2 + \text{CaCl}_2 \quad (\text{II}-10) \\
\text{Mg(NO}_3\text{)}_2 + \text{Cu(OH)}_2 & \rightarrow \text{Mg(OH)}_2 + \text{Cu(NO}_3\text{)}_2 \quad (\text{II}-11) \\
\text{MgSiO}_3 + \text{Ca(OH)}_2 & \rightarrow \text{Mg(OH)}_2 + \text{CaSiO}_3 \quad (\text{II}-12)
\end{align*}
\]

When removing magnesium carbonate hardness with calcium hydroxide two precipitates are formed, magnesium hydroxide and calcium carbonate. However, when magnesium non-carbonate hardness is removed with calcium hydroxide, calcium non-carbonate hardness is formed which must be removed as described above.

The calculations for the amount of calcium hydroxide and sodium carbonate required to remove the hardness is based on the analysis of the raw water. It is necessary to know these standard items about the water: free carbon dioxide (CO₂), alkalinity, Mg⁺⁺ concentration, and total hardness. Alkalinity is the total concentration of the concentration of OH⁻, CO₃⁻, and HCO₃⁻ ions expressed in mg/1 as CaCO₃. Total hardness is the divalent ion concentration expressed in mg/1 as CaCO₃. Magnesium ion concentration is expressed in mg/1 as magnesium. The free carbon dioxide is the uncombined carbon dioxide dissolved in the water and is expressed in mg/1 as carbon dioxide.
If the total hardness is greater than the alkalinity, the non-carbonate hardness is the difference between the two. If the alkalinity is greater than the total hardness there is no non-carbonate hardness. Excess lime is the amount used to raise the pH and supersaturate the solution to speed precipitation. Excess lime treatment may be eliminated when a water contains less than 40 mg/l as CaCO₃ magnesium hardness (A.W.W.A., 1969). Excess lime is a matter of economic importance and is different for each individual raw water.

The following scheme can be used to calculate the calcium hydroxide and the sodium carbonate requirements for waters with total hardness greater than the alkalinity (Sawyer, 1967).

**Calcium hydroxide requirement:**

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ + Ca(OH)₂</td>
<td>CO₂ (in mg/l) X 74/44 = Ca(OH)₂ (in mg/l) (II-13)</td>
</tr>
<tr>
<td>Alkalinity + Ca(OH)₂</td>
<td>Alk (in mg/l) X 74/100 = Ca(OH)₂ (in mg/l) (II-14)</td>
</tr>
<tr>
<td>Mg⁺⁺ + Ca(OH)₂</td>
<td>Mg⁺⁺ (in mg/l) X 74/24.3 = Ca(OH)₂ (in mg/l) (II-15)</td>
</tr>
<tr>
<td>Excess</td>
<td>Approximately 37 mg/l = Ca(OH)₂ (in mg/l) (II-16)</td>
</tr>
</tbody>
</table>

**Sodium carbonate requirement:**

\[
NCH = TOTAL - Alkalinity
\]

\[
NCH (in \text{mg/l as CaCO}_3) \times \frac{106}{100} = \text{Na}_2\text{CO}_3 (in \text{mg/l}) \quad (II-18)
\]

It is impossible to reduce the hardness to zero by the lime-soda ash process because of the natural solubilities of magnesium hydroxide and calcium carbonate. The minimum solubility for magnesium hydroxide...
is about 9 mg/l and about 17 mg/l for calcium carbonate. For this reason it is not possible to produce water of hardness less than 25 mg/l. In addition, both magnesium hydroxide and calcium carbonate tend to form supersaturated solutions that do not approach saturation rapidly even in the presence of precipitated material. In practice it is uneconomical to allow sufficient detention time for complete precipitation or complete settling of precipitated material already formed. So from practical consideration, waters softened by the lime-soda ash process usually have a residual hardness between 50 and 80 mg/l as CaCO₃ (Sawyer, 1967).

Dissolved solids should not be confused with hardness. A water can be low in hardness yet high in dissolved solids. For example, a salt (NaCl) solution could have 1000 mg of salt dissolved in one liter of water. The example solution has zero hardness because no divalent cations are present but has 1000 mg/l dissolved solids. This is an important plus for the lime-soda ash softening process as compared to the sodium cycle ion exchange softening. For example, for every pound of lime (CaO) added to water hard with calcium carbonate hardness, 3.5 pounds of precipitate is formed. This same pound of lime removed 2.9 pounds of hardness. This shows dramatically the amount of dissolved solids removed, but it also points out one of the problems associated with lime-soda ash process: the amount of sludge generated by this process creates quite a large disposal problem.

TYPICAL LIME-SODA ASH PLANT

A typical modern installation using the lime-soda ash process is the Claude H. Dyal Water Treatment Plant at Cocoa, Florida. The
plant softens a ground water of 375 mg/l hardness (as CaCO₃) to 85 mg/l effluent hardness. The plant has a capacity of 40 MGD. The plant consists of two 1 MG Eimco Treatment Units, two chemical mixing basins, a recarbonation basin and four filters of 10 MGD each.

The most important part of the complete treatment process is the Eimco Treatment Unit. The treatment unit is an up-flow clarifier with a rapid mixing well in the center. The sludge rakes and rapid mixing turbines rpm may be varied from 5.5 to 7.5 rpm. The maximum flow is 24 MGD giving the unit a one hour detention time.

The chemicals are fed into the center mixing well in the clarifier where they are mixed with the raw water. The lime and soda ash are delivered in the form of water solutions or suspensions. Potato starch, used as a coagulant aid, is injected into the raw water just prior to the raw water entering the mixing well.

The milk of lime solution is prepared in the lime mixing basin. The lime is fed into the basin by two shakers. In the basin it is mixed with sludge water from the sludge thickener by two mixers. The system is capable of supplying over 3000 pounds per hour of unslaked lime. From the lime mixing basin overflow, the suspended solution of lime is pumped on demand to the clarifier. The pumping rate is controlled automatically to supply sufficient lime to keep the pH in the mixing well at 10.1.

The soda ash solution is prepared in a basin similar to the lime. Water with zero hardness is used to dissolve the soda ash. It comes from the plant effluent and is softened by ion exchange. The equipment is capable of preparing over 1200 pounds per hour of dry soda ash. The overflow from the soda ash mixing basin is pumped automatically to the
Figure II-5  An example of a lime-soda ash water softening plant. Schematic of Claude H. Dyal Water Treatment Plant, Cocoa, Florida.
clarifier mixing well in proportion to the raw water flow rate. Pumping rate adjustments may be made by the operator based on the raw water hardness.

After the clarifier is the recarbonation chamber. Fluoridation is accomplished at the influent to the recarbonation chamber. In the recarbonation chamber carbon dioxide is bubbled through the water to raise the pH to approximately 8 and convert the unremoved hardness back to bicarbonates. This stabilizes the water for distribution and prevents precipitation in the filters. The carbon dioxide is provided by underwater combustion of butane and air. Chlorine is added to the recarbonation chamber effluent to control algae growth in the filters.

At the Cocoa plant there are four filters of 10 MGD capacity. These are the mixed media type with an anthracite coal layer over sand. These filters operate at a rate of 5 gallons per minute per square foot. The coal-sand filter media offers greater efficiency, particulate storage and longer runs than conventional all sand rapid sand filters. Under the filters, is a 1.25 million gallon clear well. Additional storage is provided by a 5 million gallon storage tank. Water is pumped from this storage to distribution.

PLANT INSTRUMENTATION

Instrumentation in the plant is used to monitor the processes and assure the most economical use of chemicals. Flow rate of influent water is measured for records and to control the soda ash feed. pH is continuously monitored in the rapid mixing well of the clarifiers, the clarifier effluent, the recarbonation chamber effluent, and the plant.
effluent. The pH in the clarifier mixing well is used to control the feed rate of lime. The pH measured before and after the recarbonation chamber is used to control the carbon dioxide used to stabilize the water. The pH in the plant effluent is to assure the stability of the treated water going to distribution. Hardness is measured electronically at 3 locations: the recarbonation chamber influent and effluent, and the treatment plant effluent. The two hardness measurements before and after the recarbonation chamber are to help control the stabilization process. The unit in the plant effluent is to insure final quality.

Turbidity is measured at the effluent of the clarifier, and before and after the filters and in the plant effluent. These measurements are taken on demand but can be continuously monitored. The Cocoa plant has a central control panel from which the entire operation is controlled. The plant also has provisions for a computer interface so that it could be operated entirely automatically.

The use of this information to improve the process and increase economy required a parametric study of the process and the available information from instrumentation. The operation of a softening plant depends a lot on the operator "feel" for the proper combination of parameters. It is the intent of this paper to provide a means for studying these parameters and improve the understanding of the interaction of all the parameters.
When studying a process, one of the first steps in optimizing the operation of such a process is the attempt to construct a mathematical model. It is often through mathematical models that improvements, growth, and directions are found. In this light the dynamic modeling of water softening may be an important step to understanding the process. The improvement of the economics of the process would certainly be welcomed by the public.

MODEL CHOICE

The main reactive units in the example plant as described in the previous section has the trade name of Eimco. It is a combination mixing basin and up-flow clarifier. Thus the unit is really two units in series: a mixing basin and an up-flow settling chamber which acts like a fluidized filter bed. The completely mixed flow reactor (CMFR) provides a simple and reasonable model for the mixing part of the treatment unit. More complicated models such as the plug-flow model are available for modeling situations such as is found in the up-flow clarifier. But the author feels that the added detail concerning diffusions and eddy convection would add little additional knowledge and greatly increase the difficulty of the modeling. Thus the extension of the CMFR model to include chemical and physical parameters in the
sludge blanket is justified in an effort to use the simplest possible approach with full understanding.

The completely mixed flow reactor is a control volume approach to the flow situation. The application of a mass balance to the CMFR gives the following dynamic mathematical model:

\[ \frac{dC_{mo}}{dt} = Q_i C_{mi} - Q_i C_{mo} - Vr(C_{mo}^n) \]  

(III-1)

Where:

- \( V \) = Tank volume (L³)
- \( C_m \) = Concentration of reacting species of interest (M/L³)
- \( Q \) = Flow rate (L³/T)
- \( r \) = Reaction rate (M/T)
- \( m \) = Subscript denoting species of interest
- \( i \) = Subscript denoting influent
- \( o \) = Subscript denoting effluent
- \( n \) = Order of reaction

(Weber, 1972)

The negative sign on the reaction is used because the removal of the species is desired. It would be more convenient if the reaction rate term was expressed in terms of the influent concentration instead of the effluent concentration. This is necessary for two reasons. The process operates in a feed forward control mode and Waniełista (1971) has found removal rate is dependent on influent concentration. Making this change, equation (III-1) becomes:

\[ \frac{dC_{mo}}{dt} = Q_i C_{mi} - Q_i C_{mo} - Vr(C_{mi}^n) \]  

(III-2)
THERMODYNAMIC APPROACH TO REACTION RATE

The reaction rate term is of unknown order and size. There are two approaches to the term. One approach is to collect data from an existing reactor and determine the rate term by empirical correlation. The other approach is to use the free energy of the reactants and products states to predict reaction direction and rate. The inclusion of the growth rate of precipitate nuclei to a size removable by gravity will give an overall reaction rate term.

The reaction rate term may be obtained from the application of the mass action law. The law of mass action states that the rate of an elementary homogeneous chemical reaction is directly proportional to the product of the reacting species concentrations (more rigorously, activity) (Weber, 1972). Thus, for the stoichiometric equation for two reacting ions:

\[ aA + bB \xrightarrow{\gamma} xAB \]  

(III-3)

Where:

- \( A, B, AB \) = Reacting ions or compounds species
- \( a, b, x \) = Coefficients to balance the stoichiometric equation

The law of mass action written in mathematical form is:

\[ r_m = k_m C_A C_B \]  

(III-4)

Where:

- \( r_m \) = Reaction rate (M/T)
- \( k_m \) = Theoretical reaction rate coefficient (L^3 MT^{-1})
- \( C \) = Concentration of reacting species in equilibrium concentrations (M/L^3)
- \( A, B, m \) = Denotes ion species of interest
The two reacting ions species models are used because each form of hardness is removed by the combination of two ion species to form the precipitate. This also indicates a second order reaction at least as far as the influence of ion concentration is concerned.

It can be shown from stoichiometric relations that (Weber, 1972):

\[
\frac{r_A}{a} = \frac{r_B}{b} = \frac{r_{AB}}{x}
\]  

(III-5)

Where:

- \( r = \) Reaction rate
- \( a, b, x = \) Coefficient of stoichiometric equation
- \( A, B, AB = \) Subscript denoting ion species

This implies that the rate of removal of one species causes a proportional increase or decrease in the rate of generation or removal of another.

Since the CMFR is a well-mixed environment, the concentration of all species of reactants is well distributed or uniform. Thus, concentration is an intensive property of the reactor volume.

This allows us to write:

\[
\frac{r_m}{m} = \frac{dC_m}{dt} = \frac{dC_{mi}}{dt}
\]  

(III-6)

Combining equation (III-6) and (III-4), we can write the law of mass action in differential form.

\[
\frac{dC_{mi}}{dt} = k_m C_i C_{Bi}
\]  

(III-7)

Where:

- \( i = \) Denotes influent
- \( m = \) The species on which the mass equation is written
Expression (III-7) gives the rate at which an ion is being removed and is proportional, by equation (III-5), to the rate at which the precipitate is being formed.

The term \( k_m \) may be determined thermodynamically by (Dickerson, 1970):

\[
k_m = \frac{K}{h} \frac{kT}{\exp(-\Delta G^*/RT)}
\]

(III-8)

Where:

- \( K \) = Transmission coefficient with values between .5 and 1.0
- \( k \) = Boltzmann constant
- \( h \) = Planck constant
- \( T \) = Temperature in degrees Kelvin
- \( \Delta G^* \) = Change in Gibbs free energy between states of the reacting species and intermediate complex state
- \( R \) = Universal gas constant

(Dickerson, 1970)

Some comments about the thermodynamic rate constant are in order. The \( K \) term is the probability that once the reactive complex is formed by collision and the activation energy is exceeded, that the reaction will proceed to the products instead of back to the reactants. The special Gibbs free energy \( \Delta G^* \) is the free energy in the activated state compared to the reactant free energy. Thus the reaction rate could be increased by increasing collisions, that is, increasing concentrations, increasing ionization, increasing activity, increasing temperature, and increasing mechanical agitation of the solution. The reaction rate could also be increased by reducing the activation energy as by the use of a catalysis. The Gibbs free energy difference between the
reactants and the products is the energy available to do useful work. In other words, the Gibbs free energy difference drives the reaction once the activation energy is exceeded. The equation (III-8) would be more useful to the engineer if the equation was expressed in terms of the change in the Gibbs free energy of the reaction and probability term replaced by a term giving the relative efficiency of the reaction compared to the maximum value obtained by using 100% of the free energy available. The efficiency term would contain the effects of probability plus the effects of non-uniform concentrations and other inhibiting factors introduced by a non-ideal solution. The definition of efficiency of the reaction is the ratio of the actual reaction rate to the theoretical reaction rate. Rewriting equation (III-8):

\[ k_m = \frac{-kt}{n} \exp \left(-\frac{\Delta G}{T}\right) \]  

(III-9)

Where:

\[ \overline{n} = \text{Efficiency of the reaction} \]

\[ \Delta G = \text{Gibbs free energy difference between the reactants and products} \]

The rate of growth of the precipitate to a removable size could be postulated by crystal growth. The rate of crystal growth has been investigated by several and correlated to a surface diffusion model by Bennema (1967). Bennema grew crystals of potassium aluminum alum and sodium chloride. The results of his experiment correlate well with the surface diffusion model of Burton, Cabrera, and Frank:

\[ R = C \frac{\sigma^2}{\sigma_1^4} \tanh \frac{\sigma_1}{\sigma} \]  

(III-10)
Where:

\[ R = \text{Growth rate (L/T)} \]
\[ c = \text{Constant of proportionality (L/T)} \]
\[ \sigma = \text{Relative supersaturation (dimensionless)} \]
\[ \sigma_l = \text{Relative supersaturation of surface} \]

(Bennema, 1966)

This could be used as a first approximation to the growth of the precipitate to a settleable size but the constant of proportionality must be determined experimentally. No corresponding work on calcium carbonate or calcite was found which used a quantitative approach. Therefore, it is not possible in a paper of this extent to pursue this method of determining the rate reaction term.

THE REACTOR APPROACH TO THE REACTION RATE

The second approach to the rate term is the empirical correlation of data from an existing reactor. There are two alternatives in this approach. One is to use a batch reactor and measure species concentration as they vary with time and empirically determine the constant, \( k_m \), in the mass action law. The second approach is to take an existing flow reaction and measure important variables of state in the influent and effluent. Steady state is then generally assumed and the rate constant, \( k_m \), determined on the basis of the expected order of the reaction. However, with the aid of a computer, steady state is not a necessary assumption. Applying the numerical technique available on a computer, the accumulation term can be determined and the rate term calculated directly.
THE BATCH REACTOR

The batch reactor approach is possibly the simplest means of arriving at the rate constant for the process or reaction. However, it has the following limitations. If the ion species being monitored to establish the rate constant is reacting to form an insoluble precipitate, its concentration is decreasing as the reaction proceeds. This decreasing transient concentration makes the value difficult to measure. Additionally, the rate of disappearance of the reacting ion may be quite different from the rate of appearance of the precipitate it formed. Furthermore, the ion of interest is not removed until the precipitate particle has grown large and heavy enough to be removed by gravity. This last consideration is difficult to determine in a mixed batch reactor. The batch reactor does not in any way represent the flow situation found in the Eimco treatment unit being modeled.

Considering these shortcomings, the Batch reactor test could give a technical insight into the nature of the removal process. With this understanding, the batch reactor solution is presented for the example reaction given earlier. Starting with the differential equation, (III-7) is written for the precipitate, AB,

\[ \frac{dC_{AB}}{dt} = k_{AB} C_A C_B \]  \hspace{1cm} (III-11)

Let \( C_{A,0} \) and \( C_{B,0} \) represent the concentration in reaction equivalents per liter for the reactants A and B at time equal to zero \( (t = 0) \) respectively. Let \( C_A \) and \( C_B \) be the general concentration of A and B at any time respectively:

\[ C_A = C_{A,0} - C_{AB} \]  \hspace{1cm} (III-12)
\[ C_B = C_{B,0} - C_{AB} \]  

(III-13)

Where:

\[ C_{AB} = \text{The concentration of the precipitate} \]

Substituting the relationships (III-12) and (III-13) into (III-11), differential equation (III-14) is obtained.

\[ \frac{dC_{AB}}{dt} = k_m(C_{A,0} - C_{B,0} - C_{AB}) \]  

(III-14)

For this special case when the initial concentration of \( C_A \) and \( C_B \) are stoichiometrically balanced, then \( C_{A,0} = C_{B,0} \), which is applicable to water softening because every attempt is made to feed the chemicals in correct proportion to the hardness removed. Thus, substituting \( C_0 \) for \( C_{A,0} \) and \( C_{B,0} \) and integrating equation (III-14) the following result is obtained (Weber, 1972).

\[ k_m = \frac{C_{AB}}{t C_0 (C_0 - C_{AB})} \]  

(III-15)

Thus \( k_m \) is the slope of a plot of \( t \) versus the concentration of \( C_0 \) and \( C_{AB} \) in the above relation as determined from the batch reactor. This \( k \) can be returned to the mass action expression and applied to the dynamic model with the aforementioned limitations.

Restating the mass action law for the rate expression in terms of this result with \( C_{A_i} \) substituted for \( C_0 \) is:

\[ r_{AB} = \frac{C_{AB}}{t C_{A_i} (C_{A_i} - C_{AB})} C_A C_B \]  

(III-16)
Rewriting the dynamic equation (III-2) for the CMFR gives this result:

\[ V \frac{dC_{AB}}{dt} = QC_{AB_1} - QC_{AB_o} + V \frac{C_{AB} C_A C_B}{t C_{Ai} (C_{Ai} - C_{AB})} \]  

(III-17)

The positive sign appears on the rate term because the expression is written for the precipitate which is being generated. A similar equation can be written for the reactive ions in the influent. Rigorously, the equation should be written for reactive equalivents, however, with appropriate coefficients, the concentration may be expressed as mg/l or lb/MG as CaCO₃.

DYNAMIC FLOW REACTOR

This model is the closest to the real situation. This approach used the reactor that will be found in the field and uses field operation data to determine its reaction rate.

Restating the dynamic model for the continuously-mixed flow reactor proposed for this analysis gives:

\[ V \frac{dC_o}{dt} = Q_1 C_i - Q_o C_o - VR \]  

(III-18)

Where:

\[ R = r(C_i) \] in previous equations

The reason for the change in the rate term is that \( R \) is a function of many more effects than just concentration and is more easily written. The reaction rate, \( R \), is affected by temperature, flow rate, inlet concentrations, pH, detention time and many other parameters and for this reason it was changed.
To implement this approach equation (III-18) would be written for each water quality parameter of interest. This would require four equations to model a softening process where calcium and magnesium hardness are being removed as $\text{CaCO}_3$ and $\text{Mg(OH)}_2$. In each of these four equations all the terms must be provided or determined from the others. At this point, it is necessary to choose a physical reactor, that is, physical dimensions must be assumed. For this purpose, the Emico treatment units at the Claude H. Dyal Water Treatment Plant, Cocoa, Florida was chosen. This unit has a fixed volume, thus one of the variables in the model is fixed. The flow rate is measured continuously and with the aid of electronic circuitry this information could be digitalized and recorded versus time points. The concentration of hardness ions in the influent and effluent can be measured electronically with the aid of a divalent ion sensitive electrode. Again this information can be digitalized and recorded versus time points with electronic circuitry. The rate of change of effluent quality, $\frac{dC_o}{dt}$, at each sample time point can easily be calculated with aid of numerical techniques on a computer. Thus, with information readily available from the field, the remaining term $R$ can be calculated versus time, i.e., at each sample time point, from equation (III-18). It is the reaction rate term for the entire reactor; that is, it includes the effect due to concentration, mixing, dispersion, temperature, sedimentation, flock size, and all other. It is interesting to note that no assumption of steady state is required.

More information is available than is readily evident to the casual observer. Since all the variables $Q$, $C_o$, $C_i$, $\frac{dC_o}{dt}$, $R$ are
recorded versus sample time points, they are unique to each other for each sample time point. A sample time point is the location in time when each variable is simultaneously measured and recorded. These sets of data are represented in equation (III-19).

\[
\begin{align*}
\text{Measured} & \quad \text{Calculated} \\
(t_1, Q, C_0, C_i, \ldots, dC_0, R) & \quad \frac{dC_0}{dt} \\
(t_2, Q, C_0, C_i, \ldots, \ldots) & \\
(t_3, Q, C_0, C_i, \ldots, \ldots)
\end{align*}
\]

(III-19)

That is, \( R \) could be plotted versus corresponding data such as \( Q, C_0, C_i, \) and \( \frac{dC_0}{dt} \) at each sample time point.

Hypothetical example plots of these time grouped parameters versus the reaction rate are presented in Figure III-1. It is not intended to infer these are straight lines, i.e., first order reaction, but that this type of information is available. It is very probable that \( R \) is a second order relation. Furthermore, pH, temperature, conductivity, turbidity, and stirring RPM can be measured and digitalized in a similar manner. These could also be plotted versus the reaction rate and their effect accounted for. Additionally, the rate term could be plotted versus parameters measured at some future or past time. For example, plot \( R \) at time \( t \) versus \( C_i \) at time \( t - t_D \) where \( t_D \) is the detention time of the treatment basin.

A further use of the parametric plots is to write differential equations from the plots. By means of appropriate bookkeeping and data search by the computer, it should be possible to obtain plots using three variables. Examples of such plots are shown in Figure III-2.
The mathematical statements of Figure III-2a and Figure III-2b in mathematical form are respectively:

\[ \frac{\partial R}{\partial Q} = f_a(C_1) \quad \text{and} \quad \frac{\partial R}{\partial C_1} = f_b(Q) \]  

(III-20)

By the method of composition these can be made into one equation (Wanielista, 1971).

\[ R = f(Q, C_1) \]  

(III-21)

This facilitates the inclusion in the rate term of more than one independent parameter of the system. Using the computer, this technique is quite simple because of the ability to determine the partial numerical derivatives. Plots of the partial derivative versus Q and C_1 may be made to show the functional relationships \( f_a(C_1) \) and \( f_b(Q) \). Once these functional relationships are determined they may be returned to the respective differential equation and these equations numerically integrated. Equating the integrated results and with appropriate algebraic manipulation and substitutions, the functional relation described by equation (III-20) is found (Wanielista, 1971).

Now that the rate term is determined and written in mathematical form, equation (III-20) may be returned to the dynamic model. This model can then be used to predict the effluent quality from the treatment unit.
A single time point calculation of the reaction rate has been made in Appendix B. It is based on an example water of 375 ppm initial hardness and 300 ppm of which is to be removed. This raw water and removal is similar to that found at the Claude H. Dyal Plant. The reaction rate from the dynamic model is compared to the removal rate obtained at that plant. It shows that the reaction rate of the dynamic model and the removal rate at the comparison plant are of the same order of magnitude.

**TABLE III-1**

**COMPARISON OF REMOVAL RATE**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CMFR Model</td>
<td>11100 lb/MG·D</td>
</tr>
<tr>
<td>Plant 100% Ca(^{++})</td>
<td>19300 lb/MG·D</td>
</tr>
<tr>
<td>Plant 60% Ca(^{++})</td>
<td>11600 lb/MG·D</td>
</tr>
</tbody>
</table>

The reaction rate calculated for a single time point is the same order of magnitude as the removal rate found at the Claude H. Dyal Water Treatment Plant.

The steps necessary to implement the dynamic model to any given reactor are:
1. Set up a schedule for the collection of data with consideration given to the sampling frequency to satisfy the continuity requirements in the numerical integration and differentiation techniques used in the computer. For example, sample every few seconds when the plant is expected to undergo a quick transient due to switching wells in the well field or changing pumping rate and alternately sample every few minutes under normal operating conditions.

2. Measure these parameters:
   a) Influent parameters: flow rate, hardness, Ca$^{++}$ ions, temperature, and pH.
   b) Reactor parameters: pH in mixing well, and temperature after the mixing well.
   c) Effluent parameters: hardness, Ca$^{++}$ ion, and turbidity. Turbidity is a measure of the unremoved precipitate and is related to the effluent hardness not removed.
   d) Removed sludge: check on electronic surveillance of hardness removal.

3. Write computer model of the CMFR dynamic model's differential equation to prepare the data field for computer correlation.

4. Use the computer to construct plots to correlate data to determine the proper mathematical form for the reaction rate based on second order or other appropriate reactions.

5. Compare reaction rate to thermodynamic values, plant removal rates and batch reactor results.

The systematic study of the real softening process reactor provided by the synthesis of the dynamic model should enable improvements in plant operation by providing a means to predict effluent quality. In the author's opinion, this model would include effects not accounted for in the thermodynamic, batch reactor, or present hydraulic design procedures. This is true because the removal rate is empirically taken from the field data reactor. The dynamic model could account for eddies and non-uniform mixing not accounted for in the well-mixed, uniform equilibrium conditions used in the thermodynamic development. It pro-
vides a means of modeling the flow situations directly and does not require the application of results from a non-flow situation as in a batch reactor or jar test to a flow reactor.
IV. SUMMARY, CONCLUSIONS
AND RECOMMENDATIONS

SUMMARY AND CONCLUSIONS

Economic studies have shown that water softening is worthwhile. The aesthetic value of good tasting, potable water is appreciated by everyone. The occasional reduction in dissolved solids along with the reduced detergent usage with soft water will help reduce the problems of municipal wastewater treatment. Although softening may not be required to meet public health service water quality criteria, the lime-soda ash process does have good bacteria removal characteristics.

The ion exchange process when used for municipal softening is not as economical as a lime-soda ash process. It does not provide the bacteria removal as does the lime-soda ash process. When softening turbid and iron-rich water, the pretreatment required before ion exchange softening eliminates its simplicity and operational advantages. However, lime-soda ash softening can be accomplished with the same equipment as the turbidity and iron removal. Ion exchange does have the advantages of automatic operation as well as pressure softening units which eliminate double pumping for small, safe well supplies.

The lime-soda ash softening process removes hardness by precipitation of hardness causing ions. The process follows the laws of chemical reactions and thermodynamics until the precipitate is formed. At this point the minute particles coagulate, flocculate, and settle.
Removal is presently based on the settling velocity of the coagulated and flocculated precipitate. Present designs are essentially based on empirical determination from years of trial and error. Systematic parametric study seems a rational alternative to advance the state of the art.

The dynamic time response of a lime-soda ash process was modeled. The continuously mixed flow reactor provided a reasonable model for the combination rapid mixing basin, flocculator, and upflow clarifier. Although the model does not provide for the hydraulics of the settling process it does account for the slow approach to saturation of magnesium hydroxide and calcium carbonate in supersaturated solutions. The mathematical statement of the continuously mixed flow reactor is simple enough to be easily handled by the computer and articulated enough to show details of the parameters of influence.

The classical chemical thermodynamic approach to the problem should predict the rate of formation of the precipitate. Review of the literature on the subject gave several approaches to the problem from collision theory to classical state theory using free energy. This approach has been reviewed in this paper. However, the equation for the determination of the rate of reaction requires the experimental determination of one of the terms. It is therefore concluded by the author that this approach could give no real solution to the numerical problem except for an order of magnitude feeling. The rate of growth of precipitate nuclei by the crystal growth mechanism was found to be substantiated in the literature for a surface diffusion model. However, no work was found on the growth rate of calcium carbonate of magnesium hydroxide, which simply implies the need for further research.
The second approach is the one widely used in chemical engineering: the use of a batch reactor to measure the reaction rate. This process has some shortcomings. The batch reactor in either the stirred or quiescent form is obviously not a flow situation. It is not possible by this method to account for the flow disturbances and diffusion found in a flow reactor. Difficulties arise in the monitoring of the process due to the desire to measure the removal rate by precipitation and settling as opposed to just the reaction rate. Good estimates of removal, chemical requirements and optimum precipitation conditions can be obtained. However, it would be difficult to accurately predict the removal rates of flow situations from the results of the batch reactor tests.

The third approach is the author's attempt to eliminate some of the ambiguities found in the two previous enlightened approaches. The supposition that the dynamic time-varying model for the continuously mixed stirred reactor does describe the combination up-flow clarifier and rapid mixing basin is similar to the "black box" approach to finding out what is in an electric circuit. The model is applied to input and output data from the reactor and the effect of the reactor is determined. The approach allows the detailed study of each measurable parameter such as: pH, temperature, concentration, etc.

The investigation for the development of a model begins with an existing reactor, in this case, the water softening units at the Claude H. Dyal Treatment Plant. Field data is recorded on a time point basis. That is, the parameters of the system are placed in a unique position based on their time of collection. The parametric studies of the data are made with the aid of the computer. These
parametric plots represent functional relationships between independent parameters and the dependent variable, removal rate of hardness. Several of these parametric plots could be made into one mathematical relationship using optimization, regression and composition techniques. The final result would be a mathematical model of the up-flow clarifier softening unit which could be used to predict effluent quality for a given set of influent quality and quantity data.

The rate of removal of calcium hardness for an existing plant was compared to the reaction rate for the dynamic model. The reaction rate and removal rate were of the same order to magnitude. Therefore, it may be concluded that the approach has considerable merit.

RECOMMENDATIONS

It is recommended that data be recorded from the Claude H. Dyal Treatment Plant to construct a mathematical model for the dynamic time responses of the hardness removal process. The data should be gathered in sufficient frequency to insure continuity for differentiation and integration by the computer. This can be accomplished by consulting continuity requirements of the numerical method used by the computer. Parameters that should be measured in the raw water are: flow rate, hardness, $\text{Ca}^{++}$ ion, temperature and pH. Parameters that should be measured in the clarifier are: pH in the mixing well, temperature after the mixing well. Clarifier effluent parameter which should be measured are: hardness, $\text{Ca}^{++}$ ion, and turbidity. The monitoring of sludge removal and density could be a valuable check on removal rate. The quantity and strength of the process chemical
must also be known.

A thorough understanding of the thermodynamics of chemical reaction in solutions is necessary. Further, research into the growth of crystal nuclei especially for calcium carbonate and magnesium hydroxide is warranted. Possibly microscopic examination of precipitates and floccs found in the sludge would be beneficial to an understanding of their growth. This information coupled with existing literature on flocculation and coagulation should be compared to results obtained by the dynamic modeling.

A review of reactor manufacturer's literature is suggested to see how they predict their removal rates and how these compared to the results obtained from the dynamic modeling.

The overall objective of the paper was to propose a new analytical tool for the evaluation and operation of water softening plants. It is the belief of the author that the methodology may have application to other flow processes and provide improved economics in the operation of water softening plants.
APPENDIX A

CALCULATIONS OF HOME SOFTENING COSTS

Assumptions:

Water Consumption
50 gal/person/day

Salt Cost
4¢/lb salt

Efficiency of Regeneration
101 lb salt gives 80% regeneration of 50,000 grains

Cost of Purchase:

REF: Montgomery Ward Mail Order Catalog

24,000 grains capacity unit cost $275.00 and has 10 year service life

Using straight depreciation @ $27.50 per year:

Family of 3 X 50 gal/person/day = 150 gal/day
150 gal/day X 15 grains = 2250 grains/day
80% X \( \frac{24,000}{2250} \) = 8.5 days per regeneration

365 days/year/ 8.5 day/regeneration = 43 regeneration/year

5 lb salt gives 80% regeneration
43 regeneration/year X 5 lb = 215 lb/year
215 lb/year X .04 $/lb = $8.60 per year
$36.10 per year

Purchase cost $/year/person: Family of 3 = $12.03 per year
Cost of Renting:

REF: Culligan Water Softening, salesman Larry Morgan, February 26, 1973

Rental Cost: $8.00  First tank of month
            $5.00  Second and successive tanks per month

Tank has 40,000 grains capacity
2250 grains/day/family of 3
\[
\frac{40,000}{2250} = 17.8 \text{ day/tank}
\]
\[
365 \text{ day/year/} 17.5 \text{ day/tank} = 20 \text{ tank/year}
\]

Assume: 12 tanks at $8.00 $96.00
7 tanks at $5.00 35.00

\[
$131.00/\text{year/family}
\]

Rental Cost $/year/person:
family of 3 = $43.60/year/person
APPENDIX B

The estimation of the reaction rate (R) for the dynamic completely mixed flow reactor is as follows. This estimate is necessary as a first approximation of "R" in dynamic modeling. The analysis of the water used in the estimation is given in the bar diagram below.

<table>
<thead>
<tr>
<th>TOTAL HARDNESS</th>
<th>375 mg/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>REMOVAL</td>
<td>300 mg/l</td>
</tr>
<tr>
<td>ALK</td>
<td>250 mg/l</td>
</tr>
<tr>
<td>Ca++</td>
<td>225 mg/l</td>
</tr>
</tbody>
</table>

(Concentrations in mg/l as CaCO₃)

The example water has a total hardness of 375 mg/l of which 300 mg/l will be removed. Zero carbon dioxide concentration is used to simplify the example. Two methods of doing the calculations are given. The first method is the one presented in Chapter II.

Lime Requirement (Ca(OH)₂)

\[
\text{ALK} \quad 250 \text{ mg/l} \times \frac{74}{100} = 185 \text{ mg/l or 1540 lb/MG}
\]

\[
75 \text{ mg/l Mg}^{++} \text{ as } \text{CaCO}_3 = 18.2 \text{ mg/l as Mg}^{++}
\]

\[
\text{Mg}^{++} \quad 18.2 \times \frac{74}{24.3} = 55 \text{ mg/l or 460 lb/MG}
\]

EXCESS 1 reaction equivalent = 37 mg/l or 310 lb/MG

TOTAL Ca(OH)₂ 277 mg/l or 2370 lb/MG
Soda Ash Requirement \((\text{Na}_2\text{CO}_3)\)

\[
\text{NCH} \ 50 \text{ mg/1} \times \frac{106}{100} = 53 \text{ mg/1} \text{ or } 441 \text{ lb/MG}
\]

Based on these calculations, the chemicals required to treat this water to 75 mg/1 hardness would be 2370 lb/MG lime and 441 lb/MG of soda ash. The 1.0 milli-equivalent of excess lime is added to raise the pH to the level of minimum solubility of the precipitating compounds and to supersaturate the solution. This excess can be removed by recarbonation.

An alternate method of calculating chemical requirements are as follows:

**Lime Requirements**

<table>
<thead>
<tr>
<th>Carbonate</th>
<th>Calcium Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ca}^{++}) = 4.5 mg/1</td>
<td>Requires 4.5 mg/1 (\text{Ca(OH)}_2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbonate</th>
<th>Magnesium Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Mg}^{++}) = .5 mg/1</td>
<td>Requires 1.0 mg/1 (\text{Ca(OH)}_2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Noncarbonate</th>
<th>Magnesium Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NCH} = 1.0 \text{ mg/1} )</td>
<td>Requires 1.0 mg/1 (\text{Ca(OH)}_2)</td>
</tr>
</tbody>
</table>

**EXCESS**

\[1.0 \text{ mg/1}\]

**TOTAL**

\[7.5 \text{ mg/1 as } \text{Ca(OH)}_2\]

\[
7.5 \text{ mg/1} \times 37 \text{ mg/meg} = 277 \text{ mg/1} \text{ or } 2370 \text{ lb/MG}
\]

**Soda Ash Requirements**

<table>
<thead>
<tr>
<th>Noncarbonate</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NCH} = 1.0 \text{ mg/1} )</td>
<td>Requires 1.0 mg/1 (\text{Na}_2\text{CO}_3)</td>
</tr>
</tbody>
</table>

\[1.0 \text{ mg/1} \times 53 \text{ mg/meg} = 53 \text{ mg/1} \text{ Na}_2\text{CO}_3 \text{ or } 441 \text{ lb/MG}\]
The effluent calcium concentration is estimated to be 49 mg/l as CaCO$_3$. This is based on 75 mg/l residual hardness in the effluent and the concentrations of Ca$^{++}$ and Mg$^{++}$ being proportional to their solubility in precipitate forms. The effluent calcium concentration in terms of Ca$^{++}$ instead of CaCO$_3$ is 20 mg/l calcium or 167 lb/MG.

From the example raw water, the calcium in the influent is 90 mg/l or 750 lb/MG with an additional amount of 277 mg/l or 2370 lb/MG due to the lime for precipitation. The rate of change of effluent concentration $\frac{dC_o}{dt}$ can be determined from field data. For this illustration, it is assumed to be 3 mg/l/hr or 600 lb/MGD. The clarifier unit has a volume of 1.0 MGD and the flow, $Q$, is 20 MGD. It is assumed that .75% of $Q$ or .15 MGD is drawn off with the sludge. For example, all this data would be known at each sample time point.

Solving the dynamic model, equation (III-18), for the reaction rate and substituting in the appropriate values:

$$ R = \frac{Q_i C_i}{V} - \frac{Q_o C_o}{V} - \frac{dC_o}{dt} $$

$$ R = \frac{20 \text{ MG/D} \times 750 \text{ lb/MG}}{1 \text{ MG}} - \frac{19.85 \text{ MG/D} \times 167 \text{ lb/MG}}{1 \text{ MG}} - 600 \text{ lb/MG.D} $$

$$ R = 15000 - 3300 - 600 (\text{lb/MG.D}) $$

$$ R = 11,100 \text{ lb/MG.D} $$

This is the reaction rate given by the dynamic model for this example time point.

It is important to see if the dynamic model is comparable to the existing removal rate for a given plant. The removal at the Claude H. Dyal plant reduces the hardness from 375 mg/l to 85 mg/l. Since we do not know the analysis of the raw water being treated, assume that
the hardness is 100% calcium hardness. The conversion of hardness to Ca\(^{++}\) ion is as follows:

INFLUENT \(375 \text{ mg/1 as CaCO}_3 \times \frac{40}{100} \times 8.34 = 1250 \text{ lb/MG}\)

EFFLUENT \(85 \text{ mg/1 as CaCO}_3 \times \frac{40}{100} \times 8.34 = \frac{284 \text{ lb/MG}}{966 \text{ lb/MG}}\)

The detention time is .05 day because the flow is 20 MGD and the reaction unit volume is 1 MG. The removal rate is the quantity removed divided by the detention time, thus:

Removal rate of plant = \(R_p = \frac{19300 \text{ lb/MG·D of Ca}^{++}}{0.05 \text{ day}}\)

However, if only 60% of the raw water hardness was due to calcium, the removal would be reduced by approximately the same amount. Thus, the plant removal rate for calcium for a water similar to the above example is:

Removal rate of plant = \(R_p = \frac{11600 \text{ lb/MG·D of Ca}^{++}}{0.05 \text{ day}}\)

By comparing these removal rates to the reaction rate for the dynamic model determined above, it is easily seen that they are of the same order of magnitude as desired, because the sample calculation water had approximately 60% calcium hardness.
LIST OF REFERENCES


Weber, Walter J. *Physicochemical Processes for Water Quality Control*