CHAPTER XVIII

Softening

Until the middle of the nineteenth century the chief objective of water purification was clarification. When softening was introduced it made little headway until well into the twentieth century. Once accepted, it forged ahead but in the early 1940's only one water works used softening out of every dozen that could employ it advantageously. The belated introduction of softening was not due to lack of knowledge of its possible benefits nor to ignorance of its underlying principles.* In effect if not in name it had been practiced on a small scale by rule of thumb for ages—ever since soap came into use. Potency of certain wood ashes and of earthy alkaline salts to make hard waters soft was noted by several eminent scientists during the century preceding the announcement in 1841 of what became the well-known Clark process. Most of the writers who have sketched the history of softening prior to Clark's patent have singled out Cavendish of the 1760's and Henry of the 1780's, neither of whom was primarily concerned with softening, and have overlooked Home and Rutty, of the 1750's, whose researches in this field entitle them to high standing as pioneers. Clark's lime process and its subsequent modifications, with important mechanical improvements, have been used for a century, but since 1925 have had a rival of ever-increasing importance—zeolite or base exchange.

More than two hundred years ago, Dr. Peter Shaw (1) stated, in one of his London chemical lectures of the early 1730's, that hard water becomes softer on adding to it alkaline salts.

In a classic treatise on bleaching, published in Edinburgh in 1756, Dr. Francis Home (2) described 129 experiments made by him, of which the objective of 45 was how to soften water. These tests ran from June 15 to the end of an unstated year, presumably 1755.

* This was well expressed by Baylis in notes sent to the author in 1936: "There is no reason why chemists in the latter part of the eighteenth century could not have softened public water supplies by chemical precipitation, for it appears that they understood all of the reactions involved." To which I add that although soft water was considered desirable and was sought after, particularly for industrial use, there was no insistent public demand for softening such hard waters as were being supplied to municipalities.—*M.N.B.*

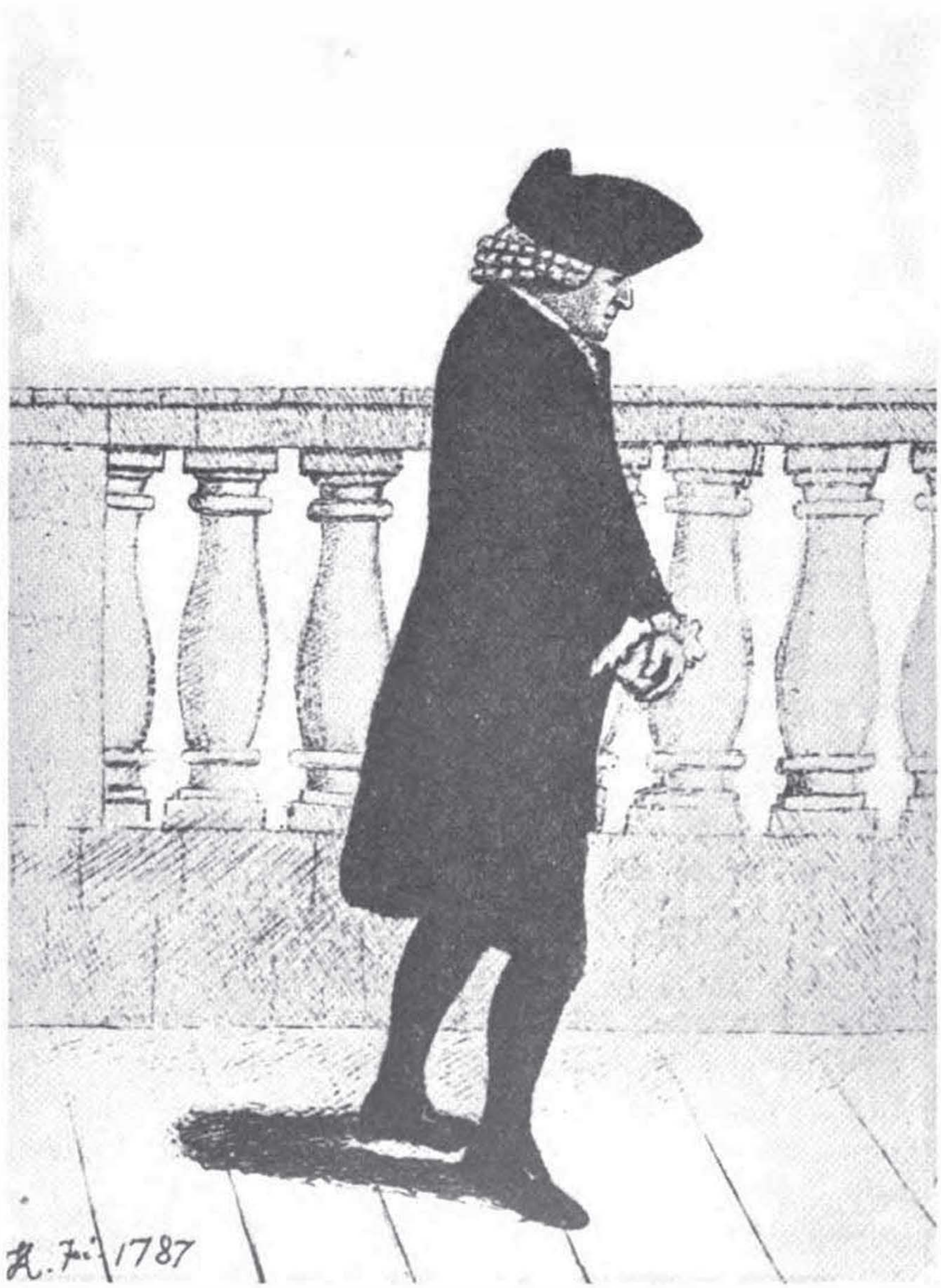

FIG. 73. DR. FRANCIS HOME OF EDINBURGH
Made earliest detailed experiments on water softening in the 1750's
(From portrait in John Kay's *A Series of Original Portraits and Caricature Etchings*, Edinburgh, 1838)

Home's method was, first, to learn what made waters hard, then to search for what could best soften them. His main standard was the soap curdling point. Of eleven hardening agents tried, he found that "the soluble part of lime" stood first, at a "soap curdling point" of 45. Then came a sharp drop to 18, for oil of vitriol, and a steady decline as follows: spirit of sea salt, 15; salt of amber, 10; spirit of nitre, 9; blue vitriol, 7; sugar of lead, 5; salt of steel, 4½; alum, 4; epsom salt, 3; cream of tartar, 1½. He ranked the softening powers of the following salts thus: fixed alkaline salts, though not of the strongest kind, 2; volatile salt of hartshorn, 1. He added: "Filtration through sand softens in proportion to the length of its course. Putrefaction softens in proportion to its degree." Summarizing, Dr. Home (2) stated:

This method which we have discovered of softening hard waters, is easy, expeditious, and cheap; qualities absolutely necessary to render it useful to the public. It is easy, as the most ignorant can do it; expeditious, as it becomes fit for all family-uses immediately, and for drinking in half an hour; and cheap, as the material costs but a mere trifle; nay, may be prepared by any person. By this change, the hard water not only becomes fit for all the common uses of life, but as beneficial as it was before hurtful to the health of man. . . . I may venture to affirm, that no other material can ever be found capable of softening hard water: and tho' one was discovered endued with the same property, it could not be of the same use to mankind, as there is none, alkaline salts excepted, to be had every where. A particular substance or plant was only to be found in particular places, but this material is to be got where-ever plants grow. So kind is the general parent of nature, that he has provided a remedy, every where to be found, for so common an evil; but, at the same time, has left the discovery to our own industry.

How much we stood in need of such a discovery, most great towns, especially those on the sea-coast, nay the greatest part of some counties, can testify. *Newcastle* is a remarkable instance of this distress. In all the pants [*sic*] or pipes there, two excepted, the water is hard; and to such a degree, that it is three times more so than the hard water which I have examined.*

Two years after the appearance of Home's book, Dr. John Rutty (3) published his large work, *A Methodical Synopsis of Mineral Waters,* which opened with a section on "common water." His first two chapters dealt with "distinguishing characters, effects and uses" of soft and of hard spring waters. They were prefaced by 38 pages of tabular data on various hard and soft waters, including "Experiments

*Dr. Home here states that since "these papers were in press" he had found "that Dr. Shaw, in his chymical discourses, has given an imperfect hint of this quality of alkaline salts, but does not inform us of the manner of doing [utilizing] it, or reasons on which it depends, or qualities of the water after it is softened" (1).

in Concert" on 38 springs of hard water in Dublin. These tables gave for each water: hydrometric readings; taste; reactions to soap, solutions of silver, lead and alum, lime water, acids, milk, flesh, syrup of violets, galls, sumach, logwood, rhubarb, ash-bark, and cale; also "contents in grains per gallon"; quality of contents (marine and other salts); and effect on bowels of human beings; besides various reaction-tests of residues on evaporation. This was certainly a remarkable exhibition of the qualities of hard and soft waters.

After noting that, without due regard to the natures of different waters, "we could not but at random be supplied with gruel, puddings and even a smooth mixture of milk and water," Dr. Rutty (3) added:

> It is of great importance in building a town to chuse a proper situation with regard to the quality of springs: Our common spring-waters, if not immoderately hard, will become soft by standing a few days; such are those at Henley, and divers others, whose waters by being exposed two days, become soft and fit to wash with; but the situation of Thame (Plot's *Nat. Hist. of Oxfordshire*) in the same county, is much worse, for there waters will not grow soft by standing two days, as the others.
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> The sacred records (2 Kings ii. 19) mention a city, the situation of which was pleasant, but the springs naught, and the land barren; which waters were not amended but at the expence of a miracle; tho' it is observable, that this was not wrought without means, viz. by salt put into a new cruse, and cast into the spring of the waters by the prophet, whereby they were healed.
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> And indeed, in the natural way, one method of softening hard water is by means of an alcaline salt, e.g. by putting into it, in a bag, the ashes of green ash or beech burnt to a whiteness; an experiment not only very useful, but illustrative of the nature of the mineral matter impregnating hard waters, viz. as being an acid united to a terrestrial matter.

Although sometimes mentioned as one of the earliest "discoveries" in water softening, that was not the object of the experiments on Rathbone Place (London) pump water made by Cavendish in September 1765 and published in 1767 (4). His experiments were made chiefly to learn why calcareous earth remained suspended in water. His main conclusion was that "the unneutralized earth, in all waters, is suspended by being united to more than its natural proportion of fixed air." The "unneutralized earth," he found, was "entirely precipitated" from Rathbone Place and other London pump water "by the addition of a proper quantity of lime water," and the exposure of the water so treated long enough "for all the lime to be precipitated." This, in effect, had been noted previously by Doctors Shaw, Home and Rutty.

The last of the eighteenth century "discoverers" of the potency of lime to soften water was Thomas Henry, in or about 1781. He opened a paper (5) on preserving sea water from putrefaction with this significant statement: "It has been frequently remarked by chemical and philosophical writers, that a new experiment is seldom made in vain. Though the operator may even fail of attaining immediate object of his pursuit, he may yet, fortuitously, acquire the knowledge of some new fact, which may be productive of improvement and advantage to science." The object of the experiment thus introduced was an appeal from "a Gentleman who had obtained a quantity of sea water, for the purpose of bathing a child, asking me to think of some expedient" to keep the water from becoming putrid. This was about the time that Henry had published a description of his method of preserving fresh water from putrefaction at sea (6).

Summing up his thirteen experiments, Henry said "It appears that quicklime, dissolved in water, precipitates the magnesian earth from the marine acid, with which it is united in the sea water, and uniting with that acid, is retained in the water, under the form of a marine selenite. What the water loses, therefore, of one salt, it gains of another. At the same time, the magnesia, being precipitated by a caustic calcareous earth, falls in a state similar to that to which it is reduced by calcination, viz. void of fixed air. In this state, I have formerly proved, by a train of experiments, that it is strongly antiseptic." (Henry's *Experiments and Observations,* p. 58.)

At Black Rock, near Cork, Ireland, water was softened by means of potash of soda, in or before 1818. This was done on the suggestion of Edmund Davy, Professor of Chemistry at Cork Institution. Later, he made experiments showing that the water of limestone districts could be softened with potash of soda or by boiling for twenty minutes (7). No earlier instance of softening water for public use has been found.

Softening, and the characteristics, advantages, disadvantages and particular uses for both hard and soft water, are given considerable space in a unique little treatise of 1830 on the properties of water by Abraham Booth, styled "Operative Chymist, Lecturer on Chymistry, Pharmacy, etc." (8). "Simple boiling," he notes, will soften waters "whose hardness consists of the carbonates of lime and magnesia . . . for as the carbonic acid is expelled . . . the earth subsides," but this "will not remove sulphate of lime, and, as this is almost constantly present in water, boiling is but a partial mode of purification. . . .

All the earthy salts which oppose the solution of soap may be decomposed by the addition of an alkali . . . the ashes of fern or wormwood, which contain a good deal of carbonate of potash, are often used for softening hard water for the purpose of washing."

Clark's Softening and Purifying Process

In 1841, Thomas Clark, Professor of Chemistry in Aberdeen University, Scotland, announced to an unready and, for a long time, an indifferent world his method of not only softening but also otherwise purifying public water supplies. In time, it came into use. He did not claim to remove permanent hardness. This was achieved later by the use of soda or by soda and lime. Mechanical improvements were provided by inventors and manufacturers. All the early plants using the Clark lime process were designed by Samuel Collett Homersham. It has been generally overlooked that Clark originated what much later became known as the excess-lime method, both for softening and purification, claiming destruction of "insects" long before the germ theory of the spread of certain diseases was accepted. Homersham's plants employed an excess of lime.

On March 8, 1841, Clark was granted a British patent on "A New Mode of Rendering Certain Waters (including the Thames) Less Impure and Less Hard, for the Supply and Use of Manufactories, Villages, Towns and Cities." His claim that the process would render waters less impure as well as less hard was elaborated by Clark in a pamphlet of 1841 (9) and the importance of purification was emphasized in a paper read in 1856 (10). In the pamphlet Clark said that, besides softening, his process would separate vegetable and coloring matter, "destroy water insects" and convert water from the Thames into a better supply for London than the new supply projected by Thomas Telford. In the paper of 1856 he declared that: "Freedom from organic matter is of still more importance than freedom from hardness. It seems a fact well established by observation, that some of the poisons producing epidemic disease find a congenial habitat in waters contaminated with organic matter."

Clark's patent covered the use of lime as a precipitant, followed by subsidence or by subsidence and filtration. "It is a triumph of chemical over mechanical art," Clark wrote in 1841, "that, by adding chalk, water would be freed from chalk, itself the largest impurity" in the London supply. Concerning other processes for softening water Clark said that boiling and distillation were impracticable while "carbonate of soda," which "on a small scale is used to prepare water for washing," would cost the London water companies £1,000 a day against £10 for lime (9).

In testimony given on June 3, 1843, before the Commissioners on the State of Large Towns, Clark described his process and deplored the indifference to it shown by the London water companies (12). In 1851, he repeated the testimony before a Commission on Water Supply to the Metropolis. This commission was composed of three men, filling chairs of chemistry in as many London colleges, all Fellows of the Royal Society. In their report (11), the commissioners stated that the Clark process was limited to the precipitation of carbonate of lime, "with a portion of the organic and colouring matter," by means of caustic lime. The commissioners had first seen the operation of the process at the Mayfield Print Works near Manchester. There 0.3 mil.gal. (Imp.) of water treated "daily at a trifling expense and with little trouble, but more for discolouration [decoloration] than softening." The water thus treated was passed through sand filters.*

The chemical commission made experiments on water then being supplied London from the New River and the Thames. These were followed by observations of a large-scale trial of the Clark process at the works of the Chelsea Co., London, directed by James Simpson Jr., Resident Engineer. The Chelsea tests and the operations at the Mayfield Print Works led the commission of chemists to conclude that the Clark process was practicable. It also was of the opinion "that no sufficient grounds exist for believing that the mineral contents of the water supplied to London are injurious to health." The General Board of Health, to whom the chemists reported, showed more concern over the hardness of the London water supply than over its pollution. It advised the use of Clark's process until a supply of naturally soft water could be obtained.

The Clark Scale of Hardness.—In a paper read May 14, 1856, Clark stated that: *"Each degree of hardness is as much as a grain of chalk, or the lime or the calcium in a grain of chalk, would produce in a gallon*

* Apparently these observations were made late in 1850. The Mayfield works seem to have been the same as "Hoyle's works at Manchester," regarding which S. C. Homersham testified in 1868. At these works, he said, he first saw the Clark process in use. These cloth printers used "fine spring water." After it had become "discoloured in some of their processes" they added lime to the water and filtered it to make it "clear enough for some of their rougher processes."

[Imp.] *of water, by whatever means dissolved."* [Italics in original] (10).

In his paper of 1856 Clark stated that the first installation of his process for municipal supply was at Plumstead where a plant had been in "successful operation for the last year-and-half" and that "Mr. Homersham is the engineer who planned these works with success." Clark might have added that Homersham consulted him. This plant, completed at the close of 1854, was the first softening plant for municipal supply in the world. Others followed slowly elsewhere in England: 1861, 1868 and 1870. All these and also plants for a castle and a hospital, states Humber, were designed by Homersham (13). All treated "spring or well water. None used filters. None attempted to remove permanent hardness."

The plant of 1854 was built by the Plumstead, Woolwich & Charlton Consumers' Water Co. to compete with the Kent Waterworks Co. operating in parts of the London metropolitan area. Both companies supplied water from wells in the chalk. Despite its softened water, the Plumstead Co. became bankrupt and was absorbed by the Kent Co. which immediately abandoned the softening plant. The Kent Co. claimed that the plant was a failure. Homersham, who designed it, testified before the Royal Commission on Water Supply in March 1868 that the Kent Co. did not operate the softening plant an hour and abandoned it for fear of a demand to provide softened water throughout its whole water supply area (14).

In his testimony, Homersham stated that in the Plumstead plant cream of lime was used as the reagent, instead of milk of lime, as used at later plants (14). Lime and water were passed through three agitators in succession, each consisting of "a pipe enlarged for a short distance, and four plates with small holes" in them. The mixture then went to a catch basin or grit chamber, then to another agitator and finally to a "depositing reservoir." The ratio of cream of lime water to the untreated water was 1 to 8 or 1 to 9. There were open depositing reservoirs, each holding about 0.22 mgd. (Imp.), each filled in about 3½ hr. and emptied in succession, the cycle taking about 10 hr. From the settling reservoirs it was lifted 160 ft. to a service reservoir on Plumstead Common. The nominal capacity of the softening plant was 0.6 mgd. (Imp.) but before its abandonment in 1861 it was worked at 1 mgd. (Imp.) in summer. The "whiting" or lime sludge was sold in its wet state to bristle manufacturers at 7 shillings a long ton (14).

The next Clark plants for municipal supply were built in 1861 by the Caterham Spring Water Co. to supply Caterham and vicinity, in 1868 by the Chiltern Hill Water Co., and in 1870 by the Canterbury Gas & Water Co. The last, says Humber (13), treated water from "boreholes" 490 ft. deep. Lime water was run into one of two reservoirs until it was 20 in. deep, then raw water was delivered through eight nozzles until the 15-ft. level was reached. From five to ten hours was allowed for sedimentation. The rated capacity of the plant was 1.44 mgd. (Imp.) but the consumption was far less.

The Colne Valley Water Co. included a Clark-process plant in works put into use in 1873 to supply suburbs of London from wells in the chalk. With enlargements this plant was used until 1925 when lack of room and difficulty of chalk disposal led to building a zeolite base-exchange plant with a capacity of 3 mgd. (U.S.). To this was added 5.4 mgd. capacity in 1932 (15).

The cases for and against water softening were reviewed by the Royal Commission on Water Supply in its report of 1869 (14). After summarizing the data given in the report of the Chemical Commission of 1851 (11) and the testimony given by a galaxy of witnesses at its own hearings, the Royal Commission concluded that "there is no doubt . . . as to the advantage of soft over hard water for washing and, with some few important exceptions, for general manufacturing purposes." Softening would be advisable for towns in the manufacturing districts, but in the metropolis there were no large demands for soft water to be used in manufacturing. The commissioners did not think that the advantages of soft water for the London district would "justify going to a great distance to obtain it, in place of the ample supply nearer at hand."

As to applying the Clark process to the metropolitan supply, the Royal Commission said that, apart from the great expense entailed, "it does not appear to be applicable to the Thames waters on a large scale. It appears more suitable for small districts supplied from chalk wells, or for use in manufactories where soft water is specially required." In reaching this conclusion, the commission seems to have been largely influenced by the testimony of Homersham, engineer for the only municipal softening plants built up to the date of the report, all of which were treating water from wells and none of which used filters. The commission may also have been much impressed by a doubting chemist who testified before it on February 28, 1868. He was Professor Edward Frankland, then examiner of metropolitan water supplies and for years one of the highest authorities on the chemistry of water. Asked for his opinion of the Clark process, Frankland said: "It is a beautiful process and a comparatively simple process, but I believe that it never could be carried out for softening such vast volumes of water as are required for the supply of London." Little did he dream of achievements to come when chemists and engineers joined hands in softening immense volumes of water—but that was decades later and in the United States. In justice to Frankland, it should be noted that six years later, as member of the Rivers Pollution Commission, he signed a report containing an estimate that £600,000 would cover the cost of softening 100 mgd. (Imp.) for the London metropolitan area by the Clark process and expressing the belief that the process was practicable for use wherever softening was needed.

"The Alleged Influence of the Hardness of Water on Health" was given eighteen pages in the Sixth Report of the Rivers' Pollution Commission, dated 1874 (16). The commission went so far as to gather general death rates for over 200 British cities and towns. These were classified by relative hardness of the corresponding water supplies and by various environmental conditions. The commission concluded that neither hardness nor softness of the water consumed affected the general death rate. This is not to be wondered at in view of the fact that the average death rate of the towns investigated, outside London, ranged from 24 (Liverpool) to 17 (Isle of Wight) with only twenty towns below 20 per 1,000. For the London metropolitan district the showing was worse: a general death rate of 24.6.

After tests of the Clark process on samples of water from the Thames, the Lee and deep wells supplied in 1870–71 by three of the London water companies, the Rivers Pollution Commission (16) concluded that "Clark's method is equally efficacious in softening all three kinds of water." It also removed "a considerable proportion of organic impurities carried by the Thames and Lee, as indicated by organic carbon and organic nitrogen" (16). Although the commission did not think hard waters detrimental to health, it strongly favored the use of "this simple and inexpensive process" of softening because of the vast saving of soap it would effect. It listed 87 British towns, including London, where softening could be used advantageously, giving the hardness of their supplies and the reductions that might be effected by softening (16).

Despite Clark's hope of 1841 that his process would be adopted by the London water companies and the favorable opinion of the process expressed by inquiring commissions, none of the companies adopted that or any other water softening process; nor has the Metropolitan Water Board done so since taking over the works in 1905. Thanks to various methods of water conservation and treatment, the vast population of the Metropolitan Water District is still supplied from the Thames and other old sources of supply.

Other British Patents

For over 40 years after 1841, the date of Clark's patent, his process held the field. This was less a tribute to Clark than proof of indifference to water softening.* There was no lack of other patents meanwhile.

In an article on softening published early in 1885, Baldwin Latham, British sanitary engineer (18), said that "as any of the alkaline earths may be used instead of, or in addition to, lime it is not surprising that, since the date of Clark's patent, numerous patents have been taken out for softening and purifying water in which lime, in combination with other alkaline earths, have been proposed." Latham mentioned about 35 British patents. First on his list of those issued up to the close of 1883 was one granted to John Horsley on April 26, 1849.†

Horsley named as reagents, "calcined or caustic barytes, phosphate of soda, oxalic acid, or one of the various preparations of those substances." In a promotion pamphlet of 1849, Horsley said that Clark's process was incomplete because it left sulfates and muriates in solution whereas by using "a solution of baryta," sulfates as well as carbonates would be extracted. Horsley stated that "there is more than enough evidence to prove that earthy or calcareous matter held in

* A popular exposition of the disadvantage of hard water and the consequent cost to Londoners appeared in the *Ladies Companion* (London) in 1850 and was reprinted in the first number of *Harper's Magazine* (New York). This was perhaps the first attempt to inform the general reading public of England and America on the evils and costs of hard water. It made little impression on either side the Atlantic (17).

† Latham's paper gave a comprehensive review of water softening up to the close of 1884, including a summary of ancient practices. It dealt, as no one else seems to have done, with the use of soap as a softening agent through the centuries, and emphasized its wastefulness compared with the far less costly modern processes of softening.

solution is the true matrix of the animalculae, ova, or germs," and that by his process "the germs are at once liberated and instantaneously destroyed, as has been experimentally determined." This went beyond Clark's claim of destruction of "water insects." No evidence of a plant following Horsley's patent has been found.

John Henderson Porter, a London civil engineer, made mechanical improvements in means for utilizing the Clark process. British patents on softening were taken out by him in 1876, 1879 and 1881 and jointly with Herbert Porter in 1884. "My invention," said Porter in his patent of April 21, 1876, "consists in the utilization of the precipitate of carbonate of lime resulting from the [Clark] process as the medium of filtration." This he proposed to do by retaining the lime on filter cloths. In his patent of May 20, 1879, he claimed mixing the reagent in a receiver and then passing the mixture into a closed vessel where the mixing was continued by causing the water and the reagent to follow a circuitous course through the vessel. The chemical reaction thus produced could be promoted, if desired, by mechanical means or by a current of air or of water. In February 1884, a London chemical journal (19) published an article on the Porter-Clark process. Installations for sugar refineries, paper mills, dyeing plants and railways were mentioned. Plants for the Northwestern Railway at Camden, Willesden and Liverpool were mentioned and one of them described. In Latham's paper on water softening, already mentioned, he said that recent inventions for "carrying out the Clark process may be described as the application of machinery to the saving of time, space and labor." Of these, the Porter-Clark process comes first in time (19).

Removal of permanent hardness from water already subjected to Clark's process of 1841 or preferably to the Porter-Clark process patented in 1876, was claimed in a British patent granted to A. Ashby on November 29, 1878. The method called for was the addition of enough soda or potash to precipitate the soluble salts of lime, magnesia, and iron, other than those which cause temporary hardness. The water might be heated when necessary.

After a half century of invention and promotion only a few municipal water softening plants had been built in England, and, as far as is known, none were built elsewhere. In 1888 one was put into use by the borough of Southampton, England. Although its capacity was only 2 mgd. (Imp.) [2.4 mgd. (U.S.)] it seems to have remained for some years the largest softening plant in the world. Chemically, it followed the Clark process, using lime as a precipitant. Mechanically, it was based on the Atkins patent of December 31, 1881. A 10 per cent solution of lime was prepared in cylinders, equipped with stirrers for occasional use. The solution then passed to a baffled mixing tank and to a softening basin. From this it went to Atkins filters consisting of "a fine layer of carbonate" gathered on woven wire cloth stretched over a disk of perforated zinc supported by a cast-iron plate covered by radial and circumferential grooves. The filter cloth was cleaned by sprays of water. The plant was designed by William G. Atkins, one of the patentees of 1881, and built by the Atkins Filter & Manufacturing Co., under the supervision of William Matthews, Superintendent of the Southampton Waterworks (20). In the early 1890's, states George W. Fuller, the Atkins wire cloth filters were replaced by cloth filters designed and patented by C. J. Harris, resident engineer of the water works (21).

Among the widely used softening processes adopted in England in the 1890's was the Archbutt-Deeley. According to a paper read in 1898 by Leonard Archbutt, who was a chemist for the Midland Railway Co. (22), this process had been in use since January 1892, by the Midland Railway at Derby, England, "clarifying and softening the sewage-polluted water of the River Derwent, reducing the hardness from 15 to 5 degrees and giving considerable purification." It had been adopted at almost 50 works in England and abroad. Lime was slaked in a tank in which the water was boiled by means of a steam coil. Anhydrous carbonate of soda was then added, the mixture boiled and stirred until the soda was dissolved. The reagent thus formed was injected through perforated horizontal pipes into a softening and settling tank.

The only municipal plants named were one at the new water works of Swadlincote and Ashby and an adoption in 1897 at St. Helens. The former plant treated a very hard well water containing "in solution a considerable amount of iron, which precipitates on exposure to light and air." By using lime only, all the iron was removed and the hardness reduced from 22 to 8½ degrees. The iron in the water aided precipitation. The softened water was "bicarbonated by means of coke." The "engineering firm" of Mather & Platt, Manchester, England, installed Archbutt-Deeley plants and controlled the American patents.

Charles P. Hoover (23) says, "The recarbonation process devised by Archbutt and Deeley . . . was employed at several plants in England to overcome difficulties due to excess causticity, such as incrustation of filter sand, clogging of service pipes and meters and unpalatable water due to excess of alkalinity." He added that the first use of recarbonation in the United States, "on successful plant scale, was in 1921, at Defiance, Ohio [Nicholas S. Hill Jr., Engineer]. Since that time practically all water softening plants have been equipped with recarbonation devices." Elsewhere, Hoover notes (24) that "recarbonation for lime-softened water was provided in the very first municipal plant built in North America [Winnipeg, Canada]."

Clark and Similar Processes in America

Except for a short-lived plant at Champaign, Ill.,* hitherto overlooked, no softening plant for a municipal supply was built in America until early in the twentieth century. Then Winnipeg, Manitoba, built a plant which was soon followed by one at Oberlin, Ohio. These were preceded by many plants for industrial supply.†

The Illinois Central Railroad equipped some of its locomotives with water softeners in or about 1879. A filter was placed in the forward dome of the locomotives. Oyster shells were found to be the best filtering medium but it was difficult to get enough of these (so far inland, in 1879). "A good substitute was found in rough scrap

* The earliest known evidence of an attempt to promote water softening in the United States is an advertisement by the American Soft Water Co., of Chicago, published early in 1887 (25). The company claimed to have "the only reliable method for softening hard [lime] water for preventing scale in steam boilers." The system was also "a perfect one for purifying water holding earthy, vegetable and other impurities in suspension." Neither process nor apparatus was described, beyond saying that filters, adapted to any pressure, were used. Designs and estimates were offered "for purifying water in large quantities for cities and villages and manufactories." No evidence has been found that this company ever installed a plant.

† For at least six months hardness was removed from the water supply of Champaign and Urbana, Ill., seat of the University of Illinois. In a letter dated January 14, 1888, S. L. Nelson, Superintendent, Union Water Supply (26), said that the National filter plant, placed at the works in June 1887, had worked satisfactorily ever since. The "combined influence of Aeration, Lime Precipitation, and Filtration." he said, "renders our water clear and bright, free from odor and vegetable matter, and sparkling in appearance. . . . It also removes the hardness of the water." At that time, the supply of Champaign and Urbana was taken from an abandoned coal mining shaft. No record of the use of a National filter can be found by the water company in question nor in the public libraries of either city. Conceivably, the filter was installed for demonstration purposes only.

iron, which is now used exclusively." Raw water was delivered on top of the filter through a rose spray (27). No record of these softeners could be found in 1938.

In September 1897, Rudolph Hering advised the city of Winnipeg, Manitoba, to get water from artesian wells and soften it instead of going 50 miles to the Winnipeg River. By the solicitation of Col. H. N. Ruttan four bids were received. The contract was awarded to the Pittsburgh (Pa.) Testing Laboratory, of which James O. Handy was chief chemist. The plant had a guaranteed normal capacity of 2.4 mgd. (Imp.) [2.88 mgd. (U.S.)] and was put in use in May 1901. The plant was cited as using the Clark or more strictly the Porter-Clark process, but, besides slaked lime, caustic soda was used, thus reducing permanent as well as temporary hardness. After receiving these reagents, the water went to filter presses. Owing to "slight but annoying incrustations on the valves and condenser of the pumping engine . . . and in a few instances deposits on meters," after the plant had been accepted (October 1902), and after a series of experiments by Handy, carbonating apparatus was installed. In this, coke was burned in a brick furnace. The resulting gases were drawn by a blower and exhauster through a water-jacketed condenser or cooler and then passed to a washing tank where sulfurous acid was removed by spraying water upon coke placed on a shelf. These and other details, including changes in the plant made up to 1904, were described by Handy in a paper prefaced by a historical review of water softening processes abroad and in the United States (28). Handy stated that the Winnipeg plant was "the first municipal softening plant in America and one of the two largest in the world." There were in the United States and Canada (early in 1904), Handy said, about 275 water softening plants, of which over 100 were in railway service. As the aggregate capacity was given as about 65 mgd., most of the plants must have been small.

The college town of Oberlin, Ohio, was the first municipality in the United States to build a water softening plant (see footnote regarding Champaign, Ill., above). It was put into use December 23, 1903. Credit for the venture at Oberlin, a town of 4,000 population, is due to W. B. Gerrish, city engineer and superintendent of water works and to the water board that backed him. Of the three members of the board, one was a professor of science and another a professor of chemistry in Oberlin College. The plant was designed by C. Arthur

Brown. Oberlin built water works in 1887, taking its supply from the Vermillion River. The water was stored in a large reservoir, from which it flowed into a small "settling reservoir," then to a pump well from which it was lifted to a steel tank supported by a masonry tower. Gerrish wrote in 1905 (29) that the water supply was of surface origin, from an agricultural district, so hard "that with possibly a half dozen exceptions each family was provided with a rain water supply in addition to the city supply."

Brown's plan, thanks partly to local conditions, was simple. The small settling basin was divided into two compartments of 0.33-mil. gal. capacity each, the daily consumption then being only 0.165 mgd. Raw water from the adjacent storage reservoir was passed through a chemical mixing box, admitted to the bottom of the first softening basin, drawn from its top through a float arm, entered the bottom of the second basin and was finally taken from the top of the latter to the pump well—all by gravity. The softened water was then forced to and through rapid pressure filters to the water tank, the filters being installed within the stone tower that supported the tank.

Average counts made November 28 to December 15, 1904, showed an extensive reduction of bacteria effected by the long period of storage (theoretically some 90 days). Softening (subsequent to storage) reduced the bacteria from 371 to 13 per ml. or about 95.5 per cent. After passing through the rapid filters, the elevated tank and the mains, there was an average of less than 5 bacteria per ml. in the water delivered to consumers. A State Department of Health count on August 18, 1904, showed 490 bacteria per ml. before and 33 after softening, a reduction of about 90 per cent. Tests for coliform organisms were positive for the unsoftened and negative for the softened water in both local and state counts.

Excess-chemical treatment for control of caustic alkalinity was introduced at Oberlin two or three years after the plant was put into operation. To this sulfate of iron was soon added. Softening was still practiced at Oberlin early in 1940, apparently with the lime and soda-ash process. Years before, however, the rapid sand filters gave way to upward-flow excelsior filters on account of cementing of the sand.

Incidental to sedimentation, from 1904 to 1915, and since then as a part of a rapid filtration plant, St. Louis, Mo., has had the benefit of a considerable degree of water softening. Within these limits, St.

Louis was the first large American city to soften its water supply (30) (see also Chaps. VI, XII and XIII).

An oft-overlooked American installation of apparatus designed for softening was put into use on April 7, 1906, at Lancaster, Pa. It was part of a purification plant built by the Pennsylvania Maignen Filtration Co., of Philadelphia, under a contract to deliver doubly filtered water from Conestoga Creek to the pumping station of the city of Lancaster. In discussing a paper on softening in 1906, P. A. Maignen (31) said that after reagents had been mixed with the water, the latter passed through two 50-ft. cylindrical tanks with concentric baffles; then upward through scrubbers and finally downward through slow sand filters covered by a filtering membrane. J. E. Goodell, Chemist at Lancaster (32), in 1940 added to Maignen's description that the amount of soda ash used was too small for softening the water being treated. When the city bought the Maignen plant in May 1924, it gave up the use of the apparatus designed for softening. The double filtration plant was abandoned when the city completed rapid filters in November 1933.

Cursed for over forty years with a hard water supply, the city of Columbus, Ohio, put a 30-mgd. water softening plant in use in September 1908. It was then by far the largest softening plant in the United States, if not in the world. It was enlarged to 54-mgd. capacity in 1923. In 1938, said Charles P. Hoover, Chemist (33), it still had the "distinction of being the largest softening plant in the world using both lime and soda ash." So objectionable had been the water supply of Columbus for years past that when the softening plant was put into use in 1908 there were over 17,000 cisterns in the city (181,511 population in 1910). Many private wells were used for drinking water.

The Columbus water works was put into use by the city on May 1, 1871. Water was taken from a filter gallery. In his first annual report, J. L. Pillsbury, Engineer, proposed that the water be softened. He suggested the use of "a solution of caustic lime," which had been approved by "Professor Wormsley." Ten years later, after an unsuccessful experience with a filter basin, Superintendent Doherty reported that office tests had shown that 1 oz. of lime added to 36 gal. of water made the city supply "superior for washing to the rain water obtained from cisterns." The water works trustees, he said, would give a sample package of lime to citizens. Plans for a supply from the Scioto

River were shelved in 1886 in favor of an extension of the filter gallery.

Subsequently, use of the river was proposed at intervals. In 1901, Samuel M. Gray again advised its use, providing it was subjected to softening and rapid filtration. Funds for this purpose were not authorized until 1904. When John H. Gregory, with Hering & Fuller as consulting engineers, took up the design of the Columbus plant, the basic principles of rapid filtration had been established at the Louisville and Cincinnati experimental plants in the late 1890's but no comparable experiments on water softening had been made. Incidentally, the Cincinnati experiments had shown that lime would not only soften water but would also reduce bacteria. At the Columbus sewage testing station, bottle and barrel studies of water softening, under the direction of George A. Johnson, then associated with Hering & Fuller, were utilized as a guide in designing the chemical phase of the softening plant. The entire purification plant, as completed in 1908, was described at length by Gregory in 1910 (34).

The plant, with facilities for recarbonation added, and with enlargement in 1923 to a capacity of 54 mgd., was described by Hoover in 1927 (35). A marked feature of the enlarged plant is the division of the entire flow of raw water into two parts, one of which flows without treatment to the baffled mixing tanks while the other constantly receives soda ash and alum needed to soften and clarify the entire volume of water. From the mixing tanks, the water goes to settling basins. Just before passing from these to the rapid filters, carbon dioxide gas is added to neutralize any excess lime. This, says Hoover, converts normal carbonates to bicarbonates, and prevents deposits in the filters and distribution system.

New Orleans, La., included softening as a part of its purification plant of 1909. Cincinnati, Ohio, provided for softening when it enlarged its filtration plant in 1936–38, but up to September 1939 softening had never been used there. It would not be needed continuously. Minneapolis, Minn., completed a softening plant in 1939, using lime and recarbonation. It is designed for an ultimate capacity of 120 mgd., has radial baffles in the precipitation tanks, extending buttress-like from the outside of the inner inverted cone (36). At St. Paul, Minn., an enlargement of the existing rapid filtration plant, completed in 1940, included a provision for softening, put into use on January 6, 1941. Lime is used (37).

Upward-flow reaction and sedimentation is one of the most notable of the recent features of water softening practice. The idea is not new but like many other conceptions it was long dormant.*

In its modern application the water is treated in a specially designed unit. Raw water and softening chemicals are mixed by mechanical stirring in the presence of previously formed sludge; the softened water is clarified in rising to the top of the clarifier where it is discharged and the sludge or precipitate is drawn off at the bottom, both continuously. Broadly, the basic principle is similar to that of the activated-sludge process of sewage treatment, but the activation in this method of water softening is chemical instead of bacterial—the formation of floc by the newly applied reagent being quickened by that remaining in the old sludge. Two types of apparatus are in vogue: The Green-Behrman Accelator (U.S. patent, December 20, 1927) and the Spaulding Precipitator (U.S. patent, November 19, 1935). In the "Accelator" the raw water is introduced on one side and the chemicals on the other side, both near the bottom of the tank below the suspended sludge level; the water and reagents rise up through a central mixing compartment, containing an agitator, then pass down through a concentric compartment, then up through an outer clarifying compartment. In the "Spaulding Precipitator," the raw water, with chemicals added, passes down through a truncated cone below which there is an agitator, then upward through a concentric inverted truncated cone at the base of which there is suspended sludge. Schematic cross-sections are given in a paper by Spafford and Klassen (38). The paper contains tabular data for accelerators and precipitators at several softening plants in Illinois and is followed by general discussion. An exposition of the "Accelator," with a cross section showing details and half-tone views of installations at Anna, Ill., and Williams Bay, Wis., are included in an article by the patentees (39).

The evolution of Spaulding's upward-flow precipitator, and its installation as part of the second water softening plant at Springfield, Ill., and the large time saving it effected compared with the first Springfield plant were told by Spaulding and Timanus in 1935 (40). Two years later, Spaulding went into the subject in more detail regarding both theory and practice (41).

* Antecedents of upward-flow precipitation were included in water softening patents taken out in England by William Lawrence (December 24, 1891) and in the United States by Herschel Koyl (July 3, 1900 and July 2, 1901).

Excess Lime

Credit has been widely given to the late Sir Alexander Houston of London for introducing excess-lime treatment of water for softening. It seems to have been entirely overlooked by Houston and by writers crediting him with having originated excess-lime treatment that all the Clark-process plants from 1854 until 1870 used what Clark himself called "excess lime" and that the same term was used by Baldwin Latham in referring to these plants in his paper of 1885. Also generally overlooked has been the adoption of excess-chemical treatment at Oberlin, Ohio, after the softening plant completed late in 1903 had been in use some three years.

In Dr. Houston's Eighth Research Report (42), he says that his studies of 1911, which led to his "discovery" of excess-lime treatment, were prompted by the failure of Parliament to authorize the full water storage program of the Metropolitan Water Board. He therefore studied means to make up deficiencies in storage at times of bad water. This led to a "new way of adding lime ('excess lime')." Quoting further:

> With hard waters it is a case of adding an excess of lime to the major proportion of the total volume, rendering the minor proportion "safe" by adequate storage, ozonization, chlorination or other method, and mixing the two together so as to neutralize the excess of lime and render the whole perfectly innocuous. With soft waters, the procedure is to treat the whole bulk of water with an excess of lime and neutralize with carbonic acid or sulphate of alumina or acid. The former operation incidentally involves "softening" and the latter may involve "hardening" the treated water.

So far as has been found, the excess-lime method has never been applied to soften London metropolitan supply, but precoagulation has been used for some years to lessen the filter burden.

In his Twenty-fifth Annual Report (1930), Dr. Houston quoted at length a description of an excess-lime softening plant treating a new water supply for Southend, England (43). The plant was put into use in September 1929. It had a capacity of 7 mgd. (Imp.) [8.4 mgd. (U.S.)]. It treated stored river water which had a temporary hardness of 94 ppm. and was liable to sewage pollution. By use of the excess-lime method nearly all the temporary hardness was removed, the water clarified and a "pronounced" disinfection effected. Whether the excess-lime process has been adopted elsewhere cannot be stated.

In the United States, Houston's experiments were immediately confirmed by Hoover and Scott in studies made at Columbus (44) and subsequently, says Hoover, at a number of other softening plants, special reference was made to bacterial efficiency. Heavy reductions in coliform averages for the year 1929 at the softening plants of Columbus, Youngstown and four other Ohio cities are listed, with associated data, by Hoover's Lime Association Bulletin 211 (23). In this booklet, he defines "excess treatment" as "overtreating with lime . . . then neutralizing the excess lime with soda ash." He defines "split treatment," for plants not equipped for excess treatment as "overtreating as large a portion of the hard water as possible to get maximum reduction of hardness and then neutralizing the excess with raw water." This was substantially what was done in the Clark-process plants designed by Homersham.

In a letter written for use here Hoover said in part (33): "I think Sir Alexander Houston deserves credit for observing the effect of lime treatment in reducing bacteria, . . . [but not] for excess lime treatment in water softening." Hoover raised technical questions concerning Dr. Houston's methods of determining excess lime in water, and in conclusion expressed the belief that "the late C. H. Koyl, Superintendent of Water Supply of the Chicago, Milwaukee & St. Paul R.R., was the man who made excess-lime water softening practicable."

That Dr. Houston was primarily concerned with bacterial reduction rather than water softening, the above quotations from him make evident. That Dr. Clark was also largely concerned in other improvements to water than softening is also evident. In his patent of 1841 he declared that his process would render water "less impure and less hard." In a promotion pamphlet of the same year he claimed destruction of "numerous water insects." Bacteria and their removal were beyond his ken, as they were beyond the dreams of Thom and Simpson fifteen years earlier when they perfected their filters. All three built far better than they knew.

Zeolite in Europe and the United States

Sixty-seven years after Clark took out his British patent on the use of lime to soften water, the first of several German patents was granted to Robert Gans for what was to become known as the zeolite or base-exchange process of water softening. After being used for a few years to treat water for industrial purposes, the process was applied to municipal supplies. By 1925, it began to rival the lime and lime and soda-ash processes. By 1940, the newer process was widely used. The antecedents and basic principles of the zeolite process have been summarized by H. M. Olson (45, 46), by a court judge (47) and by Boris N. Simin (48). Early investigators of zeolites mentioned by Olson were: Cronstedt, a Swedish geologist, in 1756, Thompson, in 1845, Way in 1850 and 1852, and Eichorn in 1858.

On April 6, 1908, says a United States District Court Decision (47), Dr. Robert Gans, of Pankow, near Berlin, was granted German Patent 197,111 for his invention of "a form of artificial zeolites" created by fusing "clays and soda ash, and hydrating them, to which he gave the arbitrary name 'Permutit.'" He "found that hard water could be continuously softened by filtration through them and that the artificial zeolites could be regenerated by washing them with a salt solution after the exhaustion of their softening bases. . . . The device first used by Gans," says the court decision, "was defective." United States patents were taken out by Gans December 14, 1909 (reissued February 17, 1914), June 7, 1910, and August 22, 1916. By a disclaimer of February 26, 1920, the third of these patents was limited, says the decision, to "a filter composed of a layer of zeolites resting on a layer of sand and quartz, downward filtration, means of cutting off the supply of water on exhaustion of the zeolites, and means of passing through the zeolites a solution of salt capable of regenerating the zeolites."

In 1911, Boris N. Simin (son of Nicholas Simin, one-time Chief Engineer of the water works of Moscow, Russia) reviewed the development of the Gans process abroad (48). He gave references to seven articles by Gans, all in German. Two early industrial installations of softening plants are mentioned by Simin. A small one in a flour mill at Kirsanaff, Russia, supplying a 110-hp. boiler, had been working since the middle of 1910. The largest zeolite plant in Germany was at a textile mill in Bremen and treated 300 cu.m. (79,000 gal.) per hour. Apparently, the earliest zeolite plants in Germany were installed in 1908. Of about 250 installations in Western Europe, most were in Germany. There were fifteen in Russia. These data by Simin do not even hint at the failure of the early form of the Gans process asserted by the court decision.

The largest zeolite plants known to D. D. Jackson, when he read a paper in May 1915 (49), were at Dresden, Germany, and Hooten, England, the first for the removal of manganese and the second for iron removal. There was also at Hooten a 1.25 mgd. (Imp.) zeolite plant for softening the municipal water supply. The latter reduced the hardness from 20 degrees to 10 degrees by bringing half of the volume to 0 degrees, then mixing it with the other half.

England led America by a decade in putting into use a zeolite plant for municipal supply. "The first public water supplies in Great Britain to be softened by this [base-exchange] process were those of the West Cheshire Water Board (1912) and the Colne Valley Water Co. (1924) to whose engineers credit is due as pioneers" (50).

The West Cheshire Water Board supplies parts of the county boroughs of Birkenhead and Wallasley and a half dozen urban districts nearby. The supply is taken from "boreholes in the New Red Sandstone," at two localities. At each of these there is a Permutit softening plant and at one a "Candy iron extracting plant."

The Colne Valley Water Co., which supplies the whole or parts of twenty London suburbs in Middlesex and Hertford counties, installed a 2.5-mgd. (Imp.) base-exchange softening plant in 1924 and added a 4.5-mgd. plant in 1932. The first of these replaced a Clark process plant installed in 1873 and subsequently enlarged. "The whole installation," it was stated in 1935, "is believed to be the largest single base-exchange plant . . . in Europe." The water treated is from wells in the chalk (15).

In 1939 there were at least twenty municipal base-exchange softening plants in Great Britain and others under construction.

In the United States, the first community to be supplied with zeolite-treated water, says Olson (45), was Wyomissing, Pa., in 1922, where soft water was delivered to city mains from a plant in a textile mill. Laurens, Iowa, is credited as having been the first American town to be provided with softened water from a plant built for city supply. This was in 1924. The first large zeolite plant in this country was put into use August 25, 1925, by the Ohio Valley Water Co. (later called the Pittsburgh Suburban Water Co.) to supply Avalon, McKees Rocks and other suburbs of Pittsburgh. Its capacity in 1938 was 7 mgd., according to H. E. Moses, Chief Engineer of the Pennsylvania Department of Health (51). The McKees Rocks plant, as this installation is called, was for a time the largest U.S. zeolite plant.

The Metropolitan Water District of Southern California, late in 1939, awarded contracts for a 100-mgd. unit of a 400-mgd. plant to soften water from the Colorado River for Los Angeles and vicinity. Lime-zeolite treatment was to be used at the start but if found advisable excess-lime and soda-ash treatment can be substituted (52). Delivery of softened water to a part of the district was begun on June 18, 1941.

Recent Summaries

The Streeter Water Purification Census of 1930–31, listed 144 softening plants in the United States but it is now known that some were omitted (53). The United States Public Health Service Census of Water Treatment Plants, issued in early 1941, showed 680 softening plants of which 510 used the lime or lime-soda and 170 the zeolite process (54). An Olson census made as of July 1, 1941, showed fewer plants: 576, of which 377 were of the older and 197 of the newer type. The North Central States (Ohio, Indiana, Illinois, Michigan and Wisconsin) led the various groups with 250 plants of all types (55). A supplemental summary and census made by Olson as of January 1, 1945, showed a gain of 89 plants to make a total of 665, of which 427 were reported as chemical precipitation plants and 238 as zeolite (56).

Canada had four softening plants in 1941. The largest of these was at Edmonton, Alberta, where lime and soda-ash were used (57).

England and Wales reported softening plants, early in 1940, in 46 towns, most of them small. Of the 33 places for which the type of process was given, about half used lime (including a few lime and soda-ash) while the other half used base exchange or zeolite. No softening plants were reported for Scotland, Northern Ireland or Wales (50). Thus, a century after Clark's softening process patent was granted in 1841, and 45 years after the Rivers Pollution Commission (16) listed 87 towns in Great Britain where softening might be used advantageously, there were less than half that number in England and Wales. For this, war and rumors of war are partly responsible. Meanwhile a number of hardening plants have been installed. These treat very soft water from moorland or other catchment areas to prevent attacks on water pipes. The Sheffield supply, which is taken from elevated moorlands and the Derment Valley, and has a hardness per 100,000 of 1.1 degrees temporary and 2.7 permanent is limed and passed through rapid and slow sand filters.

A complete bibliography of the literature of water softening would include scores of reports and papers in addition to those named in the appended list of references. *The Index of the Proceedings and Journal of the American Water Works Association, 1881 to 1939,* has about 150 entries under "Softening," some of which are duplicates of those given here.

Collins, Lamar and Lohr, of the U.S. Geological Survey, give nearly 700 chemical analyses of various public water supplies of the United States and a map showing "Weighted Average Hardness, by States, of Water Furnished in 1932 by Public Supply Systems in Over 600 Cities in the United States" (58).

Only one book devoted exclusively to water softening has been found and this is small and old (59). It contains no historical data. The only apparatus described is that of one British company. A large part of Hoover's booklet (23) is devoted to softening. A concise review of softening, containing high-spot historical data and useful references, is given in *The Manual of Water Quality and Treatment* (60). Baldwin Latham's article, "Softening of Water" (18), contains an historical summary from ancient times to 1855, including an outline of British and of a very few French and German patents, issued between 1838 and 1883.

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CHAPTER XVIII

Softening

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CHAPTER XIX

Cause and Removal of Color

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