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CURRENT PROBLEMS IN RESEARCH

Demineralization of Saline Waters

Current desalination processes and research give hope for solution of our impending water crisis.

W. S. Gillam and J. W. McCutchan

It has been stated that there are three basic water economies in the United States: The East uses water, the central states are processors of water, and the western states are water redistributors. As sources of water for use, processing, or redistribution become more scarce, the need for converted sea water comes into sharper focus.

Congress recognized the need for new sources of fresh water in 1952, passed the Saline Water Act (Public Law 448), amended it in 1955, and in September 1958 passed Public Law 85-883 calling for the construction of at least five saline-water-conversion demonstration plants. The primary objective of the Saline Water Conversion Program is to develop low-cost processes for converting saline waters to potable water. A number of surveys have indicated that within one or two decades the United States may be in real difficulty as a result of water shortages, since the population growth will triple the demand for fresh water by 1980, and since the United States has built up a large interdependent water complex that is subject to serious disruption in the event of a water shortage (Fig. 1).

Government officials (*1*) have stated that by 1980 an adequate supply of potable water may be our number-one problem. New estimates of water use and supply suggest that the critical period will begin about 10 years earlier, by 1970 (*2*). The quantity of natural fresh water which this nation can expect to have regularly available in 1980 will be about 515 billion gallons a day. In 1960 the daily use was calculated at 323 billion gallons, whereas the total dependable supply was estimated at 315 billion gallons (*2*).

Is this future demand going to be met? Justus H. Fugate, at the December 1960 National Conference on Water Pollution, said, "In spite of the effort at the Federal level, and in spite of substantial effort at the municipal and state levels, there are not now under construction or even planned for construction, by all the public and private agencies combined, sufficient water projects to provide the amount of water of acceptable quality that we will require in 1975. The naked fact is the United States faces a water crisis."

The extent of interest in obtaining additional supplies of fresh water within the United States is illustrated in Fig. 2. This figure shows the location of cities which asked to be considered as sites for the demonstration plants to be built under supervision of the Office of Saline Water, U.S. Department of the Interior. The stars indicate the sites selected for the five demonstration plants: Freeport, Texas; San Diego, California; Webster, South Dakota; Roswell, New Mexico; and Wrightsville Beach, North Carolina. The fact that this is a world-wide problem was emphasized by a survey made by UNESCO (*3*), in 1958, of institutions engaged in research on sea-water conversion. France, Hungary, India, Iraq, Israel, Italy, Japan, the Netherlands, Spain, Switzerland, the Union of South Africa, the United Kingdom and Northern Ireland, the United States, Yugoslavia, and Australia have all reported research activities at various institutions. The U.S.S.R. is also known to be actively engaged in research on the problem of demineralization of saline water.

Research Problems in Distillation

No general review of sea-water conversion would be complete without some discussion of the distillation processes. No matter how new the design of the process equipment, the fact that it is based on distillation places it in the category of development rather than that of basic research. Nevertheless, current research problems do exist. These are not new problems, but a new research point of view may be necessary for their solution.

The problems fall into four general categories: (i) studies of the composition of scale and its elimination or control; (ii) investigations of materials of construction of sea-water evaporators, from the point of view of corrosion resistance and economic life; (iii) development of means of raising the level of operating temperatures, for the hope of improving fuel economy lies in achieving an increase in temperature

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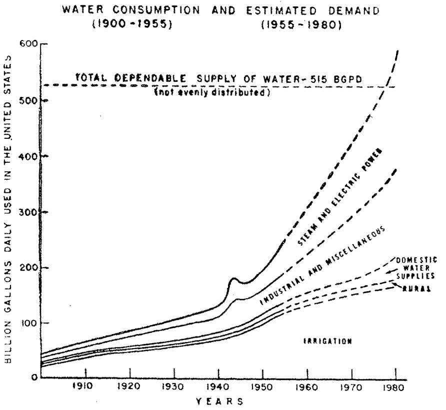

Fig. 1. Water consumption and estimated demand to 1980.

level; and (iv) a design study based on optimizing mass transfer.

The classic work of W. F. Langelier *et al.* (*4*) on scale control in sea-water distillation equipment established a means for predicting the type of scale to be expected under specific operating conditions. On the basis of this work it was found that equipment could be operated in the $CaCO_3$ or $Mg(OH)_2$ range, and that scale could then be periodically removed by acid treatment. Another answer was to use vacuum distillation, keeping the temperature below 160° to 180°F, then with a sufficiently high rate of blowdown, to operate relatively free of scale.

However, the goal of converting sea water by means that are economically competitive motivates us to look for ways of eliminating or controlling the scale problem instead of being limited by it. The work of Banchero and Gordon (*5*) at the University of Michigan, sponsored by the Office of Saline Water, represents a new effort to make a fundamental study of scale deposition on heated surfaces. As the temperature level is raised in sea-water equipment, calcium sulfate and its hydrate forms, hemihydrate and gypsum, become most important scale constituents. Gordon is currently studying calcium sulfate deposition. Kelley *et al.* (*6*) have also made an important contribution to the solution of this problem in their publication "Thermodynamic properties of gypsum and its dehydration products."

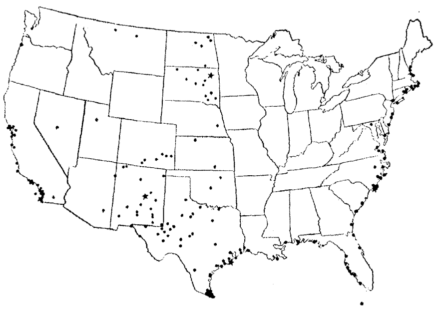

Fig. 2. Location of cities which asked to be considered as sites for Office of Saline Water Conversion plants.

A fundamental study on critical conditions for scaling of solutions on heating or cooling surfaces has just been reported by J. L. Chandler (*7*). According to his study, crystals are deposited on the surface at a rate approximately proportional to a power of the degree of supersaturation at the surface.

A survey on construction materials for handling saline waters, with special emphasis on the problems involved, was conducted by Battelle Memorial Institute under contract with the Office of Saline Water. The report, by F. W. Fink (*8*), was based on discussions with marine experts as well as on a review of current literature, such as the recent article by Bruce (*9*), entitled "Five years of experience with desalinization at Morro Bay."

From the standpoint of corrosion, it was concluded that steel probably could be used in handling deaerated sea water at temperatures up to about 250°F. However, detailed information on the corrosion behavior of inexpensive metals, such as steel, in hot water is not yet available. Aluminum-clad aluminum alloys also show promise for processing hot sea water where it is not convenient to employ deaeration. It appears that the upper temperature limit may be lower for aluminum than for steel. In order to justify inexpensive construction, the lifetime or corrosion resistance of the plant must be known in order to properly amortize the capital investment.

Metals such as cupronickels, Monel, Inconel, Hastelloy C, and titanium may have application in processing hot sea water in spite of their high cost. Available information indicates that titanium is the most remarkable of this group. It can be used in handling sea water at temperatures up to the critical point. At ambient temperatures it can resist velocities of 20 to 50 feet per second or more.

Why are we trying so hard to increase the temperature level of our distillation equipment? Thermodynamic analyses do not show necessarily that elevated temperatures are desirable. Tribus *et al.* (*10*) state, "From the point of view of the economy of a process, high temperatures may appear desirable. This statement is true because the capital costs of the irreversibilities introduced to increase plant output are often, in practice, less at elevated temperatures." Another way of looking at it may be this: thermal energy is generally available at elevated temperatures, so more efficient use is made of this energy if our process is designed to operate over the full temperature range. It should be pointed out that each increase in process temperature level carries with it new problems of scale control, construction materials, optimum size of equipment, and so on. Nevertheless, there is no doubt that at the present state of the art there is much to be gained if we can raise the operating temperature to 300°F.

It is generally assumed that if we increase the rate of heat transfer we increase the rate at which vapor is formed and transferred to the condensing surface. This is true, but it does not follow that a design based on a philosophy of optimizing heat transfer will be the same as a design based on optimizing vapor (mass) transfer. To increase heat transfer, studies have been made on forced-circulation, dropwise condensation, rotating heat-transfer surfaces, and wiped-film evaporators. For each increase in performance we have paid a price in increased capital cost

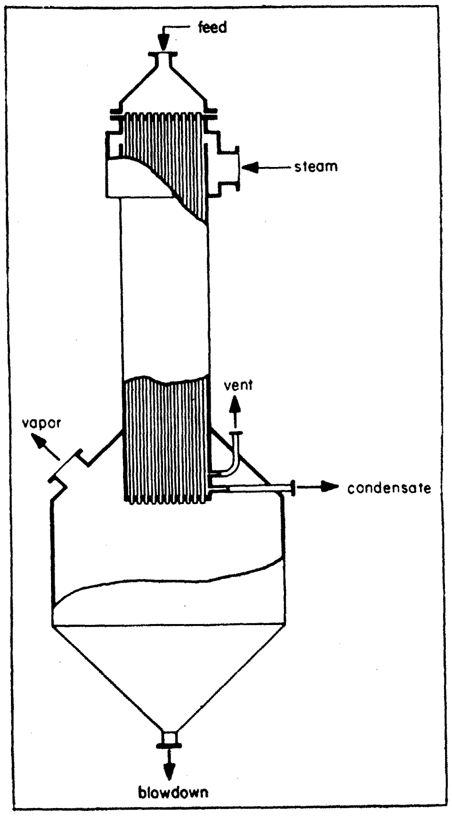

Fig. 3. Cross section of one effect of the long-tube-vertical system.

and generally in operation and maintenance cost. It is our belief that design studies can and should be made to optimize the vapor transfer in distillation equipment.

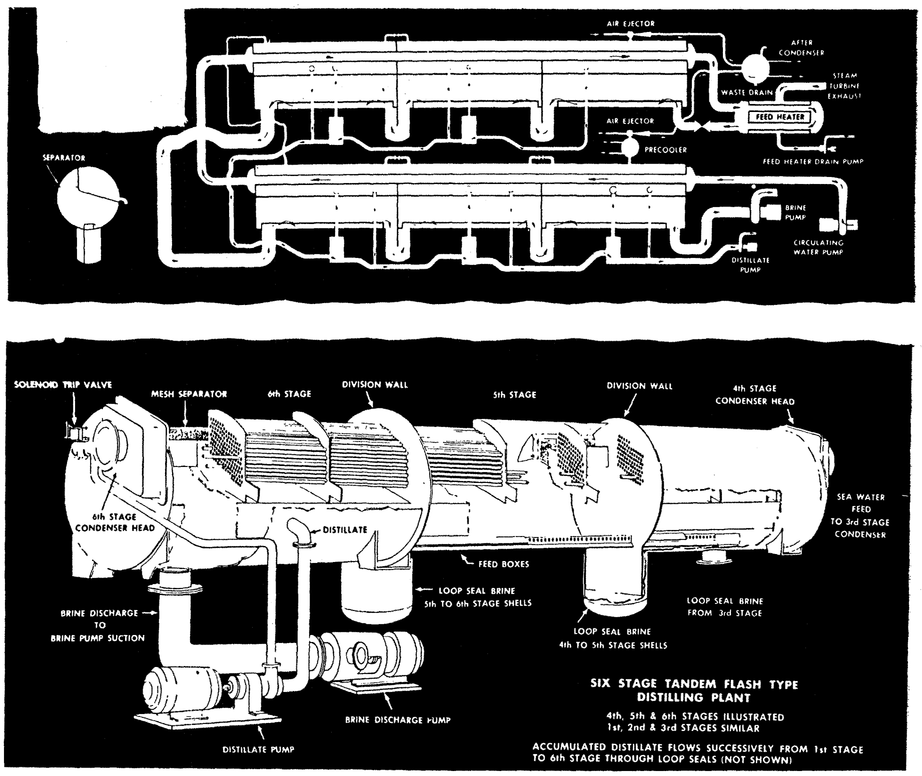

Fig. 4. Cutaway view of a multistage flash evaporating plant, similar to one under test at Wrightsville Beach, North Carolina.

Conversion Processes

At the inception of the Saline Water Conversion Program (*11*) in 1952, consideration was given to all existing and potential processes or phenomena that might conceivably be used in converting saline water to potable water. Subsequent investigations have reduced the number of processes considered potentially feasible to the point where they may be conveniently classified into four groups: distillation; processes in which membranes are used; freezing; and other types, including chemical, electrical, and biological processes.

Certainly the progress made to date will be highlighted in the demonstration-plant program. The criteria for selection of processes for the demonstration plants included two points worthy of note here. First, the process must be in an advanced stage of development to insure that the number of problems yet to be solved, that can cause long shutdowns, is minimal; second, the process should "look to the future" with respect to energy, materials, and changing conditions.

Distillation. Simple distillation is a long-established method of converting salt water to potable water. Fundamentally, the process is this: the saline water is evaporated in a closed vessel by application of heat, and the water vapor is condensed by being passed over tubes through which cooling water is circulated. Thus, the bulk of the heat needed for evaporation is carried away by the condensing water, and the balance, by the concentrated brine. Such a process requires approximately 1000 times the theoretical minimum energy requirement. There are, of course, more efficient processes than simple single-effect distillation.

Multiple-effect distillation is one method of achieving greater efficiency. A 12-effect distillation cycle was chosen for the first demonstration plant. W. L. Badger Associates, Inc. (*12*), under contract to the Office of Saline Water, has been developing this process over the past several years. It is known as the "long-tube-vertical" (LTV) system. Actually, as originally conceived, in this system the sea water was to have risen in the tubes (2 inches in diameter, 24 feet long, in this design), but tests have shown that a falling-film arrangement inside the tubes gives better heat-transfer rates. The success of this process depends in large measure upon whether or not it can be operated free of scale, and on whether low-cost construction materials can be used.

An internal-sludge stabilization technique, common to the salt and chemical industries, has been tested successfully in a pilot plant erected by Badger (*13*) at the International Nickel Company's experimental station at Harbor Island, North Carolina. Calcium carbonate and magnesium hydroxide have been controlled at temperatures up to 250°F. The Chicago Bridge and Iron Company constructed the 1-million-gallon-per-day plant at Freeport, Texas, to demonstrate this process, and it began operating in June 1961. Figure 3 is a typical cross section of one of the 12 LTV, falling-film evaporators, in which the sea water falls, by gravity, down the inside of the tubes and the steam (vapor) from the previous effect condenses on the outside, forming the product water.

In flash distillation the term *multistage* is used, rather than *multieffect*. Use of the word *stage* instead of *effect* apparently is to differentiate between the case where the sea water is heated under pressure prior to entering a series of flash chambers or stages and the case where the vapor from one effect is used to boil water in the next effect.

An excellent discussion of the reasons for the increased use of this process for sea-water distillation was published by A. Frankel (*14*). The first problem to delay the development of flash equipment was the formation of scale on heat-transfer surfaces. In a submerged coil unit, scale formation results in a reduction of output, while in the flash evaporator it causes not only a reduction in output but also a reduction in the specific heat consumption, as well as appreciable change in the flow resistance of the brine circulating system. According to present practice, these plants are operated at less than atmospheric pressure, and effective scale control has been achieved at 200°F with chemical feed treatments, such as Hagevap LP. Furthermore, on the basis of tests conducted by the Griscom-Russell Company for the Office of Saline Water, it is believed that sludge recirculation will prove as effective for multistage flash distillation as it has for the LTV, falling-film process, in which case the temperature level of operation can be raised to 250°F. The type of plant being tested by Griscom-Russell is shown in Fig. 4. The San Diego plant will be designed to test the same conditions on a larger scale.

The Fluor Corporation of Los An-

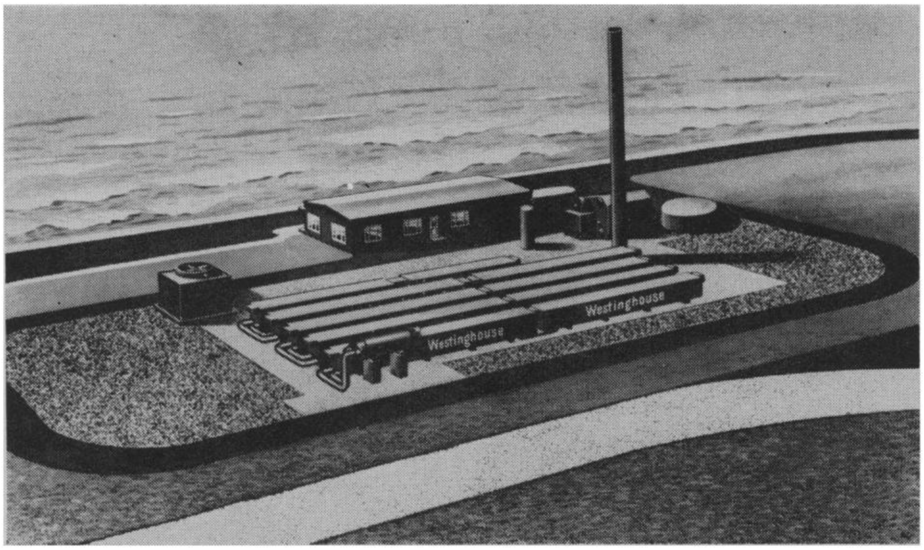

Fig. 5. Artist's conception of the flash evaporator plant to be built at Point Loma, San Diego, California.

geles is supplying the architectural and engineering services for the 1-million-gallon-per-day, multistage flash-process demonstration plant at San Diego, California. The Westinghouse Electric Corporation will construct the 36-stage plant. Groundbreaking ceremonies were conducted 19 December 1960.

Initially it was planned to combine a low-temperature nuclear reactor with the San Diego plant. Because of the experimental nature of this reactor, however, approval for it was never obtained. Therefore, the plant will get its energy from an oil-fired steam generator. Thus, this combination will not "look to the future" to the extent originally planned, but it will probably be the most reliable of the demonstration plants and, as such, will be hard to beat in this five-plant race to produce desalinized water economically. Figure 5 is an artist's sketch of the plant to be built in San Diego.

The vapor-compression process has been known for many years to be the most thermally efficient process, but it was not until World War II that the need for a "self-contained" unit was such that satisfactory units were developed. The best available combinations of engine, compressor, evaporator, pump, and heat exchanger have proved themselves in service. For a time, though, enthusiasm waned because it was apparent that scaling of the evaporator tubes was a serious problem.

However, the Office of Saline Water continued to support studies by Bliss (*15*) and by Dodge and Eshaya (*16*) on a forced-circulation vapor-compression process. This work was a factor in the decision to demonstrate this process at Roswell, New Mexico, in a plant with a capacity of 1 million gallons per day. The Catalytic Construction Company of Philadelphia is at work on the architectural and engineering specifications for this plant. The principal problem here, as in any distillation process, is that of scale control. A typical analysis of the saline well water at Roswell is given in Table 1.

This water, as compared with sea water, is high in sulfate. This highlights a problem which is not generally appreciated—that often it is more difficult to control scale in handling brackish inland waters than in handling sea water.

The choice of forced-circulation instead of thermal circulation in this process is based on data which indicate that it is easier to control scale in a forced-circulation system. In order for this process to succeed, scale must be controlled. It is hoped that as more is learned about sludge recirculation, and as these techniques are successfully applied to calcium sulfate, the forced-circulation, vapor-compression process will demonstrate the advantage of its low energy requirement and will be competitive on a unit-price basis. However, in this first plant, ion-exchange equipment will probably be specified in order to remove the calcium and magnesium. The largest existing vapor-compression installation was built by the Cleaver-Brooks Corporation for Kindley Air Force Base in Bermuda. This plant has a capacity of 200,000 gallons per day. The capacity of the Roswell plant will probably be 1 million gallons per day; thus, it will be the largest vapor-compression distillation installation ever built.

Electrodialysis. In recent years probably more has been written about the application to saline-water conversion of the electrodialysis process than has been written about any other single process. Ellis's book *Fresh Water from the Oceans* (*17*) was criticized because of its undue emphasis on this process. A timely book entitled *Demineralization by Electrodialysis* has been published recently by the staff of the Process Development Division, National Chemical Research Laboratory of Pretoria, Union of South Africa (*18*).

A more condensed discussion is presented by H. J. Cohan (*19*) of the Bureau of Reclamation, in Denver. He concluded that although the electrodialysis process has been known for a very long time, intensive developmental work to change the process from a laboratory curiosity to a practical large-scale operation has been done only in the last few years. The full potential of this process has not been realized, and will not be realized until cheaper membranes, improved flow-compartment configurations, more effective methods of scale prevention, and methods of further reducing the hazards of polarization are developed.

The Bureau of Reclamation is serving as the architectural and engineering organization for the 250,000-gallon-per-day electrodialysis plant to be built at Webster, South Dakota.

Figure 6 is a simplified schematic diagram of this process. Since the presence of manganese in the Webster well water would damage the electrodialysis membrane, the manganese will be oxidized by aeration and injection of potassium permanganate, then removed in the manganese-zeolite tanks before the stream enters the electrodialysis stack.

In the electrodialysis process, power consumption is a function of demineralization, and thus potable water, meeting health standards for salinity of 500 parts per million, can be produced from saline water containing 2000 to 3000 parts per million at a saving in energy over the distillation process. It is believed that the criterion of "a look to the future" is fully met by the electrodialysis process. The Webster plant is to be constructed by the Asahi Chemical Industry Company, Ltd., in cooperation with the Austin Engineering Company. This plant will be used to demineralize brackish well water containing 1800 parts of dissolved solids per million parts of solution, reducing its content of dissolved solids to 500 parts per million.

Freezing processes. Theoretically, a single freezing should produce potable water from sea water. However, ice formed from saline solution occludes or entraps brine between the interstices of the ice crystallites, and some brine is also adsorbed on their surfaces. Thus, one of the major problems that had to be solved before this process could be considered feasible was the development of satisfactory methods of separating the ice crystals from the mother liquor. Research sponsored by the Office of Saline Water and the work of others has shown that several separation procedures are technically feasible, and at this time at least one is economically feasible.

The fifth conversion plant, to be built on the East Coast, at Wrightsville Beach, North Carolina, will use a direct-freezing process. The specific type of direct-freezing process has not been chosen at this time, but research and development work now in progress should soon lead to a decision. The experimental programs of Carrier Corporation, Blaw-Knox, Cornell University, and Struthers-Wells–Scientific Design are continuing, and experimental work is reported in Israel and Japan. At present a number of Office of Saline Water reports (*20*) are available, as well as recent publications by Bosworth, Barduhn, and Sandell (*21*) and by Karnofsky (*22*).

Table 1. Analysis of saline well water at Roswell, New Mexico.

Solids	Concentration (ppm)
Sodium	7,452
Calcium	673
Magnesium	587
Iron	Trace
Chloride	12,606
Sulfate	2,838
Silica	Trace
Ca ("hardness") as $CaCO_3$	2,320
Mg ("hardness") as $CaCO_3$	824
Total dissolved solids*	24,360

* *p*H, 7.4.

The Carrier Corporation, under contract to the Office of Saline Water, has designed, erected, and put into operation a 15,000-gallon-per-day pilot plant, using a direct-freezing, vapor-absorption system. The initial plant installation, at Syracuse, New York, used artificially produced sodium chloride feed water with the same total saline content as sea water. The installation had good operating runs and produced water with an average salinity of less than 500 parts per million. The plant then was moved to Harbor Island, North Carolina, and operation started again on 31 October 1960. After preliminary tests, a continuous run of 500 hours was made on raw sea water to demonstrate the reliability of the design.

Other processes. Various phenomena and techniques relating to potential conversion processes or associated problems are being investigated. These studies range from effects of impressed electrostatic fields on the salt water–air interface, through commercial utilization of certain elements in sea water and the development of improved membranes, to the use of acoustical energy in an attempt to improve the economy of evaporator operation.

Heat transfer between immiscible liquids has been proposed by Woodward (*23*) as an efficient, scale-free method of raising the temperature of the feed sea water in a distillation process. The idea of using immiscible liquids in a solvent extraction process has also been studied in some detail by Hood and Davison (*24*) of the Department of Oceanography of the Texas A & M Research Foundation.

The feasibility of demineralizing water with a pair of electrodes, one responsive to the cation and the other to the anion, has been demonstrated by

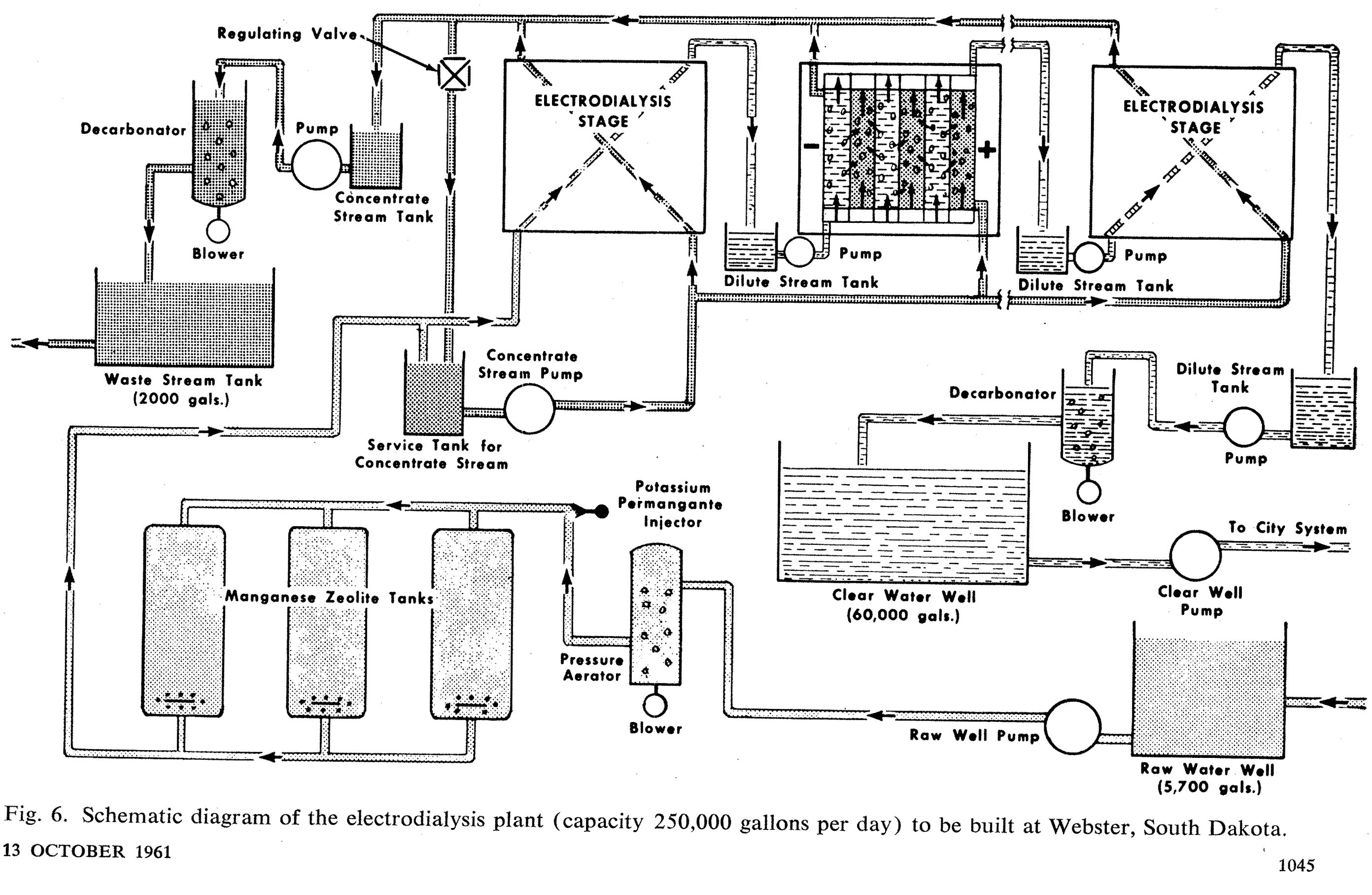

Fig. 6. Schematic diagram of the electrodialysis plant (capacity 250,000 gallons per day) to be built at Webster, South Dakota.

Table 2. Summary of estimated conversion costs (per 1000 gallons) for various processes.

Process	Estimated conversion cost ($)			
	Based on operating plants		For plant producing 1 million gal/day (1960)	For plants producing 10 million gal/day (1965)
	1950	1955		
	Sea water			
Multiple-effect flash distillation	3–4.00	1.80–2.50	1.18	0.60
Vapor-compression distillation	3–5.00	1.54–3.00	1.75	1.00
Long-tube-vertical, multiple-effect evaporation			1.00	0.60
Direct-freeze, flash evaporation			1.00+	0.60
	Brackish water			
Electrodialysis				
Total dissolved solids, 4000 ppm	1.30		1.00	0.50
Total dissolved solids, 2000 ppm	1.10		0.60	0.30

Murphy (*25*). Most commercial carbons exhibit varying degrees of cation responsivity, and the electrochemical cation capacity can be increased by treating carbons with oxidizing acids. Such carbons have capacities, per gram, of the same order as synthetic ion-exchange resins. It has also been found possible to treat carbons chemically and confer anion-responsivity on them. Preliminary cost estimates for this process indicate that it is economically feasible.

A Look to the Future

One thing is certain: when the data from the demonstration-plant program become available, we will have taken a big step toward the solution of the problem of obtaining fresh water from the sea.

However, in spite of this heartening fact, scientists and engineers do not see any possibility of a major breakthrough from operation of these five plants. Only through continued basic research can man hope to approach the theoretical minimum energy requirement of 2.89 kilowatt-hours per 1000 gallons, as calculated by Murphy (*26*). Theoreticians will immediately point out that there are inherent thermodynamic irreversibilities not included in this figure, and that a minimum of about four times this figure is all we can hope for. This still leaves plenty of room for improvement, for processes in operation today require many times this amount of energy. It is predicted that, as research and development continue along the lines discussed here, a practical limit of between 30 and 70 kilowatt-hours per 1000 gallons of demineralized water will be reached.

Even if energy were free, the cost of converting water with present equipment might still be too high. If a cheaper source of energy is found, then the emphasis in design will shift to minimizing the capital cost of the equipment as well as the cost of operation and maintenance. In the early days of the Office of Saline Water some study was made of the use of wave energy, tidal energy, wind power, atmospheric heat, and so on. The applications of solar energy and geothermal energy to the demineralization of saline waters has received some attention, but at present the capital cost of equipment to utilize these diffuse sources appears to be too great.

A current study is being made for the Office of Saline Water by Chance Vought Corporation (*27*), on the economic feasibility of utilizing radioisotopes as a source of energy for converting saline water to fresh water. It appears that the most economical radioactive source material is the calcined rare-earth fission-product cut resulting from the processing of spent reactor fuel elements. Since the cost of this material is practically zero, it should prove to be competitive with conventional fuels as a source of heat if the costs of processing and transporting it can be kept low.

Radioactive wastes are a long-lived source of heat, and of heat in predictable amounts in that the emission of energy follows certain mathematical relationships. Use of such wastes simplifies fuel logistics problems by providing energy for long periods of time with only one fuel loading. The source itself is simple in character in that the energy may be transferred to the saline water directly, without use of intermediate heat exchangers or fluids.

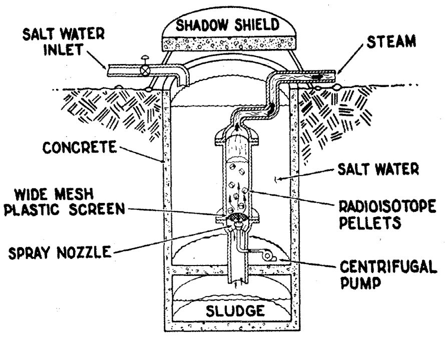

Fig. 7. Artist's concept of an energy source of the radioisotope-heat-exchanger, fluidized-bed type.

Two approaches are being pursued in the development of this energy source. The first is based on the concept of a fluidized bed in which the influent saline water is used to fluidize encapsulated radioactive pellets. The effluent from this process may be either steam or pressurized water, both being in a form suitable for supplying energy to saline-water-conversion equipment. Figure 7 illustrates the concept of an energy source of the fluidized-bed type. The other approach is that of placing the calcined radioactive-waste material in fuel rods. This approach is probably best suited for use in an indirect-cycle plant where an intermediate, nonscaling heat-transfer medium is used to transfer the energy to a conversion process such as multistage flash.

Concurrent analytical studies are being conducted on the rod and pellet configurations. The objective of these studies is to determine the optimum size and configuration of the rod or pellet array and of the heater vessel for various operating requirements, such as inlet conditions of the feed, fluid velocity, production rate, and outlet condition of the effluents. These analytical studies include thermodynamic, fluid dynamic, nuclear, structural, and chemical considerations.

In any discussion of processes the observation is invariably made that certainly reverse osmosis is the simplest, if it can just be made to work reliably. The term *osmosis* is used to describe a class of phenomena where there is a spontaneous flow of water into a solution, or from a more dilute to a more concentrated solution separated from each other by a suitable membrane. Thus, if we can find a suitable membrane we can pressurize the sea water and achieve a reversal of the normal osmotic flow.

Reid and Breton (*28*) tested a number of materials and came to the conclusion that cellulose acetate was the most promising of commercially available films. This project was discontinued when it was shown that the durability and flow rate of the membranes had to be improved before the process could compete economically with other processes. The Office of Saline Water then sponsored a basic research project with Radiation Applications, Inc. (*29*), in an effort to demonstrate the feasibility of modifying existing membrane materials both by use of nuclear radiation and by chemical means. Although the flow rates and the membrane longevity achieved to date have been lower than those required for a practical water desalination unit, the validity of the particular approach to the membrane-preparation problem has been demonstrated. Another research contract was executed with the Monsanto Research Corporation (*30*), to study the mechanism of water transmission through polymer films and to develop information which might make it possible to predict what structural and functional groups would give increased permeability and selectivity. Preliminary investigations indicate that polymeric films with appropriate micropores and selective crosslinking may meet the requirements of high water permeation, low salt transmission, and physical and chemical stability.

Loeb and Sourirajan (*31*) have been working independently at the University of California, Los Angeles, and have found that by mixing cellulose acetate with aqueous magnesium perchlorate solution and acetone, and then casting the sticky mixture cold on a glass plate, they are able to make a membrane of considerably longer life than any other yet developed. It is believed that the technique of shrinking the membrane to control pore size was the unique contribution of this project. A unit is being built, based on test data that indicate a rate of demineralization of 8 gallons per square foot per day.

The osmionic process, conceived and studied on a laboratory scale by G. W. Murphy, makes use of the driving force due to differences in concentration of brine and of the water to be demineralized. The promise of the process lies in the fact that the brine may be either natural brine or brine obtained by evaporating saline water. The sun would serve as the primary source of energy for the evaporation process. In contrast to conventional solar-energy conversion devices, no expensive fabricated structure is necessary to collect the sun's energy. No other energy source is needed, except for pumping the solutions.

The Southern Research Institute (*32*) has developed a bench-scale model of an osmionic demineralizer, shown in Fig. 8. Realization of the potentialities of this process will probably have to await development of cheaper and more selective electrodialysis membranes. With membranes currently available it has been found that promising rates of demineralization of sodium chloride solutions are obtained with the demineralizer, but that it is slightly less effective in treating solutions containing divalent ions. The bench-scale unit has contributed not only to membrane evaluation but to improvement of the mechanical design, by making it possible to determine the optimum spacing between membranes and the effect of different flow velocities in the compartments.

One of the most recently investigated methods of demineralizing sea water is one in which pure water is separated out as a solid gas hydrate. Very briefly the process is this: Any aqueous solution is brought into contact with an agent (M), such as a light hydrocarbon or a halogenated derivative, to form a solid substance of the formula $M \cdot n\mathrm{H_2O}$. This solid is a pure crystal and contains none of the constituents of the aqueous solution except the water in its lattice. One may then separate the crystals from the adhering brine and melt them, to recover the water as a product and to recover the agent for recycling to the process.

The hydrate system for desalting has many potential advantages over other methods. It is really a chemical process but is similar in some respects to a freezing process, except that the separated solid is a hydrate rather than ice. Thus, it has most of the advantages of the freezing process, such as a low energy requirement, no scale, and no membranes. It has an additional advantage over freezing processes in that it can be operated at temperatures substantially above those at which ice forms in sea water—that is, about 25° to 26°F. Depending on the hydrating agent used, the temperature may be as high as 50° to 60° thus, considerably improving the performance of the refrigeration equipment over that obtained in freezing processes.

The choice of the best hydrating agent for desalting water is based on several factors in addition to formation temperatures and pressures. The most important of these additional factors are the rate of formation of the hydrate,

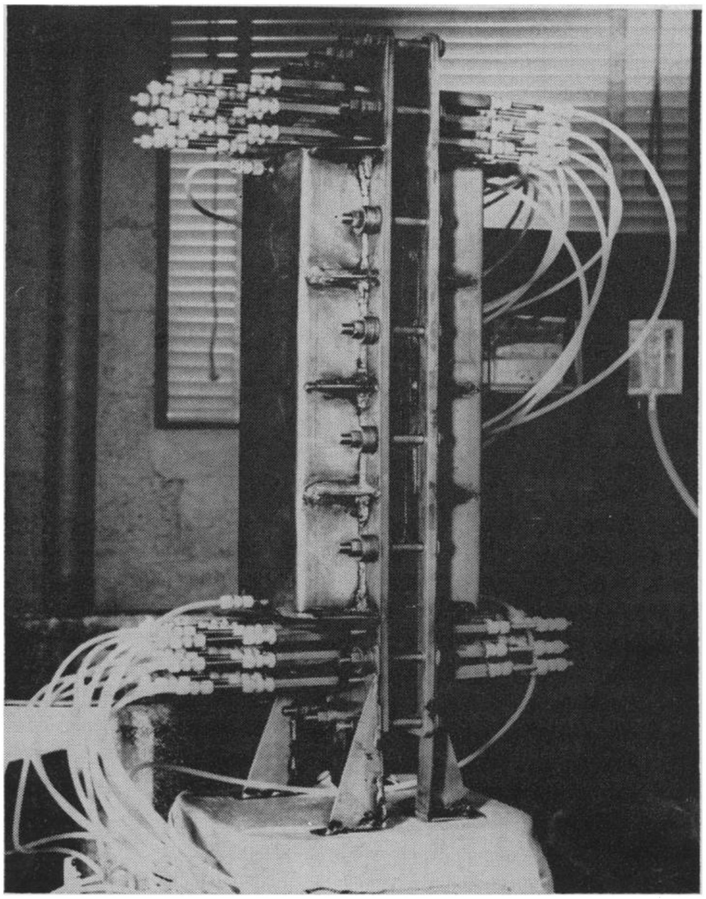

Fig. 8. Bench-scale model of an osmionic demineralizer.

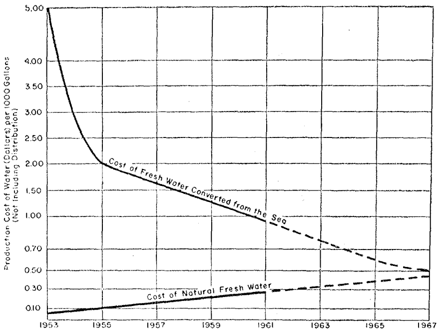

Fig. 9. Trends in the cost of developing new sources of natural and desalinized water.

the nature of the hydrate crystals, and the solubility of the agent in water. The first of these determines the size and general design of the reactor. The second determines ease of pumping a slurry of hydrate crystals and ease of washing them free of brine. The third affects the kinetics and determines the system that is needed to recover the agent from the effluent brine and fresh water.

Basic work on hydrating agents and their thermodynamic properties is being done by Barduhn, Towlson, and Hu (*33*) of Syracuse University, under contract with the Office of Saline Water. The engineering aspects of a propane system are being investigated by the Koppers Company (*34*).

This "look to the future" would not be complete without some comment on distillation. A number of new designs are being developed. Some are based on the assumption that to increase the rate of heat transfer will lead to greater efficiency. Others are based on the belief that a significant increase in rate of condensation will result in a more economical unit. The question of optimum design for distillation equipment will remain with us for some time, and improvements will probably continue to bring the cost down. However, the most convincing demonstration of progress will be the building of a plant with a capacity of the order of 50 million gallons per day, producing fresh water at a cost of 50 cents per 1000 gallons.

Costs

The estimated conversion costs for several processes and potential future costs were discussed by Gillam (*35*) at the February 1960 meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers in New York. Table 2 lists estimates that are based on data available from operating conversion equipment, or from pilot-plant studies, and anticipated future costs after the incorporation of certain modifications, as estimated from detailed engineering analyses. Such modifications might include an increase in capacity, improved heat-transfer rates, use of less expensive construction materials, alleviation of scale formation, and improved membranes.

As shown in Table 2, in 1950 cost estimates for sea-water conversion ranged up to $5 per 1000 gallons. Improved processes and equipment developed during the subsequent 5 years reduced the figure to around $2 per 1000 gallons. At the present time, additional improvements in certain distillation processes and the development of freezing processes appear to justify projection of a cost of $1 per 1000 gallons. It appears quite likely that future conversion costs for large installations will be considerably less than $1 per 1000 gallons.

A final point is one made by T. B. Noland, director of the U.S. Geological Survey, speaking at the Fourth National Watershed Congress. According to Noland, we can say emphatically that we will have water to meet our needs, except for irrigation needs in arid or subhumid regions, in the immediate future, but we can say with equal emphasis that there is not the slightest possibility that we can obtain new supplies of water at the cost of the water we use today. "This is not a matter of inflation," said Noland, "it is the law of diminishing returns. In resource development, the best and cheapest sites are utilized first, so inevitably increased use is accompanied by increased cost."

This point is made graphically in Fig. 9, which gives a comparison of costs of natural fresh water and fresh water from converted sea water. Already a few localities have found that these curves cross, or that the margin has become so narrow that the need for a dependable source has caused them to look to the sea. An economic analysis should be made for each site that is considering conversion of saline water. An article by A. W. Bruce (*36*) on the decision to install sea-water evaporators at the Morro Bay Steam Plant in California is a study of the type suggested.

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