Geothermal Chemical Engineering

ROBERT C. AXTMANN
and
LAWRENCE B. PECK

Department of Chemical Engineering
Princeton University
Princeton, New Jersey 08540

A major, national program to exploit geothermal energy requires creative chemical engineering solutions to a wide array of difficult problems. With some overlap, most of the problems fall into these categories: resource development and management, energy extraction and utilization, power cycle design and optimization, environmental engineering, and corrosion and scaling of equipment. Reinjection of waste fluids, insofar as it proves feasible, will affect the shape of the solutions in all categories.

Convective hydrothermal reservoirs, the most accessible and well characterized of geothermal resources, are immense, permeable media in which heat and mass transport are coupled with chemical reaction. Despite decades of effort, no satisfactory physical or mathematical model exists for any reservoir. Even less is known about the hot rock and geopressured resources, which also may be utilized ultimately.

Electric power production receives primary emphasis in the United States, both in terms of current utilization and of research and development. Worldwide, however, the total power devoted to agricultural activities, space heating and cooling, and process heat applications is greater than that to electric power conversion.

Because hydrothermal reservoirs are low temperature (<350°C) sources of corrosive fluids, much current development effort aims at power cycles that promise enhanced efficiencies and that avoid some of the problems of corrosion and scaling. Among the candidates are several binary cycles which employ secondary working fluids, and the total flow concept, which utilizes two-phase flow from the production wells.

Once thought to be all but negligible, the environmental effects of geothermal installations have recently been subjected to informed scrutiny and found nonnegligible. Among the problem areas are gaseous effluents including hydrogen sulfide, mercury, radon, ammonia, and H_3BO_3 and aqueous emissions that contain heavy metals. Reinjection of waste geothermal fluids would ameliorate many environmental impacts but could be complicated by silica deposition in equipment and in the underground reservoir.

A national need to develop indigeneous energy sources has quickened interest in the potential of geothermal energy for the production of electricity and of district and process heat. In the past 4 yr, the federal geothermal budget has climbed from virtually nil to approximately $\$75 \times 10^6$, nearly twice that of the thermonuclear fusion budget for 1972. Despite a plethora of legal and regulatory obstacles, the private sector is following apace.

Many of the technological problems that impede even a modest expansion in the geothermal base are chemical engineering ones. Ironically, the field has attracted few chemical engineers. The main purpose of this review is *to describe those areas within geothermal engineering that* appear most ripe for the application of chemical engineering skills. We eschew a comprehensive description of geothermal science and technology because such are available from many sources, some of which we shall remark.

Possibly the gentlest introduction to geothermal energy is Ellis' brief and lucid survey (Ellis, 1975). Despite an emphasis on electric power generation to the near exclusion of other uses and a bias toward geological aspects (the author is a geochemist), the article is an excellent summary of the current worldwide status of geothermal power.

Correspondence concerning this paper should be addressed to Robert C. Axtmann.

LITERATURE

Key elements of a geoethermal engineer's library include the proceedings of three United Nations symposia (Rome, 1963; Pisa, 1970; San Francisco, 1975), a special UNESCO publication (Armstead, 1973), and a volume that grew from the proceedings of a 1972 meeting of the American Nuclear Society in Las Vegas (Kruger and Otte, 1973). All are mixed bags, but each contains vital reference papers. Several monographs scheduled for publication during 1976 were not available for this review. The only refereed journal devoted exclusively to the field is *Geothermics*, published on an irregular schedule in Pisa, Italy. The rest of the better work is splattered all over; the largest portion appears in geochemical, geophysical, or geological journals. An American magazine, *Geothermal Energy,* began publication in 1973; 40% of the August, 1975, issue comprised advertising.

The technical report sector of the geothermal literature is vast and burgeoning; the quality follows a longitudinal rule; that from New Zealand (near the International Date Line) and Iceland (not far from the Greenwich meridian) is generally excellent, while reports from intermediate regions seldom attain mediocrity. An exception to the rule is a recent survey of geothermal resources in the United States (White and Williams, 1975).

As a result of recommendations made at the First Geothermal Implementation Meeting at Wairakei, New Zealand, in April, 1974, an international link has been established between geothermal data centers at Pisa, the Lawrence Berkeley Laboratory, California, and the U.S. Geological Survey in Reston, Virginia.

RESOURCES

United States geothermal resources include hydrothermal convective systems, the only type in present use anywhere; hot igneous systems, both of the molten magma the the hot dry rock varieties; and conduction dominated systems, most particularly, the geopressured zones of the Gulf Coast.

Recently, the United States Geological Survey has published an authoritative assessment of the potential for all three types (White and Williams, 1975). The methodology relies on site-by-site geochemical, geophysical, and geological data together with clearly stated assumptions to justify extrapolation or interpretation of the data. This procedure has the advantage that it may be updated easily when further exploration provides new field data. The results of the survey differ significantly from earlier, broader-brush approaches (for example, that of Rex and Howell, 1975).

The USGS survey is cautiously optimistic. It reports, for example, that the geothermal equivalent of twelve 1 000 MW(e) power plants with 30 yr lifetimes could utilize known reserves with present-day (geothermal) prices and technology. The onshore portion of the geopressured zones could support another 30 to 115 GW(e) generating capacity and might provide an equal amount of energy from methane dissolved in the geothermal fluid.

The potential total resource in hot igneous systems is of staggering magnitude, equivalent to 6 900 billion barrels of oil, but whether or not it will become available is a speculation. Exploitation must await development of a difficult technology which involves drilling and fracturing at advanced temperatures and at depths down to 10 km and beyond. Banwell argues, however, that a fraction of the funds that will be necessary ultimately to develop thermonuclear technology would suffice to ensure an equivalently infinite source of energy from crustal heat (Banwell, 1975).

All existing commercial geothermal installations extract heat from hydrothermal convective systems, that is, from permeable reservoirs that contain hot water, steam or both. Such systems occur in regions of recent or developing volcanism, crustal rifting, and recent mountain building. White and Williams delineate four subtypes within this genre, which are displayed in Table 1. Also included in the table are the numbers of identified United States sites of each subtype in all fifty states (Renner et al., 1975).

Only the first two subtypes listed in the table have found use as sources of electric power. The sole commercial installation in the United States, that at the Geysers field north of San Francisco, has a generating capacity of about 500 MW(e) and is of subtype (a). The Mexican Plant at Cerro Prieto, near the United States Border in Baja, California, has a 75 MW(e) plant and is of subtype (b-1). So, too, is the geothermal resource in the Imperial Valley of southern California, possibly the most likely locale for a significant increment in the United States geothermal electric capacity.

TABLE 1. IDENTIFIED UNITED STATES HYDROTHERMAL CONVECTIVE SYSTEMS

	Subtype	T_{max} °C	Number
a)	Vapor dominated	~240	3*
b)	Water dominated		
	(1) High	>150	63
	(2) Intermediate	90-150	224
	(3) Low	<90	†

* Two of these, at Yellowstone and Mt. Lucas National Parks, are unavailable for exploitation.
† Total unknown, but many have been catalogued (Waring, 1965).

A lower temperature, (b-2) resource at Klamath Falls, Oregon, has provided district heating for many years. Other such reservoirs are distributed widely over the western, continental United States with additional sites in Hawaii and Alaska (Renner et al., 1975). In addition, a determined minority of the geothermal community holds that there may be a vast resource below the Appalachian belt (Finn, 1975), but the available data (White and Williams, 1975) lend little support to the notion.

ECONOMICS

Economic analyses of geothermal power seldom transcend engineering cost studies (for example, Armstead, 1973), but a few authors have taken a broader view. Robson (1974), for example, has examined the capital requirements implicit in some of the rosier scenarios for expansion of the geothermal base. Banwell (1975) argues a compelling economic advantage for geothermal energy over all competitors, particularly in developing countries. The latter point has been made many times, perhaps most eloquently by Barnea (1972) who champions the development of nonelectrical end uses. A recent technology assessment examines the macroeconomic impacts of geothermal resource development in the United States (Futures Group, 1975).

"Net energy analysis," a new but controversial* approach to the assessment of competing technologies, involves the computation of the ratio of delivered energy to the energy value of material, environmental, and processed energy subsidies. Gilliland (1975) has made a detailed application of the procedure to the geothermal case. Not surprisingly, perhaps, she found that the net energy ratio for geothermal resources far exceeds that for oil shale.

PRODUCTION OF GEOHEAT

Reservoir Mechanics

In any high temperature geothermal power system, the actual production of the steam is clearly among the fundamental problems to be considered. It would certainly be desirable to be able to estimate the total recoverable energy in a particular hydrothermal reservoir before we risk the substantial investment required for development. Once a production system is operational, one would like to be able to predict the future productivity of the field and to evaluate the effects that various field management strategies would have on productivity.

In order to facilitate such estimates and predictions, a

* The scientists/environmentalists who invented net energy analysis (Berry and Fels, 1973; Odum, 1975) like it; many economists (Langham et al., 1976; Huettner, 1976) do not. In any case, the United States Congress has mandated the procedure for the evaluation of federal energy proposals (Public Law, 1974).

mathematical model of the geothermal reservoir is needed. Except for low temperature fields where the theory of single-phase flow in porous media may be applied, no satisfactory model of a producing geothermal reservoir yet exists.

Any adequate reservoir model would include heat and mass transport in permeable media, coupled with chemical reaction and, possibly, such effects as ground subsidence and environmental stresses. A substantial body of literature concerning heat and mass transport in porous media already exists. Much of this work relates to the production of crude oil, particularly with regard to in situ combustion (Gottfried, 1965) and hot fluid injection or steam flooding (Lauwerier, 1955; Marx and Langenheim, 1959; Martin, 1967; Davidson et al., 1967; Chappelear and Volek, 1968; Spillete and Nielson, 1968; Shutler, 1970; Kuo et al., 1970; Clossman et al., 1970). The most significant phenomena for oil production, however, are not the same as for steam production. For example, the pertinent viscosities differ by several orders of magnitude, and heat transport becomes more significant in steam production. Thus, the body of literature related to crude oil production is not directly applicable to modeling of hydrothermal systems.

Another related area is groundwater hydrology. Early, relevant contributions include the development of the appropriate differential equations and the study of steady state heat conduction (Phillip and De Vries, 1957; De Vries 1958). Stallman (1963) and Bredehoeft and Papadopulos (1965) have calculated rates of groundwater movements from temperature profile measurements using theories of heat flow in porous media. Bredehoeft and Pinder (1973) have used the digital computer for simulating aquifiers using a two-dimensional (areal) model.

More closely related to geothermal systems is the work of several authors who have modeled undisturbed natural hydrothermal systems. Early attempts at modeling the hot springs in Iceland were made by Einarsson (1942) and Bodvarsson (1949, 1954) who used a model of vertical cross section and attempted to account for transport mechanisms and sources of liquid. A similar model has been used by White (1957) and more recently by Donaldson (1968, 1970). Wooding (1957, 1963) has modeled the effects of heat using flow in porous media. While this work is closely related to the problem of geothermal energy production, it fails to account for any effect of the production itself on the system.

If only the work that directly concerns producing geothermal systems is considered, the literature is very limited. The first attempt to apply overall heat and mass balances to geothermal production was made by Whiting and Ramey (1969), who used data from the Wairakei, New Zealand, field. Other attempts at modeling the Wairakei field have been made by Marshall (1966, 1970) and by Brigham and Morrow (1974), again using lumped parameter models. All of these authors succeeded reasonably well in matching the actual trends of the reservoir but were unable to account for any spatial variations in the parameters.

Very recent attempts have centered on using distributed parameter models in an effort to develop a detailed simulation which would account for spatial and temporal variations in the heat and mass flows. Some analytical solutions to simplified mathematical models have proved useful (Kassoy, 1975), but for a detailed model of a producing reservoir, numerical solution techniques with digital computers become necessary. Solutions to the heat and mass transfer problems have been attempted by using a variety of numerical techniques (Mercer et al., 1974; Garg et al., 1975; Lasseter et al., 1975; Mercer et al., 1975; Faust and Mercer, 1975), but the complexity of the governing equations has forced a trade off between simplification and computation time.

None of the existing models takes into account the chemical reactions that occur in a geothermal system, yet some of these reactions (for example, silication) present problems hindering exploitation. Also, no satisfactory model of a system utilizing reinjection of heat depleted water has been developed, although specialized cases have been investigated (Gringarten and Sauty, 1975). A reinjection model will be necessary to determine the feasibility of this environmentally favorable technique. Clearly then, much basic chemical engineering work remains to be done if a suitable model of a producing geothermal reservoir is to be realized.

In the absence of satisfactory physical models, it is nonetheless imperative to develop and operate a reservoir in such a way as to maximize its ultimate usefulness and/or profitability. Empirical methods for rational management of geothermal reservoirs rely on careful records of discharge rates from individual wells, wellhead and downhole pressures and temperatures, geochemical observations, and certain physical measurements, for example, of gravity and ground levels. Bolton has described the evolution of such methods at the Wairakei field (1970, 1973, 1975), and Budd has sketched them briefly for the Geysers field (1973). One of the most important parameters involved in such attempts is the rate of mass recharge to the reservoir, a subject which Healy has recently illuminated (1975).

A very special challenge to the art of reservoir mechanics is posed by the Hawaiian hydrothermal reservoirs. These are believed to be overlaid with a freshwater aquifer (the Ghyber-Herzberg lens) and to interface with the oceanic waters surrounding the islands. Early attempts to model this interesting configuration physically have been reported recently along with an overview of the entire Hawaiian Geothermal Project (Shupe, 1976).

Flow Optimization. Well drilling is a major item of capital cost for any geothermal installation. While we exclude drilling technology from this review, the optimization of flow in a given well is clearly an important subject of chemical engineering interest.

Because the thermal conductivity of rock is low, geothermal fluids reach the surface with approximately the same energy content as that at which they enter the borehole from the formation. Water below 100°C or dry steam will emerge at the wellhead with little change, although the former must be pumped if artesian pressures are insufficient. Waters entering the well at $T > 100°C$ or steam-water mixtures boil as they ascend, losing temperature and pressure in accordance with saturation conditions; the flow rate and the proportion of steam at any elevation in the well are functions of the enthalpy and pressure of the mixture (Dench, 1973).

Flashing in high temperature boreholes begins about two thirds of the way to the surface in a typical well. The fluid in the upper portion will then have a lower density so that hydrostatic pressure in the formation drives the fluid out (self-flow). The flow rate stabilizes when the sum of the wellhead pressure, the weight per unit area of the fluid in the well, and the frictional resistance pressure equal the downhole pressure.

Possibly the best published discussion of two-phase flow in geothermal wells is a cogent amalgam of intuition and field data from the Wairakei borefield (James, 1970*a*). Because the maximum attainable flow rate is limited by the sonic velocity of the steam-water mixture, James suggested that it might be profitable to increase the well diameter over the upper portion of the well where steam flashing occurs. Recently, Elliott (1975) reported a more detailed examination of the proposal, but, so far as we are aware, it has not been tested in the field.

Elliott has also analyzed the prospects for increasing borehole energy output rates through use of downhole pumps. The latter would be driven by turbines which are powered by steam separated at the surface. Considering the limiting cases of pure water and 30% brine, he found that the pumps would provide more net power output than would self-flow for geothermal fluids at 150°C, but rather less for fluids at 300°C.

Other proposed schemes for enhancing borehole output power include the use of downhole heat exchangers, deep injection of hydrocarbons (for direct contact heat exchange to feed the binary cycle, see below), and injection of inert gases deep in the well to induce self-flow without phase change, that is, with minimal temperature lowering (Futures Group, 1975, pp. 52-3). None of these methods appears to have been examined in detail.

As the title of this section implies, optimum borehole flow need not correspond to maximum flow, an important point made in an early, seminal paper (James, 1967) and later amplified (James, 1970*b*). For steam and hot water fields that use a single stage of flashing for electric power generation, James shows that wellhead pressures (that is, steam separation pressure in the case of hot water) should be no lower than 65 to 85 $lb/in.^2$ gauge. At lower pressures, the flash steam flow rate will be greater but the intrinsic power potential less. Arguing from simple reservoir models, James also demonstrates that the same wellhead pressures lead to the greater integrated power yield over the lifetime of the reservoirs.

There is relatively little in the open literature about optimal flow in steam fields, although Budd (1973) has discussed briefly the experience at the Geysers field.

USES OF GEOHEAT

Present, worldwide utilization of geothermal energy is tiny on any scale save the most local. The United States is now first in electrical production with approximately 500 MW(e) from an input of about 3 600 MW(th). Iceland leads in district heating by servicing 127 000 people at a peak load of nearly 590 MW(th) (Einarsson, 1975). The U.S.S.R. devotes 5 000 MW(th) to agricultural production that totals 10^6 tons of vegetables per year (Tikhonov and Dvorov, 1970). In Hungary, geoheat is applied to animal husbandry (heating and cleaning milkrooms, cattlestalls, pigsties, and chicken houses) at a rate of 200 MW(th) (Boldizsar, 1970). Only New Zealand applies geothermal steam at rates greater than 100 MW(th) to an industrial process, the pulp and paper mill at Kawerau (Smith, 1970). Smaller scale, nonelectrical applications for a multitude of purposes have recently been tabulated by Howard (1975*a*).

That the nonelectrical applications of geothermal resources have been slow to develop may be due, in part, to two persistent myths: that industrial, commercial, or domestic heat sinks must be located adjacent to the geothermal reservoir and that geothermal reservoirs are always located far from population centers or convenient transportation thereto. Einarsson (1973) notes, however, that several installations exist where water at less than 100°C is piped from 10 to 20 km and believes that water at 150° to 180°C could be transmitted for space heating purposes as far as 50 to 75 km. While it is true that many, if not all, of the world's major developed geothermal fields for electrical generation are located in remote regions, hydrothermal reservoirs do exist close by or under Paris, Nairobi, Butte City, and Boise, Idaho. Indeed, a recent United States report contains the remarkable statement: "As geological information continues to be developed, it appears that the availability of low-grade heat in or near the major towns or cities of the Intermountain West is the rule rather than the exception" (Kunze et al., 1976).

The geothermal technology of district heating has but minor chemical components, namely, corrosion and scaling. Suffice it to note that 120000 people in Reykjavik currently obtain geothermal space heating at 25% of the cost for heat derived from light fuel oil at current prices (Bodvarsson, 1976) and that the Iceland district heating experience has received ample recent documentation (Einarsson, 1973, 1975).

The remainder of this section emphasizes applications to chemical industry and the power cycles involved in the generation of electric power. The ordering chemical electrical rather than the reverse is not arbitrary but does reflect dismay at a national plan that places primary emphasis on electrical energy conversion (Kruger, 1976) and the conviction that, ultimately, the more crucial United States problem will be lack of oil, not of generating capacity. Oil can produce electrical power at efficiencies that approach 40%; geothermal efficiencies have yet to exceed 15%. It would seem prudent, then, to apply geothermal energy to situations where its heat content utilization is limited by heat transfer rather than by the second law. By that token we would not exclude use of geothermal heat for boiler preheat in fossil fueled plants, nor in conjunction with fossil fueled superheat. As we point out below, however, neither possibility has yet been adequately explored.

Applications to Process Industries

An excellent, overall summary of the geothermal potential for process heat usage, as it was perceived at the time of the 1970 U.N. Conference at Pisa, is available (Lindal, 1973). In it, the author proposes a provocative yardstick for indicating the economic viability of using geothermal steam: the amount of steam used per unit value of the product. The index is high for seawater desalination, heavy water via the hydrogen sulfide process, ethyl alcohol from either sulfite liquors or wood waste, and solid caustic soda via diaphragm cells. The major applications at present (Lindal, 1973) include the production of pulp and paper (100)*, diatomaceous earth (35), salt from seawater (2), boric acid (15), dry grain (2), and dry seaweed (3).

A more recent report gives annotated tabulations of processes which either are or have been used commercially or have been examined for economic merit (Howard, 1975*b*). One of the most promising of the latter is the freeze drying of food which, conceivably, might be combined with other geothermal agricultural activities in an hybrid installation. Unmentioned is the use of carbon dioxide, a major component of geothermal fluids, as a feedstock for methanol synthesis (Axtmann, 1975*a*). An economic study of the extraction of carbon dioxide from either the atmosphere (0.036 v/o carbon dioxide) or from seawater ($\sim 10^{-5}$ g moles/l) identifies at least three processes that are economically competitive with limestone calcination (Steinberg and Dang, 1975). Much of the cost of these processes may be attributed to separative work. A 200 MW(e) at the Broadlands field in New Zealand would emit 3600 tons/day of carbon dioxide (Axtmann, 1975*b*), which is equivalent to about 10000 barrels of methanol/day. The carbon dioxide concentration in the gas ejector effluents at the Wairakei plant is approximately 50 v/o (Glover, 1970). Depending upon

* Numbers in parenthesis in this paragraph are the associated thermal power in megawatts delivered to the process.

its design, a Broadlands plant might produce carbon dioxide at concentrations even higher. It is noteworthy that, in the two decades after 1934, 100 000 tons of carbon dioxide for dry ice production were mined from geothermal wells near the Salton Sea in California (Koenig, 1970).

A potentially profitable process for the production of sulfur from hydrogen sulfide effluents is described below.

Beginning in 1966, the National Research Council of Iceland has sponsored studies of an extraordinary enterprise called the Sea Chemical Complex. To be situated over rich hydrothermal deposits on the Reykjanes Peninsula, the complex would be fueled by both geothermal steam and fuel oil and would utilize geothermal waters, shell sand, titanium ore, and seawater as raw materials. Products could include magnesium chloride, potassium chloride, calcium chloride, bromine, magnesium, sodium, and titanium metals, soda ash, chlorine, and, possibly chlorinated hydrocarbons. In the course of the development, a unique bicarbonate process for the production of magnesium metal from geothermal brines has evolved (Lindal, 1975).

Except for the Icelanders, most knowledgeable workers who have examined the prospects for demineralizing geothermal waters at a profit have been discouraged (Ellis, 1974). This is an area, however, that may have to be reexamined as various material shortages evolve. For example, projected demands for lithium metal for either lithium-sulfur storage cells or for thermonuclear fusion reactors far outstrip known lithium reserves (Hammond, 1976). Yet geothermal waters from the Salton Sea area contain greater than 300 p.p.m. of lithium (Ellis, 1975). A single 150 MW(e) plant at the Salton Sea would discharge on the order of 25 tons/day of lithium, and the incentive to extract this material might become overwhelming.

Many studies of the prospects for desalination of seawater have been published (Laird, 1973; Table 9 of Howard, 1975*b*), but the only active pilot studies of which we are aware are those sponsored by the Spanish government on the Island of Lanzarote in the Grand Canaries (Pendas, 1975).

Two final applications highlight the frequent geographical juxtaposition of hydrothermal resources with other mineral resources. One is a project at the Rotokawa field on the North Island of New Zealand in which a modified Frasch process is under test to employ hot geothermal fluids for extracting sulfur (Smith, 1970). The second would involve the calcination of gypsum with geothermal heat in those western states where both gypsum and hydrothermal deposits are reasonably close (Holditch, 1976).

Electric Power Generation

Extant Equipment. Figure 1 depicts the equipment configuration for the open Rankine cycle in use, with minor variations, at most of the world's operating geothermal plants. Fluid from a borehole passes through a pressure reducer at the wellhead to a cyclone separator which removes entrained water and solid debris. Wastewater, if any, flashes to atmospheric pressure through noise silencers; the residue is either reinjected or otherwise disposed of.

High pressure steam (>75 lb/in.^{2} gauge) from the cyclone exit stream joins a manifold, which may be fed by many other wells, and thence flows to the power station. Energy conversion takes place in a conventional, single-stage, turbine generator which is, typically, of 50 MW(e) capacity or less. The largest such unit in operation during 1976 was the 100 MW(e) generator at Unit #11 at The Geysers.

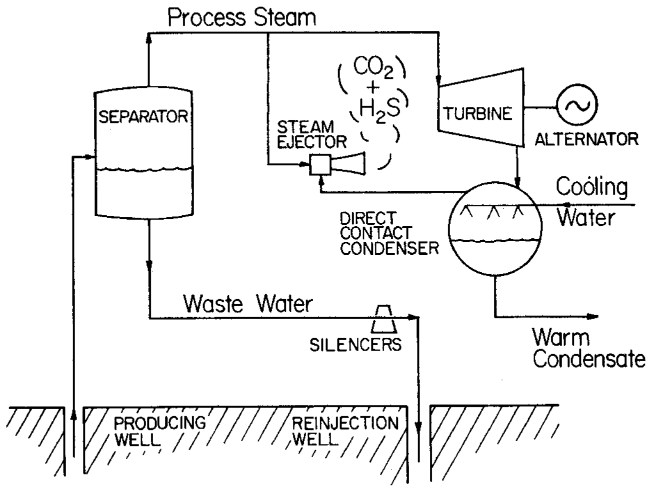

Fig. 1. Schematic diagram of a geothermal power plant at a liquid dominated reservoir with reinjection. The cooling water and condensate steams may come from and go to either cooling towers or to a natural water body. At vapor dominated fields, the separator is a simple steam trap, and the portion of the condensate that does not evaporate in the cooling towers is either reinjected or otherwise discarded.

Waste heat removal takes place in direct contact condensers, either of the low level (Finney, 1973) or barometric types. Most of the larger installations provide condenser cooling water from open cycle cooling towers: mechanical draft at Cerro Prieto and The Geysers, natural draft at Larderello, Italy. In either case, the steam condensate is more than sufficient to provide makeup water for evaporative losses in the towers. The Wairakei Plant in New Zealand is located on the banks of a swift river and is unique in that it utilizes once-through, condenser cooling.

Mechanical exhaustors or steam ejectors remove noncondensable gases from the condensers. At the Monte Amiata field in Italy, however, the noncondensable gas fraction is so large that gas ejection is uneconomical; a direct, opencycle (Brayton) system exhausts *spent steam* and noncondensables directly to the atmosphere (Anonymous, 1973).

Other variations occur. In 1973, for example, the Wairakei Plant started up a second-stage flash unit which feeds intermediate pressure steam from several wells to mixed pressure turbines. The modification increased the plant's output by approximately 15% (McKensie, 1974).

More complete descriptions are available for the larger plants: The Geysers (Finney, 1973), Larderello (Ciapica, 1970), and Wairakei (Haldane and Armstead, 1962). The last is particularly valuable because it gives, in unusual detail, the rationale for various design decisions.

All existing geothermal power stations are miniscule in comparison with modern fossil fueled or nuclear plants. The economics of scale which apply to the latter are inoperative at geothermal reservoirs where steam must be gathered from several square miles of equivalent surface area to provide feed for, say, a 75 MW(e) plant.

Geothermal installations, moreover, have all developed piecemeal; in no case was the full extent of the resource known when construction began. Add the fact that the world's total installed capacity is still of the same magnitude as the output of a single, large, nuclear plant, and it should not be surprising that almost no geothermal process equipment development has occurred until very recently. All the individual units indicated schematically in Figure 1, save only the noise silencers, were off-the-shelf items decades ago. Except for the substitution of low level condensers for barometric ones, the basic cycle of the eleventh unit completed in 1974 at The Geysers is identical to that of the first, which was constructed in 1960 (Finney, 1974).

The Binary Cycle. An alternative to the open steam cycle already described is a closed Rankine cycle that utilizes a secondary fluid such as isobutane. The overall scheme has been termed the vapor-turbine cycle (Anderson, 1973) and the organic Rankine cycle (Holt and Brugman, 1974), but most of the technical report literature refers to it as the binary cycle. A small plant that uses freon as the working fluid was built in the U.S.S.R. (Moskvicheva and Popov, 1970), but, so far as we are aware, no operating data have appeared.

Binary cycle development in the United States has been pursued by Magma Energy, Inc., of San Francisco and the Ben Holt Company of Pasadena. The original concept (Anderson, 1973) appears most applicable to low temperature (< 200°C) reservoirs, utilizes downhole pumps (instead of self-flow), and involves tubular exchangers to transfer heat from the geothermal brine to the working fluid.

Heat exchanger tests in 1974 with hot brines from the Salton Sea area disclosed serious scale deposition (Holt and Brugman, 1974), and cost studies indicated that the heat exchangers, in any case, might account for as much as 40% of the total plant investment (Sheinbaum, 1975; Giedt, 1975). As a result, recent versions of the binary cycle have included flashing the geothermal fluid (Holt and Brugman, 1974) and/or use of direct contact heat exchangers (Sheinbaum, 1975; Boehm et al., 1975). The latter technique would result in a hybridized cycle, since the secondary and primary fluids would intermix. Both schemes obviously open up the binary cycle's applicability to high temperature reservoirs.

The binary cycle has not yet been proof tested in the United States and, meanwhile, suffers the arrows of skeptics (for example, James, 1975). A recent, comparative study of the power conversion efficiencies of eight different cycles (Elliot, 1975) indicates that the binary cycle, and most particularly the binary flash cycle, are inferior in performance to all of the competitors considered except the single-stage steam flash system, that is, the cycle in use at all operating plants. Elliott's study did not compare costs, nor did it include noncondensable gas effects, which are least deleterious to the power conversion efficiency of the binary cycle.

Total Flow. A major program at the Lawrence Livermore Laboratory of the University of California is directed at the development of another new approach to geothermal power conversion. Termed the total flow concept, it involves the expansion of the wellhead, brine-steam mixture through a mixed phase expander which drives an electrical generator (Austin et al., 1973). The candidate expanders include tangential, axial, and radial flow impulse turbines, reaction devices, and positive displacement devices. Whereas the conventional steam flash cycle discards a large fraction of the available heat in the separated water, the total flow device does not. Insofar as the latter is capable of converting that enthalpy to electrical energy, the method should provide superior overall conversion efficiencies.

The program currently focuses on high temperature and high salinity applications, specifically, the resource in the Salton Trough zone of the Imperial Valley in California. In principle, however, the concept might find application with any hydrothermal resource (Austin et al., 1975).

Open Cycles. As described previously, the gassy Monte Amiata field employs an open Brayton cycle as a matter of economy. Armstead (1975) argues that such schemes could be applied more generally and particularly for low cost, peak loading service.

Regenerative Closed Brayton Cycle. Workers at Brookhaven National Laboratory have proposed an exotic configuration in which hydrogen gas is compressed in an absorption/desorption cycle on metal hydride beds (Powell et al., 1975). Low temperature ($T \sim 100°C$) geothermal heat drives the compression cycle, while high temperature fossil fueled or nuclear heat ($\sim$ 700°C) provides expansion work in a turbine. The authors claim that $\sim$ 90% of the high temperature heat would convert to electricity, and about 3 kW of low temperature heat would be required per kilowatt of electrical output. The overall energy conversion is estimated at $\sim$ 60%.

Miscellany. We have dealt with distinctly different thermodynamic cycles for the generation of electricity. Now we discuss hybrid cycles and diverse process or equipment developments which might enhance the operating characteristics or the efficiencies of any of the cycles mentioned. Some of them could also find utility in the nonelectrical applications that are treated more fully earlier.

Two authors have examined the possibility of adding a fossil fueled superheater to a geothermal steam plant. Both found lower electrical unit generating costs than for either separate geothermal and coal plants of the same total capacity as the combined plant (James, 1970*c*) or a totally geothermal plant that was expanded for peak power purposes (Armstead, 1970). Both studies were colored by transportation and fuel supply problems peculiar to New Zealand and by the characteristics of the Wairakei field. Both authors, moreover, warn against applying their results to other situations.

The general question of how fossil fueled superheaters would affect the economics of geothermal power is surely amenable to an elementary system analysis, but, apparently, no one has yet attempted one.

A related, equally unstudied question is whether geothermal sources could or should supply preheat to boiler feedwater in fossil-fueled plants. In Utah and Nevada, for example, coal fields are quite close to promising geothermal resource areas. The maximum utilization of geothermal heat in this application would not be Carnot limited, since only heat exchange between two fluids is involved. Thus, the geothermal utilization efficiency could approach that of the electrical cycle efficiency of the fossil plant multiplied by the exchanger efficiency, or perhaps as large as 30%. This is approximately twice the utilization at the Geysers plant.

The implementation of geothermal preheat would not be as simple as replacing the existing feed heaters. Modern plants employ the preheat cycle to increase the overall efficiency of the fossil plant (Sherry, 1971). Thus, new design and optimization work are required, and perhaps this cycle would be practical only for plants not yet constructed.

Corrosion and scaling problems in the heat exchangers might prove difficult, but no more so than in the original binary cycle concept (Anderson, 1973) nor in many of the nonelectrical applications discussed above.

An ambitious undertaking at the Los Alamos Scientific Laboratory aims at extracting heat from hot rocks several miles below the earth's surface (Smith, 1973). An encouraging, preliminary test of the concept was reported in early 1976 (Sullivan, 1976).

The hot rock system involves drilling two adjacent wells, hydrofracturing the rock at the bottom, injecting water into one well, and withdrawing it from the other. Others have suggested that fracturing with nuclear explosives might be more effective (Burnham and Stewart, 1973). A useful summary of the concept is available with references to the original reports (Futures Group, 1975, pp. 41-44).

To maximize energy extraction in hot rock systems, Brown has proposed a dual-cycle system consisting of a closed, topping cycle with steam and a bottoming cycle that employs an isobutane turbine (Brown, 1973). The cycles are driven with separate heat exchangers in series; both turbine condensers are air cooled because freshwater is expected to be in short supply in those regions where hot rocks are found.

Bodvarsson has recently made an econometric analysis of low temperature resource usage in the Pacific northwest and makes a case for enhancing the potential of the resources through use of novel recovery techniques that resemble those which would be used in the hot rock scheme (Bodvarsson and Reistad, 1975).

The largest operating plants at hot water fields, those at Wairakei and Cerro Prieto, both separate steam at the wellheads and there discharge wastewater. A series of papers (James, 1968*a*, *b* 1970*a*) propounds the advantages, in terms of enhanced power output, that would accrue from transmitting the two-phase mixture to the powerhouse and employing a double-flash process. The supposed disadvantages of two-phase flow (for example, cavitation, water hammer, silting, or scaling of the pipes) have proved ephemeral, at least at the Kawerau paper mill installation in New Zealand (James, 1974). In any case, the proposers of the total flow concept appear sanguine about the scheme.

ENVIRONMENTAL EFFECTS

1975 marked the end of a romantic era during which geothermal resources were perceived as founts of "clean power from inside the earth" (Lear, 1970). In that year, two on-site, environmental impact analyses of operating plants appeared. The first is a study of the Wairakei, New Zealand, plant which utilizes a liquid dominated reservoir (Axtmann, 1975*a*); the second analyzes northern California's Geysers plant which derives energy from a vapor dominated field (Reed and Campbell, 1975). Axtmann stresses operational problems with an emphasis on chemical aspects. Reed and Campbell pay more attention to impacts during exploration, drilling, and development and take particular note of physical phenomena, for example, noise pollution and soil erosion. Between them, the two reports catalogue an extraordinary range of impacts. Both make two important points: every field presents a unique mix of environmental problems, and most of the worst impacts are avoidable. In short, each geothermal installation presents abundant opportunities for creative environmental engineering.

The environmental literature of geothermal energy is sparse but growing rapidly. Two review papers from the Second U.N. Symposium include useful bibliographies on physical (Swanberg, 1975) and chemical (Axtmann, 1975c) effects. So, too, does an earlier report (Axtmann, 1974).

Gas Emissions

Geothermal steam at the world's five largest power plants (Geysers, United States; Larderello, Italy; Wairakei, New Zealand; Cerro Prieto, Mexico; and Monte Amiata, Italy) contains from 0.15 to 30% noncondensable gases including carbon dioxide, hydrogen sulfide, hydrogen, methane, nitrogen, boric acid, and ammonia. Some carbon dioxide and sulfur emission rates rival those from fossil fueled plants on a per megawatt-day basis (Axtmann, 1975*b*).

Hydrogen Sulfide. If unabated, the sulfur emission rate at the Geysers Plant would be 28 metric tons/day (Reed and Campbell, 1975). The daily emission rate at Cerro Prieto is approximately 55 metric tons/day (Axtmann, 1975*b*). In most plants, the hydrogen sulfide partitions between the gas ejector exhaust (Figure 1) and the cooling water in the direct contact, turbine condensers.* The major fraction of the hydrogen sulfide then reaches the atmosphere via cooling tower plumes or by evaporation from a natural water body.

A hydrogen sulfide emission control scheme developed for the Geysers plant combines incineration of the gas ejector exhaust (followed by scrubbing) and precipitation of elemental sulfur by means of an iron based catalyst injected into the inlet stream to the cooling towers (McCluer, 1974). The efficiency of the system may approach 90% (Reed and Campbell, 1975).

A second approach to hydrogen sulfide emission control would make use of a modified Claus plant for the production of elemental sulfur but would require indirect contact condensers at the turbines in order to concentrate all of the hydrogen sulfide in the gas ejector stream (Axtmann, 1975*c*). Preliminary cost studies indicate that for plants which emit more than about 25 tons of hydrogen sulfide per day, and which are located in areas with a firm market for sulfur, the emission control scheme could reduce the costs of geothermal power. A positive factor in the economics of the arrangement is the steam that is produced in the waste heat boiler of the Claus plant.

Hydrogen sulfide in geothermal steam may contribute to fatigue corrosion in the turbine blades of the power plant, a phenomenon that contributes to low load factors at the Geysers plant (Reed, 1975). A case can thus be made for developing steam pretreatment methods that would remove the bulk of the condensables before they reach the power plant. The Battelle Pacific Northwest Laboratory is investigating the use of metal oxides, for example, zinc oxide, as sorbents for hydrogen sulfide, and the EIC Corporation of Newton, Massachusetts, is studying a steam scrubbing process in which copper sulfate solution produces a sulfide slurry which may then be regenerated to the sulfate (Anonymous, 1976).

Carbon Dioxide. Carbon dioxide emissions, while copious (70 to 95% of total noncondensables) do not appear to present first-order environmental problems. An exception could occur in the case of condenser cooling water that is discharged to a natural water body; dissolved carbon dioxide may make a significant contribution to the growth of noxious weeds in a lake near the Wairakei plant (Axtmann, 1975*a*). A potentially profitable use of the carbon dioxide effluent is described above.

Trace Gases. Abnormally high atmospheric levels of mercury vapor exist near several hydrothermal areas (Siegel and Siegel, 1975); a few wells at the Geysers field were drilled within an abandoned cinnabar mine, a circumstance that may cause troublesome ambient mercury concentrations if the wells are placed in service (Reed, 1975). Very recent measurements at Cerro Prieto indicate mercury concentrations in the steam condensate in the range from 30 to 40 p.p.b., a result which indicates that the greater bulk of the mercury present flashes to the steam fraction (Robertson, 1976*a*).

Radon, a radioactive noble gas, is a decay product of uranium, which is frequently present in geothermal rocks. Steam at The Geysers contains radon concentrations as high as 8.3 picocuries/l; the Californian Department of Health requires that radon concentrations in uncontrolled areas be less than 3 picocuries/l. Field measurements show that ambient levels fall within the regulation in areas of normal human access (Reed and Campbell, 1975; Stoker and Kruger, 1975). Wollenberg has written a valuable re-

* Only at Monte Amiata, which employs an open Brayton cycle, do all the noncondensable gases emerge from the turbine exhaust.

view of the radioactivity anomalies associated with hot spring systems and presents evidence that systems in which deposition of calcium carbonate predominates give rise to gamma ray exposure rates two orders of magnitude greater than systems in which silica deposition predominates (Wollenberg, 1975).

Aquecus Effluents

The total mineral content of geothermal waters that have been flashed at atmospheric pressure varies from a few thousand parts per million (for example, at Wairakei) to as high as 256,000 p.p.m. at the Salton Sea area in the Imperial Valley, California. The geochemical basis for the composition of geothermal brines is complicated but fairly well understood. Ellis has published a recent treatise on the subject (1976) as well as a briefer summary at an elementary level (1975).

While the bulk of the dissolved solids are the relatively benign alkali halides, trace amounts of heavy metals are also frequently present. Published analyses of geothermal fluids, however, seldom include concentrations much below the parts per million level. As a result, the potential hazards of trace metals have only recently become a matter for study and concern (Sabadell and Axtmann, 1975; Robertson, 1976*b*). For example, mercury and thallium levels in waters from the Broadlands field in New Zealand are lower than the limits of detection (0.01 p.p.b.), yet amorphous silica precipitates from borehole discharges at the same field contained as much as 200 p.p.m. of mercury and 1 000 p.p.m. of thallium. Apparently, mercury ion exchanges on the silica precipitate surface, while thallium coprecipitates with SbS, which is formed when the hydrogen sulfide containing waters are cooled while flowing past the silica (Weissberg, 1969).

Routine disposal methods for the wastewaters from liquid dominated reservoirs include ponding (Cerro Prieto), discharge to a river (Wairakei), discharge to the ocean (El Salvador), and reinjection (Otake, Japan). As discussed in more detail previously, only the latter procedure is likely to find environmental acceptability in the United States.

In the case of both vapor and liquid dominated fields, dissolved chemicals are present in the blowdown from cooling towers. At The Geysers, for example, approximately 80% of the steam condensate evaporates in the tower, while the remaining water contains dissolved ammonia and boric acid, one or both of which have proved deadly to a steelhead trout population when the effluent discharged to Big Sulfur Creek (Finney, 1972; Reed and Campbell, 1975). Similarly, at Larderello, boron concentrations in the condensate exceed permissable levels for discharge to streams adjacent to agricultural areas. In both locations, reinjection has proved to be a satisfactory solution.

Environmental Dosimetry

Both the magnitudes and the pathways of polluting geothermal discharges change markedly as a geothermal area progresses from its natural state (frequently characterized by significant discharges of hydrogen sulfide, mercury vapor, and radon from fumaroles or hot springs), through exploration, drilling, field testing; to periods of production, maintenance, shutdown, and decommissioning. Unlike more conventional power sources, geothermal areas may extend over many square miles. From the perspective of both industrial hygiene and public health, it would be desirable to develop cheap, reliable, integrating instruments for measurements of low concentrations of hydrogen sulfide, mercury, boron, radon, heavy metals, and, possibly, silica vapor (Axtmann, 1976).

CORROSION AND SCALING

The chemical impurities found in all geothermal fluids are potential agents for corrosion and scaling. Of the two, corrosion is probably the easier to handle, for example, through use of corrosion resistant materials. General materials specifications appear impossible to compile, however, because the identities and concentrations of the corrosive constituents vary so widely from site to site. The bulk of the dissolved solids are alkali halides with smaller amounts of heavy metal salts; the dissolved gases may include hydrogen sulfide, hydrogen fluoride, carbon dioxide, and ammonia.

Banning and Oden (1973) have collated data on the brine compositions at several of the larger operating plants, as well as the corrosion resistance of many metals and alloys of likely interest. They make few suggestions, however, on how to choose the proper material systematically. Ongoing projects at Oak Ridge National Laboratory and at Battelle Pacific Northwest Laboratory are investigating the role of individual constituents in corrosion with the hope of identifying synergistic effects (Anonymous, 1976). A group at Lawrence Livermore Laboratory is concentrating on particular problems posed by the highly concentrated brines from the Salton Trough region in southern California.

Hydrogen sulfide presents difficulties if it reaches the turbine of an electric power plant; at sufficiently high concentrations, it appears to cause fatigue corrosion of the turbine blades (Reed, 1975). Steam pretreatment methods for hydrogen sulfide removal are the subject of studies at Battelle Pacific Northwest Laboratory, the Environmental Impact Center (EIC), and the Dow Chemical Company (Anonymous, 1976).

Another approach to corrosion control is via the use of corrosion resistant coatings. The Brookhaven National Laboratory has proposed a polymer-concrete composite for such applications (Steinberg, 1972), and some tests are reported to be in progress (Steinberg, 1976).

The second problem, that of scaling or buildup of minerals in plant equipment, is not as amenable to solution by existing technology. The major contributor to scale formation is amorphous silica. Silica exists as dissolved silicic acid in deep hydrothermal fluids at concentrations that correspond to the solubility of quartz at the appropriate temperature. As the fluid rises to the surface and is cooled and/or flashed, the silica concentration exceeds the solubility of the amorphous form, and precipitation occurs via the formation of polymeric silica structures. The mechanism of polymerization and its relationship to scale buildup are not fully understood. To review previous work in the area is beyond the scope of this paper, but Krauskopf (1956) provides a comprehensive review of the work prior to 1956, and recent, concise reviews of the problem are presented by Owen (1975) and Hoffman (1975).

Two approaches to studying the problem of silica scaling have emerged. On the one hand, several groups have begun fundamental research into the mechanism and kinetics of silica polymerization and the influence on this reaction of the many variables such as temperature, *p*H, dissolved silica concentrations, and concentrations of other constituents of geothermal brines. It is hoped that by understanding the complex process by which dissolved silica deposits as scale, the problem may be eliminated or at least controlled. Olin (1975) finds that for the Salton Sea geothermal fields, controlling the *p*H and decreasing the residence time of the fluid in the plant may retard, but probably not eliminate, deposition. Peck and Axtmann (1975) have proposed that the reaction may best be described as a nucleation and growth of particles followed by agglomeration, a suggestion that finds support in the data of Harvey et al. (1976) who have recently reported on experiments with synthetic geothermal solutions at 95°C.

Other workers have taken a more pragmatic approach and have investigated methods of silca scale control without the benefit of a complete knowledge of the scaling process. An early attempt at reducing deposition involved dilution of geothermal fluids with pure water before district heating systems were fed (Thórhallsson et al., 1975). This procedure reduced the deposition rate but did not eliminate scaling. Yanagase et al. (1970) showed that ponding of discharge waters is accompanied by formation of colloidal silica, which could then be discharged without silica deposition. This method would be unsatisfactory, however, for use with reinjection procedures. Ragnars (1975) describes the use of a direct contact heat exchanger to heat freshwater by the hot geothermal fluid. In this way the corrosive gases are removed and scale buildup lessened owing to dilution. Rothbaum and Anderton (1975) propose the removal of silica by addition of quicklime, which precipitates silica as calcium silicates, a useful by-product. The process was successful in removing silica and thus preventing deposition in field tests at the Broadlands field. Shock and Duba (1975) investigated the possibility of using electrical potentials to control deposition. Scale due to metal ions could be greatly increased on a negative electrode, and silica scale was somewhat reduced.

Another novel approach to the elimination of silica scaling was demonstrated on a laboratory scale by Kunze et al. (1976). They heat exchanged a synthetic geothermal fluid with a second working fluid, using a fluidized bed of sand particles as the heat exchanger and the hot geothermal fluid as the fluidizing agent. Abrasive action of the sand effectively eliminated scale buildup on the heat transfer surfaces, and very high heat transfer coefficients were maintained. Subsequent field studies at the Raft River, Idaho, geothermal field (Grimmett, 1976) revealed that most of the silica was removed from the fluid by passage through the bed, while other minerals remained in solution. This result has been experimentally verified in laboratory experiments with synthetic solutions by Morgan and Axtmann (1976), and the procedure appears to be one of the more promising thus far investigated.

Other, less widespread, scaling problems are caused by calcium carbonate deposits (Ellis, 1975) and by heavy metal sulfides (Jackson and Hill, 1976). Calcite deposition may be eliminated by maintaining carbon dioxide pressures (Kunze et al., 1976) or by lowering the water temperature (Hoffman, 1975). Jackson and Hill (1976) offer several methods for reducing heavy metal sulfide deposition.

REINJECTION

As discussed in the Section above entitled *Environmental Engineering* and in more detail elsewhere, Axtmann (1975*c*), the reinjection of spent geothermal fluids at liquid dominated reservoirs amounts to an environmental imperative. The reinjection procedure is deceptively simple: pump the wastewater down a nonproducing well into the aquifer. Not only would contaminants be kept out of the environment, but the unusable enthalpy and mass would be returned to the reservoir, thus reducing thermal pollution and perhaps prolonging the reservoir lifetime.

Reinjection is currently practiced at The Geysers field (Budd, 1973) and should be easily implemented at any other vapor dominated field. The major advantages of reinjection, however, accrue at water dominated fields where reinjection is hampered by the silication reactions which produce scaling in plant equipment. If silica polymer is present in cool reinjection water, it may eliminate or drastically reduce the permeability of the formation surrounding the reinjection well. Ultimately, the procedure might destroy the overall permeability of the aquifer (Owen, 1975; Ellis, 1975).

Several years ago a full scale reinjection experiment was performed at the El Salvador installation (Einarsson, et al., 1975). Silica precipitation was prevented at the cost of reinjecting only high temperature ($\sim$ 150°C) water. No adverse effects on the nearby producing wells were noted, but the hotter reinjection temperature forced a lower energy recovery rate (approximately 50%) and, in any case, would not be practical for low temperature resources.

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THE AUTHORS

Robert C. Axtmann is Professor of Chemical Engineering at Princeton University and a founding member of the Center for Environmental Studies at that institution. A graduate of Oberlin College, in 1950 he received the Ph.D. degree in physical chemistry from the Johns Hopkins University, where he worked with Professor Donald H. Andrews. His interest in geothermal power received strong stimulus from Annabell H. Axtmann who, quite reasonably, insisted that they spend his academic leave during 1974 in New Zealand.

Lawrence B. Peck is a candidate for the Ph.D. degree in Chemical Engineering at Princeton. He graduated in Chemical Engineering from Purdue University in 1974. At Princeton, he has found that graduate research that is contingent upon government funding furnishes an excellent excuse for improving his golf game.

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Scopolamine Permation Through Human Skin *In Vitro*

The sorption and rate of permeation of scopolamine base in human skin have been measured as a function of drug concentration in aqueous solution contacting the stratum corneum surface of the skin. The sorption isotherm is nonlinear, and the apparent penetrant diffusivity computed from steady state permeation data is greater than that estimated from unsteady state (time lag) measurements.

By assuming that sorption occurs by both ordinary dissolution and binding of penetrant to immobile sites in the membrane, the experimental sorption isotherm can be predicted, and the disparity between steady state and time lag diffusivities can be reconciled.

S. K. CHANDRASEKARAN
A. S. MICHAELS
P. S. CAMPBELL
and
J. E. SHAW
ALZA Corporation
Palo Alto, California

SCOPE

The unique molecular transport and barrier characteristics of human skin, which provide our protection against most toxic substances in the environment and have frustrated efforts to use the surface of the body as a route of entry of drugs for disease treatment, remain incompletely understood. In an earlier paper (Michaels et al., 1975), we employed the principles of membrane permeation and a simplistic two-phase representation of skin microstructure to evolve a model of the transdermal permeation process which was shown to be rational and useful for predicting the permeability of skin to various micromolecular substances.

In this paper, we examine another property of skin affecting its permeation behavior: its tendency to sorb and bind substances during the process of permeation. The extent and nature of the binding phenomenon is of great practical importance in determining the unsteady state kinetics of transdermal mass transport and the efficiency