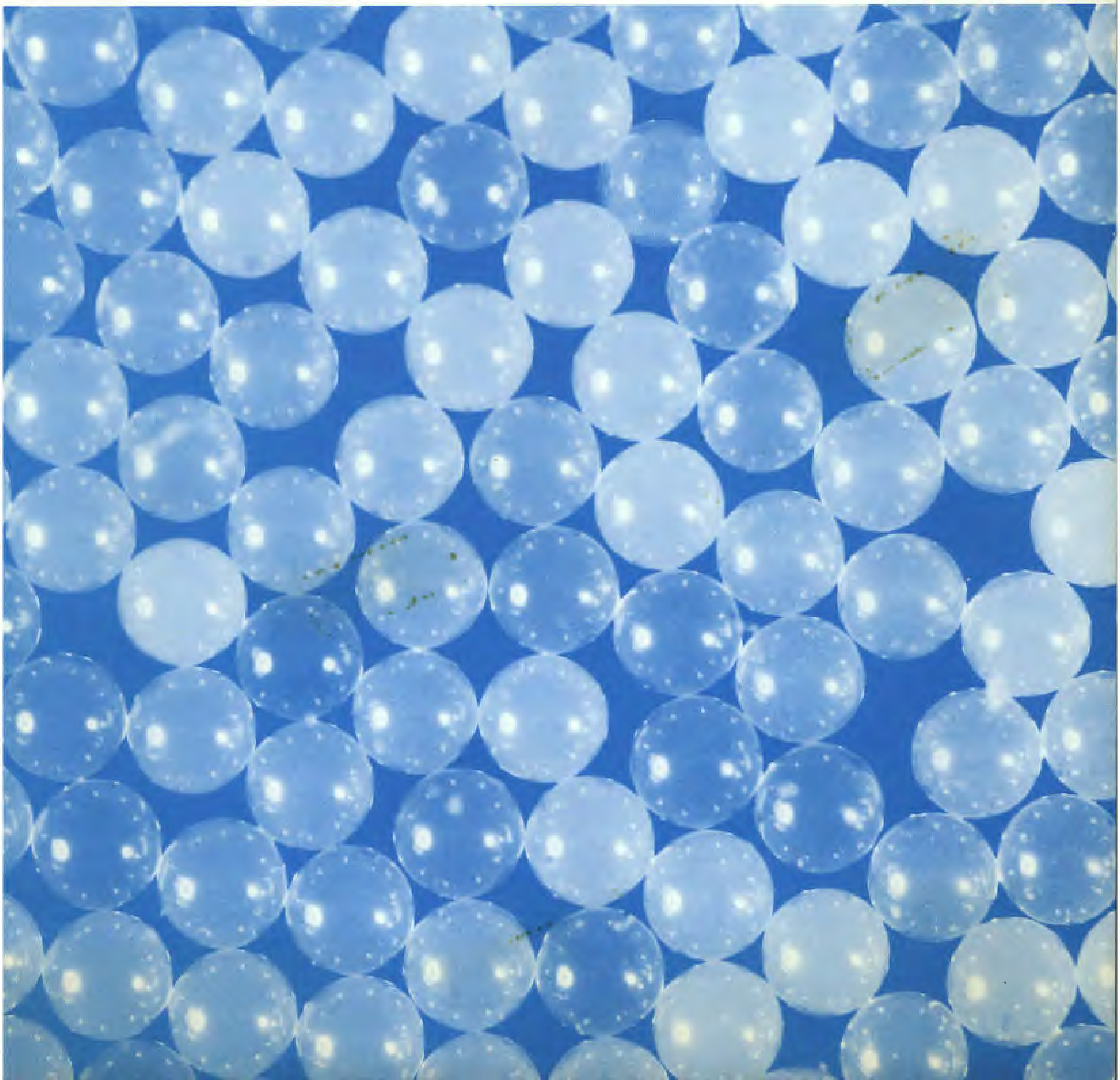
Review

FALL 1973

OAK RIDGE NATIONAL LABORATORY



Review

OAK RIDGE NATIONAL LABORATORY

VOLUME 6, NUMBER 3 **FALL 1973**

FEATURES

THE COVER: The remarkable uniformity of these 355-μm thorium oxide microspheres was achieved by vibrating the nozzle through which they are sprayed as a sol. Paul Haas, who, with Sam Clinton, both in Chemical Technology Division, devised the process, discovered that if the vibration of the nozzle is kept to a specific resonance, the droplets dry out to gel microspheres of just the desired size. Paul Kasten tells the whole story on facing page.

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Assistance is provided by Graphic Arts, Photography, and Technical Publications Departments of the ORNL Information Division.

The *Review* is published quarterly and distributed to employees and others associated with the Oak Ridge National Laboratory. The editorial office is in Room 149, Building 4500-North, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee 37830. Telephone: 483-8611, Extension 3-6900 (FTS 615-483-6900).

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

Paul Kasten has covered a lot of ground since he was awarded his doctorate in chemical engineering by the University of Minnesota in 1950. Coming directly to ORNL, he was immediately plunged into reactor physics and moved from there to reactor analysis and development programs. He spent over a year in Jülich, Germany, in 1963 and 1964 as Guest Director of the Institute for Reactor Development at the Nuclear Research Center, joined the U.S. Reactor Evaluation Team to India in the spring of 1967, was a U.S. delegate to the IAEA Thorium Utilization Conference in Vienna in 1968, taught a course in thorium reactor evaluation at the Institute of Atomic Energy in São Paulo, Brazil, in the fall of 1969, spent the academic year of 1968–69 on the faculty of the University of Tennessee as professor of nuclear engineering, and just this fall took a flying trip to visit the gas-cooled reactor programs being carried out at the Dragon Project, Winfrith, England, and at the KFA in Jülich. He has been director of the Gas-Cooled Reactor Programs at the Laboratory since 1970.
at the Laboratory since 1970. Here he confers with J. H. Coobs (r.), Assoc. Dir. of the GCR Programs.

The Interesting Fuel for the HTGR

By PAUL KASTEN

High temperature gas cooled reactors (HTGRs) are now being marketed commercially by Gulf General Atomic (GGA); however, an important factor in their acceptance as a power source is the ability to recycle HTGR fuel economically. Fuel recycle is particularly important to those reactors operating on the thorium cycle, which is the preferred cycle and the one used in GGA-designed systems. Use of the thorium fuel cycle rather than the uranium cycle improves the fuel burnup efficiency of the reactor and promises improved economic performance if commercial fuel recycle is available.

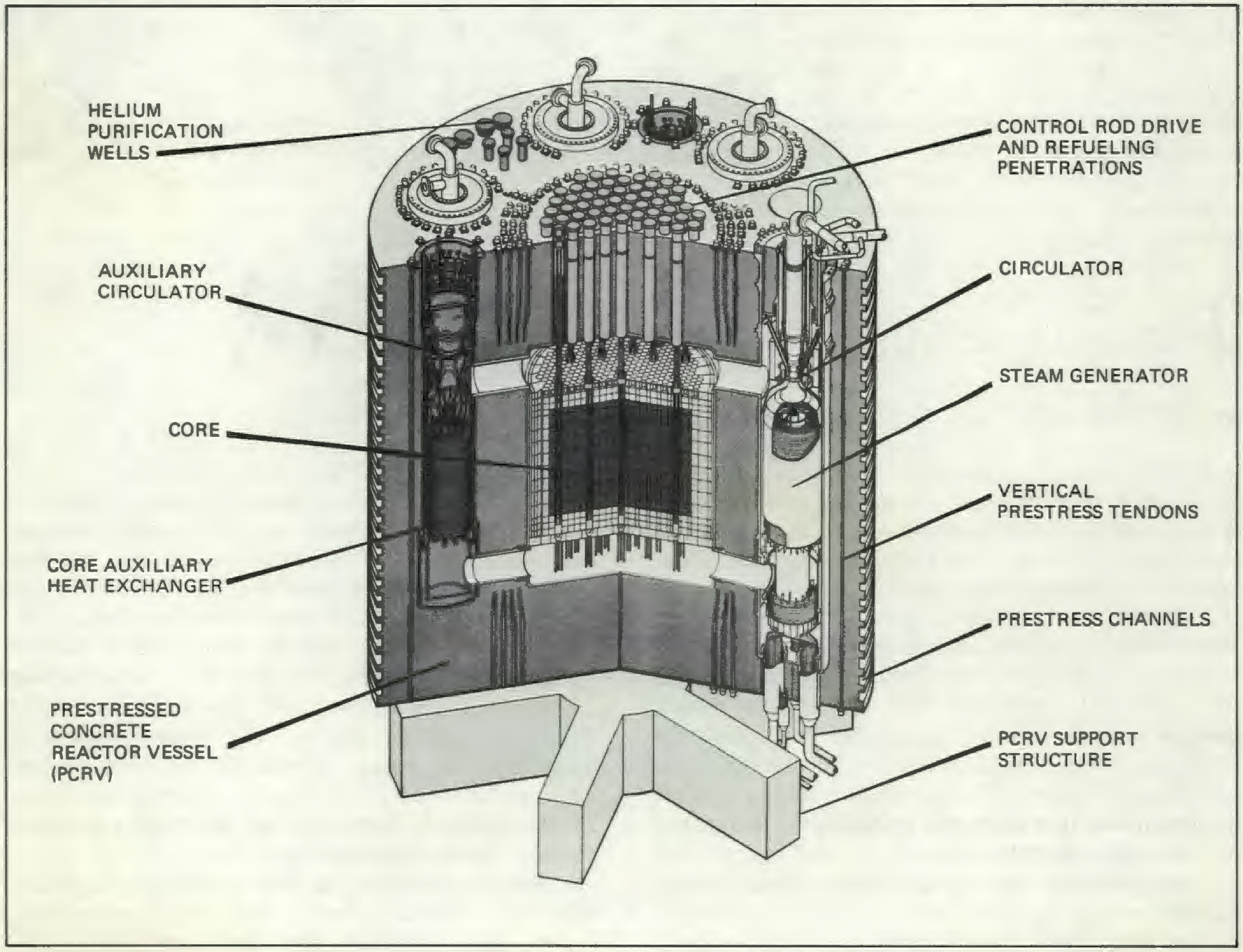
Development of HTGR fuel recycle technology, under the direction of Ray Wymer, Chemical Technology Division, and A. L. Lotts, Metals & Ceramics Division, is a major effort of the Gas Cooled Reactor Program at ORNL. Also involved are AEC-supported programs at GGA and the Idaho Chemical Processing Plant (ICCP). The ORNL work dates back about seven years.

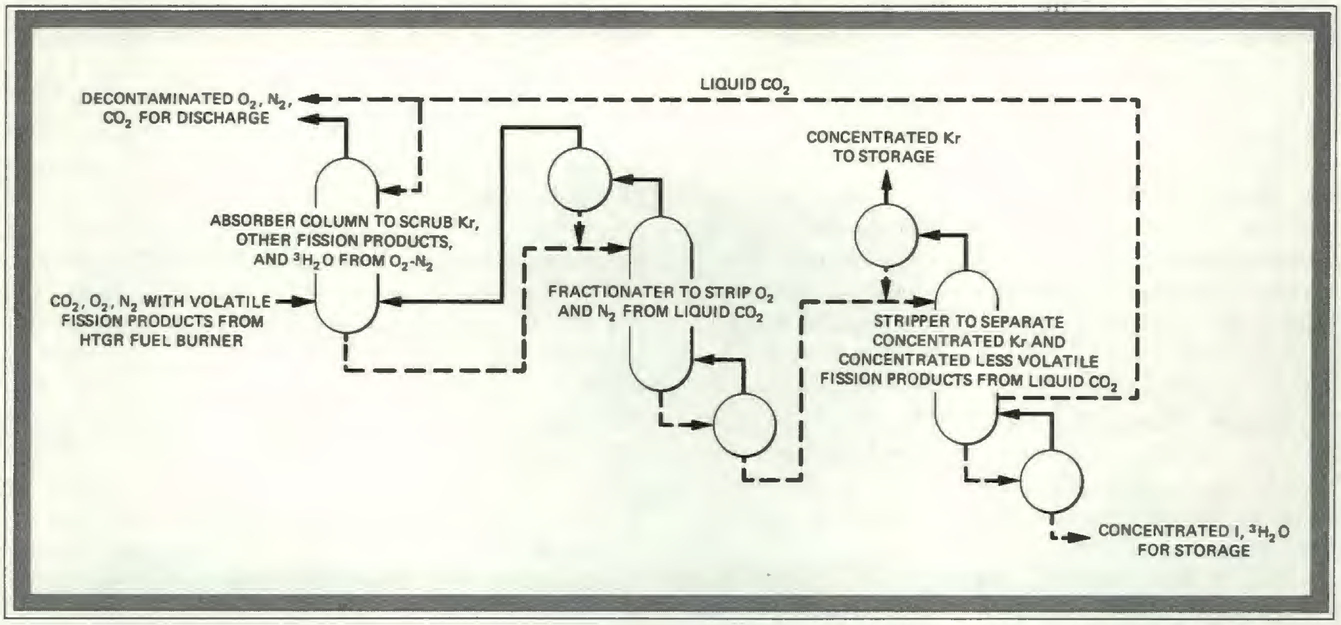
To date, six large HTGRs have been sold, with operation of the first of these units to begin about 1980. An HTGR prototype, the 330-MW(e) Fort St. Vrain reactor, is to start generating power in early 1974. Three experimental gas-cooled reactors are operating successfully: the Dragon reactor in England, the AVR reactor in Germany, and Peach Bottom I near Philadelphia.

The HTGR core assembly consists of fueled graphite elements. Coated fuel particles are fabricated into fuel rods that are then placed into channels of a graphite moderator block. The reference initial fuel contains fissile UC_2 and fertile ThO_2 particles about the size of grains of table salt. The fertile kernels are coated first with a low-density pyrolytic carbon layer followed by a high-density pyrolytic carbon layer — the so-called Biso coating. The fissile kernel is coated with a low-density pyrolytic carbon layer and with a silicon-carbide layer sandwiched between two high-density pyrolytic carbon layers; this is the Triso coating. These coatings serve as pressure vessels and retain fission products; the fissile kernel's silicon-carbide coating retains heavy metal fission products such as strontium and cesium in fuel that goes to high burnup. The coated microspheres are mixed with matrix material containing pitch and graphite filler to form fuel rods about $^5/_8$ in. in diam and 3 in. long. These rods stack end to end in the fuel holes of the hexagonal graphite moderator block that stands about 31 in. high with 14-in. flats (8-in. faces).

A recycle element is similar to the initial fuel except the fissile particles consist of Biso-coated kernels of (Th, ^{233}U)O_2, having a Th/U ratio of about 4. The use of Triso-coated particles for initial fuel permits the separation of "burned" ^{235}U particles from the ^{233}U which is bred into the fertile particles; such a separation leads to the selective removal of the ^{236}U generated in the initial fissile particle during reactor exposure, thus preventing that nuclear poison from accumulating in the reactor. Separation of particles isn't necessary for the recycle fuel element, since neutron capture in ^{233}U leads to generation of a fertile

HTGR nuclear steam system





The KALC (Kr Absorption in Liquid CO_2)process for decontaminating off-gases from fuel processing

material. These fuel features need to be considered in the fuel reprocessing operations.

The overall operations of interest in HTGR fuel recycle are those that take place between the discharge of spent fuel elements from the reactor and the return of refabricated fuel elements to the reactor. Factors that have to be considered are shipping, handling, and storage; recovery and purification; fuel element refabrication; and waste management. Fuel recycle developmental work thus involves reprocessing and refabrication processes, design of associated equipment, and development of operating procedures. Furthermore, operations must be performed on a pilot plant scale in order to integrate processes, equipment, and operation properly and to demonstrate practicality. Such a demonstration includes proof testing of refabricated fuel elements in commercial reactors. Finally, cost analyses, which include such factors as plant design, fuel performance, and recycle processes and equipment, are performed to help choose alternatives and to extrapolate the technology to commercial scale.

Current fuel recycle operations involve crushing irradiated fuel elements and burning the graphite and the particle coatings in a fluidized-bed burner. This operation leaves the Triso-coated fissile particles intact in a silicon carbide coating, but exposes the kernels that had only carbon coatings. Leaching of the burner ash by a solution of nitric acid plus a small amount of hydrofluoric acid dissolves all fuel but that protected by SiC. This is the first step in the Acid-Thorex process, first developed at ORNL by a team from the Chemical Technology Division led by A. J. Gresky, R. H. Rainey, and Bob Lowrie. The solution is treated by means of solvent extraction to separate fission products from the fuel and to separate uranium from thorium. The product uranyl nitrate is mixed with thorium nitrate and then undergoes nitrate extraction to produce a sol of ThO_2-$^{233}UO_2$ having a Th/U ratio of about 4. This is the Solex process, developed by A. D. Ryon and John Moore. This sol is then passed through a nozzle to form droplets; as water is extracted from them by an alcohol drying agent, they turn into gel microspheres, which are dried and calcined to become the recycle fuel kernels. This sol-gel process was developed by Paul Haas and Sam Clinton.

The kernels are coated with a low-density pyrolytic carbon when they are heated to around 1400°C in a fluidized bed that has acetylene gas passing through it. The high temperature thermally decomposes the acetylene and causes carbon to deposit on the fuel kernels to form the buffer coating. This porous buffer layer provides volume for fission gases and also absorbs fission product recoils, minimizing damage to outer coatings. Following deposition of the buffer coating, propylene is used to deposit a high-density pyrolytic carbon layer on the buffer layer, which serves as the pressure vessel for the fuel and associated fission products. (If Triso coatings are needed on fuel recycle particles, additional coatings are deposited, employing processes similar to those just described.)

The coated recycle fuel granules, which are Biso-coated thoria and Biso-coated (Th, ^{233}U)O_2 particles, are then mixed to homogeneity with diluent particles and placed in a fuel rod refabrication machine; matrix material of graphite flour and pitch is then warm-pressed into the bed of coated particles to form the fuel rod. The rods are stacked in the fuel holes of the graphite moderator element and capped with graphite plugs. The whole block is raised to high temperatures to carbonize the "green" fuel, and, after inspection, the product elements are ready to be shipped back to the reactor as recycle fuel.

This process entails numerous fuel handling and transfer operations and many measurements related to quality assurance and control of fuel inventory. Further, the fuel processing and fuel refabrication operations need to be performed remotely behind heavy shielding because of the presence of fission products during the former and ^{232}U decay products during the latter. The problem is how to do the remote operations economically.

Developmental work in HTGR fuel recycle has many aspects. In developing the basic technology for fuel recycle, specific demonstrations in "hot" pilot plants are planned. The R & D work on the fuel crushing and fluidized-bed burning operations is being performed at GGA, where a "cold" pilot plant is under construction. The hot pilot plant for fuel reprocessing, which would demonstrate fuel crushing, burning, and fuel recovery, will be at ICPP. Results from GGA's cold head-end processing pilot plant will be used in the hot pilot plant at Idaho.

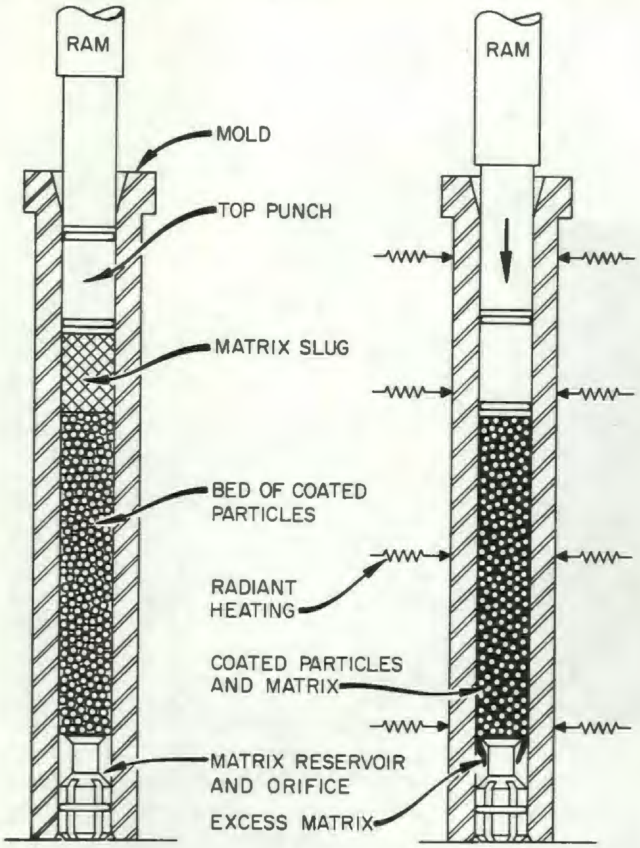
The ICPP operation will also demonstrate handling and cleanup of off-gases from burning the fuel. A primary contaminant of the off-gas after filtering is radioactive krypton. The technology for off-gas cleanup is being developed by Ron Glass and others in the Chemical Technology Division, using the KALC process (krypton absorption in liquid CO_2) originated by the division's director, Don Ferguson. In this process the burner off-gas which is primarily CO_2 is liquified and then used to absorb krypton and xenon; subsequent fractionating and stripping operations remove these and other radioactive noble gases. This process also looks promising for removing iodine and tritium. The KALC process will be employed in the ICPP pilot facility.

The method used at ICPP for separating fuels and fission products is to be the Acid-Thorex process. This involves separation of the uranium and thorium from the fission products in an extraction column, followed by separation of the uranium from the thorium in a partitioning column. The uranium is then separated from the organic solvents in a stripping column and after evaporation is put through a denitration step to solidify the product. The Acid-Thorex process was demonstrated by Earl Shank in 1954 in a pilot plant operation at ORNL, using fuel that had had only a low exposure, but the fuel processed at ICPP will have been highly irradiated in the Fort St. Vrain HTGR. The influence of high fission product concentrations on fuel recovery operations is under study by Karl Notz in the Chemical Technology Division using irradiated fuel capsules as the fission product and fuel source. Leaching operations on unirradiated fuel after burning the graphite and carbon are being conducted by GGA. The Idaho plant will use the information gained from these studies in its hot pilot plant work, which also will include waste treatment, disposal, and material handling operations.

Fuel fabrication development is the responsibility of ORNL, specifically of John Sease, Metals & Ceramics, and Notz. As with reprocessing, the effort involves development of technology, followed by demonstration in a hot refabrication pilot plant. The Thorium-Uranium Recycle Facility (TURF), completed in 1967 under the direction of A. R. Irvine, project engineer, will be used for this. TURF will be equipped with a pilot plant that is being designed by a team directed by J. W. Anderson, project engineer, of UCND Engineering, and A. L. Lotts, project manager, of the Metals & Ceramics Division. Staff members on the team include J. W. Snider and Frank Harrington of Chemical Technology Division; Sease, Paul Jarvis, and Frank Davis of UCND Engineering; and Howard Cochran of Instrumentation and Controls Division. The pilot plant's collection of shielded hot cells is equipped for the variety of operations associated with fuel refabrication.

Recycle fuel fabrication starts with ^{233}U in the form of uranyl nitrate recovered from HTGR fuel processing operation. The uranyl nitrate is mixed with thorium nitrate, and mixed-oxide microspheres are prepared by the sol-gel process

Slug technique for making bonded bed fuel sticks



already described. In fabricating fuel microspheres, careful control of kernel size is important in order to assure control of coating thickness, as well as better separations between fissile and fertile particles. The process has recently been significantly improved by Haas to give excellent control of kernel diameter. By vibrating the nozzle or orifice at a frequency in resonance with the natural frequency of drop formation, remarkably good size control has been achieved.

The fuel kernels are then coated as described, in a coater that has to be operated remotely, as does all the other refabrication equipment. This requires special equipment and maintenance design, not to mention material handling and inspection operations. Since coater operation results in soot deposits throughout the system and a consequent need for frequent parts replacement, coater development at ORNL has emphasized a system designed for low heat absorption to facilitate rapid changeout of parts. Mack Lackey of Metals & Ceramics is currently developing a prototype of the coater to be used by the pilot plant. Inspection operations, such as determination of coating density, thickness, and structure, are difficult enough in an ordinary laboratory, but the remote operation requirement makes inspection a challenging assignment. Bill Perkins, Metals & Ceramics, is working on this task. One development, by Perkins and Lou Thacker, of Instrumentation & Controls, is a particle size analyzer which determines particle size to better than ± 1% at a rate of 20,000 particles per minute.

In fabricating fuel rods, matrix material needs to be dispersed among coated fuel particles. The process developed at ORNL by the Metals & Ceramics Division's Ron Bradley and Sease, called the Slug Injection process, involves pouring coated particles into a mold, placing a cylinder of preformed matrix material on the bed of particles, and warm pressing the the matrix into the particle bed. A laboratory-scale fuel fabrication machine, designed by Don Cannon of UCND Engineering, is automated to perform this process and is in routine operation in Metals & Ceramics. On it, a rotating table has different stations where the various operations of particle loading, heating, intrusion, cooling, and rod removal are carried out in series. This is planned for use in refabrication of fuel in TURF.

After fabrication, the rods are stacked into channels in the graphite block, and the whole element is raised to carbonizing temperatures to drive off the non-carbon constituents of the fuel matrix; this requires ventilating and off-gas handling. The product element is then ready for return to the reactor for use.

The ultimate success of a refabrication process is in the fuel's satisfactory performance under reactor operating conditions. In order to determine the permissible refabrication process conditions, an irradiation testing program of recycle-type fuels is being carried out at ORNL by Jim Scott and Walt Eatherly of Metals & Ceramics and John Conlin of the Reactor Division. They are conducting capsule irradiation tests in the HFIR and the ORR; elsewhere tests are going on in the Peach Bottom HTGR and some have been performed in the Engineering Test Reactor in Idaho. These tests not only lead to better understanding of the fuel's performance in the reactor, they also result in a quantity of irradiated materials for use in testing fuel reprocessing methods. Postirradiation studies are in the hands of Frank Homan of Metals & Ceramics. Full-sized HTGR fuel recycle elements will be fabricated in the TURF hot pilot plant and exposed to reactor operating conditions to verify them as a satisfactory fuel.

Automatic fuel rod machine (Capacity approximately 4,000 per day)

The TURF pilot plant offers a scaled operation, providing a balance between size and cost. Further, all operations have to be comparable to those needed in a commercial facility, with characterization of material at many stages during fuel recycle. Methods for quality control, assay analysis, materials handling, maintenance demonstration, and waste handling must be adequate. The entire fuel recycle operation has to be an economic one on a commercial scale, and evaluations are being made to assure that the developing technology is pertinent to a commercial fuel recycle plant. It is important to factor into the equipment design the operating requirements of a large commercial plant and at the same time to consider safety and environmental factors.

Since savings in fuel recycle costs are realized with large-scale plants, there is an economic incentive to delay fuel recycle until the scale of operations is large. Therefore, the timing of HTGR fuel recycle development is related to HTGR power growth, as well as to the costs for fabricating, processing, and refabricating fuels. At the same time, delay in fuel recycle leads to an increase in the initial and makeup fuel costs as well as in the fuel storage needs. Thus, for a given HTGR power growth pattern there is an optimum time to initiate fuel recycle that is based on a balance among the above cost items. Cost analyses based on three different (but reasonable) HTGR power growth curves during 1980—1990, on estimated costs of fuel fabrication and fuel recycle as a function of plant throughput, on a 10% discount factor, and on other nominal economic ground rules, indicate that the most economic year to initiate HTGR fuel recycle is about 1985 for the three different build schedules considered.

Taking into consideration the time required to develop recycle technology, to design, build, and check out a fuel recycle hot pilot plant, and to operate the pilot plant successfully, it will be 1980—81 before recycle technology will have been demonstrated satisfactorily. This technology then has to be translated into the design of a commercial recycle plant. Since the time between the starting of design work and the beginning of operation of a commercial facility is estimated to be about seven years, it will be difficult to assure a commercial fuel recycle plant as early as 1985. Thus, it is appropriate that emphasis is now increasing on HTGR fuel recycle development. It is anticipated that ORNL will continue to play an important role in this effort.

Alex Zucker, associate director of the Laboratory for physical sciences, speaks here on a subject very close to his heart. He is known to readers of this magazine for his reviews of current books, but in this issue he lines out an architecture for full utilization of basic and applied research in the country's search for solutions to the energy shortage.

Physical Research:

A three-tiered strategy in support of energy R & D

By Alex Zucker

A question scientists rightly ask in these days of high concern for the future of the country's energy supply is, "What is a sensible basic physical research strategy in support of a national energy R & D program?" A detailed answer must await a set of national plans for energy R & D, when the particular physical research tasks can be enumerated and when priorities and levels of effort can be assigned.

If we cannot now make detailed plans, we might usefully examine the role of physical research in terms of some reasonable energy R & D model. Even if we cannot say with any degree of precision what research should be carried out, we ought to be able to say how we should approach the problem.

We will postulate a reasonable energy R & D model and propose in its support a three-tiered strategy for physical research: the first tier to provide crucially needed data for nearly complete technologies, the second tier to provide us with expected but not at all certain discoveries needed for new technologies, and the third tier consisting of basic multifaceted research underpinning the entire energy R & D enterprise.

Consider the following two-phase energy R & D model: A near-term program to reduce dependence on imported oil and gas by 1985 to 10 or 15% of our total consumption, and a long-term goal to advance our energy base, through a variety of technological developments, to satisfy the expectations of the population for the next fifty years.

The model needs some elaboration. For the near term, it suggests that we substitute coal, of which we have abundant reserves, for oil or gas in nearly all central generating stations. Further, it

"A second component of the near-term strategy requires that we develop with great haste a viable coal hydrogenation technology..."

suggests that we accelerate the installation of nuclear power reactors and concomitantly increase the effort in mining and enriching uranium. The underlying notion is to substitute electrical energy for oil or gas whenever possible and to generate electricity from uranium or coal. A second component of the near-term strategy requires that we develop with great haste a viable coal hydrogenation technology (liquefaction and gasification) to supply between 10 and 20% of our total oil and gas requirements as soon after 1985 as possible. We mention, but do not explore in detail, the serious problems that are raised by some requirements of this model: tripling the production of the coal mining industry and making an equally demanding increase in uranium mining.

The long-term strategy is very different. We can pursue many more options: uranium or thorium breeder reactors, thermonuclear fusion reactors, geothermal energy, solar energy, storage batteries, large-scale hydrogen production, superconducting transmission lines, etc. There is a danger that the word "long-term" will be taken to mean that this part of the program is not urgently needed. No such thing is implied. It signifies merely that we can not expect from it an impact on energy systems before 1985 and in many cases not before the end of the century. In this model, the long-term energy R & D program will advance on many fronts and must be so designed that it can absorb failures and shift its center of gravity to exploit new inventions or follow developing social patterns. The chief thing to bear in mind is that energy systems are large and ponderous; they take a very long time to develop. The automobile-highway system took about 50 years, the fission breeder technology will take a similar time span from the time it was conceived until it contributes significantly to the national economy in the 1990's.

All this is by way of an overlong but necessary introduction to what is really our purpose: to develop a strategy for basic physical research. We discern that the near-term program of the model must perforce exploit technologies that are nearly complete. The important word here is "nearly". In almost every instance, there are weak points in these technologies. They must be resolved, and scientific research is the best method we have to resolve technical difficulties. A few examples will illustrate the point. Coal liquefaction technology is not far from complete. Several processes have been developed and we can now design pilot plants that can be expected, in a few years, to result in full-scale commercial plants with a daily capacity to convert 10,000 tons of coal to about 30,000 barrels of synthetic crude oil. The goal of our model is to produce three million barrels/day; this implies that we expect to build about 100 such plants near our coal

"The chief thing to bear in mind is that energy systems are large and ponderous; they take a very long time to develop."

mines as soon as possible. One technical problem: to liquefy a ton of coal we will use between 100 and 300 gallons of process water which will contain, let us say, 2000 ppm of phenols and smaller amounts of other substances. For a 10,000-ton/day plant, we are faced with treating a million or more gallons of water a day, with a phenol content of over 2000 ppm which must be reduced to less than 0.1 ppm. We have ideas how to accomplish this, but research is needed to identify the most economical large-scale methods. Moreover, it is unlikely that the same methods will be used in the arid western environment as in the Appalachian coal fields. This example illustrates two significant points: one, that even fairly complete technologies have critical points in need of research, and in need of it now if any of our plans are to produce results; and, two, that in vast enterprises whose goals are measured in hundreds of millions of tons per year, the environmental and health aspects tend to be controlling. We are learning this fact, all too painfully, in reactor development and siting. Unless we take care at the outset, we will have the same situation when we try to mine 1500 million tons of coal annually or try to locate hundreds of coal hydrogenation plants.

We add a few more examples of research needed in the near term according to our model. The coal hydrogenation processes need research in kinetics of the relevant chemical reactions, evaluation of possible catalysts, analytical techniques to determine the by-products of a hydrogenation process, etc. Even in the deeply researched reactor business, which in our model will expand mightily in the next ten years, there exist crucial problems in radioactive waste handling, nuclear safety, and security against diversion, which need attention and where physical research promises to solve outstanding problems.

For the near term there exists then a class of nearly complete technologies: the basic discoveries have been made, yet there remain important and often critical go, no-go areas where additional knowledge must be gained through research. This kind of research – high-priority, limited in scope, and in direct support of near-term technological goals – forms the first tier of our physical research strategy. It is characterized by its specificity, urgency, and close ties to the R & D program. Needless to say, it must get off the ground immediately and be funded at a level that will make useful results highly probable.

The long-term technology R & D in the model is basically different in character; most of it depends crucially on a discovery that has not yet been made – a probable discovery to be sure, but nevertheless one that is not in hand. So, for example, the whole scheme of abundant energy from fusion rests on our belief that physicists

"...scientific research is the best method we have to resolve technical difficulties."

can devise a plasma of sufficient duration, density, and temperature or that they can heat a deuterium pellet to the required temperature without destroying the surrounding wall. Both these discoveries may be probable, but neither has been made. Also, it would be marvelous to be able to extract hydrogen from water at an economically acceptable price. Perhaps this can be done by electrolysis or by some yet-to-be-invented chemical process or by new biological or biochemical methods. It seems reasonable that one of these avenues will lead to success. But we can hardly count on it in planning for the year 2000. And again, a projected network of superconducting electrical transmission lines awaits the discovery of a cheap superconductor with a high critical temperature, and the large-scale deployment of electric automobiles a cheap high-energy-density battery.

Research in support of the long-term technology then constitutes the second tier in our program. The objectives are still specific, but the approach is multifaceted. Results are probable, but no single discovery is crucial in a model that can shift priorities and adjust its goals to correspond to the realities of science, economics, and social forces. Our controlled thermonuclear research program is a good example of this kind of strategy. Research now advances energetically on three fronts: mirror machines, theta pinches, and tokamaks. Competition is keen, but it is still not clear which scheme for magnetic confinement, if any, will prove successful and translatable for an energy-producing technology.

Second-tier research must not be regarded as a sort of strategic reserve in a campaign for long-term energy. It too has to be deployed at once, with clearly described objectives, but with longer lead times. No specific line of research can guarantee results, but we can guarantee overall failure if research is not advanced with vigor and substantial resources.

We come now to the third tier of our research strategy. While we are still concerned with energy-oriented research, the approach here is disciplinary. The goals are to gain new knowledge, to develop new ways of systematization, and to reach new insights into those fields of science that have a bearing on the whole energy problem. Disciplinary research is more theoretical, broader, with more room for unexpected developments. From this kind of inquiry we can get results that are useful for problem solving with which we are concerned in the first tier or for the new discoveries that we confidently expect from the second tier. But there is more. Disciplinary research may uncover really new phenomena; in the past it has led to the discovery of antibiotics, nuclear fission, and the band theory of solids, each of which has changed human destiny in a fundamental way. We depend on the results of disciplinary research to maintain our energy bases in the near term as well as in the long term and to uncover hidden aspects of the natural world. Some examples of disciplinary physical research are: catalysis, electrochemistry, atomic physics, organic chemistry, and solid state physics — an array of research fields obviously related to a successful development of energy technology.

Thus our strategy: three tiers of research of equal importance drawing one from another, underpinning the massive engineering efforts, and providing a sound base for the enormous amounts of capital investment that our energy program requires. It is self-evident that changes in the energy R & D model do not require changes in research strategy. No doubt the priorities will change, but we will always have to provide urgently needed answers for nearly complete technologies, new discoveries will be needed and can be confidently expected in the longer term, and a broad base of scientific knowledge must advance apace if we are not to find ourselves moving from manageable crisis, to catastrophic crisis, to abhorrent constrictions of the human condition.

Electron Spectroscopy for Chemical Analysis

The History and Promise of ESCA at ORNL

By TOM CARLSON and LESTER HULETT

In the last few years electron spectroscopy has been developed as a highly versatile tool, of interest to many disciplines (physics, chemistry, biology) and providing important services to both basic and applied research. The field, however, is not a new one. Before World War I, physicists were using magnets to ascertain the momenta of the newly discovered β particles, and until recent years beta spectroscopy has been an important means of studying nuclear properties. However, the real interest lately has been in the study of low-energy electrons, 2000 eV or less, and the information they yield on molecules, atoms, and solids.

Electron spectroscopy is the analysis of electrons according to their kinetic energy. In the study of matter, electrons are produced by being

Tom Carlson joined the ORNL Chemistry Division in 1954 with a doctorate in chemistry from Johns Hopkins University, moving to the Physics Division five years later. There he worked with A. H. Snell and Frances Pleasonton on charge spectroscopy, an interest that has led him to his present position as head of the electron spectroscopy group in the division. He is currently coeditor of the *Journal of Electron Spectroscopy.* In 1970, he and Les Hulett, of the Analytical Chemistry Division, joined forces to study the application of electron spectroscopy to specific problems. Hulett, whose Ph.D. in physical chemistry was earned at Louisiana State University, worked first in the Solid State Division before transferring to Analytical Chemistry in 1969. The two of them collaborated on the accompanying article, which purports to show the promise of electron spectroscopy for chemical analysis, with particular emphasis on the role played by ORNL researchers in the development of the field. In the photograph on page 11, Carlson makes an adjustment on the machine he has developed for the current ORNL work, as Hulett looks on.

ejected from the material by x rays or other sources of excitation. Then, by passing through an electrostatic or magnetic field, the electrons can be separated according to their kinetic energies, or momenta. After separation, they are detected and information is stored as to the number of electrons formed as a function of energy.

Many subdivisions of electron spectroscopy have sprung up (e.g., uv photoelectron, x-ray photoelectron, electron impact, Auger, and a special technique known as Penning ionization), but this article is about only one, x-ray photoelectron spectroscopy, and how it can be used for a wide variety of research problems. The field achieved its recent impetus primarily through the work of Kai Siegbahn and his colleagues at Uppsala, Sweden. It was Siegbahn who first coined the acronym ESCA, from electron spectroscopy for chemical analysis, by which the process is commonly known today.

Scientists at Oak Ridge also played important roles in the early history of ESCA. Manfred Krause, now in the Chemistry Division, pioneered the use of x-ray photoelectron spectroscopy for gases in 1965. One of the first electrostatic spectrometers to be built in the United States especially for ESCA was constructed in 1968 in the Physics Division. Some of the earliest studies using x-ray photoelectron spectroscopy for environmental problems were carried out by the authors. There are right now over 200 groups throughout the world involved in ESCA research. To help handle the outpouring of reports in this field, the *Journal of Electron Spectroscopy* was established, and the U.S. contributions are being edited here at Oak Ridge.

What Is It?

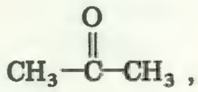
Just what is ESCA? Simply, it is the use of monochromatic x rays to measure atomic and molecular binding energies. From the familiar photoelectron effect elucidated by Einstein, we have the relationship

$$E_e = h\nu - E_B$$

where E_e is the kinetic energy of the ejected photoelectron, which is measured with a high degree of precision using an electron spectrometer; $h\nu$ is the x-ray energy which is well known (usually K_α x rays of Al, 1487 eV, or Mg, 1254 eV); and E_B is the electronic binding energy that one hopes to obtain. X rays can be used to eject electrons from the inner or "core" shells of the atom as well as from the valence (outer) shell. Since the atomic binding energies are characteristic of the element, x-ray photoelectron spectroscopy is a powerful tool for elemental analysis. However, as we mean to show, it is much more than that.

The core electrons of atoms in molecular components behave for the most part as if they were in purely atomic orbitals, unaware of the molecular binding. However, when electrons are plucked out by photoelectric ejection they sense the chemical environment of the atoms as a net charge. A positive charge, such as will occur with an oxidized species, will reduce the kinetic energy of the photoelectrons, and a higher binding energy is recorded. A negative charge will have the opposite effect. ESCA can measure the shifts in the binding energies of the core electrons and thus determine the chemical environment of each element in terms of electron density.

One can view ESCA as an analytical technique with a new dimension. An unknown material may be examined not only for the elements that may be present (qualitative analysis) or for how much of each element is present (quantitative analysis), but also for an evaluation of its chemical environment in terms of a net charge. For example, in acetone,



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3\ ,$$

one finds photoelectron peaks corresponding to the 1*s* oxygen and 1*s* carbon atomic orbitals. From the intensity of the peaks one further deduces that there are three carbon atoms to one oxygen atom in acetone. But in addition, two photoelectron peaks for carbon indicate two chemical environments. The intensities are in the ratio 2:1, with the less intense peak corresponding to a higher binding energy and thus to a more highly oxidized form. (From previous experience we also deduce that the binding energies of the two carbon 1*s* shells are consistent with a hydrocarbon group and a carbonyl group.)

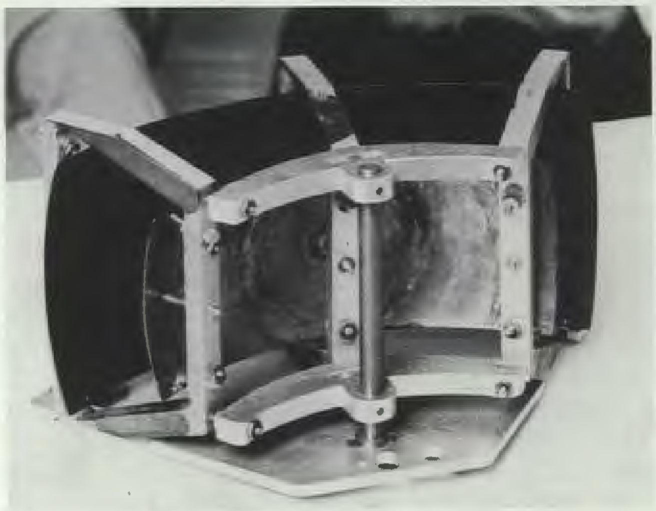
Before turning to the types of research that have been aided by ESCA, take a look at its capabilities. First, any element in the periodic table can be studied for its core binding energies by ESCA, which is to say that only hydrogen and helium, lacking a core shell, are not amenable for such study. Second, in addition to identifying the element, ESCA can determine the chemical environment from the small shifts in the core binding energies. Third, although one peak is associated with each subshell of the atoms, extra lines may appear, indicating transitions to various excited states of the ion. These extra or satellite lines are most interesting from a fundamental understanding of photoionization and may also have importance for studying chemical binding. Fourth, electrons normally studied in ESCA have a mean free path in solids of about 10 to 20 Å. This means that measurements are made only on the first few atomic layers. Thus, we are dealing with a surface technique. This sometimes is a nuisance, but often can be turned to advantage, if the specific nature of the surface is of prime importance.

Fundamental Research

X-ray photoelectron spectroscopy has much to offer both fundamental and applied research. In physics, for example, there is the question of the photoelectron cross section as a function of photon energy and angular distribution. There is also the question of the basic nature of binding energy, for example, the problem of how a molecule or solid reacts to the creation of a hole. Other important physical questions are the changes of electron densities and spin densities in different solids as determined, respectively, from shifts in the core binding energies and from splitting of the photoelectron peaks. These results can be correlated with Mössbauer isomer shifts and hyperfine splitting. In the Physics Division, the Mössbauer group under Felix Obenshain and the electron spectroscopy group are currently engaged in a joint effort on this problem. The nature of excitation in photoionization processes can be deduced from satellite lines. This problem has been of longstanding interest at Oak Ridge. Characteristic energy losses such as plasmon losses can be seen in the photoelectron spectrum as satellite bands, a field pioneered by Rufus Ritchie of the Health Physics Division. The density of states in the conduction band may be studied by x-ray photoemission, and molecular physics is served by the study of photoionization in the valence shells of free molecules.

Both organic and inorganic chemists have profited widely from ESCA. The electronic structure of organic molecules can be deduced from photoelectron chemical shifts; and, in particular, the effects of substitution can be evaluated. Reaction products can be identified. The structure of new compounds can be deduced. As a spectroscopy, ESCA has rather poor resolution in comparison, for example, with nuclear magnetic resonance. However, ESCA is highly versatile and can handle small samples (1 mg or less), and its results can be interpreted in a straightforward manner. Not only simple organic compounds can be studied with profit, but complicated systems as well. For example, we determined from ESCA studies that a substantial charge separation in the nitrogen atoms of some nucleosides occurred simply by the addition of a methyl group, which completely altered the resonance structure of the molecules. These compounds are of particular interest because they are frequently associated with mutagenesis. ESCA studies on the effect of metals on DNA are contemplated with the help of Ron Rahn in the Biology Division.

The fact that ESCA can be applied to virtually all the elements makes this technique a natural one for inorganic chemists. Even binding energies in highly radioactive materials have been measured in microgram quantities of the actinide compounds. Chemical shifts as a function of the periodic table have been widely studied, and it is possible to equate the relative magnitude of the chemical shift per change in effective charge with the calculated atomic radii. Inorganic chemists have been busy studying the changes in charge density that come about as the oxidation states change and have carefully tested the concepts of electronegativity. In addition to shifts in the core binding energies arising from changes in chemical bonding, shifts also occur as a consequence of changes in the crystal potential, and these changes have been studied in a number of salts. Besides simple salts, inorganic complexes have received attention. Chemical shifts can be interpreted in terms of ligand field theory. For paramagnetic compounds containing transition metals, rare earths, or actinides, extensive satellite structure is apparent in the photoelectron spectra. These satellites are strongly dependent on the chemical binding, and the study of their properties promises to be of great value in the investigation of the behavior of this important group of compounds. With the help of students from the Universities of Tennessee and Illinois and of participants from Mexico, France, Norway, and Finland, the nature of satellite structure in photoelectron spectroscopy is being vigorously pursued, both in the Chemistry and Physics Divisions at ORNL — a truly international as well as interdisciplinary venture.

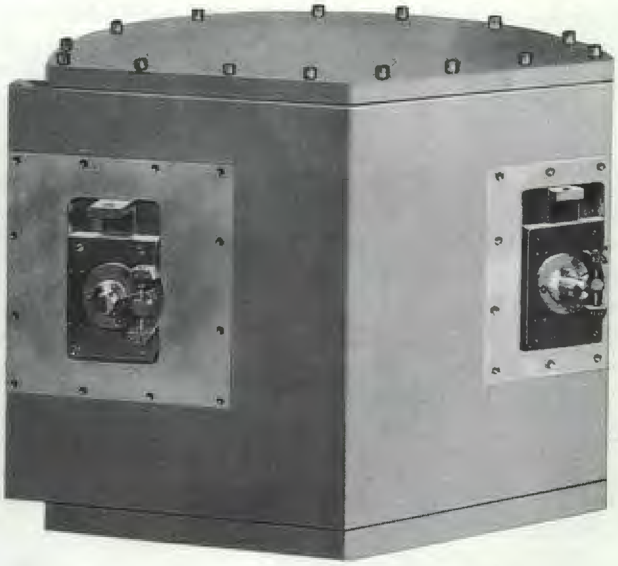


The three illustrations across the top make up a capsule history of electron spectroscopy at ORNL. Above are original electrostatic plates built by Snell and Pleasonton in 1954 for study of charged ions from nuclear decay, first practical application of Purcell's original design, used by Krause in 1965 for low resolution electron spectroscopy.

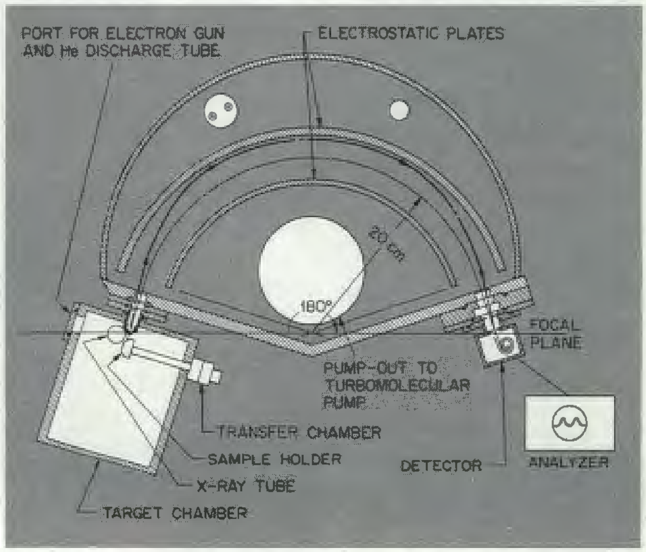
Applied Research

As mentioned earlier, the ESCA technique is a versatile method of surface analysis. For the first time, elemental analysis of surfaces can be performed routinely on many kinds of solids, whether insulators or conductors. The shifts of core binding energy and satellite structure provide additional information about the chemical environment of elements present on the surface. These new capabilities have made it possible to solve in a short time many problems that were almost intractable only a few years ago. In corrosion studies, for example, the determination of the composition of protective oxide films is often desired. Tony Bacarella in the Chemistry Division and John Griess, Chemical Technology Division, found that copper alloys having 30% nickel were much more corrosion resistant than pure copper. They knew that the resistance was due to a protective film; their question was whether the film was copper oxide, nickel oxide, or a mixture of both. Photoelectron spectra showed clearly that the film was

The double-focusing electrostatic plates, designed by Carlson and built by Frank Ward, Plant and Equipment Division, in 1968. The plates have the same basic design as those on the left but are machined for higher resolution.



An electron spectrometer currently being built commercially, based on design of instrument in Physics Division at ORNL.



The three basic components of x-ray electron spectroscopy. (1) Target chamber is where photoelectrons are produced by irradiating sample with x rays. (2) Electrostatic plates separate photoelectrons according to their kinetic energy. At given voltage on the plates, only electrons of given kinetic energy are focused at the exit slit. (3) Detector counts each electron passing through slit, and these data are stored. Counting rate, measured as a function of plate voltage, gives photoelectric spectrum.

mostly nickel oxide with a small amount of copper oxide. Large concentrations of silicates, however, totally unexpected, were also present on the surface.

The ion etching technique is commonly used in conjunction with photoelectron spectroscopy. Bombardment with argon ions can remove the outer surfaces of solids in a controlled fashion, permitting the underlying substrate to be examined. Ernie Long and Helen Henson in Metals and Ceramics Division gave us a problem that required this approach. They were studying corrosion films on hafnium in a NaK loop. X-ray diffraction patterns had indicated the presence of hafnium nitrides. When we examined the specimen we found a surprise: On the outermost surface there was no hafnium. Instead we found carbon, oxygen, nitrogen, and tin. Nitrogen was present in three forms: nitrate, nitrite, and nitride. Carbon and oxygen are expected contaminants. We still don't know how the tin or nitrogen got there. After about 20 atom layers were removed from the specimen surface, the tin peak no longer appeared, and the carbon and oxygen peaks were much reduced. The hafnium peaks became very prominent. Only one form of nitrogen, nitride, remained on the surface. In the recent past, surface analyses such as this were in the province of only the fundamental researcher. Now they can be commonplace and routinely available for the solutions of applied problems.

Catalysis is an obvious area for the use of photoelectron spectroscopy. In the past three years a very large number of commercial spectrometers have been sold to oil companies and other industries because of their interest in solid—gas and solid—liquid catalysis. Environmental pollution research often involves solid—gas catalysis also. Birney Fish, formerly at ORNL and now with the Environmental Pollution Control Agency of Kentucky, and Jack Durham of the EPA brought us such a problem involving the interaction of SO_2 on atmospheric particulate matter. We found, by exploiting the chemical shift phenomenon of ESCA, that when SO_2 is adsorbed on transition metal oxides in the presence of air, it is rapidly oxidized to sulfate. For alkaline earth oxides, however, the oxidation of SO_2 to sulfate occurs very slowly.

Environmental pollution monitoring is also well served by the photoelectron spectroscopy technique. On particulate matter collected in Knoxville many toxic materials such as lead, sulfate, chlorine, and organic amines have been found. Now that surface analysis is routinely available through photoelectron spectroscopy, we are arguing strongly that surface analysis data should be a routine supplement to the more conventional bulk analysis. Birney Fish convinced us of this by pointing out that most particulate matter that remains as such under weathering conditions is necessarily insoluble in water. This means that toxic materials in the interiors of the particles are not readily transmitted to plant or animal life upon contact. The material on the surface of the particle may be easily transmitted, however. Birney's thesis was vindicated in our study of fly ash: bulk analysis indicated only one part per thousand sulfur, but ESCA peaks of the samples were almost as intense as those of pure potassium and calcium sulfate. This means that most of the sulfur in the particles was concentrated at the surface, giving it a high degree of chemical aggressiveness.

In the Environmental Sciences Division, Tsuneo Tamura, Fred Sweeton, and Ernie Bondietti are studying the adsorption of cadmium on kaolinite and montmorillonite clays. An understanding of the surface reactions is the central goal. The past year Larry Wilson, of the Ohio Wesleyan University faculty, worked with us and studied the cadmium-kaolinite system. He found a reciprocal relationship between cadmium and calcium peak intensities. This is in keeping with the idea of cadmium adsorption by ion exchange with calcium on the clay surface. Probably the most interesting discovery of Tamura et al. was the synergistic effect of iron in cadmium adsorption. They found that if kaolinite is treated with iron the uptake of cadium can be as much as 20 times as high as for untreated clay. Work is in progress to try to understand this effect better.

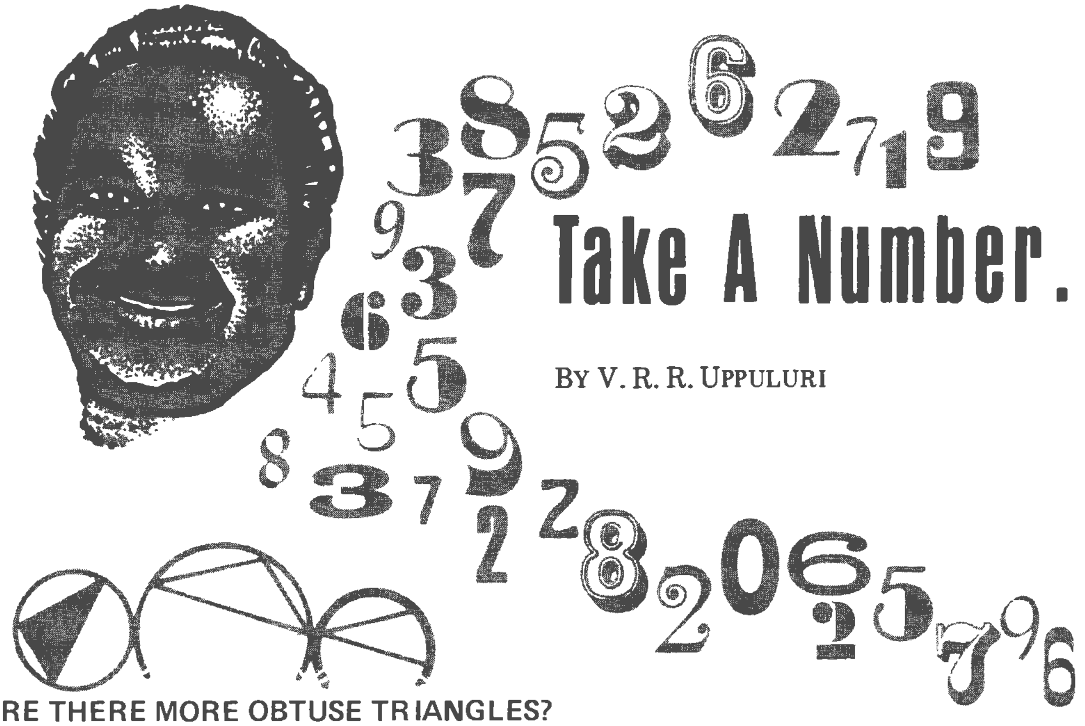
Energy Research

Photoelectron spectroscopy will have many applications of these types in the expanded energy research planned by the Laboratory. In nuclear reactor research there will be many more cases, such as those of Long and Henson and Bacarella and Griess, where film analysis will be desired. In the thermonuclear program it will be necessary to protect materials from tritium impregnation by thin films. Laboratories performing solar energy research will find that thin film technology is again important in the design of high efficiency collectors of sunlight. In coal liquefaction and desulfurization the method will be very useful for studying catalysis, corrosion, and chemical states of sulfur, nitrogen, and other elements.

The Future

Although x-ray photoelectron spectroscopy has already proven to be a valuable and versatile tool, new improvements in equipment design give hope that much more can be accomplished. Position sensitive detectors are being developed at ORNL to increase the sensitivity a hundredfold. Monochromators promise a fivefold improvement in resolution, at least for gases, which should permit detection of subtle changes in chemical bonding. Ultrahigh-vacuum systems, which will insure clean surfaces, are being built for use with ESCA. Radiation from synchrotrons may serve in the future as an ideal photon source. In addition, x-ray photoelectron spectroscopy is being put to new uses, such as Manfred Krause's technique of turning the photoelectric effect into an x-ray spectrometer.

As ESCA has been developed at ORNL, it is an ideal example of interdisciplinary activity. Born out of basic physics, it has expanded to many other areas of research, both fundamental and applied. With the interests of the Laboratory undergoing expansion, and the need for scientific interaction being stronger than ever, electron spectroscopy ought to play an even larger role in the future.



Take A Number.....

By V. R. R. Uppuluri

ARE THERE MORE OBTUSE TRIANGLES?

Take three points at random on the circumference of a circle. The triangle formed by these three points can be either acute or obtuse with positive probability. It can be shown that the probability that the three points form a right triangle is equal to zero, but it is surprising that the probability with which we find an obtuse triangle is $3/4$.

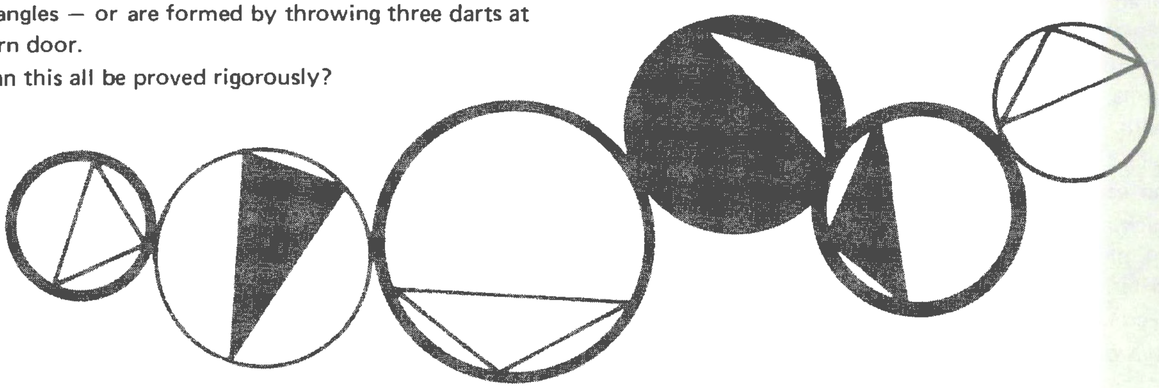
Monte Carlo studies done at the University of Minnesota indicate that the probability of finding an obtuse triangle is greater than half, even if the three points are taken at random inside circles, triangles, or rectangles — or are formed by throwing three darts at a barn door.

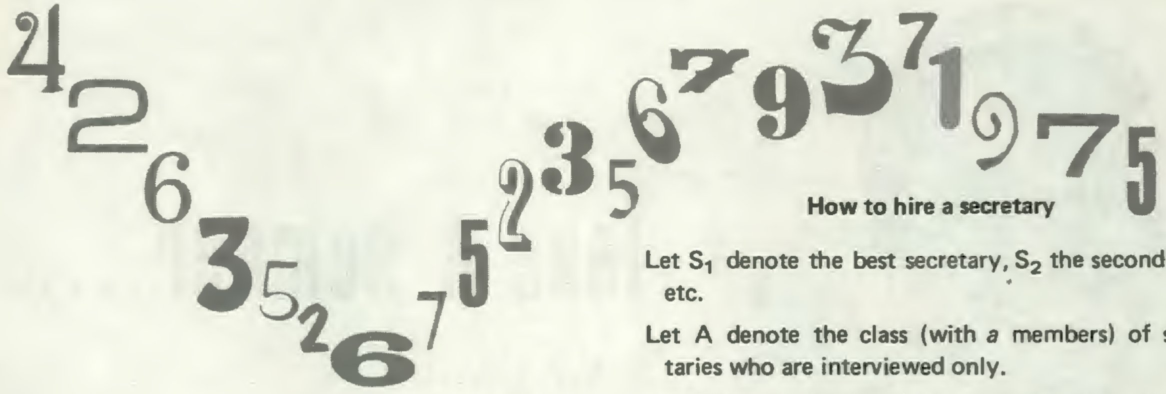
Can this all be proved rigorously?

A PARADOX

Consider a circle whose circumference is normalized to be unity. Choose two points A and B at random on the circumference. The expected length of the arc AB and the expected length of the arc BA are each equal to $1/2$.

Now, consider an arbitrary but fixed point P on the circumference. Only one of the two arcs will contain P. It is interesting that the expected length of the arc containing P is equal to $2/3$.





DR. UPPULURI'S FAN MAIL

Dr. Venkata Ramamohana Rao Uppuluri (as he is known to South Central Bell) has enhanced his already international renown in the short time that he has been providing the *Review* with his elegant little mathematical curiosities. Among his more distinguished fans is the director of Lawrence Berkeley Laboratory, Dr. Edwin M. McMillan, and scarcely an issue of the *Review* is printed that Ram does not hear from Dr. McMillan in acknowledgement or augmentation of the latest poser. The following, in reference to "The Secretary Problem" of the last issue, is a sample of this rich correspondence:

Dear Dr. Uppuluri,

I have written up my treatment of the "secretary" problem, in a very condensed form, and enclose a copy. By computing exact values of P for small a + b, one finds that the result is not very sensitive to a/(a + b) in the vicinity of e^{-1} and that it converges rather rapidly to $P \sim e^{-1}$.

This strategy was originally designed for a parlor game, in which the only player is given a set of cards with different numbers on them, and the goal is to pick the highest number. One outcome could be that no card is picked, which is not more of a loss than picking a nonmaximum number. However, in the case of picking a secretary, there may be the additional criterion that a choice must be made because a secretary is needed. Then the strategy must be altered in a way that I have not tried to figure out.

How to hire a secretary

Let S_1 denote the best secretary, S_2 the second best, etc.

Let A denote the class (with *a* members) of secretaries who are interviewed only.

Let B denote the class (with *b* members) from which one is hired.

The circumstances in which S_1 is hired are:

(1) S_1 is in B, S_2 in A. The probability of this is

$$\frac{b}{a+b} \cdot \frac{a}{a+b-1}.$$

(2) S_1 and S_2 in B, S_3 in A, and S_1 comes before S_2. Probability:

$$\frac{b}{a+b} \cdot \frac{b-1}{a+b-1} \cdot \frac{a}{a+b-2} \cdot \frac{1}{2}.$$

(3) S_1, S_2, and S_3 in B, S_4 in A, and S_1 comes before S_2 and S_3. Probability of this is

$$\frac{b}{a+b} \cdot \frac{b-1}{a+b-1} \cdot \frac{b-2}{a+b-2} \cdot \frac{a}{a+b-3} \cdot \frac{1}{3}, \text{ and so on.}$$

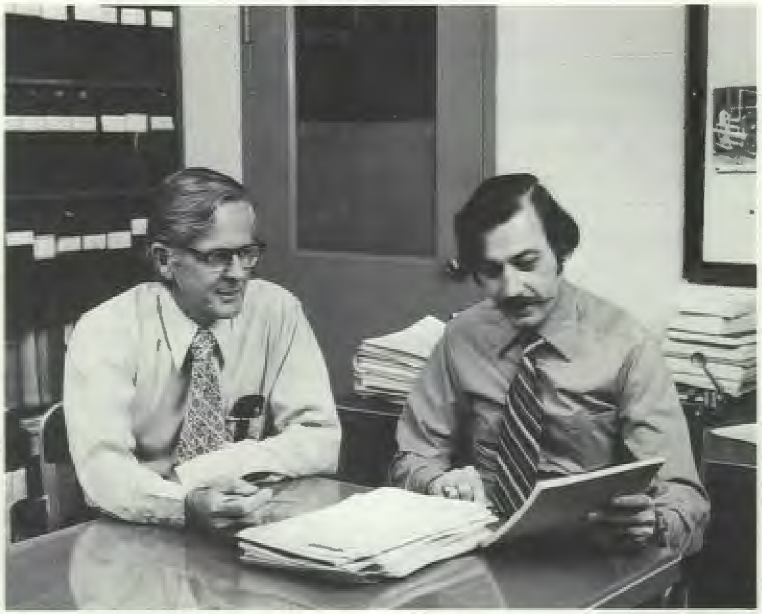
The total probability of hiring S_1 is the sum of these, a series with *b* terms. Call this sum P. As *a* and *b* become large,

$$P \rightarrow \frac{a}{a+b} \cdot \sum_{n=1}^{\infty} \frac{1}{n}\left(\frac{b}{a+b}\right)^n = \frac{-a}{a+b} \cdot \ln\left(\frac{a}{a+b}\right)$$

$P_{\lim}$ has its maximum value at $a/(a+b) = e^{-1}$, where $P_{\lim} = e^{-1}$.

– Edwin M. McMillan

Truman Anderson, shown right, with co-author John Michel, has been a nuclear engineer in the Reactor Division of ORNL for 15 years. A product of the University of Missouri at Rolla, with a M.S. from the University of Tennessee and a diploma from the Laboratory's School of Reactor Technology, he has moved from involvement in early nuclear power developments, both for the public utilities and the military, to such studies of nuclear energy applications as he writes of here. This particular work was performed with Michel at the request of AEC Division of Reactor Research and Development in 1972 and includes contributions from Claude Haws, Chemical Technology Division, and Oran Culberson, consultant from the University of Tennessee. Michel has since left the Reactor Division for a position with Uranium Enrichment Associates in Oak Ridge. Anderson is currently associate director of the Nuclear Desalination Program.



The Reactor as a Source of Industrial Energy

By TRUMAN D. ANDERSON and JOHN W. MICHEL

The emphasis by both government and industry in the development and application of nuclear energy has been primarily on central station electric power. In view of recent concern about our supply of energy for almost every sector of the economy, the question arises as to whether nuclear energy could be applied on a significant scale to industrial needs in addition to central station power. Industrial energy use, as a potential candidate, is examined here in detail with particular emphasis on heat-dependent processes.

Of all the economic sectors, industry is by far the largest single user of energy, accounting for about 41% of the total. The term "industry" includes many diverse activities ranging from small food processors to giant chemical complexes, and their needs are met in a variety of energy forms such as process steam, direct furnace heat, electricity, and fossil fuels for feedstock. The largest amount of industrial energy is consumed in the form of process steam. In fact, the primary energy consumption related to process steam production is nearly 17% of our total national energy use — a figure two-thirds as large as the energy consumed to produce electric power.

It is evident that industry is far from a monolithic entity, and a realistic assessment of where nuclear power fits must consider the fine structure of industry in relation to the inherent characteristics of nuclear energy sources. Nuclear steam supply systems are large, require a sizable capital investment, involve a long period of planning and construction, and generally have design characteristics intended to match the requirements for central station power plants. Reactors are commercially available in discrete sizes ranging from about 1600 MW(t) to 3800 MW(t) and with prime steam temperatures of 515°F to 950°F. The time required to construct a reactor and put it into commercial operation at present ranges from seven to ten years.

Although industrial energy consumption is large, the average size of individual blocks of industrial energy is small relative to the size of nuclear units. We examined boiler capacity and average size of boiler sold to selected industrial groups over a six-year period and found that even though the total capacity is impressive, the average size of individual units is not. For example, the paper industry bought over 14,000 MW(t) of boiler capacity in the 1965 to 1971 period, but the average size boiler was about 43 MW(t). For all industrial boiler sales, only 6% of the capacity was in units larger than 150 MW(t).

The size question coupled with the extensive planning required for nuclear plants leads to one obvious conclusion: if nuclear power plants are to have a large role in the future supply of industrial energy, industrial complexes with dual-purpose nuclear plants will be required. But an industrial complex would be difficult to implement if the only basis for it is a multitude of small industrial energy users. What would seem to be required for each complex is at least one large consumer — a pivotal industry that in itself could justify the planning required to build a nuclear power plant. Once such a firm planning basis were established, the addition of smaller industries to the complex would be relatively easy. In essence, then, the question of nuclear power for industry becomes a search for large industrial energy consumers. Even though the energy used by the very large plants may be a small part of the total energy involved, the large plants, nevertheless, are the key to industrial uses of nuclear energy.

The Large Consumers

If we examine energy consumption by industrial category, we find that two-thirds of industrial energy consumption is by six industries. These are, in order of energy consumption: primary metals, chemicals, petroleum, food, paper, and stone. The combined energy consumption of the next four largest consumers — textiles, lumber, rubber, and machinery — is about the same as the smallest — stone — of the top six.

For detailed study, let us look at chemicals, paper, and petroleum from these top six. For various reasons, food, primary metals, and stone are not as suitable for the nucleus of an industrial complex. The food industry uses large quantities of process heat, but the industry is highly dispersed and many food processing plants, being of a seasonal nature, have a low use factor with respect to energy supply. The primary metals industry uses energy in the form of coke for iron ore reduction and in the form of high-temperature furnace heat. Similarly, most of the energy used in the stone industry, including the manufacture of glass, cement, bricks, and gypsum products, is in the form of high-temperature furnace heat. Both the primary metals and stone industries might, with modified processes or advanced reactors, offer opportunities for the use of nuclear energy, but we did not evaluate such advanced applications.

Paper

The paper industry is the fifth largest industrial energy consumer. Production of paper and paperboard is about 58 million tons/year, with an expected rise to about 102 million tons by 1985, a growth rate slightly more vigorous than the GNP.

Almost 80% of the energy consumed by the paper industry is in the form of process steam and the remainder is electricity. Process steam pressures commonly in use throughout the paper industry are 150 psig or less. The low pressure steam (~50 psig), about half the total consumption, is used in drying while high pressure steam is used in pulping and other operations. The low steam pressures suggest that a dual-purpose (electricity and steam) plant might be applicable, and, indeed, most large mills generate their own electricity in fossil-fueled, dual-purpose plants.

A paper mill of 1000 tons/day capacity is considered to be very large; the largest mill has a capacity of 2800 tons/day. Currently there are 34 mills with capacities larger than 1000 tons/day. The purchased energy requirements for each installation vary rather markedly depending on the paper product, the age of the mill, and the extent of use of waste products (bark, etc.) to generate steam. Based on the national average, purchased fuel is burned at a rate of 264 kW(t) for each ton per day of plant output. Thus, today's large mills consume purchased fuel at rates up to about 700 MW(t), and the trend is to even larger installations.

The anticipated increase in production by 1985 implies the need for additional capacity equivalent to over 50 of today's largest paper mills. The corresponding new energy production capacity is equivalent to the output of more than 10 reactors of the maximum size now available.

It is, of course, unrealistic to assume that all the new paper capacity would be supplied by nuclear plants, but the paper industry would seem to be a promising potential application for nuclear energy.

Petroleum Refining

The petroleum refining industry is a very large consumer of energy — the third largest in the industrial sector. Refineries start with raw materials, primarily crude oil, and convert them into automotive and aircraft fuels, fuel oils, lubricants, coke, and chemical feedstocks. The kinds and quantities of individual products vary among refineries, and, consequently, the characterization of energy consumption for a typical refinery is difficult. The industry average is an input in the form of thermal and electrical energy of about 700,000 Btu per barrel of crude processed; this is equivalent to 12% of the energy content of the crude. Refineries vary in size from 300 barrels/day to 434,000 barrels/day. In January of 1972 there were 247 refineries with a total capacity of 13 million barrels/day, for an average size of 53,000 barrels/day. Thus, based on industry-wide energy data one might expect the "average" refinery to have an energy use rate of about 450 MW(t) and the largest refinery would require about 3700 MW(t).

Refineries produce waste-product hydrocarbon mixtures which are normally used as fuel; these fulfill about 36% of the energy needs. The remaining 64% is provided by fuels with market value such as natural gas, fuel oil, and petroleum coke. It is the marketable fossil fuels that could potentially be displaced by nuclear fuel.

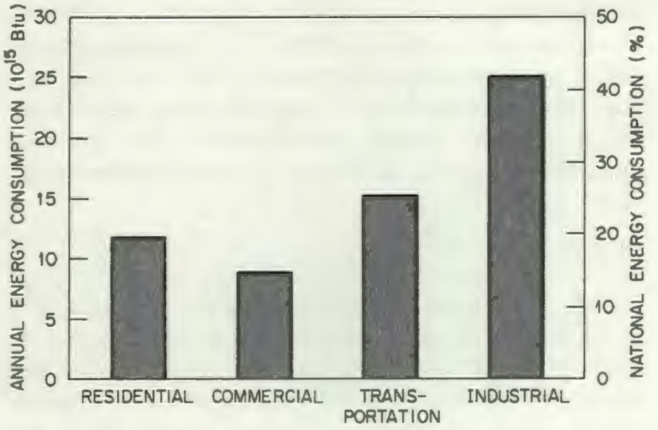
To get a better understanding of the fine structure of energy consumption, we examined energy data for a specific large modern refinery and for individual processes within the refinery. In this case, about 80% of the thermal energy generated is in the form of furnace heat and the remaining is in the form of process steam. The process steam requirement could easily be met by present-day light water reactors, but the furnace heat requirement could not. The bulk of the energy consumed in radiant furnaces is used to heat streams of the refinery process to 700 to 1000°F. The high temperature gas cooled reactor would appear to be a potential candidate for supplying this energy. But some modifications to the current HTGR design might be required for petroleum refining applications.

Projections about the future of the petroleum refining industry indicate a significant expansion. The National Petroleum Council predicts that, during the 15 years from 1970 to 1985, refining capacity must increase by 10 million barrels/day if the industry is to meet the anticipated demand. The corresponding increase in process energy capacity is over 85,000 MW(t). This new capacity will predominantly be contained in very large refineries and would seem to be a promising market for high-temperature nuclear systems, especially the HTGR.

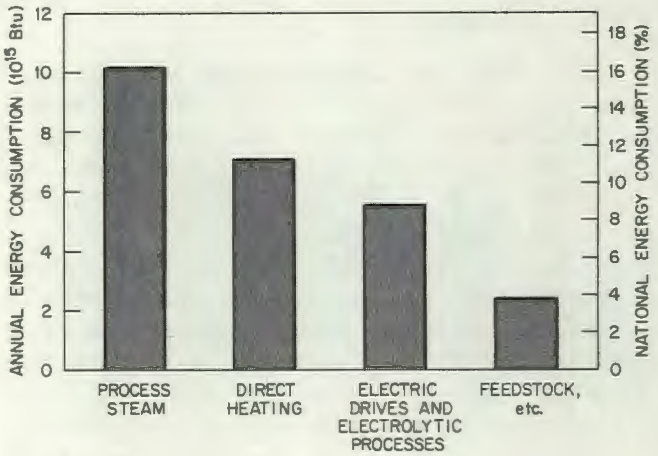
Chemicals

The chemical industry is second only to primary metals in the consumption of energy. It is at once the most complex to analyze and the most promising in regard to the potential application of nuclear energy. The complexity arises from the multiplicity of products which makes it difficult to characterize energy needs for typical plants. There are thousands of chemical compounds: alkalies and chlorine, fertilizers, pigments, industrial gases, synthetic fibers, plastics, soaps and detergents, organic intermediates, pharmaceuticals — the list is nearly endless. Seldom does a plant produce a single product. The promising aspects of the chemical industry relative to the application of nuclear energy stem from the following factors: first, the industry consumes a large amount of energy; second, it is not difficult to find individual plants with energy consumption rates of 500 to 1500 MW(t) and chemical complexes with rates of several thousand MW(t); and third, the chemical industry among all industries has shown the greatest awareness of impending fossil energy shortages and the most willingness to examine alternatives. An illustration of the latter point is the planned use of nuclear process steam from the Consumers Power nuclear plant at Dow's Midland, Michigan, chemical complex. This, incidentally, is the only example to date of the planned use of nuclear process energy in industry.

Although, as noted previously, it is difficult to characterize the chemical industry with respect to energy consumption, we did examine energy needs on a total-industry basis and obtained data on energy consumption rates for specific plants and complexes. Industry-wide energy consumption by end-use is distributed approximately among process steam (52%), furnace heat (24%), and electric power (24%). It should be noted that this distribution does not include the energy content of the



Energy use by four economic sectors, 1968.



Industrial uses of energy by form, 1968.

fossil fuels that are used for feedstock, i.e., the raw material for chemical processes; the feedstock segment is almost as large as all other energy inputs combined, and of course in this function, fossil fuels cannot be replaced by nuclear energy.

Presumably most of the steam requirements for the chemical industry could be satisfied by the quality of steam available from present nuclear reactors. Part of the furnace heat could probably be supplied by nuclear plants, but the distribution of temperature requirements is not defined well enough to comment on the magnitude of this market.

Another interesting aspect of energy use in the chemical process industry is the relatively large electric energy component. In 1970 the industry consumed 31% of the total U.S. sales and industrial generation of electricity. At its present rate of growth, the industry will be needing nearly four times the 1970 power consumption of the entire U.S. by the end of this century.

Our examination of specific plants included four large petrochemical plants. Fuel use rates averaged about 1000 MW(t) for the four plants. About two-thirds of the fuel is used to generate steam and the remainder to make electricity and fire heaters and furnaces. The steam generation segment could potentially be supplied by dual-purpose nuclear plants.

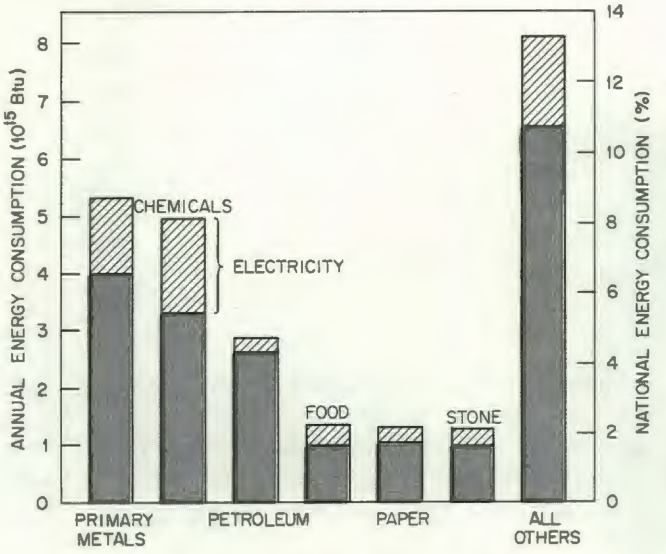
Because one chemical product is, in many cases, the raw material from which another chemical product is made, the chemical industry is its own best customer. This situation has led to some very large multiplant complexes. The magnitude of such operations can be seen at Geismar, Louisiana, and Deer Park, Texas, to take two examples.

The Geismar complex is located on the east bank of the Mississippi River about midway between Baton Rouge and New Orleans. It consists of eleven contiguous plants owned by different chemical companies. Although precise figures are not available, it is apparent that the Geismar complex consumes energy at the annual rate of several thousand MW(t).

The Houston, Texas, ship channel is another area having a high concentration of chemical plants. Among these is the complex at Deer Park, which comprises six chemical plants and a petroleum refinery. The total energy consumption rate for the seven-plant complex appears to be on the order of 4000 to 5000 MW(t)/year.

It should be noted that the two complexes cited above are not unique. For example, both banks of the Mississippi below Baton Rouge are covered with numerous chemical plants and petroleum refineries. Additional analysis might identify other complexes with energy requirements equal to or exceeding the needs of those mentioned. The chemical industry would seem to be a very promising future application of nuclear energy, partly because the idea of complexing has already been accepted.

Industrial uses of energy classified by industrial category, 1968.



The Question of Cost

The energy supply situation is currently in such a state of flux that no matter what one says about cost, it is likely to be wrong. Certainly economics plays a strong role in the selection of energy sources for industry, but short-term economic considerations must be tempered by other factors. Environmental acceptability is important and so is an assurance of long-term supply. It is desirable to choose the most economical fuel that will meet environmental standards and that will have a favorable long-term supply outlook. Nuclear energy would appear to be reasonably promising relative to environmental and long-term supply considerations.

Many industrial energy users are currently reporting that process steam costs, based on fossil fuels, are upwards of $1.00 per million Btu (MBtu) and projected to go higher, especially if more stringent environmental standards are imposed. Of course, the actual costs vary widely and are dependent on many factors including location.

In our study of energy costs from nuclear plants, the main emphasis was on dual-purpose plants (electric power and process steam) because most industrial applications require steam in quantities and at conditions such that the thermodynamic and economic benefits of dual-purpose operation can be achieved. The incremental cost of producing process steam in a dual-purpose plant depends strongly on the steam conditions, i.e., temperature and pressure. At 350° F, a temperature typical of many process steam applications, the incremental production cost with a light water reactor may be about 40¢/MBtu (1972 cost basis). To this cost must be added other expenses associated with conveyance, distribution, backup, and isolation (reboilers or isolation loop). Such additional costs are highly dependent on the application. Nevertheless, it would appear that for many applications process steam could be delivered for less than $1.00/MBtu, and the nuclear alternative would be competitive with fossil sources.

Conclusion

There is reason to believe that large nuclear power plants can and will be applied to industrial energy needs especially for new plants in the paper, petroleum refining, and chemical process industries. In most applications nuclear plants would be operated as dual-purpose plants supplying electricity to a power grid and process energy for local use. Such plants offer appreciable overall savings in energy relative to single-purpose plants and can, in many cases, relieve the demand for fossil fuels and the environmental problems associated with their use.

Whether nuclear energy will contribute significantly to our total industrial energy requirements will depend on the success of implementing industrial complexes. A prerequisite for each complex would seem to be one or two large industrial plants which require enough energy to provide the firm planning basis necessary for the construction of a nuclear power plant. Industrial plants of the necessary size will be commonplace in the near future.

Obstacles to industrial nuclear energy are: (1) the time required to construct a nuclear plant is at present four to seven years longer than the time required to build most industrial plants; (2) the planning of nuclear plants for industry will in most cases involve a utility and one or more private companies which presents organizational problems; and (3) the siting, safety, and environmental considerations for nuclear plants and some industrial plants may be conflicting. Although these obstacles are not trivial, we believe they can be overcome. Certainly the incentives for overcoming them will be great if present trends toward higher cost and uncertainty of long-term supply of fossil fuels continue.

LAB ANECDOTE

NOTHING COULD BE SIMPLER
or, THE CASE OF THE LEFT-HANDED GIs

"Could you make 100 curies of barium-140 for us?"

"Nothing could be simpler."

Such is the answer Charles Coryell of Clinton Laboratories reported he gave to Robert Oppenheimer, director of the Los Alamos Laboratory, in 1943. Coryell had considered building hot cells to separate fission products, and with Oppenheimer's need, the authorization for Building 706-C came through. In the DuPont numbering system, all research laboratories are numbered 706, and this was the third research laboratory at the Clinton site. Today the sign reads "Chemical Separations Laboratory" for the west half of Bldg 3026, but it is still called the C Bldg from its wartime designation. The fourth such building, 706-D, is now the east half of Bldg 3026.

Before the C Bldg went up, 100 millicuries of a beta or gamma emitter was a big source. Henri Levy and Edward Brady (now associate director of the National Bureau of Standards) scaled everything up 1000-fold and designed operational cells for as much as 100 curies. They had plenty of input from the prospective users, who included Coryell's section that studied fission products and Waldo Cohn's section that prepared radioisotopes for biological work. And within a year they prepared not just 100 curies but 900 curies of barium-140 for a single shipment.

The first big job in the C Bldg was a study of the Hanford plutonium separation process at small volume but at full radiation level, done by Vernon Cannon and Edouard Shapiro. The second big job produced 200 curies of barium-140 in September 1944; it required the judicious addition of lead sheets for radiation shielding. The chemical procedure, which ended with the precipitation of barium chloride from a strong hydrochloric acid solution, was basically the separation used by Hahn and Strassmann five years earlier when they discovered nuclear fission. Metals can't contain the strong acid; thus one cell was filled with a handblown glass system. The Stang reactor was pioneered here; it uses fritted glass filters with air support as a valve. The procedure was to discharge a half ton of uranium fuel slugs each day and ship them downhill to the C Bldg, on a half-ton truck of course. The 12.8-day half life of barium-140 meant the work had to go fast and delivery to Los Alamos had to be swift; the strong gamma rays from the daughter lanthanum-140 meant careful shielding and a heavy shipping container.

The work had its unexpected and lighter sides. For one thing, all the controls and periscopes and manipulators were mounted on the cell walls (modern practice puts most of them on a separate panel). For an unplanned reason the controls were more conveniently used by a left-hander than a right-hander; and lo, many of the soldiers assigned to the program were left-handed. It must be said that the Army's personnel men had done their jobs well and had sent science or engineering majors to the Clinton Laboratories. Of that GI crew in the C Bldg, Ed Nicholson is a senior man still at ORNL, two are professors of chemistry, and at least two more remained in the AEC's work for many years. Another episode involved a welder who very carefully welded a Monel metal valve into a stainless steel acid delivery line; not every welder can do it. But in the first test run the nitric acid had no difficulty finding the mistake and dissolving the valve right out of the system. And Coryell, who worked forty hours straight on the initial "hot" run except for a nap at the old Whippoorwill Hotel, followed the letter of company regulations, which stated that all time on shift is credited to the day the work began, by entering forty hours of work on his timecard for a single Saturday.

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What was the Whippoorwill Hotel? It was the house at the SW corner of Bethel Valley Rd and West Portal Rd, of the farmer (uncle of present Anderson Co. Judge Joe McGill) who worked part of the present X-10 site and was forced to sell it to the Army Engineers. For hotel use it was fitted with Army cots and no plumbing.

The C Bldg produced not only new isotopes but new elements as well. Promethium, discovered by two members of Coryell's team, was named by his wife, Grace Mary. The discoverers, Larry Glendenin and Jack Marinsky (then a soldier), began with a fission-product concentrate from Waldo Cohn's work. The first ponderable quantities of technetium and of promethium were made by George Parker and colleagues. Xenon-135, of enormous importance in high-power reactor operation, was separated here by Simon Freed, George Parker, and Ralph Brosi for the cross section measurements at the Graphite Reactor by Seymour Bernstein and Maurice Shapiro. Sizable amounts of neptunium were produced here for research.

Of another importance was the work of Waldo Cohn whose group made radioactive isotopes for biological work. Out of that program grew the isotopes sales program that quickly became a big business at ORNL. Initially in the C Bldg the separations were standard analytical chemistry, which is after all the preparation of small quantities of highly pure materials. Ion exchange soon proved to be a general method for remote handling of small quantities, as did liquid-liquid extraction with complexing agents. (One exuberant chemist did so well with the complexing agent TTA that he sounded like a soap commercial with his chant, "TTA does everything.") The first price lists and isotope catalogs were prepared in the C Bldg by Waldo Cohn and Ralph Overman, along with Paul Aebersold of the Manhattan District, and given public announcement in 1946. Even before that time there had been some cloak and dagger shipments. The Berkeley cyclotron, the principal source of phosphorus-32 for the United States, was completely preoccupied with highly secret uranium experiments for Oak Ridge. So every few weeks Oak Ridge prepared and shipped to Berkeley fractions of curies of carrier-free phosphorus-32, made by irradiating sulfur in the Graphite Reactor, to be released from there on a business-as-usual basis.

The C Bldg first made it possible to dedicate the Graphite Reactor to the country as a whole (whose reactor is it anyhow?), and not just to a few local scientists, by selling its neutrons as radioisotopes for medicine and industry and research. The isotope sales program outgrew the cells of the C Bldg. New buildings went up, now numbered 3028 to 3038, to handle the administrative side and the technical side of the work. Isotope production sales is now principally a commercial business using other reactors and other accelerators than ours. Isotope development is no longer a line item in the AEC's budget. And Bldg 3026 needs a new coat of paint. — Herbert Pomerance

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George Scatchard, Professor emeritus, physical chemistry, Massachusetts Institute of Technology 1892–1973

Dr. Scatchard's association with ORNL began with his participation in the Modern Chemistry Symposium sponsored by the Laboratory in the summer of 1950. He subsequently spent many summers and shorter periods in residence in the Chemistry Division, consulting principally with groups working with aqueous solutions and with molten salts. Among many outstanding physical chemists of about his generation who consulted at the Laboratory, he was distinguished particularly by his deep and sustained participation in the problems which were presented to him. A great deal of work in his fields of interest at ORNL has been influenced by his contributions. His scientific help will be greatly missed, but even more than that, his many friends will miss the pleasure that his visits always brought to them.