Chapter 11
Physical Chemistry and Materials

Background

Given the thousands of materials or chemical processes that SRI has explored over its lifetime, selecting just a few as representative becomes an impossible task. Nevertheless, this fairly eclectic chapter examines a few new materials, several processes and their modeling, and an SRI service that for years was the largest information source in the world on the availability of a wide range of materials. But first, to help represent the wide range of this type of SRI work, I will briefly mention a few materials research projects here. They are indicative of many that should have been mentioned had there been enough time and space.

During the late 1950s, SRI had a metallurgy group headed by Dr. Rudy Thielemann. One of his specialties was superalloys, materials with superior strength that were capable of operating in high-temperature environments (>2000°F) without appreciable oxidation or corrosive effects. One use for such materials was in jet engines. In work for the Tungsten Institute and for the American-Marietta Corporation, Thielemann and his group invented a series of new alloys of steel that employed tungsten, cobalt, nickel, and a host of more minor elements. These alloys made their way into the manufacture of jet turbines. Names like WI 52, SM-200, and SM-302 were among the alloys that either originated or were significantly improved at SRI. After leaving SRI in 1961, Thielemann continued in this field, and in 1980 an international quadrennial conference on superalloys was dedicated to him and his contributions.

A second example relates to something every housewife or cook understands: the difficulty in cleaning an oven. But because of an opportunity from the Whirlpool Corporation and some technical insights at SRI, that chore has been eased significantly. In the early 1990s SRI performed a very detailed study on why pyrolized food (i.e., food that has been chemically decomposed by heat) adhered to different surfaces through mechanical, chemical, and even ionic bonding. The research not only sought to find low-adherence, cleanable surfaces but also considered their cost of manufacture. More than 30 potential oven materials were tested for their ease of cleaning plus susceptibility to abrasion. The answer came in recommended changes to the porcelain enamel surface used in ovens and how it is applied. The recommended process improved surface smoothness, added material with low ionic content, treated the surface to enhance the presence of chemically inert nitrides, and added a basic film that turns fat and fatty acids into water-soluble esters. These SRI improvements have made their way into most of today's consumer ovens.[A]

Finally, there is a more current illustration involving the burgeoning world of portable power sources: the ubiquitous battery or its equivalent. Over the past decade and under the leadership of Dr. Subhash Narang, SRI has been researching more capable and useful energy sources. One of the first was removal of the flammable gel in lithium-ion batteries that made them dangerous to use. The solution was a polymer electrolyte that SRI announced in 1998. Building on that experience, SRI began to explore new and more flexible forms of the lithium-polymer battery. This work has led to batteries of arbitrary shape, and even to the potential of a battery fiber that will allow clothing to act as a power source. Batteries that can assume other roles in portable devices will afford a considerable reduction in both size and weight. More recently, SRI began research into miniature hydrogen-based fuel cells whose energy density exceeds present battery technology. SRI has created laboratory fuel cells that operate more efficiently and have lower manufacturing costs. These new technologies are still emerging but seem promising enough that SRI has launched a new company called PolyFuel. PolyFuel has announced a new membrane material, a critical component of hydrogen fuel cells, that is more power efficient and significantly lowers the now prohibitive cost of fuel cells for their biggest market, the automobile.

One of the most unusual alternatives to consumable power sources such as batteries is SRI's innovative use of a material called electroactive polymer. This elastomer material, sandwiched between compliant electrodes, can create a voltage source when deformed, or, inversely, it will deform itself when a voltage is applied. This technology has enormous applications, from flat acoustic speakers to battery replacement. The DARPA is sponsoring research to place such material in the heel of a soldier's boot. The expected result: every 8 hours of walking using a 2-watt boot generator (4 watts for both boots) saves approximately 200 grams of battery weight while adding no additional carried weight. SRI researchers, such as Dr. Ron Pelrine, Joe Eckerle, and Roy Kornbluh, are on the threshold of several products, and, consequently, SRI has just formed a new company called Artificial Muscle to commercialize their efforts.

Before proceeding with more detailed project accounts, however, I would like to mention an important, multifaceted person in the early growth and character of SRI.

Dr. Thomas C. Poulter (1897–1978)

While this book is primarily about SRI's research and innovations and not individual people, one person of the SRI Sciences Group deserves special mention—Dr. Thomas C. Poulter, known as "Doc." Doc Poulter was already a prominent scientist and explorer when he came to SRI, along with Dr. Jesse H. Hobson, about 2 years after its founding. Both were leaders at Chicago's Armour Research Foundation, and both would be instrumental in the early growth of SRI.[1] As SRI's second director, Hobson was a strong leader who brought SRI through its first period of significant growth. As associate director, Poulter helped SRI bring in its first funding for seismic and geologic research. Over the next 30 years, Poulter would become one of the most highly respected leaders at the Institute.

Poulter had been second in command in Admiral Richard Byrd's 1933 expedition to Antarctica and became the leader of the mission that would rescue Byrd when he was dying alone of carbon monoxide poisoning in a small shack near the South Pole. Following that first trip to Antarctica, Poulter became scientific director of Armour. He also made a second trip to Antarctica with Byrd in 1939.[2] During World War II, Poulter was a consultant to the Secretary of the Navy, helping to develop the use of sonar on submarines. After the War he returned to Armour, and in March 1948, joined SRI as its associate director.[3]

Poulter's life at SRI was one of both leadership and the pursuit of his own investigations. The eclectic Dr. Poulter did research into the phenomena of explosions, examined seismic wave probing in everything from glaciers to potential oil reserves, and investigated the design and effects of explosive charges. After stepping down from management, he spent 14 years trying to understand the aural and sonic capabilities of undersea mammals and, ultimately, how to implant a new, bionic cochlea that would allow the deaf to hear.

An outgrowth of Doc Poulter's interest in the engineering use of explosives was a legacy called the Poulter Seismic Method.[B] This

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[1] Armour Research Foundation became Illinois Institute of Technology Research Institute in 1963.

[2] A popular story about Doc Poulter needs retelling here from a write-up by Steve Miller who worked for Poulter in his early days at SRI. During Byrd's second expedition to Antarctica, a seismic scientist reporting to Poulter brought, as part of his equipment and supplies, fifty cases of whiskey. Poulter learned of this after the ship had left Antarctica, so he arranged with the US Navy to fly an airplane, a Ford Tri-motor, into Little America for the first time ever. The plane brought in the needed seismic supplies that had been displaced by the liquor and left with the hapless scientist aboard. Poulter then personally poured all fifty cases through a hole in the ice, knowing that anyone with a high alcohol blood content could die in the extreme cold. Now, missing a seismic scientist, Poulter himself worked out how to launch plane seismic waves into the ice and earth. This seismic approach has come to carry his name.

[3] Poulter, while traveling in California, heard that the new SRI was looking for a leader. He returned to Armour Research Foundation where he was working and mentioned this to its director and his boss, Dr. Jesse H. Hobson. They both were disenchanted with Armour and came to SRI on March 1, 1948 (see Appendix B).

approach used an array of explosives placed atop a line of poles to approximate a plane wave acoustic signal that was better able to probe the earth or things resting on it, like glaciers. SRI used this method in the early 1950s on glaciers in Alaska and Greenland and to look for oil reserves in the Edwards Plateau in Texas.

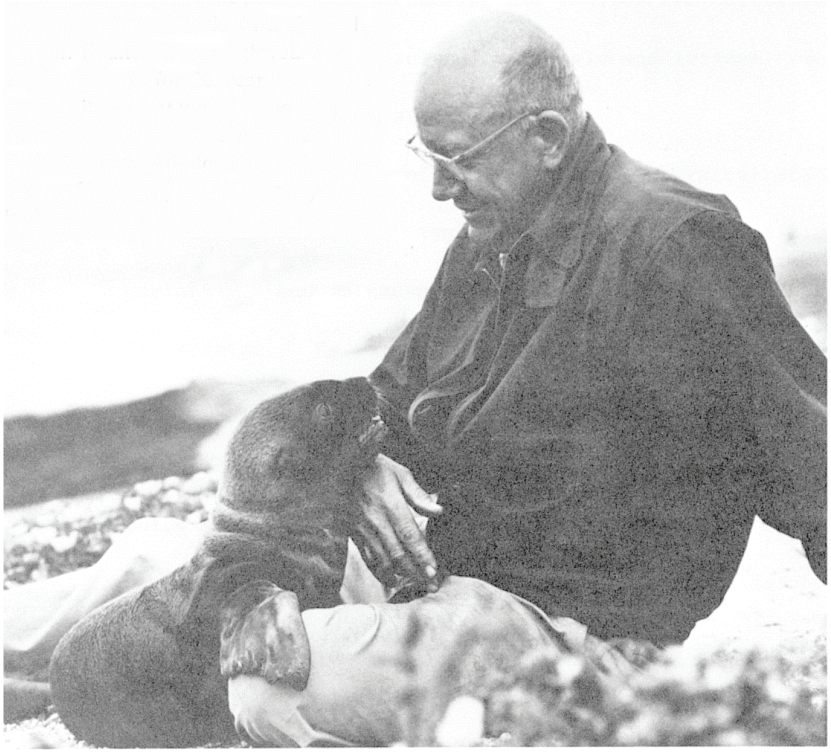

Figure 11-1. Dr. Tom Poulter with an Año Nuevo Pup.

In 1953, to continue to exploit this technology, Poulter formed a group called the Extreme Pressure and Explosives Laboratory with an initial staff of about six people. This was the beginning of 50 years of research conducted around the theme of explosives, their effects, and related phenomenology. The group grew rapidly, and in March 1954 in formal recognition of Poulter's contributions, the SRI Board voted to change the lab's name to Poulter Laboratories. That name was later changed to its present one, Poulter Laboratory.

In 1961, Poulter visited an uninhabited island, Año Nuevo, off the California coast about 12 miles north of Santa Cruz. He was looking for a place to do atmospheric probing with sensors housed aboard missiles. But the island was full of seals and sea lions and he became so captivated by them (see Figure 11-1) that he soon abandoned his interest in upper atmospheric weather and became engaged in learning about these creatures. Though he would later come to investigate the role their sounds had in both communications and biological sonar, he first moved to protect this island so important to their breeding.

By May of 1962, Poulter had applied for and received a permit from the California Division of Parks and Recreation to study the marine inhabitants of Año Nuevo. Shortly after receiving the permit, Poulter applied to the National Science Foundation (NSF) for a grant to rehabitate the island and convert it to a marine biological research facility that would study the six marine mammals that frequented the island. Although his proposal was unsuccessful, he and colleagues from the California Academy of Sciences and the University of California at Santa Cruz continued the work, reporting it in papers dated from 1965 through 1967. They then recommended that the State set Año Nuevo aside as a reserve to protect its unique marine life. Their recommendation was accepted, and on June 29, 1967, the island was closed to the public. Their research continues today under the management and guidance of marine biologists at UC Santa Cruz.[C]

As a more formal means to pursue these interests, Poulter started the SRI Biological Sonar Laboratory in about 1964 to investigate the remarkable ability of sea mammals such as seals and sea lions to detect and discriminate between objects under water. With other colleagues like Ronald Schusterman, Richard Hubbard, Danny Del Carlo, and Richard Jennings, he developed the first laboratory in North America devoted primarily to the study of the behavior and physiology of sea mammals.[D] Creating an underwater acoustic laboratory in an abandoned Nike antimissile site just off the shore of San Francisco Bay, Poulter would be among the first to assert that these mammals could use echolocation—that is, active sonar—to locate food. In thousands of trials in light and total darkness, California seals would be fed fish in acoustically anechoic chambers equipped with hydraphones. These tests showed for the first time a seal's ability to use underwater clicking sounds to quickly locate live or dead fish.[E] While some have questioned this sonar-like ability, most researchers now accept it.[F]

In 1967 Poulter turned to whale recordings by visiting the calving grounds of the gray whale off Baja California. Here he carefully sorted out the whales' variety of emissions from those of other creatures and from background noise coming from within and out of the water. He was able to isolate several gray-whale vocalizations including one that sounded like a loud rasp followed by a Chinese gong. It seemed to be an alert signal emitted when a helicopter or plane would pass at a low level. This signal caused the immediate cessation of all other whale sounds. The silence would then be ended with a series of echolocation clicks.[G]

In his pursuit of understanding sea mammals, Poulter was to record and analyze about 600 miles of magnetic tape of such sounds from seals, sea lions, and whales. He made 15 trips to the Arctic and 3 to the Antarctic pursuing the various species and their habitats.

One account of Poulter's insight in biological acoustics comes from Ted Griffin, who in 1962 became the first person to extensively interact with and train a killer whale, one he called Namu, for the British Columbia town near where it was captured. Griffin had been observing the whale for some time and had shown that it was not dangerous to humans. His dealings with Namu had gained media interest, and one day a film producer came to Seattle and suggested that, if Griffin could swim with Namu and show some conviviality, he could make a documentary about it. To explore this possibility, Griffin's brother jumped in the water first, some filming was done, and he emerged unscathed. Then, as Griffin started to swim with Namu, he was wondering how far the interaction could go. Would the whale come when he called? Would the whale call him? Would the whale indicate whether it was hungry?

Over the first few days in the water, the whale—no matter where he was—would come to Griffin, even in the dead of night. Not knowing exactly where Namu was, Griffin could sense its presence and would reach out, find his nose, and then caress Namu across its body. They became friends. Further, he would squeak to the whale and it would squeak back. So that he might learn more about communicating with Namu, Griffin asked Poulter to come and take some recordings and lend his insight. After several days of observations Poulter surprised Griffin by concluding that he, Griffin, was not sounding like the whale, but the whale was altering its normal vocalization to sound like Griffin's whale imitations! Griffin was astounded. The whale was consciously trying to reach out to him. Thereafter, their communication was enriched, as the whale would do its best to imitate Griffin even when he was doing tasks underwater not related to Namu directly. This little episode underscores Poulter's insight into the vocalization of undersea mammals.[H]

Doc Poulter died in 1978 at the age of 81 while working in his laboratory. One of his associates, George Duvall, who had come to lead Poulter Laboratory for a time, summarized his respect for this genuinely caring, imaginative, and energetic man with the three principles Poulter lived by:

- Never look back; that is, don't waste time regretting your mistakes. Learn what you can from them and go forward.
- Do not let your visions be bounded by the limitations imposed by your present knowledge and skills. If you want to do something worthwhile that requires knowledge or skills outside your present limits, learn what is needed if you can, get others to help where you can't, and forge ahead.
- Let your enthusiasm flow out and engulf others. It will inspire them and let your work go faster; it will be reflected and will also regenerate your own.[I]

He was one of SRI's best-loved people.

Radiation Chemistry

Very early in its history, SRI undertook several research contracts with the Atomic Energy Commission (AEC). Some of these were from the AEC's reactor division, which was searching for industrial uses for its radioactive waste. From these explorations came a working relationship with the AEC that would lend SRI some privileged positions in exploring the uses of radiation chemistry. One of these positions occurred in August 1954 when SRI became one of only three sites in the United States—and the only one in the West—to receive a very large public depository of unclassified AEC reports of interest to industry. This library was appropriate to SRI because of its ongoing interest in the industrial application of radiation. But it was a bit earlier, in late 1952, that SRI received from AEC-Brookhaven the largest radioactive source then outside the government. It was a 4,500-curie cobalt 60 gamma-ray source that SRI housed in an elaborate facility appropriate to its safe and effective use.[4, 5, J] Figuratively, part of that housing was the formation of a new laboratory in radiation engineering (see Figure 11-2).

The potential uses of radiation in industry were many, involving areas of biology, chemistry, and related engineering disciplines such as electronics. Some of the early research directions at SRI were

- Nondestructive testing of metal casings
- Nonthermal sterilization of foods and drugs whose composition precluded heating
- Prevention of sprouting in onions and potatoes
- Triggering of commercially important chemical reactions
- The structural effect of radiation on some plastics.

While only its earliest insights arose at SRI, this last area would come to have great influence on the local economy and would become the basis for a very large industrial company.

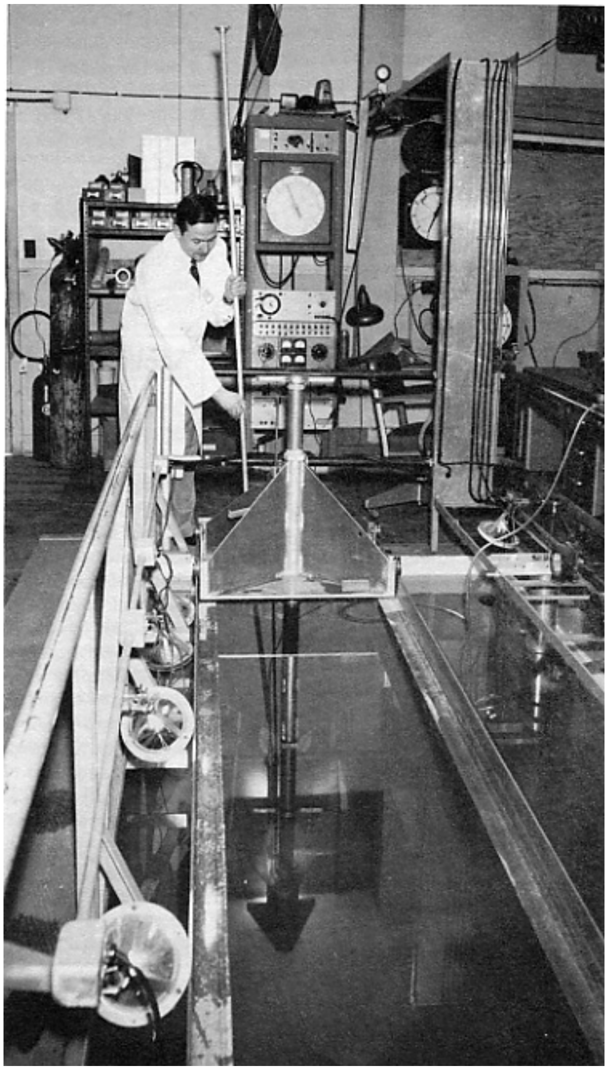

Figure 11-2. SRI's cobalt radiation "swimming pool" (Dr. Ed Kinderman with the pole).

The person who was to head the SRI Radiation Engineering Laboratory was MIT chemical engineering graduate Paul Cook. Arriving in 1948, Cook became instrumental in the growth of radiation chemistry at SRI and saw in some of its results important commercial potential. As it would turn out, starting companies was simply a natural inclination for Cook. Before coming to SRI he had founded a wire company with his brother, and in 1951, while still affiliated with SRI, he started another company to provide lighter weight wire to the aircraft industry. Cook's new company, called Sequoia Process Corporation, was located in nearby Redwood City. As time progressed, and building on insights he was gaining from some of his SRI work on the radiation of plastics, Cook introduced that technology at Sequoia. The relevant latent product from the SRI experience had to do with polymer-based wire insulation, in particular, polyethylene.

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[4] This cobalt source was powerful enough to be lethal if fully exposed to a human for 7 seconds. Therefore, part of the physical housing was a 720-cu-ft concrete underground storage chamber holding 5,400 gal of water. This was the cobalt storage area and adjacent to it, also underground, was an instrumentation room in which experiments could be run remotely. Joining the two rooms was an aluminum "window" to which both the source and the target could be moved for precisely controlled radiation exposure. (SRI's *Research for Industry*, 5(2), 1-9, January 1953).

[5] According to Ed Kinderman, a researcher in the same group (phone conversation, January 28, 2003), the cobalt source arrived not quite "as advertised." The neutron bombardment of the cobalt at Brookhaven was incomplete and thus developed only about half of its labeled output. Sam Taimuty of SRI got them to rebuild it and in turn helped set up the instrumentation to do the dosimetry for the whole chamber.

Polyethylene was light, cheap, and had good electrical insulation properties. It was a polymer in that it consisted of very long molecules that formed tiny, quite independent polymer crystals. The plastic didn't, however, hold up well under high temperature, and it didn't have much flow above the melting point of the crystals. Based on observations that dated back to the Manhattan Project and early 1950s work at General Electric, Cook and others began to explore how the properties of polyethylene were changed under radiation.[K] For example, how could the temperature-tolerant properties and the structural strength of such a plastic increase dramatically as a result of gamma radiation?

The main structural effect from radiation was called cross-linking, which would have two consequences for the polymer. One was greater stability at high temperatures, and the other was something called structural memory. As cross-linking implies, it is the forming of bonds between individual polymer molecules. Under radiation, hydrogen atoms were knocked off the polymers, permitting a cross-molecule bond to form. This connection essentially transformed the plastic from a two-dimensional structure to a three-dimensional structure, increasing its stability under high temperature. Irradiation also improved another weakness of polyethylene, stress cracking. Removing that weakness improved its electrical insulation property.

These and other innovations, including improving polyethylene's oxidation properties, grew in part out of a joint effort between SRI and Sequoia that began in early 1955 and involved four projects totaling about $60,000 in just over 2 years. From these efforts came the formulation for a new wire insulation product at Sequoia called Hyrad that could withstand continuous temperatures in the vicinity of 300°F (see Figure 11-3). Remarkably, the close working relationship helped the concept move from the laboratory to an online production state in less than one year.[L] While running Sequoia, Cook continued to participate at SRI until the spring of 1953.

However, within a few years an SRI board member, who had funded Sequoia to the extent of holding a controlling share, took over operation of the company. At this point, in 1957, Cook mortgaged his house and founded a second company to exploit this use of radiation chemistry. He called it Raychem and immediately began selling a flame retardant polyethylene coated wire, reaching profitability within seven months.[M]

At Raychem, the resourceful Cook also returned to the second important property of irradiated polyethylene—structural memory. This property was recognized during the time irradiation work was going on at SRI. [N,O,P] To realize this other attribute of cross-linking, the polyethylene mix, as augmented by the work mentioned above, is extruded at the desired

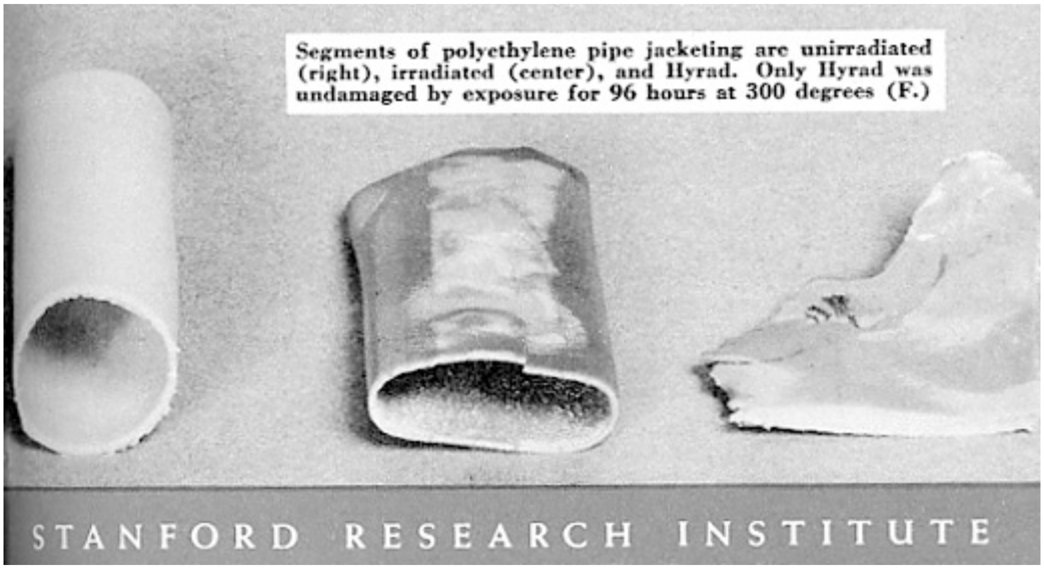

Figure 11-3. Temperature Consequences of unradiated versus irradiated polyethylene (SRI's *Research for Industry*, 8(4), 1-2, May 1956).

final diameter and irradiated. Then the tube is heated to soften it enough to expand it to a level that stretches but does not break the cross-link structure. Allowed to cool, it remains stable at this expanded diameter. This constitutes the packaged product. When the tubing is used, and on being reheated to about 125°-150°C, the tube returns to its original and smaller diameter, where it again stabilizes. This memory property enabled a brand new product line called heat-shrink tubing. With this and a continuing stream of useful products, Raychem grew to become a Fortune 500 company with revenues of $2 billion.

After many years of growing the company, Paul Cook rekindled his penchant, the founding of start-ups. After his tenure at Raychem was over, he also returned to the chairmanship of SRI and while here left this same entrepreneurial imprint on his alma mater (see Appendix B). Today, the indefatigable entrepreneur is again immersed in starting companies not necessarily related to SRI work but here on its campus.

Rod Polymers

Here, from the Internet is a description of a new type of sailcloth called Zylon, manufactured by Toyobo in Japan:[Q]

> For 1996, a new ultralight mainsail made from Dimension Polyant's PBO/Zylon cloth, a new 0.6 oz. nylon runner, and a heavy # 1 genoa were added to the inventory. PBO is a new cloth available from Dimension that exhibits 40% less stretch than traditional Kevlar. Even more impressive is its breaking strength. PBO has more than twice the tenacity of Kevlar. This allowed us to produce by far the lightest main possible. The 12,000-denier cloth used (normally 18,000- denier is used) is lighter than the material that would usually be used in a J-29 main. Built using Ultra Bond construction, the sail weighed only 28 lbs! It has performed extremely well due to its construction and minor changes in last year's design. Constant improvements in our spinnaker designs continue to make Banks spinnakers the fastest available.

From the *Denver Post* of September 27, 1999, the following describes the use of Zylon to protect fans at auto racing events:

> "Today's spectators can expect warm weather. And thanks to the IRL's 2-race-old tethering system, spectator injury or death because of on-track Indy-car accident debris might be tragedies of the past.
>
> The Suspension & Wheel Management System (SWEMS) is required on every car competing in the Radisson 200. IRL officials, along with car constructors Dallara, G Force and Riley & Scott, have worked vigorously to minimize the possibilities of wheel assemblies becoming detached during high-speed accidents. The SWEMS principle utilizes multiple restraints attached to a car's chassis and suspension. The

Figure 11-4. A Zylon spool and sails made from it (from the Toyobo web site, www.toyobo.co.jp).

restraints are made of FIA-approved Zylon, which has a breaking strength of 5 tons.”

We are surrounded by and, to no small extent, composed of polymers. Some are natural such as silk, natural rubber, cellulose, and proteins. Others are synthetic such as plastics, nylon, and synthetic rubber. Polymers are extremely large molecules composed of many structural subunits, called monomers, which are linked repetitively into long chains. A polymer molecule may contain from 1,000 to more than 250,000 atoms and have a molecular weight as high as several million. By contrast, a molecule of methane, CH_4, has a weight of 16. Polymers have a lot of forms and display an enormous variety of useful properties such as films, membranes in the body, wool, violin strings, and solid fuel rockets. The repeating units of a polymer, composed primarily of carbon and hydrogen, can also be linked together in a linear fashion to give the extremely long molecules useful in fibers. Those necessary for cloth and fiber-like forms are called rod polymers and are the root of an important SRI contribution known as the PBZ family.

In the early 1970s, Dr. Jim Wolfe was a polymer chemist at the Air Force’s Wright Laboratories in Dayton, Ohio. He had been working on rod polymers there in search of an ultra-light, ultra-strong material for military aircraft. He came to SRI in early 1977 with ideas on how to continue that research and sought sponsorship from the Air Force Office of Scientific Research and his former lab.

The SRI team built a new class of polymers whose properties were sufficiently novel that several patents were issued on their composition and synthesis. The family is called PBZ— for poly(2,6-benzothiazole)—and its synthesis is difficult. It involves selected monomers that interact in a phosphoric acid bath to form the so-called doping polymers that are then used in another solution and drawing process to form the final fiber. The PBZ axial ratios may be very high—that is, very long and very thin—and, in this case, provide the basis for building a very strong fiber (see Figure 11-5).

The polymerization process carries some risk. Bock Loo, a former engineering assistant in the lab at SRI where this process was invented, mentions that the monomers were not only difficult to make but were somewhat toxic.

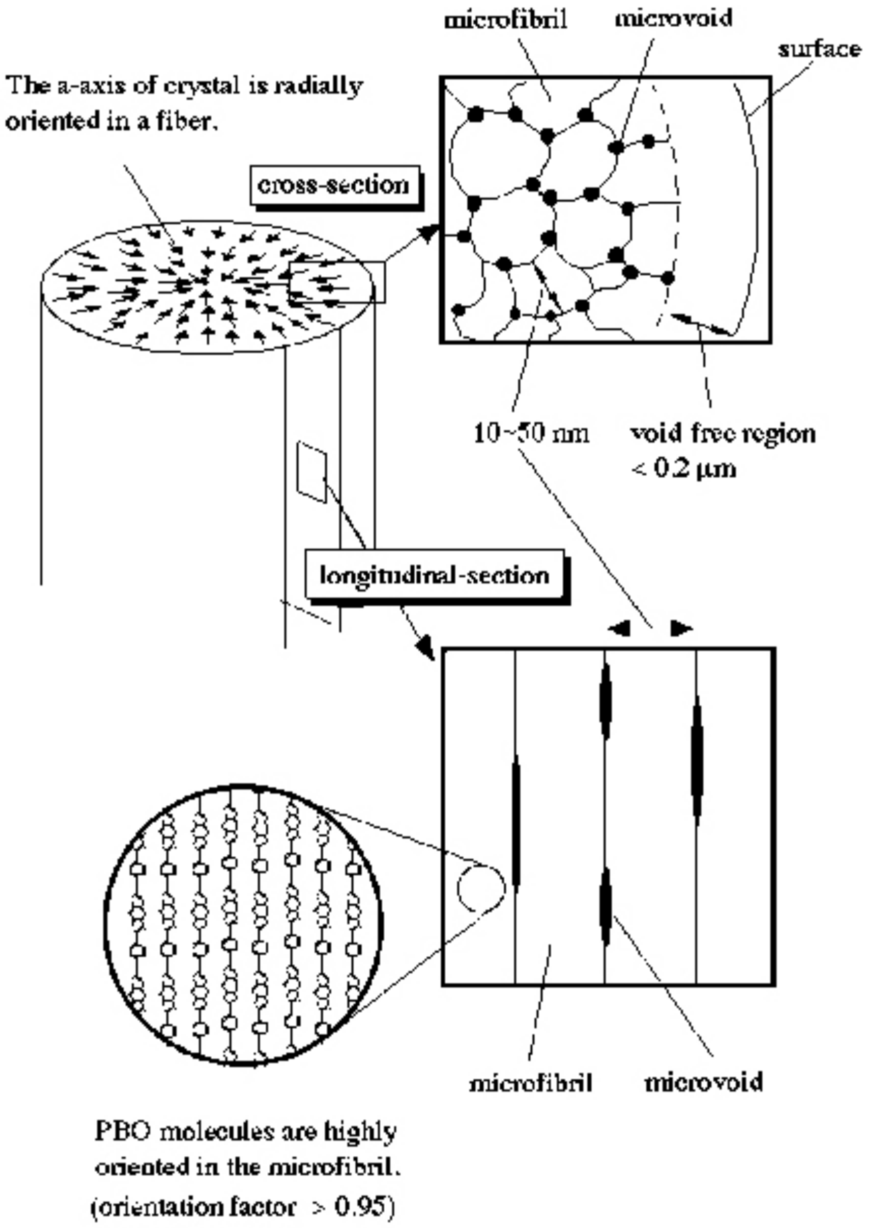

Figure 11-5. A depiction of the polymer molecules within the fiber.

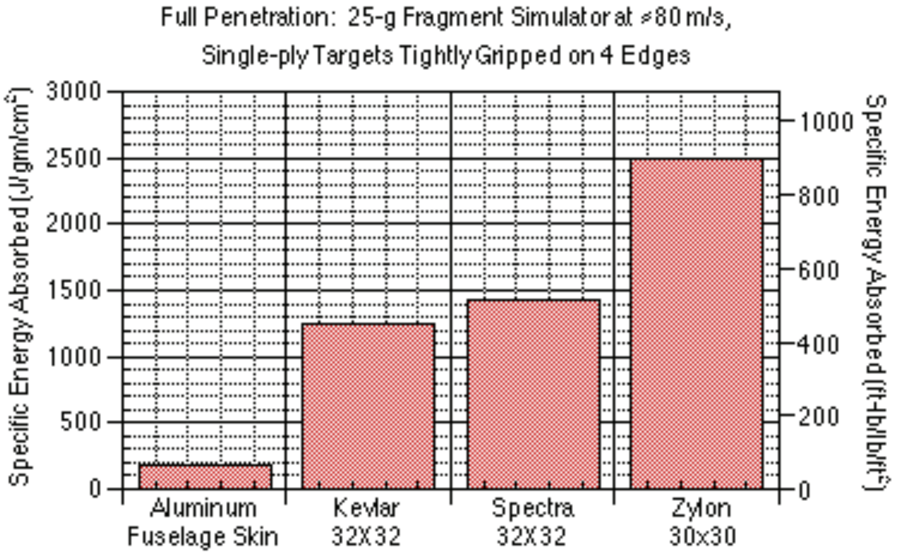

Figure 11-6. Comparison of kinetic energy absorption by various barriers.

Masks were required because the mere presence of the yellow material made everyone sneeze; getting any of it on ones clothes meant an immediate trip to a sink to wash it off. Thus, most of the work was done under exhaust hoods. As the properties improved, the batch sizes grew from grams to as much as 30 pounds.[R]

Early fibers from the PBZ family displayed encouraging properties: light weight, stretch resistance, very high strength, heat resistance, and nonabsorption of water. To help converge on the best combination of product and process, Wolfe's group tested each fiber created and recorded the process and the end results. These were then subjected to computer analysis and the process was repeated. SRI received several patents in this area with awards from 1980 to 1988. The specific one for the PBZ family was applied for in 1982 and issued in August of 1985.[S]

In the late 1980s, SRI licensed the manufacturing process for its rod polymer to Dow Chemical. After investing about $1 million to reach a manufacturing capability, Dow gave up and licensed it in turn to the Japanese textile company, Toyobo.[6] By 1998 Toyobo had placed Zylon, its product name for the SRI polymer, on the market. Zylon is now appearing in a wide range of applications where strength and lightness are critical. As one might expect, Zylon's main competitor is Kevlar™, but as will be shown in the few applications to follow, Zylon's attributes surpass Kevlar and other alternatives.

One of the important uses of Zylon is now being explored at NASA and SRI: the protection of airline passengers from the lethal release of turbine blades from engine failure. Normal insulation-filled aluminum airplane skins are not very effective against such failures. Zylon sheets, however, are so strong that adhering them to the outside of the interior airplane walls can be an effective aid in increasing passenger protection. In SRI gas gun tests, 25-gram projectiles, simulating turbine fragments, were accelerated to 80 meters per second against aluminum and several fabrics made of high-strength polymer yarns. These tests demonstrated that aramids (Kevlar™), polyethylenes (Spectra), and polybenzoxazole (Zylon) absorbed over 5 times more kinetic energy than aluminum fuselage skin on an area density basis. The specific energy absorption (SEA), which we define as the energy absorbed per unit area density, of one particular Zylon weave was 15 times that of 2024-T3 aluminum, as shown in Figure 11-6. Results of experiments to investigate the effect of weave tightness and multiple fabric plies suggest that SEA increases linearly with a real density, independent of weave tightness and number of plies.

Similar advantages over Kevlar can be seen from the ballistic tests at NASA's Glenn Research Center shown in Figure 11-7. Here 1.9 lb titanium discs were fired at 1,600 feet per second at the inside of a cylindrical aluminum structure simulating a section of a jet engine fan enclosure. The wall consisted of a thin aluminum skin, five layers of either Zylon or Kevlar™, and on the outside, a 1-inch-thick

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[6] This technology was one pursued by SRI's exclusive commercialization agent at the time, CommTech International. When Dow was ready to abandon the manufacture of rod polymers, it was CommTech who solicited Toyobo's interest and facilitated the relicensing. This license had produced considerable royalties for SRI since about 1998 and Toyobo is still trying to enter Zylon's perhaps most lucrative market, bullet-proof clothing. (Conversation with Bonnar Cox, May 20, 2004.)

layer of honeycomb aluminum. The tests again show the superiority of Zylon.

Other, more fundamental properties of Zylon are those shown in Figure 11-8 from the Toyobo web site.

A very recent and interesting application for Zylon is in golf clubs. Though it may seem a natural for golf club shaft design, and it is, that's not the unusual aspect of its use. Instead, it's in the club head design itself. Today's large-faced metal "woods" are made of very strong lightweight materials such as titanium. But the hollow or lightly filled volume of these heads undergoes a distortion at impact that represents an energy loss. The tension on steel reinforcing rods in concrete construction gave David Boone, club designer for Zevo Golf, the idea of putting the club head permanently under tension. In a very innovative step for golf club design, he tied the top and base of the head together through a stretched membrane of Zylon. Zylon's lightness and high tensile strength have made this new driver a novel addition to golf.[T]

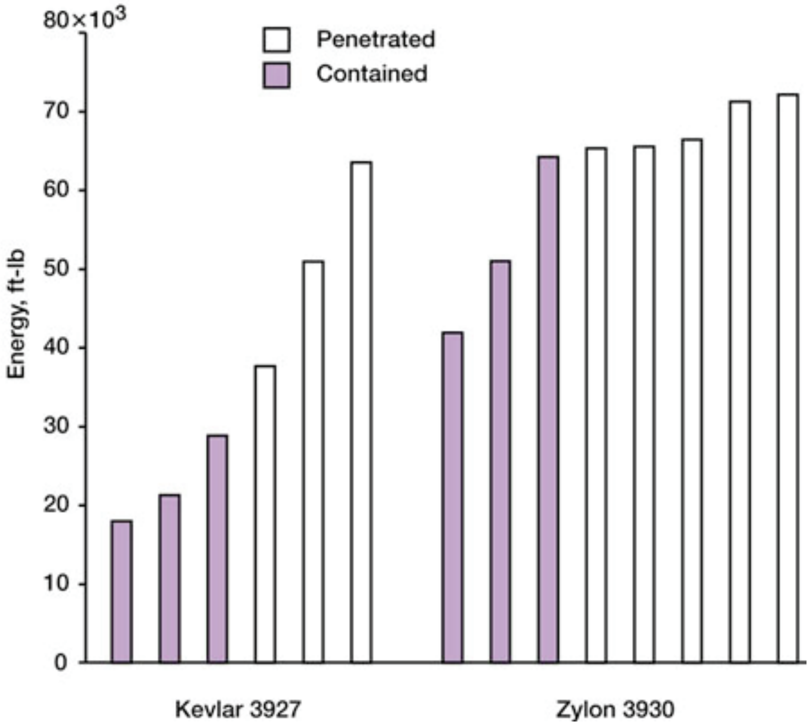

Figure 11-7. Projectile tests at NASA comparing Kevlar™ with Zylon.

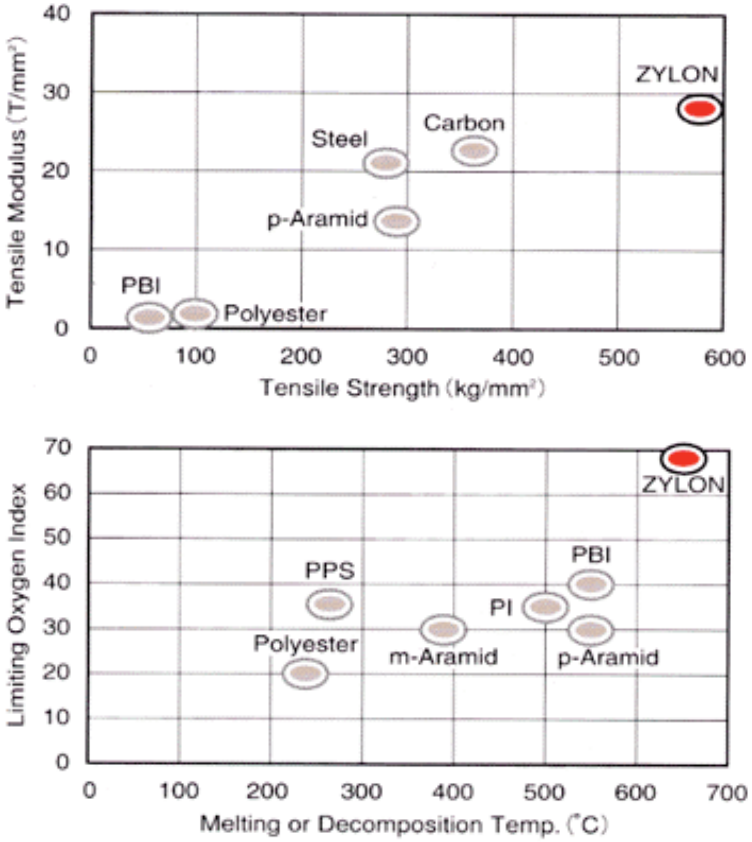

Figure 11-8. Comparative tensile and melting characteristics of Zylon (from the Toyobo web site).

Modeling Chemical Processes

As with many aspects of present day science and engineering, mathematical models and available computing power are combining to play a huge role in the design of chemical processes.[U] Often there are a variety of ways to manufacture a substance, so it is important to discover the most efficient means, the process with the least environmental impact, or the one that yields the purest product. Today, a lot of this exploration uses a computer code developed by Stanford professor W.C. Reynolds, called STANJAN. The main objective of the code is to calculate the chemical species composition that result when a given elemental input composition has been brought to thermal equilibrium at temperatures and pressures of interest. Using that code, however, requires a set of thermodynamic input parameters associated with every elemental or molecular species involved in the chemistry of the system.[7] It is in this later area of measuring or evaluating the needed parameters that SRI's Materials Research Lab has contributed for over three decades. Here are a few examples.

Much of the SRI work surrounds high-temperature reactions such as those used in combustion or refining processes. One long-term client, the Gas Research Institute, has a continuing interest in catalysts that will not only produce the most efficient flame but will not be consumed prematurely in the combustion process. SRI has modeled the behavior of a range of metallic catalysts, showing which will or won't have commercially acceptable lifetimes.

There is another, more pervasive combustion process in the engine of your car. In the early 1920s, the Ethyl Corporation introduced tetraethyl and tetramethyl lead to effectively increase the octane or anti-knock performance of gasoline. Those additives, along with MTBE, have serious environmental impacts and have been generally outlawed. Another, somewhat less toxic additive, called MMT, contains manganese and has been used in limited amounts overseas, in Canada, and to a lesser extent in the U.S. (under a waiver granted by the U.S. Environmental Protection Agency or EPA). But the emission of elemental manganese in the exhaust gases could be a problem, and SRI has worked for Ethyl to clarify this issue by modeling the combustion process when MMT is present. The SRI work indicates that manganese can be captured prior to emission as a solid, manganese phosphate. But the complex four-way interchange between the suppliers of additives, the automobile industry, environmental groups, and the EPA concerning MMT is ongoing.

In the meantime, another SRI effort reflecting environmental concern is that for the government's National Renewable Energy Lab. This work involves the complex chemical processes in the energy conversion of biomass. Here SRI has developed a STANJAN thermodynamic database for the 20 or so constituent elements that occur in various biomass compositions for NREL to use in modeling the various combustion and gasification processes.

The last two efforts to be mentioned here are the production of titanium metal and the white pigment in paint, titanium dioxide. The importance of titanium and its alloys to our national defense prompted DARPA to investigate more cost-effective processes for its production. In this case SRI has developed a new fluidized-bed chemical vaporization process for the deposition of pure titanium or its alloys using intermediate compounds (precursors) like titanium tetrachloride. SRI's chemical modeling of the vapor deposition process was key to the development of that fluidized-bed process. Curiously, another process in which titanium tetrachloride is an important intermediate is the production of the all-important ingredient in paint, titanium dioxide. This oxide is the principal whitener in all paints and because it is a very important product of Du Pont, they asked SRI to help refine both the chlorination and oxidation steps of that production process. Not only did SRI successfully complete that modeling

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[7] Needed for each atomic or molecular species are the various energy absorption and production parameters, such as enthalpy and entropy, important when heat, pressure, and temperature are varied. These thermodynamic parameters are often determined experimentally at SRI using mass spectrometry in specially designed chambers called Knudsen cells. While the species to be examined are chosen by clients, the results are often placed in the large international database for such information called the JANAF tables.

investigation, but in doing so found previously unknown chemical species that helped more accurately model the chemistry of Du Pont's manufacturing process.

These few examples, out of hundreds, depict a range of important contributions SRI is making to the chemical process industry and the mitigation of such processes on the environment.

Oxidation Chemistry

There is no more important element to us than oxygen. By weight, it comprises about half of our bodies and, curiously, half the planet itself. Through the dynamic processes that oxygen enables, it is essential to all living things. When we inhale, oxygen forms the basis for our energy absorption and the temperature stabilization of our anatomy. But as much as anything, oxygen is associated with what we normally think of as aging, the decomposition of almost all materials into oxides. Our adapting and modulating those processes for different purposes, from near-benign environmental protection to explosive energy release, has been the focus of the SRI's chemistry laboratories for several decades. We will mention here just a few of those lab's notable accomplishments.[V]

High Energy Materials

In the core of the solid propellant rockets that put the space shuttle into orbit there is an oxidation process of extremely high energy. Given a certain rocket size, that process effectively determines the allowable payload of the shuttle. Today that reaction consists mainly of a fuel made up of powdered aluminum and hydrocarbons, an oxidizer of ammonium perchlorate (AP), and a binder to hold them evenly dispersed. The energy potential and efficiency of such a fuel mixture can be viewed in terms of the velocity of the exhaust gas. For obvious reasons, this fuel-oxidizer combination also needs to be as stable as possible prior to ignition.

Around 1990, the SRI Chemistry Lab was working for the Office of Naval Research (ONR) on a program to develop new explosives, specifically by exploring those oxidizers that had high energy but didn't involve the caustic and other negative properties of chlorine. They had been concentrating on a particular type of organic structure called cubanes, from the cubic form in which eight carbon atoms were arranged. Because of the inherent high bonding strain of this structure, the ONR community believed it would have very high energy potential. The particular form of the cubanes ONR had targeted involved compounds of nitrogen called N,N-dinitramines. But no one in that community, including SRI, had been able to synthesize them.

SRI senior chemist Dr. Jeffrey Bottaro had an insight. He believed that the dinitramide salts themselves, without the difficult covalently attached cubane configuration, would be more easily synthesized, have the needed stability, and provide the energy performance sought over the chlorine-based oxidizers in use. He synthesized a new compound called ADN, or ammonium dinitramide with the formula $NH_4N(NO_2)_2$. When ADN was put in propellant form, this new oxidizer would demonstrate both an increased stability and a predictable increase in lift capacity over current propellant formulations. Dr. Rob Schmitt, Bottaro's colleague and supervisor, calculated that ADN would provide an 8% percent increase in the shuttle's payload. Even better, the avoidance of chlorine in the formulation meant that it would be more environmentally friendly, produce none of the chlorine-based compounds inimical to the upper atmosphere, and have fewer "contrail" signatures than the present oxidizer used in the shuttle. The lack of an exhaust trail signature would also be a strategic advantage for rocket-based weapons.

SRI received four patents on the material and its manufacturing processes. When this new propellant will be introduced is uncertain, but the Army and Navy are exploring the use of ADN for both environmental and efficiency reasons.[W] The Navy also believes ADN will reduce the weight of rocket motors by 40% and so is trying to reduce the manufacturing cost of ADN to about $100 per pound.[X] Morton Thiokol is currently working with the Navy to increase the specific impulse (effectively the exhaust velocity) by about 20% over the AP oxidizers through the addition of aluminum hydride as a fuel.[Y]

An interesting aspect of this story flows from the competitive intricacies of the Cold War.[Z] Bottaro and his SRI colleagues were attending a 1993 meeting of the American Institute of Aeronautics & Astronautics (AIAA) when they heard a group of Russians giving a paper on the same ADN-based propellants that they had built. As it turned out, the Russians had been secretly using such propellants in the missiles of the former Soviet Union since the 1970s and the Russian delegation was in this country ultimately hoping to market them. Their presentation was a solid affirmation of the SRI approach, but their history of secrecy, of course, meant there was to be no challenge to the SRI patent position. Schmidt and Bottaro later tried, unsuccessfully, to bring these Russian scientists to SRI to continue work on ADN along with SRI researchers.

The future prospects for ADN are emerging and amazingly varied. The European auto supplier Autoliv developed the salt guanylurea dinitramide as a state-of-the-art airbag propellant devoid of any physical or toxicological hazards, only to have TRW patent the same material, precluding worldwide marketing of guanylurea-based airbags by Autoliv. In the military area, the British are exploring ADN as a potential propellant for air-to-air missiles, and ADN offers unparalleled performance prospects as a major ingredient in torpedo warheads.

There are even medicinal applications for this broadly useful compound. In the spectrum of psychoactive drugs, most are nitrogenous and in the physiology of the brain have a negative (base) pH. They are also in the form of positive ions that have difficulty in transitioning the barriers between the blood and the brain. Usually, complex indigenous proteins aid this transition, but they have a very narrow range of drugs with which they can work. Dinitramide salts, however, have the unique ability to transport a wide range of organic ions across such biological membranes. Thus, ADN shows promise as an agent for delivering pharmaceuticals to the brain in situations not previously enabled. SRI is now obtaining a patent on this pharmacological use of ADN. So, the technological possibilities for this simple material are substantial.

Oxidation in Environmental Chemistry—Organic Compounds

When considering ways to clean up or prevent harm to the earth's environment, at least two questions about the oxidizing transformation of organic materials are important to answer:

- What are the chemical processes that can occur?
- What are the rate constants of such reactions?

The answer to the first question identifies what products lie in the chain of decomposition, including which of those are toxic. The answer to the second question defines how long these products will be around. Simply put, but extraordinarily complex, the net rate of change in concentration of a given chemical is the sum of all the equilibrium and kinetic processes that affect it in a specific environment. (See box for a partial list.[AA])

Unfortunately, observations and measurements intended to extrapolate or generalize are not all that useful. For example, measuring the depletion rate of most chemicals is not very helpful because isolating the entangled processes and adequately defining what is often a complex environment make extrapolation to another site almost impossible. The relative contribution of different processes can change with location and season. This difficulty leaves only the option of trying to identify the few, most important processes involved with a given chemical in either water or air and then trying to understand and quantify them in the laboratory.

Although we think easily of oxygen's attraction to metals, as in the rusting of iron, oxygen actually has a much greater affinity for organic compounds. Given that the world now produces a billion tons of organic chemicals each year, some of it will be inadvertently introduced into the streams, rivers, and coastal waters around industrial cities or areas of concentrated use. Once such material is introduced into ground or surface water, there is ample opportunity for the hydrolysis of such compounds (their reaction with the H^+ and OH^- ions of water) with unknown consequences. Because of the implied threat to our environment, SRI has been exploring the hydrolysis of organic chemicals for at least two decades.[BB]

Process	Parameters
Atmosphere	
Photolysis	Light Intensity
Oxidation	Oxidant concentrations
Rain out	Precipitation rate, sticking coefficient
Transport	Wind velocity
Surface Waters	
Volatilization	Preference of substance for air or water, surface roughness
Sorption/bio-uptake	Organic/lipid content of sediments, organisms
Hydrolysis	pH, temperature
Photolysis	Light intensity
Biotransformations	Organism population, nutrients, temperature, and pH

Because the transformation of many organic chemicals under hydrolysis can either reduce or increase their potential toxic effects on biological communities, the government agencies responsible for water quality, such as the Environmental Protection Agency (EPA), are very interested in such processes. And because some of the inimical products can have half-lives ranging from seconds to centuries, we need to fully understand these processes in both fresh and marine waters. Let's look at some examples of the EPA's long relationship with SRI in this area.

SRI has contributed to EPA regulations both by developing the general methods and protocols for testing the presence of questionable material as well as by determining the properties of certain individual, potentially harmful chemicals as they are created and transformed in the earth's environment. For the past 20 years SRI's chemistry labs have helped EPA and its overseas counterpart, the Organization for Economic Cooperation and Development (OECD), define test methods for hydrolysis, photochemical reactions, and sorption in soil[8] as well as vapor pressure and volatilization models for dispersion in air. These SRI methods were incorporated into EPA testing procedures starting in 1982 and have continued to the present. Also, the 2002 OECD methods for photochemical protocol were developed at SRI.

One example of the pursuit of individual chemicals is the case of a specific member of the family of dioxins. Certain important toxins in our modern environment come from a family called polychlorinated dioxins. Among other sources, these are the byproduct of pesticides or the incineration of chlorinated wastes. One such highly toxic member of that family is called tetrachlorodibenzodioxin or TCDD. It was one of the many toxic chemicals that oozed to the surface in New York's Love Canal episode in the late 1970s. Several years later, at the request of the EPA, SRI set out to learn more about how this hazardous chemical behaved in the natural environment. If it indeed were a present threat, how long would it remain so? Two relevant properties were examined: (1) how easily would TCDD evaporate, that is, what was its volatility in both water and air and, (2) what were its persistence properties under photolysis or exposure to sunlight?[CC]

To gauge the former, Tom Podoll, Helen Jaber, and Ted Mill measured the vapor pressure, solubility, and diffusion properties of TCDD under a variety of conditions. From these measurements they could estimate that TCDD in water would have half-lives of about 32 days

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[8] Soil sorption is the integration of a chemical into soil either by absorption or by adherence to its surface.

in lakes and ponds and about 16 days in rivers. Given some assumptions, its persistence in air and soil were also estimated. The results of this work became part of the EPA's assessment of TCDD and other dioxins that, among other things, led to the EPA's emissions standards for flue gas in 1993.

The Experimentation, Science, and Utility of Explosions

When you first learn that something as violent, rapid, and turbulent as an explosion has very predictable and often precise utility, even at large scale sizes, it seems counterintuitive. The shocks from such events are literally over in a flash and the effects on materials are varied and complex. Nevertheless, for the past 50 years SRI's Poulter Laboratory has followed and contributed to the experimental and theoretical science of explosion-produced shock waves and their effects on all kinds of materials and structures. SRI's investigations have covered the control and influence of a very wide range of sizes and types of explosions as well as their use in simulating very high-energy events that could not be housed in an affordable experimental setting.[DD]

This research capability began with what are called terminal observations, a repetition of similar explosions or shots in an attempt to characterize what happened. This method used optical instruments to image effects observable on the outside surfaces of materials. Then came the ability to directly measure some of the parameters of the explosion itself and the response of materials to it. Finally, with the advent of computer modeling, each shot can incur greater experimental design, much more sophisticated and multi-dimensional monitoring, as well as more detailed post-experiment analysis.

The evolution of techniques for studying explosive effects at SRI began in the mid-1950s and continues today. One of the early uses of explosives in Poulter Lab was to simulate the effect of nuclear radiation on ballistic missile nose cones. SRI undertook years of investigation for the DoD to determine the resilience of missiles to a variety of explosions under real and simulated conditions. To conduct the simulations, SRI built an experiment site in the foothills east of San Francisco Bay. There, explosive charges could be fired safely with minimal disturbance. As urban development drew closer, the site was moved eastward to a new 480-acre location near Livermore, CA.

As the modeling and understanding of explosive effects grew, so did the range of problems Poulter Lab could address. From the idealized nose cone environments of the outer atmosphere that enabled the simulation of shock loading from x-rays, the work moved to the more complex interactions near ground level. Here, the Lab's increased modeling and experimental capabilities were extended to address damage to structures, vehicles, and military systems from the airblast produced by nuclear weapons. Figure 11-9 shows Poulter Lab's 8-foot-diameter, 250-foot shock tube, driven by explosive charges, to simulate nuclear airblast conditions on specific targets. Obviously, this work helped us better understand how different materials and

Figure 11-9. SRI's Corral Hollow test site near Livermore, CA, showing the eight-foot shock tube in use.

structures could survive a nuclear attack.

Not all of SRI's nuclear test experimentation would be simulated. As the United States continued its nuclear testing program after World War II, SRI became involved in assessing directly the blast and shock effects of a nuclear explosion. SRI's involvement started with high-explosive preparatory tests at Dugway Proving Ground in Utah very early in the 1950s, later moving to the Mercury Nevada Test Site north of Las Vegas, and to a lesser extent in the Pacific Proving Ground where much larger weapons were tested. SRI would be one of the few laboratories outside the government to make measurements on such tests, which would eventually include atmospheric, near-ground, and under-ground locations.[9] The relevant SRI groups were Poulter Laboratory and the Physics Division. After the moratorium on above-ground tests in the 1960s, Poulter Laboratory continued measurements on underground tests and in the process developed new measurement techniques sensors, and gauges that would find a wide range of uses.

With this brief background, then, in what way did these laboratories make their greatest contributions? Very conservatively, one could easily recognize three: instrumentation, overpressure load simulation, and modeling material failure. We will cover them briefly in that order.

Instrumentation

The first instrumentation problems were associated with measuring the shock wave effects in the air and ground surrounding a detonation. It was 1951 when SRI first tried using commercial equipment to instrument and record a nuclear test. It quickly became clear that the commercial sensors and instruments of that day could not cope with the range or magnitude of the variations witnessed. So, SRI immediately began a program of gauge design, construction, and use that would continue for over two decades. At first, the engineers were delighted when even one gauge survived the nuclear blast long enough to record even one millisecond of data. SRI went on to build gauges that would accurately measure the displacement and velocity of the ground movement and the important pressure dynamics induced by the primary damage mechanism, airblast.

Next, given the multiplicity of such sensors needed across the test site, SRI designed a clever and cost-saving data acquisition system. These arrangements multiplexed data retrieval onto the power leads to the remote sensors and then to the instrumentation vans where data recording took place. The system had variable bandwidths, high dynamic range, and its multiplexing design saved enormously in instrumentation costs. The system remained in use until about 1982.

Even with ground and airblast results now in hand, the complexity of extending them into exactly what would happen inside the affected materials was difficult. Thus came the second area of SRI contribution to instrumentation, the amount of stress and strain in the affected materials.

To learn something about how much strength was needed in a material for it to survive some specific blast, it was necessary to become quantitative about that material under shock-wave impact. Keep in mind two things about instrumenting material in this environment. One is the extremely high pressure involved and, just as important, the range of pressures that must be accurately recorded. These meant that the instrument not only had to survive but had to accurately and dynamically measure a pressure span of as much as 4 or 5 orders of magnitude. The SRI-built material-impact sensors were novel indeed. They were small and thin enough to be attached to or even easily embedded inside a material. For the first time, then, the effect of shock waves could be measured *within* the material being examined rather than from visual inferences of its outside surfaces. Today, the manganin and ytterbium piezoresistive transducers that SRI invented are the standard by which all other sensors used in dynamic pressure measurement are judged.[10, EE] Next, then, comes the question of simulation.

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[9] Other SRI participation was in the areas of radar and communication effects. These involved the high altitude nuclear tests of 1958 and, after the Soviet moratorium violations, those of 1962. See Chapter 9.

[10] SRI's Dr. Douglas Keogh and his colleagues designed many of these novel sensors. One of the most notable was a gauge that would linearly sense an overpressure of over one megabar (a bar being ~14.5 psi), perhaps a thousand times what existing gauges could do. It used the piezoresistive characteristics of a copper-manganese-nickel alloy called manganin and under that name it remains the principal choice for any strong overpressure measurement.

Overpressure Simulation

Computer modeling and simulation helped build and make practical a theoretical basis for shock waves and their predictable impact on materials and structures. This development lent a greater value to experimental design and a basis on which to explain results. For example, Poulter Lab pioneered the development of above-ground conventional explosive techniques to simulate nuclear airblast and ground shock effects. Similarly, sheet explosives could simulate x-ray loading on specific materials and structures. To represent the effect of slower-moving shock waves, the large shock tube in Figure 11-9 was built and instrumented. Other shock wave simulations were successfully applied underwater in large pools added to the SRI test sites. These pools were used to study the effect of underwater shocks on submarine models, underwater mines, and obstacles in surf zones and on beaches.

Another dimension to simulation is the use of scale models and how to interpret their behavior in terms of the structure they represent. Poulter Lab became a world leader in understanding the advantages and limitations in this field, and that work is continuing. Some examples include the modeling of missile silos subjected to nuclear attack, underground tunnels being attacked by conventional weapons, nuclear reactors undergoing core disruption, trains in derailment accidents, and the safety of automobiles under various crash scenarios.

Modeling Material Failure

Finally, there is the damage to material itself. Members of Poulter Laboratory developed a class of material models that describe how materials fail. This class, called nucleation and growth and fragmentation (NAG-FRAG) began with physical observations of microcracks and voids that occur naturally in materials and that grow and coalesce under shock wave loading. The models were originally developed to describe the nucleation and growth flaws in space heatshield materials but were then extended to cover several materials, even rocks. This SRI work has made a lasting theoretical and practical contribution and is described at greater length in a later section.

Shockwave-Produced Diamonds

A more modest use of explosions occurs in a laboratory or factory setting where they can create the very high temperatures and pressures used in metallurgy. It was 1959 and SRI metallurgist Paul De Carli was trying to make high-pressure versions of some minerals by using explosions to shock-load them.[FF] One of the minerals he chose was graphite. In the post-shock residue, Paul noticed some particles that were hard enough to scratch sapphire, had a density higher than fully dense graphite, and revealed faint lines of the x-ray diffraction pattern of diamond superposed on the pattern for graphite. This was an exciting discovery but since De Carli's technical director, George Duval, had just read a classified report that said that diamond could not be synthesized by shock methods, it took two years before the result could be published.[GG] Concurrent with the submission of the paper for publication, and in one of its early excursions into trying to profit from its intellectual property, SRI applied for a patent in July 1961. The diamonds produced by the SRI process had no relevance to gem production but were appropriate for the coating of abrasion tools whose value industry was just beginning to discover.[11]

A vice-president of Allied Chemical saw the paper and contacted SRI. By mid-1962, this led to a $250,000 research contract, complete with a royalty clause. Allied became so eager that it started pilot plant production of shock-synthesized diamonds before the scientific basis of the process was fully understood.[12] As that understanding grew, and after exploring a British patent on shock synthesis, a continuation-in-part was filed on the patent. U.S. Patent 3,328,019 was issued to SRI on March 1,1966.

But Du Pont was also working on the shock synthesis of diamonds. Their Patent 3, 401,919 was granted in 1968, and it appeared to infringe on SRI's. To restrict entrance to a budding market, Du Pont had also bought up the rights to the earlier British patent and, rather than

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[11] In 1955 researchers at the GE Laboratory developed a very high pressure and temperature process (about 1 million psi and 3,000 degrees F) to create synthetic diamonds. That is the leading industrial diamond production process today, with only a small fraction of that being produced using shock techniques.

[12] According to an online reference (www.mrw.interscience.wiley.com, September 4, 2004) shock-produced diamonds were first manufactured in 1961, making the Allied effort perhaps the first.

sorting out their respective rights, Allied and Du Pont decided to sign mutual cross-licensing agreements. Unfortunately for SRI, Allied then decided that the market was still too small to support both large companies and Allied dropped out. As it has turned out, the market has grown considerably since.

Du Pont treated shock synthesis like a small business and spun off a quasi-independent small division to commercially produce industrial diamonds. With the expiration of the patents, Japanese and Chinese companies have also been making shock-synthesized diamond. In the end SRI had secured a very early patent on an increasingly important process but, in retrospect, its license agreement simply failed to protect its interest.

Other Applications

SRI's measurement insight and experimental innovations became a springboard for many other types of practical research applications. Explosives and propellants have been used to develop a technique for simulating the ground motions produced in earthquakes. To characterize the hazards associated with a pipeline rupture and subsequent ignition, Poulter Lab conducted the world's largest natural gas fire test in an isolated section of the Canadian pipeline. In anticipation of the growing interest in hydrogen as a fuel, SRI has performed extensive studies of hydrogen explosions.

Other studies include ways to neutralize terrorist bombs and to harden structures against their use. One such application relies on special methods for strengthening existing windows so that glass fragments do not fly inside the building from a bomb outside the building. Another is the lining of airplane fuselage and baggage containers with another SRI invention, the rod polymer called Zylon (see a previous section on rod polymers). Innovations and experiments such as these have kept SRI's Poulter Laboratory vital for nearly the entire history of SRI.

The Modeling of Fractures—FRASTA

To most of us, a crack is just a crack, perfectly random, and the only story it tells is that whatever broke wasn't strong enough. But to Don Shockey and Takao Kobayashi of SRI's Center for Fracture Physics, a crack is a special kind of fracture with an intriguing story to tell.[HH] When an aircraft engine turbine disc fractures or a bridge or building collapses or a refinery vessel fails, considerable damage or loss of life can occur. Whenever the collective costs are high, it becomes critical to determine why a failure happened. For this field of fracture analysis, SRI has built one of the world's best tools for probing fractures and for using their characteristics to find not only what weakness caused the fracture but also the time history of the event itself. The name of this tool is FRASTA, which stands for Fracture-Surface Topography Analysis.

To easily see the utility of such an analytical tool, take the case of a crack opening on just one side of the wall of a 22-year-old boiler tube in a fossil fuel power plant. Using FRASTA, SRI was able to tell when the failure process began, the rates and growth history of the crack, and the effects on such growth of any chemical cleanings and hot starts. All this information helped define the future operating conditions and maintenance procedures needed to prolong the life of the plant.[13,II]

The foundation for developing the FRASTA system began over 30 years ago in work SRI was doing for the Department of Defense. Part of one study on whether an antiballistic missile defense system was feasible was the question of the kill mechanisms for incoming warheads. To the extent that another nuclear device was to provide that mechanism, it was necessary to understand how the heat from the x-rays of a nearby explosion would affect the material of the incoming warhead. The likely effect would be a heat-induced shock wave in the impacted material. But would the material be destroyed?

In 1967, SRI staff members Dick Crewdson, Lynn Seaman, and Troy Barbee began working on simulation experiments using a gas gun to generate shock waves whose features could be specified. They tested various target specimens and then tried to give consistent, quantitative characterizations to the fractures and other damage they saw. It was metallurgist Barbee who drew the relationship between the

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[13] More recently, FRASTA was used in settling several lawsuits, where it helped pinpoint the source of very costly failures.

Figure 11-10. Dr. Takao Kobayashi and a FRASTAscope.

observed fractures and the well-studied field of metallurgical phase evolution—equations that described how fractures grew under tensile stress. Would they apply in the case of temperature-induced stress? The answer was yes, and the team developed a mathematical basis for the nucleation[14] and fracturing of several materials under different impact intensities. Although Crewdson and Barbee left SRI in 1969 and 1971, respectively, Don Curran and Don Shockey joined the effort and succeeded in developing crack nucleation and growth (NAG) rate models. The models were verified for simple metals whose fractures arose from x-ray bombardment in underground nuclear tests. But, when used successfully to predict failures in nonmetallic objects such as phenolics, on various size scales, in purely kinetic impacts as well as static loading, the model's greater generality became appreciated. NAG became the basis for crack propagation predictions by focusing on the small microstructure failures occurring at the tip of a macrocrack. The technique would be applied to a wide range of failure problems for the next 20 years.

At the time, most failure analysts routinely examined and interpreted fracture surface features to ascertain the fracture origin, the propagation direction, and the general type of loading. But these evaluations were heavily qualitative. Being able to suggest improvements in structural design that would deny future failures required more quantitative information about the loading conditions and the nucleation and growth history of the crack. That information just wasn't decipherable at the time. Additionally, most fractures involve three dimensions and any comprehensive model needed to reflect those dimensions.

In 1982, Takao Kobayashi came to SRI having the notion that three-dimensional, quantitative modeling of fractures was possible (see Figure 11-10). With the help of his SRI coworkers Don Shockey, Yvonne Wu, and Jim Kempf, he was able to offer a major advance in fracture mechanics. He understood that the three-dimensional roughness of fracture surfaces held the needed information about the loads that caused the failure as well as the kinetics of the fracture event itself. More significantly, he thought the information could be extracted. As a material is loaded, it first deforms elastically. Upon further loading, certain sites of defect or points of geometric load concentration begin to deform inelastically. Still more loading produces microcracks around the inelastic zones. At points where small separations arise, the material becomes stress-free and—very important—the material captures in its topography the preseparation deformation. This process proceeds in the direction of crack formation, leaving a trail of inelastic

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[14] Nucleation in fractures is the process whereby specific points in a material, where the material becomes inelastic, become the sites of fracture initiation. It has to do with the microcomposition and structure of the material, the type and configuration of stress it is under, and even the loading that produced the damage.

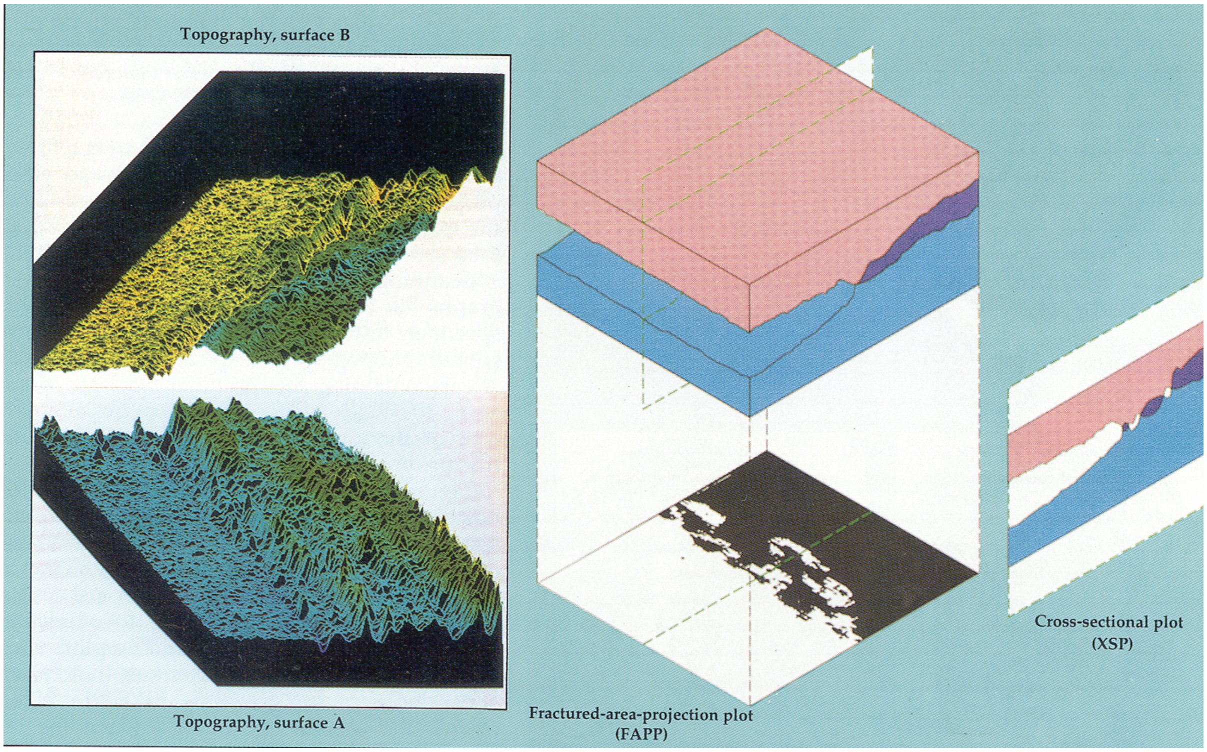

Figure 11-11. FRASTA images depicting the analysis of a fracture.

deformations that vary with distance from the nucleation point. That variation encodes the crack history.

With this understanding, the question became one of illuminating those traces. After trying several approaches, Kobayashi arrived at the notion of using a scanning laser microscope to map topographically the fracture surfaces. The group first developed three-dimensional tools to reassemble (mate) the conjugate surfaces. Then they created small, variable offsets between the pair and the ability to examine them in projected and isometric views. These views, it turned out, permitted the fracture event to be reconstructed. This approach was a major advance in fracture analysis and gave SRI the ability to extract from topographic fractures a quantitative picture of what had happened.

This set of imaging and analytical tools became FRASTA. Figure 11-11 gives an example of a specific analysis, starting with a three-dimensional scan of the two "halves" (conjugates) of the fractured specimen. This is done using the scanning laser microscope called a FRASTAscope. When the two halves are "reassembled" virtually, this assemblage reveals, by means of projections like those shown, the microcrack initiation sites and several other characteristics of the fracture. The time history of the fracture is a sequence of the individual projections, only one pair of which is shown in the figure.

The technology of FRASTA has come to the attention of the fracture analysis community around the world. As with many SRI innovations, the government provided most of the development money. However, both commercial and government organizations are now using FRASTA or asking SRI to use it for analyzing their failure problems. As of March 2004, four FRASTAscopes have been sold and the team is exploring whether the techniques could be made to work when only one of the two surfaces is available.

SRI's Chemical Economics Handbook

This story is not about the science of materials but their supply and demand on a global scale.[JJ] From the Institute's earliest days, it has provided a service that has illuminated the production and use of a very wide range of industrial chemical and related materials. The service was spawned in the Institute's economics environment but has benefited over

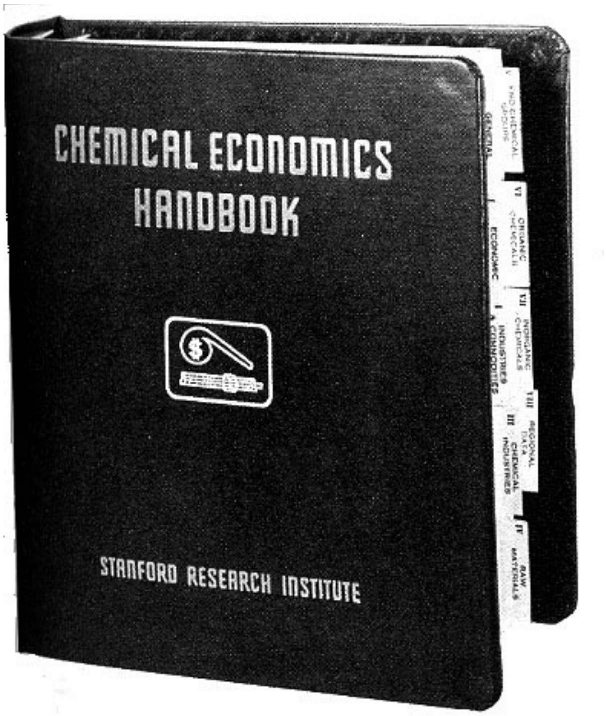

Figure 11-12. First issue of the *Chemical Economics Handbook* (1950).

the years from the technical insights of the chemists and materials scientists in sister SRI organizations. The centerpiece of this service is the SRI *Chemical Economics Handbook* (CEH). Started in 1950, the *Handbook* has become the standard global source on the production, use, and economic aspects of virtually all chemicals of commercial importance. For over a half century, the SRI program producing the CEH has been supported by 200 to 300 organizations in more than 25 countries. Throughout the world, SRI's "Chem Handbook" has come to be recognized as the bible of the industry. Given such a presence, how did this unique resource begin at SRI?

The CEH was the brainchild of Dr. Raymond Ewell.[15] Before joining SRI in March 1950, Dr. Ewell worked in an area of Shell Chemical that performed economic evaluations on materials important to Shell's industry. Inside Shell, the group's chemical market assessments were highly regarded as rigorous and Ewell brought that discipline to SRI. By 1950, advances in technology and the lure of new products, such as plastics, which had started replacing metals, paper, glass, and other traditional materials, suggested to Ewell the need for comprehensive but simple, industry-relevant information. A better knowledge of the availability of chemicals would have an appeal to any company needing to use them. Collecting such information from open sources and removing its inconsistencies was a tedious process, easily put off by companies for less precise estimates.

In a nutshell, Ewell saw in the burgeoning chemical industry a critical need for timely, detailed, and accurate information about the production, sales, shipment, and price of its constituent materials.

Companies that were expanding their present production or contemplating new products would profit from a standardized inventory and availability of the materials they needed. He was right. Those companies soon saw the value in such a service because their decisions about the size and timing of their large capital investments, typical in the chemical industry, were crucial to profitability.

That initial CEH staff numbered five, and the annual subscription fee was a very modest $250. The service started with a 250-page volume that gave basic information on the production and price of major chemicals. There were 51 initial subscribers to the *Handbook*, and it became one of the first attempts at systematic industrial marketing research by an independent organization anywhere in the world.[KK]

However, there was an obvious problem. A little arithmetic shows that, with such pricing, the annual gross income from subscriptions of $12,750 amounted to just a bit over $2,500 for each of the five people. Clearly, this effort was not going to be profitable even in the 1950s. So why was it started? Between the beneficent words of the SRI charter and the clear need, the SRI managers had found sufficient justification at the time to proceed. The CEH was started not to make money but to serve an industry and hopefully provide a lead-in to single-client work for some of the member companies. This orientation would continue for quite a few years, abetted by an accounting system that couldn't quite address the net income of a subscription type of project.

Most of the early CEH compilations were simple tabulations or semi-log graphs of the

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[15] After launching the handbook, Dr. Ewell went to India for SRI to help establish a small business presence with Dr. Gene Staley (see Chapter 15). He left SRI in 1957; by 1963 he was assistant director of the National Science Foundation, and by the spring of 1971 was Chancellor for Research at SUNY—Buffalo.

supply side of a relatively few important chemicals and essential raw materials. The work consisted mainly of updating these from available sources, converting quantities to standard metrics and format, and periodically distributing them. Still, keeping accurately abreast of a growing industry took a lot of attention. The CEH also came to add data on the general economy, accounts of other industries important to the chemical industry, as well as the earlier statistical profiles on chemicals.

The compilation work was very rigorous. A research analyst tabulated data from available sources. These data were then verified by someone else, and then verified yet again, so that they were essentially free of compilation errors. This was a very important point: From the very start, CEH established a reputation for accuracy, reliability, and thoroughness. But these procedures also were adding cost to an already unprofitable arrangement whose price was still just $365 or so per year by 1960. If SRI was going to charge more—and it had to—some value proposition had to be made.

After several years of operation, the SRI staff became so familiar with their chemicals that a couple of things started to happen. The data and graphs became heavily footnoted with ancillary information and insights and, more important, they began to look into the consumption or demand side of the market. This new perspective, however, revealed some inconsistencies between aggregate production and consumption. The reasons for these discrepancies were aggressively pursued. It was 1957 and with this investigation in progress, Mimi Erskine joined the group and also began to explore these inconsistencies and their patterns. In analyzing both ends, so to speak, she and others were able to reconcile the differences. Her method became a check and balance for a given chemical and even further improved the overall veracity of the CEH. This new, more comprehensive representation also enabled other important changes in the CEH and its SRI operations.

While this new insight was developing in the late 1950s, the CEH still continued its unprofitable operation. About 1960, in one of SRI's belt-tightening moments, the CEH group was asked to work its way out of subsidization.[16] John Strickland, who had taken over leadership in 1955, became an advocate for expansion and profitability. As a means of attacking the financial problem, he saw in the expanded knowledge they were compiling and, from the creative offerings of Mimi Erskine, the potential for a set of new reports to take to their subscribers. He felt it would be worth repackaging the explanatory notes about the markets for specific chemicals, the information about the industries that relied on them, the analyses of producing companies and their capacities, the supply/demand relationships, and the end-use patterns. The increasingly reliable contacts in the producing and consuming industries were also adding a lot of value.[17]

All this access and in-depth awareness were giving the individual SRI analysts their own global reputations in their chosen chemical groupings such as fertilizers or organic chemicals. This combination of information and expertise, then, was evidenced in a set of new prototype reports taken to the client community in the early 1960s to test their interest. The samples were personally shown to the project's domestic clients, and foreign clients were contacted by telephone and mail. Armed with this new value, Strickland and colleague Tom Gunn were looking for an increase in subscription price to $1,800 per year to reach break-even.

The response was almost totally positive. Even some who had not joined before were now attracted. So these expansive reports were added to the CEH in 1964 and soon comprised the single most important feature of the *Handbook*.[LL] In Tom Gunn's words, "This was really a major turning point. The program went from being a 'look-it-up' type of research resource to an interactive service. Our [staff] was contacting people in industry with all sorts of questions and those in industry were doing the same with our staff."[MM]

To help justify the cost, each client would now receive two additional sets of the CEH to distribute inside the company. Some wound up inside the research and development operations

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[16] SRI's new President, Karl Folkers, noticed the unprofitability of the CEH program and actually advocated selling the operation. However, plans to make it profitable were under way and so it remained in operation. That option would, however, be revisited.

[17] Not so incidentally, this willingness of industry people to yield private facts about their operations comes, almost certainly, from SRI's nonprofit objectivity—something the staff zealously guards.

as guides to the design of new products.[18] So by 1975 the annual fee was $4000, which covered three copies of the CEH to each subscriber. The expanded use, size, and update rate of the *Handbook* continued to be promoted by its successive directors.[19] With all this effort, the CEH continued its pattern of wide acceptance and, internally, attained consistent profitability.

As a measure of the CEH scope, by 1975 more than 130 chemicals and chemical products were covered in the expanded "Marketing Research Reports," each issued on a three-year cycle. In addition, over 550 chemicals were addressed in data sheets and smaller marketing reports. Researchers spent a considerable time reviewing findings with industry specialists to ensure quality work. The new reports also included coverage on technology and environmental issues. The CEH, now produced by 34 staff and consisting of 19 volumes containing 7000 pages, had broadened its coverage to include the following chemicals and allied products, with examples:

- Petrochemical feedstocks (ethylene, propylene)
- Organic intermediates (ethylene oxide, propylene oxide)
- Plastics (includes about 25 in all)
- Elastomers (styrene-butadiene, neoprene)
- Fibers, (including polyesters, nylons)
- Derivative products (dyes, pigments, adhesives, surface coatings)
- Agricultural chemicals (fertilizers, pesticides, animal feeds)
- Inorganic commodity chemicals (industrial gases, chloralkali products)
- Specialty chemicals (plastics additives, surface-active agents, fluorocarbons).

Industry growth was also proceeding both in the quantity of material manufactured and in its globalization. As examples of the former, U.S. production of petroleum-derived benzene increased from about 50 million gallons in 1950, to about 1 billion in 1975, to almost 2.4 billion in 2000. Production of high-density polyethylene (HDPE), used to make milk bottles, film, pipe, and many other goods, increased from about 50 million pounds in 1950, to 2.5 billion pounds in 1975, and to 14.3 billion pounds in 2000.

Industry growth was also coming from globalization. During the 1970s, the chemical industry began to globalize. The disruptions caused by two shocks in crude oil prices and developments in less industrialized countries also changed the nature of the industry. In 1950, when the CEH started, the European and Japanese sectors of the industry were just rebuilding and the vast majority of chemical production was in the United States. Over the next 25 years, the economies of Western Europe and Japan expanded significantly, and these areas reappeared as important chemical producers. But soon globalization would also encompass lesser-known producers. For example, in 1975 the United States and Europe made about 40% of the world's HDPE, with Japan producing half that much. By 1975, about 40% of the HDPE, was made in the U.S., 40% in Western Europe, and 20% in Japan. In 2000 the U.S. share had shrunk to 28%, Europe, 23%, and Japan 6%. The displacing producers at about 5% each were the Middle East, South Korea, Canada, and China.

As a consequence of this globalization, the CEH practice expanded geographically to meet the increasing demand for information. Offices were opened in Zurich and Tokyo to provide more complete data on Western Europe and Japan. The *Directory of Chemical Producers (DCP)* was initiated by SRI in the 1960s to give clients extensive lists of U.S. producers with their locations and products; the information was cross-referenced to list the producers and locations of all products. By 1980, the DCP for Western Europe was available, and by 1990, DCP Eastern Asia made its debut.

A group of SRI chemical engineers started the *Process Economics Program (PEP)* to provide clients with the technology and economic evaluations of many chemical processes.[20] In the mid-1970s, the SRI Chemical Consulting practice started the *World Petrochemicals (WP)* program to provide extensive supply/demand

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[18] Tom Gunn tells of an episode that reveals the utility of the CEH material. He was visiting the manager of market research of Sun Oil and in the process met a new member who had good industrial experience but was not very familiar with the CEH. When this new member said he was working on a report on ammonia, Gunn handed him a copy of a recent CEH report on ammonia by Tom Blue. After examining it for only 5 minutes, he claimed it would save him 2 months work.

[19] In 1961, Tom Gunn became editor of the *Handbook* and was followed in 1968 by Kirt McCaleb, John Dean in 1972, and Fred Chan in 1974. More recently came Betty Johnson, Tom Gunn again, then Sara Soder, and today's director, Eric Linak.

[20] *PEP* was started by Ken Lund with help from John Strickland and Bill Sutphen.

and producer/capacity databases on ethylene, propylene, butadiene, benzene, methanol, and all their derivatives in virtually every country of the world. In the late 1970s, the *Specialty Chemicals Update Program (SCUP)* began providing analyses of the critical factors for success, profitability, outlook, markets, and trends for 35 specialty chemical markets.

To alleviate the physical bulk of the printed CEH, evident in Figure 11-13, clients can now elect to receive all five programs via the Internet or on CD-ROMs. The DCP program now covers Canada, Mexico, South America, India, China, and the Middle East. SRI also began offering CEH-type analyses in the *China Report: Chemical Product Trends* and *Asian Report: Chemical Industry Trends*.

The SRI chemical economics practice became the largest and most respected service of its kind in the world. Approximately 100 full-time professional and support staffers continue to update CEH, DCP, WP, PEP, and SCUP reports on a regular basis. Additional offices were opened in Houston and in Beijing, China. The CEH now covers about 250 chemicals in 38 binders. Clients pay almost $30,000 per year for monthly updates of 5 to 8 reports.

A number of famous companies have subscribed to CEH for all 50 years: Dow Chemical, Du Pont, Chevron, Eastman Chemical, Procter and Gamble, Hercules Chemical, PPG, Monsanto, Union Carbide, Bayer, and General Electric. The subscriber base has changed somewhat in the last 15-20 years, as the number of chemical producers has decreased due to mergers and about a fifth of the subscribers are now financial institutions, government agencies, engineering companies, or other consultants. About half the subscriber base has headquarters outside of the United States. Also, along the way, there has been some competition to the CEH from companies like Chem Systems, Parpenelli Tecnon, and Chemical Market Analysis, Inc. But none has been able to match the breadth and depth of SRI coverage, and it has become virtually impossible for a major chemical or materials company to launch a major new initiative without the substantiation of CEH numbers.

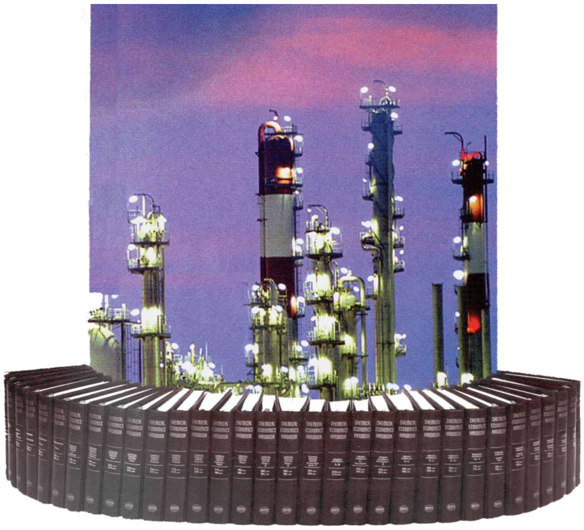

Figure 11-13. The printed form of the SRI *Chemical Economics Handbook* (circa 2001).

All that having been said, and in spite of this long and distinguished history, in January 2004 SRI sold its stake in the CEH and related services. The buyer was a broadly based information services company, Access Intelligence, headquartered in Maryland. This transfer ends, then, at least for now, the last vestige of the Business Group at SRI.

In concluding this piece about a successful SRI service, there is one, perhaps instructive, character issue. The success of the CEH rested on the ability of SRI staff to draw out information from its sources that would otherwise be proprietary. That trust afforded SRI by its sources is the result of deliberate and continuing attention to an obligation that all of SRI takes very seriously: objectivity and the integrity that it, in turn, demands.

The Monsanto Million Dollar Challenges

The chemical industry has more than its share of difficult production problems, particularly in managing the waste byproducts it produces. Monsanto, headquartered in St. Louis and one of the larger members of the industry, conceived of a way to address some of its bigger waste management challenges. The idea was to pose one of Monsanto's technical or manufacturing problems and invite the worldwide technical community to help solve it by competing for a million dollar prize. The winner would receive $500,000 to use in finding a solution to the problem, and if that solution was successfully applied, a second $500,000 would be awarded.

The first such competition, initiated in late 1994, was a search for a way to remove ammonia from the wastewater of some of Monsanto's plants. Out of 180 applicants, SRI came in first, with a proposal written by Drs. Abhoyjit Bhown, Ron Smith, and Luke Schneider. SRI successfully completed the initial design phase.

The second competition took place a year or so later and involved another difficult waste management problem: finding a practical, cost-effective technology that would recover high-purity amino acids and phosphoric and phosphorous acids from a particular waste stream, leaving clean sodium chloride. Recovery of these materials could lead to recycle and reuse by the company. Again, out of 34 applicants, an SRI proposal by David Bomberger, Neeraj R. Pakala, Charles K. Hiebert, and Eugene R. Moore was evaluated highest. During the final stages of internal review, however, a Monsanto vice president refused to approve the award to SRI because it had won the previous year's award and should not get it two years running. He then asked that the award go to the second place proposal. Alas, that was also from SRI, a proposal written by Bill Asher! The vice president therefore reversed himself and made the second award to the first-ranked SRI proposal. This second award was announced at the Fifth World Conference of Chemical Engineering in July 1996.

Figure 11-14. The Monsanto trophies won by SRI.

As it turned out, neither of the plans was ever implemented, due not to their lack of efficacy, but because of the changing business patterns within Monsanto. These consistent awards, though, among worldwide competition, reflect not only SRI's considerable talents in chemistry and chemical engineering but also its excellent ability to address real-world technical challenges.

Endnotes

[A] As related by Dr. Angel Sanjurjo and from B.J. Wood, A. Sanjurjo, S.M. Johnson, B.R. Taylor, T. Kobayashi, and Jacques Giovanola, *Improved Coatings for Ovens*, Final Report to the Whirlpool Corporation, July 1992.

[B] Phyllis Flanders Dorset and Stephen Miller, "*A Finite Difference—A Short History of the SRI Physics Division*," author-published, copyright 2003.

[C] From the notes of Earle Jones, a retired SRI Vice President and docent at Año Nuevo, March 1, 2001.

[D] Biography of Ronald Schusterman (www.pbs.org/safarchive/3_ask/archive/bio/93_schusterman_bio.html) and *SRI Intercom* 6, April 7, 1965.

[E] T.C. Poulter, "Whiskers and the Penguins," *SRI Journal* 26, 8-14, June 1969.

[F] T. C. Poulter, Marine Mammals, in *Animal Communication*, T. A. Sebeok, Ed., Indiana University Press, pp. 405-465, 1968 and T. C. Poulter, Underwater Vocalization and Behavior of Pinnipeds, in *The Behavior and Physiology of Pinnipeds*, R. J. Harrison, R. C. Hubbard, R. S. Peterson, C. E. Rice, and R. J. Schusterman, Eds., Appleton-Century-Crafts, New York, pp. 69-84, 1968.

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[H] Taken from www.pbs.org/wgby/pages/frontline/shows/whales/interviews/griffin.html, January 14, 2001 and *SRI Intercom*, 23, December 1, 1965.

[I] From *Poulter Laboratory Celebration—1954 to 1986*, held at SRI on September 5, 1986.

[J] Dorset and Miller, op. cit.

[K] Interview with Paul Cook on February 14, 2003.

[L] SRI's *Research for Industry*, 8(4), 1-2, May 1956.

[M] Paul Cook, op. cit.

[N] From an account of several interviews of Bruce Graham, founding director of SRI's Life Sciences Division, taken over 1997 and 1998 by Elmer Reist and Gordon Newell.

[O] James B. Meikle and Bruce Graham, Electrons Produce High-Temperature Dielectric, *Electronics*, 29(5), 146-150, May 1956.

[P] SRI's *Research for Industry*, 8(4), 1-2, May 1956

[Q] Toyobo web site, www.toyobo.co.jp.

[R] Conversation with SRI's Bock Loo, November 9, 2000.

[S] Patent No. 4,533,724, James W. Wolfe et al., Liquid Crystalline Poly (2.6-Benzothiazole) Compositions, Process, and Products, issued August 6, 1985.

[T] Wyatt Haupt, Staff Writer, *North County Times*, San Diego, CA, June 5, 2002.

[U] This description of SRI work came from an interview with SRI physical chemist Dr. Don Hildenbrand.

[V] Much of this account derives from material sent by and conversation with Drs. Ted Mill and Jeff Bottaro.

[W] www.serdp.org/research/PP/PP-1058.pdf

[X] www.ih.navy.mil/emtc2.pdf

[Y] Referenced in the Navy's 1999 Report to Congress on dual use technology (see www.dtic.mil/dust/cgr/navy00cgr.htm).

[Z] Advanced Energetic Materials Emerge for Military and Space Applications, *Chemical and Engineering News*, pp. 18-22, January 17, 1994.

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[CC] T. Podoll, H. M. Jaber, and T. Mill, Tetrachlorodibenzodioxin: Rates of Volatilization and Photolysis in the Environment, *Environmental Science and Technology*, 20(5), 1986.

[DD] This all too brief story was compiled from the writings of Poulter Lab leaders, George Abrahamson and Jim Colton, and from the informative history of SRI's Physics Division by Dorset and Miller (op. cit.)

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[FF] Most of this section came from discussion with Paul DeCarli in September 2004.

[GG] P.S. DeCarli and J.C. Jamieson, *Science*, 133, 1821-22, 1961

[HH] Some of this section came from discussions with Dr. Don Shockey.

[II] *SRI Highlights*, page 3, January/February 2000.

[JJ] Material for this account came from a 25-year summary of CEH operations, a telephone interview and correspondence with former CEH head, Tom Gunn, an article by Bob Schwaar for the *SRI Alumni Newsletter*, and input provided by Eric Linak, the current CEH director.

[KK] Conversation with Eric Linak, current CEH director.

[LL] K. E. McCaleb, "The Biography of a Chemical Economics Handbook Report," paper presented at the National Meeting of the American Chemical Society, Los Angeles, CA, March 30, 1971.

[MM] Tom Gunn, personal communication, June 3, 2001.