Development of Chemical Processes and Equipment to Recover Curium-244 and Californium-252

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Abstract

In the mid 1960s, ^{244}Cm and ^{252}Cf were produced at the Savannah River Site (SRS) from ^{239}Pu starting material in nuclear reactor irradiations designed for successive neutron capture. Both solvent extraction and ion exchange processes and equipment were developed at the Savannah River Laboratory (SRL) to separate and purify curium and californium from irradiated plutonium-aluminum fuel tubes. High-pressure ion exchange proved more suitable than a solvent extraction process with tertiary amines ("Tramex") for the final stages of purification. A combination of high-pressure displacement and elution development cation exchange chromatographic processes was able to separate and purify 100 g quantities of ^{244}Cm and milligram quantities of ^{252}Cf. Curium-244 is suitable as an isotopic power source for remote applications, and ^{252}Cf is an intense neutron source for medical and industrial applications.

Introduction

In the mid 1960s, kilogram quantities of ^{244}Cm and milligram quantities of ^{252}Cf were produced by irradiating ^{239}Pu in a Savannah River Plant (SRP) reactor. The ^{239}Pu was converted to ^{244}Cm, and, in turn, ^{252}Cf and other transplutonium elements were converted by successive neutron captures and beta decays during irradiation of the aluminum-plutonium fuel tubes:

$$Pu \rightarrow Am \rightarrow Cm \rightarrow Bk \rightarrow Cf \rightarrow Es \rightarrow Fm$$

The SRP program for producing transplutonium elements in several stages is depicted in Figure 1. In the first irradiation, ^{239}Pu captured neutrons to produce heavier isotopes. The resulting mixture of plutonium isotopes was recovered (Curium I Campaign) and fabricated into aluminum alloy targets for a second irradiation in which a portion of these plutonium isotopes was converted to ^{242}Pu, ^{243}Am, and ^{244}Cm. The bulk of the ^{244}Cm from targets of this second irradiation (Curium II Campaign) was separated and purified for evaluation as an isotopic power source for remote applications such as space satellites. The ^{242}Pu and ^{243}Am were recovered and re-irradiated along with some of the ^{244}Cm to produce

^{252}Cf and other transplutonium elements such as berkelium, einsteinium, and fermium. The spontaneous fission mode of radioactive decay of ^{252}Cf makes it an ideal portable neutron generator for medical and industrial applications.

SRL developed a pilot-scale two-stage solvent extraction process using (1) tributyl phosphate (TBP) in the first stage to recover plutonium and separate a crude actinide-lanthanide mixture (Curium I, II Campaigns) and (2) tertiary amines (designated Tramex and conceived at Oak Ridge National Laboratory) in the second stage to purify curium and americium from rare-earth fission products (Californium I Campaign). Californium was contained in the curium fraction.

The Tramex solvent extraction process consists of three cycles of extraction with a tertiary amine to separate the trivalent actinides from the lanthanides. This process requires high-concentration chloride solutions and proved difficult to control. A 'skunk works' effort was begun at SRL to demonstrate the technical feasibility of an alternative approach based on ion-exchange chromatography. In 1968, Nat Stetson (manager, SR Operations Office), Lom
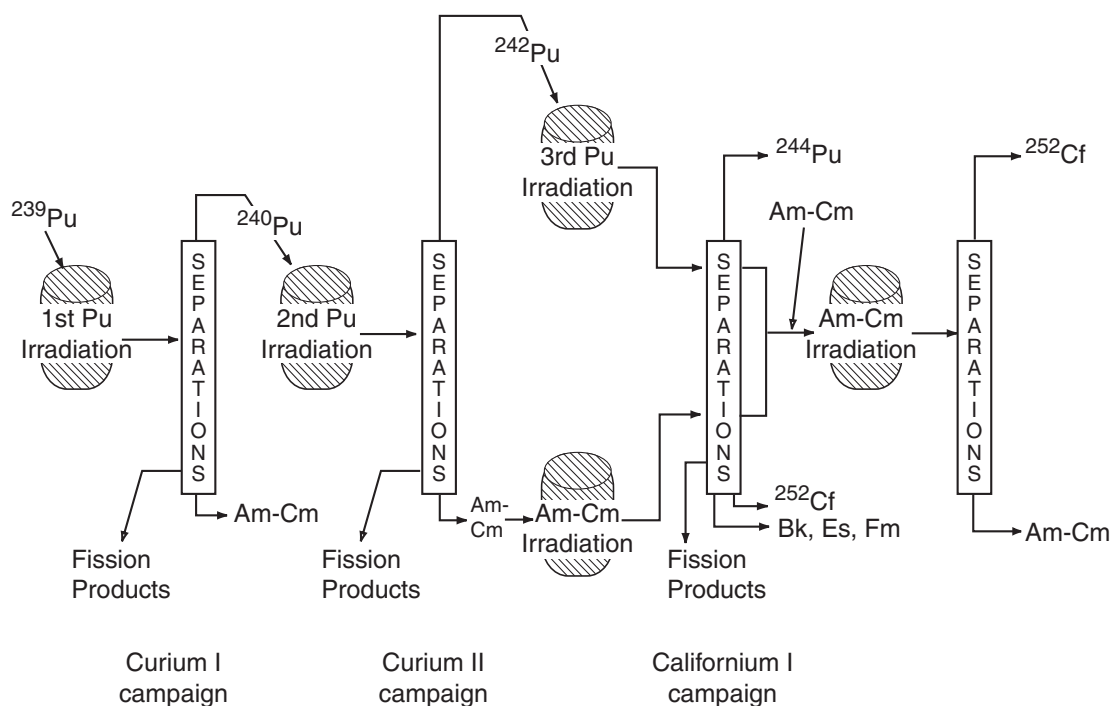
Figure 1. Outline of the transplutonium elements production program at Savannah River Plant

Squires (manager, AED), Clark Ice (director, SRL), and Bill Hale and John Lowe (research chemists) met in Washington, D.C., with Glenn Seaborg (chairman of the Atomic Energy Commission) to review initial positive results of a new approach, high-pressure cation exchange chromatography for separation and purification of curium and californium. Armed with Seaborg's endorsement, SRL launched a major effort to develop a large-scale high-pressure cation exchange chromatographic process. What followed was an excellent team effort between the AEC and Du Pont with leadership and support from Frank Baranowski, who headed up the AEC Division of Production, to successfully produce and purify large quantities of ^{244}Cm and ^{252}Cf.

Advantages of High-Pressure Cation Exchange

Conventional low-pressure cation exchange was an effective method both for separating

transplutonium actinides from lanthanides and for separating adjacent transplutonium elements. However, low-pressure cation exchange proved ineffective for large quantities of highly radioactive materials such as curium, americium, and californium because of the relatively long residence time on the column. The localizing heating and radiation due to radioactive decay energy degrades the resin material, and radiolytic gases generated by radiolysis of the solution physically disrupt the resin bed. Pressurizing the cation exchange system reduced the residence time of these highly radioactive feed materials and dissolved the radiolytic gases, suggesting that separation and purification of curium and californium were theoretically possible.

Pressurized cation exchange also has advantages over solvent extraction processes. The pressurized cation exchange process requires less accurate control of concentration and flow rates than the solvent extraction process. In addition, cation exchange requires only stainless steel

equipment, whereas tantalum or Zircaloy-2 is required for the chloride solutions in the alternative solvent extraction methods.

In developing a high-pressure cation exchange process suitable for curium and californium, optimal operating parameters needed to be developed for resin particle size, elutriant flow rates, column length, pressure levels, elutriant composition and concentration, feed concentrations, column temperature, and lanthanide/actinide elution sequence. In high-pressure cation exchange, finely divided resin particles (5-10 or 30-60 mm) are used instead of 100-200 mm or larger resin particles in conventional cation exchange. Elutriant flow rates from 1-50 ml/min-cm^2 have been obtained with positive displacement pumps pressurizing the feed and elutriant solutions up to 2500 psig. A pressure limit is finally reached where a further increase in pressure does not result in increased flow due to resin compaction.

With small-particle resin, equilibration between solution and resin is rapidly attained and results in potentially better separations than in conventional cation exchange. Rapid equilibration for small-particle resin results from decreased diffusion distances in both the resin particles and in the aqueous film surrounding the particle. The use of small-particle resin improves kinetics and gives a more uniform flow, which allows fast flow rates for the loading and elution steps. These high flow rates drastically reduce the time necessary to attain a given separation. The decreased residence time of highly radioactive feed materials in the resin reduces radiation damage to the resin, especially during the loading step. Also, localized heating due to radioactive decay energy being deposited in the system is reduced.

To achieve the fast flow rates possible with small-particle resin, elutriant and feed solutions are pressurized, which has the additional advantage of dissolving the radiolytic gases produced. In highly radioactive solutions, radiolytic gases are generated by radiolysis of the solution primarily by alpha particles and fission fragments from decay of transplutonium actinides.

Radiolytic gases can cause resin bed disruptions, which may result in irregular flow and channeling. Some gassing may occur at the bottom of the column, but the high pressure keeps bubble size small and removes the gas immediately. When the columns are operated at elevated temperatures, solution viscosity is reduced, and the pressure drop is lower for a given flow rate.

Because cation exchange resin shows little selectivity among lanthanides and actinides, a chelating agent must be used to separate cations of the individual elements into separate bands. Two types of chromatographic development were used in the actinide separations: displacement development and elution development. Displacement development is superior for large-scale separations. Rates of band movement and product concentrations in displacement development are approximately tenfold greater than those in elution development.

Displacement Development Chromatography

Displacement development involves the following steps:

- The resin is loaded with a cation (the barrier ion) that has less affinity for the resin than the ions to be separated.
- A mixture of the ions to be separated is loaded onto the column.
- A chelating agent having different chemical complex stability with each of the cations to be separated is pumped through the column.

The cations of each element in the actinide-lanthanide mixture form separate bonds and are eluted with the elements forming the strongest chemical complex with the chelating agent coming off ahead of the others. There is a binary zone, or overlap region, between each band of pure component because the column is not at equilibrium.

In 1968-69, a high-pressure displacement development cation exchange chromatographic process was developed at SRL to replace the Tramex solvent extraction process for separation of large quantities of transplutonium actinides. As much as 250 mg of ^{252}Cf and 190 grams of ^{244}Cm were separated in a single batch from americium and lanthanide fission products using Zn^{2+} as the barrier ion and 0.05M diethylenetriamine pentaacetic acid (DTPA) at pH 6.0 as the chelating agent. The system consisted of four 4-foot columns in series with decreasing diameters from 4 inches to 1 inch. Each column was loaded with 25-55-μm-particle-size "Dowex" 50W cation exchange resin (synthetic polymer containing sulfonic acid groups) at 70°C. Successively smaller columns were used because the length of the overlap zone is independent of diameter, but the amount of material in this zone decreases with diameter. A high pressure (900 psig) pump forced the DTPA solution through the columns at a flow rate of 16 ml/min-cm^2.

The results of a typical displacement development separation, which took 8-16 hours, are shown in Figure 2. Californium-252 elutes ahead of ^{244}Cm and is not shown in this figure. Three kg of ^{244}Cm, 1.3 kg of ^{243}Am, and 8 mg of ^{252}Cf were separated using this system.

Elution Development Chromatography

Elution development consists of the following steps. The cation resin is conditioned, and a mixture of the ions to be separated is loaded onto the column to form a narrow band near the top of the column. Complexing agents that form chemical bonds of different stability with the various ions to be separated are used to achieve selective elution from the resin. There exists a competition between the resin and the complexing agent for each ion, and if the column is run close to equilibrium conditions, each ion will be exchanged between the resin
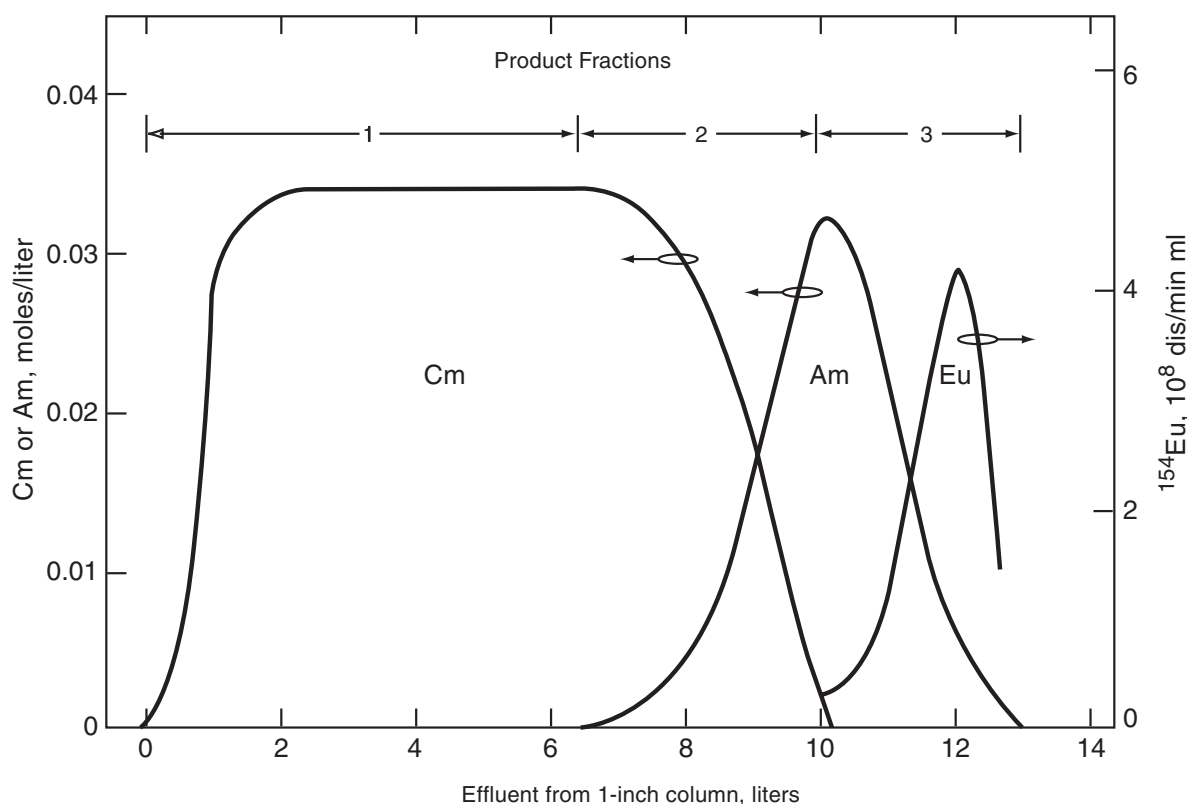

Figure 2. Typical displacement development diagram

and complex form many times as it moves down the column. As the various absorption bands move down the column, their spatial separations increase until finally the ion from the lowest band appears in the effluent from the column.

In 1968-69, a high-pressure elution development cation exchange chromatographic process was also developed at SRL for separation and purification of ^{252}Cf containing fractions from both Tramex and DTPA displacement development processes. Milligram quantities of ^{252}Cf, submilligram amounts of ^{249}Bk, and subnanogram amounts of ^{253}Es and ^{254}Fm were separated from multigram quantities of ^{244}Cm and ^{243}Am using 0.4M alphahydroxy isobutyrate (AHIB) partially neutralized with NH_4OH to a pH of 3.4 as the elutriant. The pH of this AHIB solution was increased stepwise during the elution as shown in Figure 3 to effect a sharper separation. The system consisted of one 120-cm-long, 5-cm-diameter column loaded with 20-40-μm-diameter Dowex 50W cation exchange resin at 75°C. A high-pressure (700 psig) pump forced the AHIB solution through the column at a flow rate of 8 ml/min-cm². The results of a typical elution development separation, which took 5 hours, is shown in Figure 3. Over a two-year period, 3.5 mg of ^{252}Cf were purified from Tramex solvent extraction feed material, and 5.5 mg of ^{252}Cf were purified from DTPA displacement development cation exchange feed material.
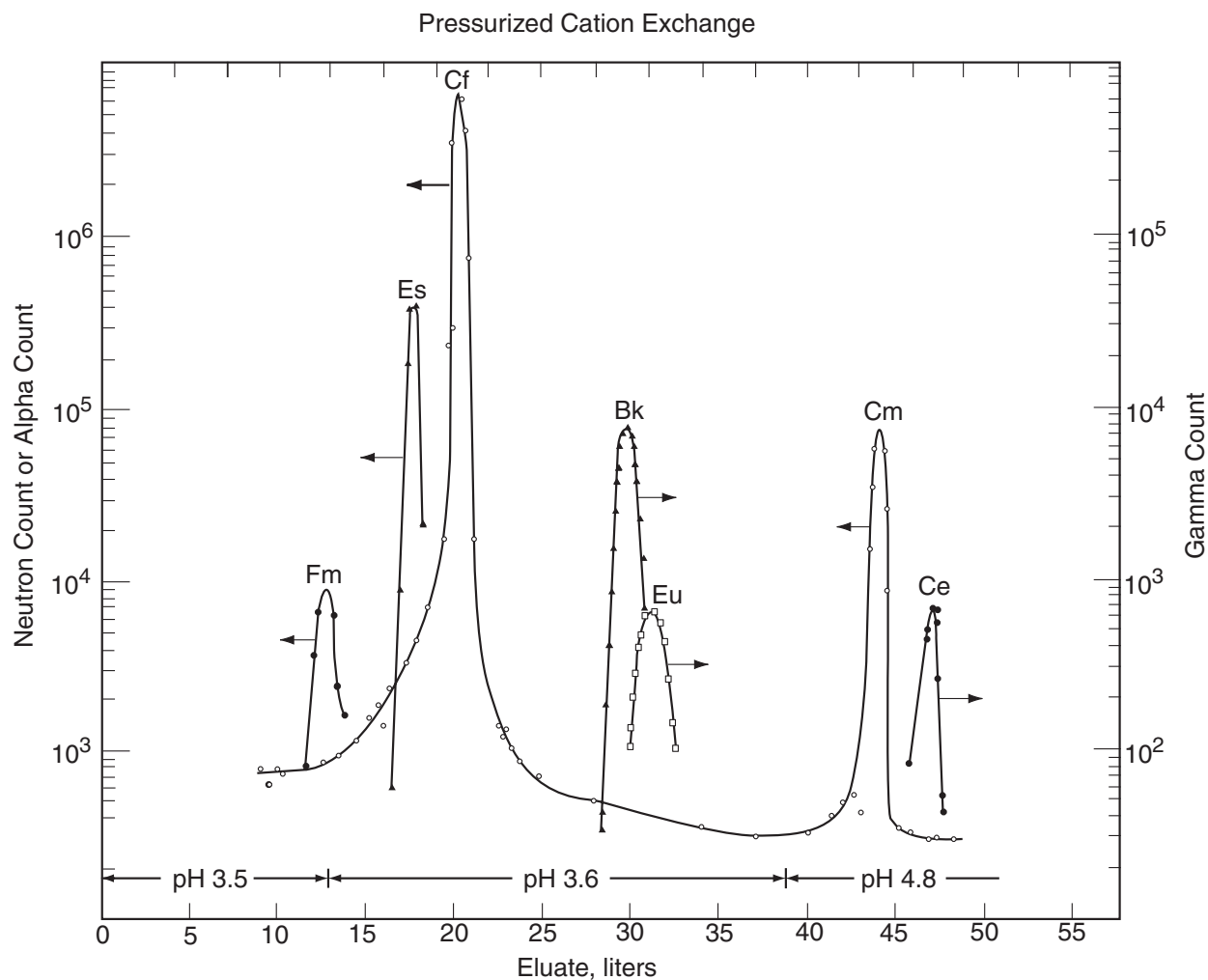
Pressurized Cation Exchange

Figure 3. Typical elution development diagram

Uses of ^{252}Cf and ^{244}Cm

Californium-252 is a unique source of neutrons because it yields a highly concentrated and reliable neutron spectrum from a very small assembly. During the past 40 years, ^{252}Cf has been applied with great success to cancer therapy; neutron radiography of objects ranging from delicate flowers to massive objects, such as entire aircraft; startup sources for nuclear reactors; elemental analysis of coal, nuclear fuel, explosives, and the human body; and many other beneficial uses. For many of these applications, ^{252}Cf is unique and irreplaceable. From 1965 to 1995, 8 g of ^{252}Cf have been produced, 3.6 g were shipped, and 600 mg were sold. A Market Evaluation Program sponsored by the Department of Energy determined that at that volume of usage, the large-quantity production capability of ^{252}Cf at SRL was not required. Therefore, the Oak Ridge research facility continues to meet present and projected near-term ^{252}Cf requirements at a price of $50/mg. Californium-252 is also produced in Russia.

Curium-244 was made available for development and demonstration of SNAP generators and of isotopic power fuels for deep space probes, but these uses have not come to fruition. Small quantities have been used as a gamma source, but its primary use has been as target material for producing ^{252}Cf. Curium-244 has a specific heat generation rate of 2.8 w/g and decays with an 18-year half-life. Curium-244 sells for $185 per milligram and can also be purchased from Oak Ridge National Laboratory.

Site Impact

The Site impact of the Curium and Californium Campaigns included several reactor cycles at SRP to produce sufficient quantities of ^{244}Cm and ^{252}Cf. Each reactor run was followed by work in the separation areas to do initial solvent extraction separations.

The development of the TBP and Tramex solvent extraction separation processes for this application was done at SRL. The novel high-pressure displacement and elution development cation exchange chromotographic separation and purification processes were also developed at SRL.

Biographies

Robert M. Harbour

Robert Harbour worked at SRL from 1968 to 1973, first as a research scientist, then as a research supervisor. During the balance of his 25-year Du Pont career, he worked in Petrochemicals and Imaging Systems Departments in a variety of research, manufacturing, marketing, and business management positions both domestically and overseas. From 1984 to 1985, he succeeded Frank Kruesi as Director, Technology Division for AED.

Post-Du Pont, Mr. Harbour managed an early-stage venture capital firm in Sydney, Australia, and currently has a management consulting firm in Santa Fe, New Mexico, focussed on assisting high-growth, technology-oriented companies.

Mr. Harbour graduated from Macalester College, St. Paul, Minnesota, in 1964 with a B.A. degree in chemistry, and from the University of Missouri, Columbia, Missouri, in 1968 with a Ph.D. in physical chemistry. He did post-doctoral work at Oak Ridge National Laboratory, Oak Ridge, Tennessee, before joining Du Pont at Savannah River Laboratory (SRL).

Clark H. Ice

Clark Ice worked at the Hanford site from 1947 to 1950 as an analytical chemist before arriving at SRP's Laboratories Section in 1952. In 1954, he moved to SRL as senior supervisor in the Analytical Chemistry Division. He subse-

quently held positions as research manager, Chemistry Division; director, Separations Chemistry and Engineering Section; and assistant director, SRL, before becoming director, SRL.

Following his retirement from Du Pont, Mr. Ice worked for General Public Utilities (GPU) from 1979 to 1989 as a member of the Three Mile Island (TMI) 2 Technical Advisory Group and the TMI 2 General Office Review Board.

Mr. Ice graduated with a B.S. from Central State Teacher's College, Edmond, Oklahoma, in 1938. In 1941, he received a Master's Degree in chemistry and in 1952 a Ph.D. in biochemistry, both from the University of Oklahoma, Norman, Oklahoma.

William H. Hale

William Hale worked at SRL from 1966 to 1976, first as a research chemist, then as a research supervisor and research manager. During the balance of his 28-year Du Pont career, he held a variety of management positions in Petrochemicals and Information Systems Departments before moving to Conoco in 1988 as Vice-President for Conoco Information Systems. Following his retirement in 1993, he was Director of the National Supercomputing Research Centre in Singapore during 1994-1996. He currently works as a consultant with Du Pont Safety Resources and with E. G. Mahler & Associates.

Mr. Hale graduated from The University of Texas in 1963 with a B.S. in chemical engineering and from the University of California-Berkeley in 1966 with a Ph.D. in inorganic chemistry. He attended the Stanford Executive Program in 1990.

John T. Lowe

John Lowe worked at the Savannah River Laboratory from 1965 to 1971, first as a research chemist, then as a research supervisor. After a series of management assignments in the Petrochemicals Department, he returned to Savannah River in 1983, sequentially as program manager, laboratory director, and plant manager. In 1991, he returned to the Petrochemicals Department as director of research and development.

Following his retirement from Du Pont in 1993, he was director of the process industry practices initiative, a consortium of 30 major owner and contractor firms developing a common set of engineering standards for the process industry. He is currently associate director of the Construction Industry Institute, and is a consultant with E. G. Mahler & Associates.

Mr. Lowe graduated from Georgia Institute of Technology in 1962 with a B. S. in chemistry, and from the University of Illinois with a Ph.D. in physical chemistry in 1965.

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