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L'ÉNERGIE ATOMIQUE  
DU CANADA LIMITÉE

**AECL RESEARCH PROGRAMS IN CHEMISTRY**

**Programme de recherche en chimie de l'EACL**

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Chalk River Nuclear Laboratories

Laboratoires nucléaires de Chalk River

Chalk River, Ontario

September 1980 septembre

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RÉSUMÉ

Des recherches fondamentales et de soutien sont effectuées en chimie dans les laboratoires de l'EACL pour mieux comprendre les processus en jeu dans les systèmes actuellement employés en énergie nucléaire et pour rester au courant des progrès réalisés aux frontières de la recherche chimique afin que l'on puisse tirer parti des innovations dans les futurs travaux de l'EACL. Le présent rapport donne un aperçu des programmes actuels de recherche, sous les rubriques suivantes:

- Chimie sous rayonnement
- Séparation des isotopes
- Chimie des solutions à haute température
- Chimie du retraitement du combustible
- Chimie analytique

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ABSTRACT

Fundamental or underlying research in chemistry is being done in AECL laboratories to further the understanding of processes involved in current nuclear energy systems and maintain an awareness of progress at the frontiers of chemical research so that new advances can be turned to advantage in future AECL endeavours. The report introduces the current research topics and describes them briefly under the following headings:

- Radiation chemistry
- Isotope separation
- High temperature solution chemistry
- Fuel reprocessing chemistry
- Analytical chemistry

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## AECL RESEARCH PROGRAMS IN CHEMISTRY

### INTRODUCTION

Developments in chemistry and atomic energy have been tightly intertwined ever since the discovery of nuclear fission in 1939. Indeed, the relationship can be traced further back to pioneer research on the nature of radioactivity. Since then the new knowledge about the radioactive elements and the chemical changes induced by nuclear radiations are but two of the many advances in atomic energy research which have broadened and strengthened our understanding of chemical phenomena. At the same time, chemical research has helped to make atomic energy safe and economical through its contributions to the design and operation of nuclear reactor systems, the production of the special materials needed for reactors and the management of nuclear wastes.

Chemical research relating to nuclear energy is done in university, industrial and government laboratories throughout the world and every major nuclear energy research centre has extensive chemical programs. Together they advance the study of chemistry on a very broad front. Canada cannot and need not be actively doing research across the whole front. Rather, our research is directed towards areas of special relevance to the CANDU reactor and its support systems. In addition we strive to be aware of advances in chemistry which may become important to Canada's nuclear program in the future and do research in selected areas where the potential gains are large. Our underlying or fundamental research is coordinated at two sites, the Chalk River Nuclear Laboratories (CRNL) and the Whiteshell Nuclear Research Establishment (WNRE) and the programs at both laboratories are described in this report, but to put the research in context a brief description of a CANDU power reactor will be given first.

A simplified diagram of a CANDU power reactor is shown in Figure 1. The fuel is natural uranium in the form of uranium dioxide. Natural uranium is a mixture of three isotopes, 99.3% of U-238, 0.7% of U-235 and a trace of U-234. Isotopes are atoms of the same element which differ in mass because of a different number of neutrons in the atomic nucleus and are designated by a number attached to the chemical name or symbol, e.g. U-238. Differences in the number of neutrons in the nucleus can give isotopes of the same element widely different physical properties even though the chemical differences may be small. Uranium-235 in natural uranium undergoes fission after capturing a neutron in the reactor. Uranium-238 does not behave in this way; after capturing a neutron it eventually transmutes to an isotope of plutonium, Pu-239, which happens to be fissile like U-235.

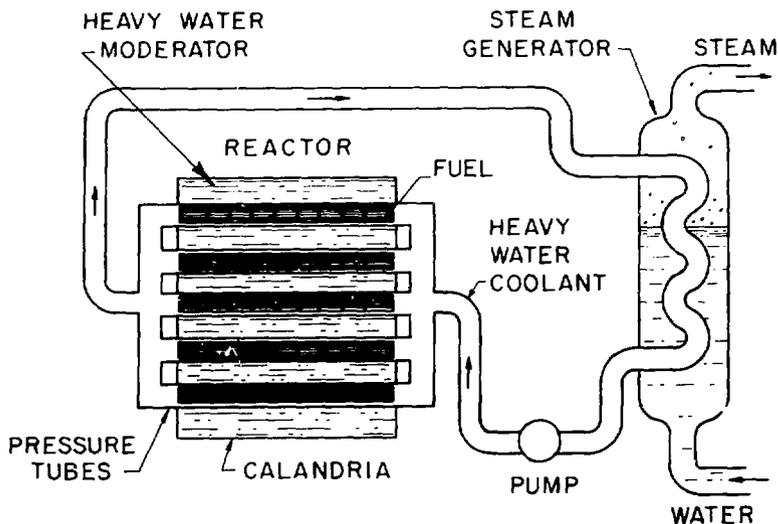


Figure 1: A simplified flow diagram of a CANDU power reactor. Only five of the many pressure tubes and one of the numerous pumps and steam generators are shown. Steam from the steam generator drives a turbine to make electricity.

Fission produces heat energy in the reactor as well as the neutrons required to keep the fission chain reaction going. Not all neutrons lead to fission; some are wasted and a feature which makes CANDU reactors better than others is the efficiency with which the neutrons are used. Because of the economical use of neutrons, natural uranium can be used as fuel.

The neutrons born in fission are very energetic, i.e. "fast", and to be effective in a CANDU reactor they must lose most of their energy because it is low energy or "slow" neutrons that produce fission in U-235. For this reason the fuel is surrounded by a slowing down medium called a moderator, heavy water, as shown in Figure 1. Heavy water is composed of the elements hydrogen and oxygen as in ordinary water but instead of the natural isotopic composition of ordinary water, i.e. 7000 parts of mass 1 (protium) to 1 part of mass 2 (deuterium), the hydrogen in heavy water is nearly pure deuterium. The energetic neutrons produced in fission are slowed down or moderated by a series of elastic collisions (such as billiard balls make) with deuterium atoms. Deuterium is the key to the good neutron economy of the CANDU reactor. Deuterium is a good moderator, second only to protium, and absorbs few neutrons compared to protium or other materials. When deuterium does absorb a neutron, tritium, the mass 3 isotope of hydrogen, is formed. Tritium occurs naturally in small amounts in the atmosphere since it is produced by the interaction of cosmic rays with nitrogen. It is radioactive and decays with a 12.3 year half-life by the emission of an electron ( $\beta$ -particle). It is interesting to note in passing that only the isotopes of hydrogen, of all the elements, have been given names of their own.

The moderator is held in a tank, called the calandria, through which fuel channels pass. A small vapour space above the heavy water is filled with a cover gas, which is mostly helium. The moderator operates at 60-80°C and the cover gas is slightly above atmospheric pressure.

A coolant picks up the heat produced by fission in the fuel and flows from the reactor at 300°C and 1200 pounds/square inch pressure (12 MPa). Any water is a good heat transport medium but heavy water is chosen for reasons of neutron economy as already discussed. The coolant gives up its heat in a steam generator and the steam drives a turbine to make electricity. An alternative coolant, an organic liquid called terphenyl, which gives a higher thermal efficiency since it can operate at a higher temperature than water, and at lower pressure, has been developed by AECL and is ready for testing in a prototype power reactor.

The calandria, the pressure tubes which hold the coolant, the sheathing which contains the fuel, and other structural members of the reactor are all made of alloys of zirconium. These alloys are chosen because they combine good strength and corrosion resistance with acceptable neutron absorption properties. Thus zirconium is consistent with the CANDU concept of good neutron economy. The parts outside the reactor are steel and other conventional structural materials.

As already mentioned, fissile Pu-239 is produced when U-238 absorbs a neutron. In the same way, another fissile isotope, U-233, can be formed in a reactor from Th-232, the isotope which makes up natural thorium. These fissile isotopes can be used to extend our natural resource of U-235. In order to do so, however, it is first necessary to separate the Pu-239 and U-233 from the non-fissile materials in a fuel reprocessing step to which reference will be made later.

Clearly, a great deal of research and development has gone into the unique CANDU power reactor system and refinements continue to be made. The R&D work directly applied to reactors and their components is described in other reports in this series. The research programs discussed in the present report underlie and support the applied programs but the reader may observe overlap in some areas because the boundaries between the underlying and the more applied sectors of research are just as hard to define in written descriptions as they are to distinguish in laboratory work. The bibliography in the final section of this report lists additional reports and papers giving more detailed accounts of topics introduced here.

## 1. RADIATION CHEMISTRY

Various forms of radiation are present in a nuclear reactor, namely alpha particles, beta particles and gamma rays emitted by radioactive nuclei, and fission fragments and neutrons emitted in the fission process. Before being slowed down (moderated), fast neutrons lead to the presence of energetic protons via collision or "knock-on" processes in hydrogen-containing material such as

water. These various radiation types are referred to as "ionizing radiation" (the X-rays used for medical examinations are another example) because they involve high energy, and when traversing matter, deposit energy in sufficient amount to induce atoms or molecules to become ionized, i.e. form a positively charged ion and an electron. The same processes can also lead to formation of electronically excited atoms or molecules. There follows a series of chemical events involving times covering the range from millionths of a second to seconds and days. To understand the overall chemistry we have to study the identity and behaviour of short-lived transient species, as well as the stable final products. This field of science is called radiation chemistry.

We study the radiation chemistry of various liquids and gases which function as reactor coolant, moderator and cover-gas in order to understand existing or potential problems and to solve or avoid them. Such knowledge is essential for the design of future systems and necessary to maintain an informed body of consultants. It is also important to understand the effect of radiation on the world around us so that the radiation chemistry of air and water is studied. The latter plays an important role in the radiation chemistry of biological systems. Furthermore, there have been many contributions to basic chemical knowledge applicable to other areas of chemistry, e.g. the chemistry of ions and electrons and short-lived molecular fragments. One aspect of our programs is the study of model systems in order to build up a unified picture of the physical and chemical phenomena occurring in the radiation chemistry of gases and liquids (related research on solids is discussed in the report on materials science). Future advances rely heavily on our basic knowledge and understanding and our ability to monitor what goes on in the scientific world around us.

Since the earliest days of CRNL, radiation chemistry has been a thriving research topic in AECL and the need for the work continues. Similarly, there are related programs in seven Canadian universities and several other government laboratories. In the early days, the radiation chemistry of water received a lot of attention because heavy water is the moderator in the CANDU reactor and water is a major constituent of plants, animals and humans. In addition, the organic-cooled reactor (OCR) developed by AECL led to considerable effort during the 1960's in understanding the radiation chemistry of organic coolant and model organic molecules.

Excellent experimental facilities are available for research in radiation chemistry including several types of high energy electron accelerators (Van de Graaff, Febetron), and a Cobalt-60 gamma-ray source, together with techniques for observing the behaviour of short-lived species (millionths of a second) and stable final products. The work is reported in reputable scientific journals and at national and international conferences. Several international conferences have been held at AECL sites on radiation chemistry.

Over the past 30 years major achievements have accumulated from the work, of relevance to not only the nuclear program but also to our fundamental understanding of the chemical behaviour of highly reactive, short-lived chemical species which are commonly encountered in nature and in many scientific or technological situations. These are briefly summarized below:

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- understanding and control of radiolytic (i.e. radiation-induced) decomposition of reactor moderator and reduction of oxygen formation (a cause of corrosion).
- understanding the radiolytic and pyrolytic (heat-induced) high temperature decomposition of terphenyl, the organic coolant in the OCR.
- fundamentals of the radiation chemistry of liquid water, water vapour, oxygen, nitrogen, nitrogen oxides, air, carbon dioxide, ammonia and a number of the other inorganic gases.
- fundamental radiation chemistry of simple organic liquids and vapours.
- basic physics and chemistry of the solvated electron in inorganic and organic liquids and solids.
- reduction of radiolytic decomposition of CAN-DECON solutions, which are used to clean radioactive deposits out of reactor components.
- reactor dosimetry (measurement of the intensity of various types of radiation at various points inside a nuclear reactor).
- radiation chemistry at solid surfaces vs. that in the bulk of a material, e.g., interaction of metal oxides with gas molecules in the presence of a radiation field.
- effects of radiation dose (total amount) and dose rate (intensity).
- hydrogen/deuterium isotope effects in reactions of short-lived chemical species.
- computer simulation of radiation chemistry. A very efficient computer program has been developed enabling simulation of events covering the whole range of times. This is a very useful diagnostic and predictive tool in both our research and our role as consultants, and incidentally, can be used in any field of chemistry.

The need for the work continues and we look forward to carrying out important studies in various basic and applied research areas which involve radiation chemistry such as many of the above-mentioned. A few additional topics for the future are: the role of radiation chemistry and photochemistry in tritium fixation in the atmosphere; the chemistry of radio-iodine; and the effects of radiation on complex formation and distribution coefficients in fuel reprocessing chemistry (see also sections 4 and 5), nuclear waste management, corrosion, and on polymers (plastic insulators, gaskets and protective coatings).

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## 2. ISOTOPE SEPARATION

The mass difference between isotopes of the same element can cause a small but significant difference in chemical reaction rate, or a shift in a chemical equilibrium, as well as a difference in physical behaviour such as neutron absorption, ability to slow down (moderate) neutrons in a nuclear reactor core, absorb neutrons or undergo nuclear fission or fusion.

In the Canadian nuclear program, there is current or potential interest in processes for separation or concentration of certain isotopes of both heavy and light elements, summarized in Table 1.

Table 1

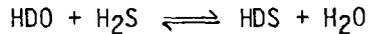
### Isotope Separation Processes of Special Interest

- separation of deuterium from natural sources for use
  - (a) as heavy water in reactors and
  - (b) as a fuel for the fusion energy reactors of the future
- separation of tritium from heavy water to reduce biological health hazards and for use
  - (a) in self-illuminated signs and watch dials
  - (b) as a fuel for the fusion energy reactors of the future
- removal of the neutron absorbing isotope (Zr-91) from natural zirconium to further improve the neutron economy of CANDU reactors
- concentration of the fissile isotope U-235 from natural uranium for use as a reactor fuel
- preparation of isotopes for use in medicine, agriculture, industry or research.

Some of these separation processes are discussed below.

## Hydrogen Isotope Separation Processes

Heavy water is produced at the rate of about 1000 metric tons a year from three Canadian plants. The Girdler-Sulphide (GS) process used in these plants is described in detail in other reports in this series. It is based on the isotope exchange equilibrium between liquid water and hydrogen sulphide gas that in chemical parlance is written:



The formula HDO could, for example, represent the one molecule containing deuterium among the approximately 3500 H<sub>2</sub>O molecules which together make up natural water. The position of this equilibrium, i.e. the proportions of HDO and HDS in the mixture, depends on the temperature: lower temperatures favour deuterium in HDO while higher temperatures push the equilibrium to the right and favour HDS. To take advantage of this temperature dependence, the huge towers characteristic of GS plants (90 m high, 10 m diameter) are divided into an upper, cold (32°C) and lower, hot (130°C) section. Hydrogen sulphide gas bubbles up through water passing down from the top over a series of trays. Deuterium is extracted from the water and enriches the hydrogen sulphide at the top of the hot section, a fraction of which is withdrawn and routed to a smaller second stage column where the process is repeated. After three stages the water contains about 15% deuterium and it is then economical to distill it to achieve 99.8% D<sub>2</sub>O, reactor grade water. Through R&D at CRNL and elsewhere the GS process has been made to work well but there is always scope for more efficient, cheaper or more flexible processes.

### (a) Hydrogen-Water Process

One such possibility that has been thoroughly researched at CRNL is analogous to the GS process in that water is brought in contact with hydrogen gas. Here the isotope separation is fundamentally more efficient but it is slower than the GS process and a catalyst is needed to speed up the exchange reactions involved. Such a catalyst was invented at CRNL in 1969. Over the intervening years the catalyst has been further developed in the laboratory and tested in large scale engineering equipment and it forms the basis of several processes discussed elsewhere in this series of reports.

Atoms of protium and deuterium exchange between water and hydrogen gas molecules very slowly under normal conditions but do so much faster on catalytic metal surfaces, of which platinum is best. The key to the invention was the application to the platinum surface of a waterproof plastic coating which prevents liquid water from forming a film on the catalytic surface but is porous enough to let water vapour and hydrogen molecules reach the surface easily. The details of this concept have been the subject of much basic research at CRNL and the knowledge gained has been used to optimize the catalyst configuration, the utilization of platinum and the waterproofing treatment. In practical applications the catalyst is usually deposited on the surface of alumina balls or other ceramic shapes which are packed in a tall, thin column. Water trickles

down through the catalyst bed and hydrogen flows up; deuterium is extracted from the water and is concentrated in the hydrogen flowing from the top of the column. Factors such as water and hydrogen flow rates, hydrogen pressure and column dimensions are important and have been investigated over the ranges of interest.

There is world-wide interest in the catalyst and its applications, and AECL has patents on these in 10 or more countries. A Canadian firm is licensed to manufacture and sell the catalyst and cooperates with AECL in the development program. Two applications are described below.

#### (b) Combined Electrolysis-Catalytic Exchange Process

When water is electrolysed to form hydrogen and oxygen by the passage of electric current, the deuterium concentration in the hydrogen is less than in the water from which it is produced, by a factor of 6 or more. This scientific fact is the basis for a process which has been used in a plant operated at CRNL for many years to upgrade the concentration of deuterium in heavy water to reactor grade. Research on hydrogen isotope separation by electrolysis has been done at AECL to provide technical support and improve this upgrading process. With the invention of the wetproofed catalyst it was possible to unite the two processes, electrolysis and hydrogen-water exchange, into a combined process which benefits from the advantages of both. The combined process is being tested in a small plant designed to upgrade the heavy water in a research reactor at CRNL.

Currently, a good deal of attention is being directed world-wide to the use of hydrogen as an "energy carrier", or "currency", in the future. According to this concept, hydrogen would be produced where energy was available, e.g. at nuclear power stations, hydroelectric sites, etc., and used as a fuel in airplanes or buses, or as pipeline gas for domestic and commercial applications. The only proven way to make hydrogen for this concept today is by electrolysis. It has been proposed in AECL patents and papers that such electrolysis plants in the future could be easily adapted to the combined electrolytic catalytic exchange process to make heavy water as a valuable co-product of hydrogen production. A consortium of Canadian firms has assessed such a scheme for application in central Canada and, although no technical difficulties were found, it was concluded that the economics are not yet favourable.

#### (c) Tritium Separation Process

As mentioned in the Introduction, when deuterium in reactor heavy water absorbs a neutron it is changed to tritium, a radioactive isotope of hydrogen. This results in a gradual buildup of tritium in the heavy water, as DTO. At a level of about 3 atoms of tritium for every million atoms of deuterium, it is desirable to remove the tritium in order to assure that accidental releases to the environment continue to be negligible, and that tritium exposure of nuclear power station personnel is kept well within the levels considered tolerable. Research has demonstrated that the wetproofed catalyst can be used to extract tritium from heavy water in a process analogous to the extraction of deuterium from light water. In a similar application tritium can be removed from the ordinary water used in the reprocessing of spent reactor fuel and this is being

studied in American, European and Japanese laboratories. We collaborate with the U.S.A. in this program. The tritium can be further concentrated by low temperature distillation, and combined with a metal such as zirconium to form a stable solid substance suitable for long-term storage. Alternatively, it can be sold for commercial applications such as the illumination of signs, watch dials, etc.; in the future the demand will be increased many-fold if tritium comes into use fusion reactors.

#### (d) Catalysis Research

In the hydrogen-water process the actual exchange of hydrogen and deuterium atoms between molecules of water and hydrogen occurs when the molecules are adsorbed together on a platinum crystal surface. The way such molecules are adsorbed and react, the role of the metal surface and the influence of foreign molecules are all subjects for detailed research using advanced surface science techniques, some of which have been pioneered at CRNL.

Not all exchange processes require a solid catalyst; in some, a dissolved catalyst is effective. One process that uses a dissolved or homogeneous catalyst involves the exchange between hydrogen and an organic chemical called methylamine. This process and related processes have been studied extensively at CRNL.

These programs have been complemented by a series of research contracts with the University of Ottawa, McMaster University and Queen's University.

#### Advanced Methods of Isotope Separation

Part of our scientific responsibilities in the area of isotope separation is to keep informed of, and to evaluate, potential new processes based on ideas conceived within AECL, or derived from recent scientific literature or meetings with colleagues from other organizations, often from other countries. This function is performed with respect to isotopes of hydrogen, zirconium and uranium, on an on-going basis. Around 1970 we became aware of the potential of laser photochemistry for isotope separation.

Photochemistry is a close relative of radiation chemistry. The basic difference is that light rays (ultraviolet, visible or infrared) are involved and their energy is very small compared to that of the particles or rays of radiation chemistry. Before the development of lasers it was usually impossible to photochemically induce ionization of atoms or molecules except when extremely short wavelength (far ultraviolet) light sources or certain special molecules were used. However a laser can be a very intense source of light rays such that a given molecule can be made to absorb many light rays essentially simultaneously so that the individual energies add up. Thus lasers offer the prospect of ionization or electronic excitation of atoms and molecules, and of vibrational excitation of molecules.

One difference in physical properties of isotopes, not mentioned above, is very small wavelength shifts in optical absorption spectra (ultraviolet, visible

or infrared regions) between atoms or molecules with different isotopes of the same element.

These phenomena, plus the laser property of emitting intense light of a single wavelength, make it possible to stimulate in a highly selective fashion the excitation or ionization of atoms or molecules in a complex mixture involving a desired isotope. Subsequent dissociation, chemical reaction or physical processes such as electrical or magnetic extraction (of ions) have allowed the separation on a laboratory scale of the desired isotopic component from a mixture. The basic attraction of such processes is that the single-step isotope enrichment factor may be very high (e.g. 1000-10,000 for deuterium/protium separation) compared to low values (2-10 for deuterium/protium separation) for conventional methods such as the chemical exchange equilibria discussed above. In this way, laboratory-scale separations have been observed for isotopes of a large number of elements, e.g., hydrogen, boron, carbon, nitrogen, oxygen, sulphur, chlorine, bromine and uranium.

The program at CRNL has thus far concentrated on the use of infrared lasers to selectively decompose molecules in order to separate protium and deuterium. The work has concentrated on understanding the fundamental physics and chemistry of such processes and it is at the very frontiers of the topics: interaction of molecules with intense laser beams and molecular dynamics of chemical reactions. The work has been complemented from 1977-1980 by a research contract at the University of Toronto. In 1980 a research contract was placed at McMaster University to develop a molecule containing zirconium suitable for research on laser isotope separation of zirconium. The very latest in laser developments have been incorporated via a \$140,000 contract with a completely Canadian firm, Lumonics Research Ltd. of Ottawa. In late 1979 they completed development and commissioning of a prototype short-pulse carbon dioxide laser for CRNL, the first such commercial laser of its type. Some expertise in laser development has also evolved within CRNL as a result of the research programs.

Apart from the relevance of the results to potential future methods of separating deuterium for heavy water production, they are also applicable to tritium recovery processes. Furthermore, the expertise acquired will enable us to do work related to separation of isotopes of heavy elements such as zirconium and uranium, if it becomes important to the Canadian nuclear power program.

### 3. HIGH TEMPERATURE SOLUTION CHEMISTRY

As mentioned already, the heavy water coolant leaving a CANDU reactor is at 300°C and high pressure. The temperatures of process streams in heavy water and fuel reprocessing plants range up to 180 and 120°C, respectively, and the temperatures in geological storage vaults may fall in this range as well. In reactor safety analyses temperatures as high as 1000°C or greater may be important. It is therefore important to know how solutions of various substances in water will behave at high temperature. Much of this knowledge is lacking because it has been difficult to make measurements at the pressures required to

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keep water liquid at high temperatures. Equipment and techniques are being developed for this purpose, however, and the success of the continuing program in this area is illustrated by the more than 30 papers on solution chemistry at elevated temperature which have been published by AECL in the fundamental and applied literature since the program began in the early 1970's.

The fundamental properties of solutions are described by "thermodynamic variables" and these are systematized in a well-developed branch of science called chemical thermodynamics. The research at WNRE extends the extensive knowledge of the thermodynamic variables of room temperature solutions to higher temperatures and forms the basis for predicting the way other thermodynamic properties, such as the solubilities of system components and the electrical potentials of possible corrosion reactions, change with increasing temperature. We recently acquired a solution microcalorimeter for measuring solution heat capacities above 100°C which is one of only two such instruments in the world.

Because experimental measurements are so difficult, the development of theoretical computer models for predicting the thermodynamic properties of high temperature solutions is a continuing priority. Several methods capable of extrapolating room temperature data above 150°C are now available. Their usefulness was recently demonstrated, for example, by their ability to predict the detailed high temperature thermodynamic properties of 100 uranium and plutonium dissolved and solid species which are needed for environmental assessment studies in the nuclear waste management program. A new, more theoretical approach, which may soon be applied to solutions, has successfully been used to predict the properties of liquid water and compressed steam to 900°C.

Some of the experimental research is aimed at providing data needed to develop these methods. For instance, electrical techniques are being used to determine the thermodynamic properties of single ions at elevated temperatures. Many substances dissociate into pairs of positively and negatively charged ions when dissolved in water. The experiments separate the properties of pairs of ions into their single ion components which, in addition to being valuable in their own right, provide the data needed to deduce the properties of additional single ions from conventional thermodynamic measurements for comparisons with theory.

Uranium ions become associated with a variety of other ions in solution forming complexes with distinct thermodynamic properties of their own, altering the character of the solution and changing the solubility of uranium compounds. Complex formation is typical of the family of elements to which uranium belongs; it is called the actinide family and includes thorium, plutonium and other elements important in the nuclear program as well as uranium. Uranium dioxide solubility measurements and studies of uranium complex formation with carbonate and other common groundwater ions are extending the present experimental data base at room temperature to temperatures ranging up to 300°C.

The experimental measurements and theoretical descriptions for solubility and related properties also include chemical compounds of elements such as iron, nickel and cobalt because, as mentioned earlier, the part of the system which carries the heat away from the reactor is made of alloys containing these metals.

Hot water causes some corrosion of these alloys but of more serious concern is the fact that the corrosion products which are carried around the system are made radioactive in the reactor and eventually become distributed outside the reactor shielding, thus increasing the radiation hazard to the staff. Through a knowledge and understanding of the properties of these substances, chemical control methods can be improved to minimize the hazard. This information is also of use in understanding and optimizing the systems used for reactor decontamination and boiler water chemistry control.

The thermodynamic properties of selected fission product elements are also being studied at elevated temperatures. One such element is technetium which is formed in the fission process but was unknown prior to the nuclear age (no stable isotope exists). Under some conditions, technetium is very difficult to remove from aqueous systems - a very desirable property when used as a radioactive tracer but undesirable when disposing of technetium in geologic storage. Thus experiments are being done to understand and control technetium behaviour. In a slightly different category are iodine, selenium and palladium. A good deal is known already about these fission products but not under all conditions encountered in reactor systems and waste repositories.

The knowledge and understanding arising from research on the thermodynamics of high temperature water solutions strengthens the foundations for present and future development of CANDU reactor systems, waste management, fuel reprocessing and accident analysis. In addition, this information will be valuable in a variety of other Canadian applications. Two diverse examples are high temperature water for *in situ* mining of oil sands, and corrosion in the pulp and paper industry.

#### 4. FUEL REPROCESSING CHEMISTRY

Classical chemical thermodynamics has been successful in its treatment of the properties of dilute solutions but further research is required to extend its application to concentrated solutions. This is because the properties of the solvent or of particular solutes can be significantly affected by solutes present in high concentrations and current solution theory cannot predict these effects. Highly concentrated solutions would be used in the reprocessing of spent reactor fuel if Canada finds it necessary to extend nuclear fuel supplies by this means. Consequently the chemistry of such solutions is being studied at WNRE to provide the fundamental knowledge needed for eventual process development. The program emphasizes thorium solution chemistry because the thorium fuel cycle is an attractive option for CANDU reactors in the future, but thorium spent fuel reprocessing will differ from uranium reprocessing technology developed abroad. To be able to exploit this option, we need to acquire the necessary knowledge and expertise. Current work is on thorium nitrate-nitrite acid solutions in water at 25°C; the temperature will be pushed up to 50°C in the future and other solvents will be investigated.

The established method for reprocessing spent fuel to recover the desirable actinides from the unwanted fission products involves partitioning the dissolved fuel components between two immiscible solvents, e.g. oil and water. The two liquids must be capable of forming a suspension of fine droplets, one in the other, with a large interfacial area, so that the fuel components will migrate and partition to the appropriate solvent quickly; but it is also essential for the two liquids to settle quickly in two layers later in the process to effect the final separation. The WNRE research program is aimed at understanding the factors controlling the interfacial areas in liquid mixtures of the sort used in solvent extraction processes as well as the transfer of solutes across these interfaces.

## 5. ANALYTICAL CHEMISTRY

As mentioned in the Introduction, our research is focussed on the requirements of the CANDU reactor and related technology; no topic illustrates this more clearly than analytical chemistry. Continuing research over the years has built up a battery of methods and techniques for the analysis of CANDU materials. These include the determination of a wide variety of properties including chemical compositions, isotope ratios, radioactivity, surface characteristics and spatial distributions in heterogeneous materials. Noteworthy advances have been made in methods for the analysis of radioactive materials such as irradiated fuel in support of fuel engineering and reactor physics; the determination of protium-deuterium ratios and the establishment of heavy water standards; the determination of impurities in coolants, both heavy water and organic coolant; and the chemical characterization of fuel reprocessing and waste management experiments.

Improvements to the accuracy and precision of the methods are, of course, continuing concerns. At the same time improvements to speed and efficiency receive special attention to reduce the time and effort required to analyze the thousands of samples arising from programs at CRNL and WNRE. To this end there has been a good deal of work done on methods for determining several elements simultaneously in a single sample. These usually rely on characteristic emission or absorption by the element in question in the appropriate region of the electromagnetic spectrum. To increase the speed and thus provide quick responses to changes in conditions, research has yielded a number of special instruments which continuously analyze liquid and vapour streams in reactor circuits, heavy water plants and fuel reprocessing experiments.

There is a steady demand for the analysis of one-of-a-kind samples from the R&D program, e.g. specimens used in nuclear physics or solid state research, deposits in reactor circuits and environmental samples. Frequently these require small research programs for their completion and call for versatility and flexibility in their solution.

An example of analytical chemistry development that has been of extraordinary importance to the perfecting of CANDU reactors over many years is

the refinement of techniques that permit accurate measurement of the number of atoms of the isotopes of uranium, plutonium and other transuranic elements, and the associated fission product elements, in samples of reactor-irradiated fuels, both experimental and operational. The success of this program has been dependent upon the ongoing, concurrent evolution of techniques in physics, chemistry and computation. The modern mass spectrometer for the analysis of inorganic solids was invented for nuclear work, and some of the earliest spectra of plutonium were obtained on a CRNL-built instrument.

Separative techniques being developed at CRNL today permit measurement of as little as  $10^{-12}$  grams of an inorganic element in one millilitre of solution. Such techniques are valuable not only to nuclear power, but ultimately in many other areas of human concern, for instance in measuring the purity of environmental materials such as the waters in rivers and lakes.

An unusual example of response capability in analytical chemistry was the work done at WNRE, on the fragments of the Russian Cosmos satellite which fell in Northern Canada in 1978. A very large number of chemical, isotopic and surface analyses helped the authorities to establish the hazards posed by debris from its reactor.

We will continue to strive through research in analytical chemistry to meet the ever-changing requirements of research and development. Emphasis is being directed toward better methods for surface analysis, toward faster, cheaper, non-destructive methods for the analysis of radioactive materials such as nuclear fuels, and toward means of conducting analyses within operating systems. In-system and on-line analysis research offer the prospect of better or more efficient reactor and chemical plant operation. Recently we have successfully demonstrated the automatic boiler chemistry control of a Saskatchewan power station. This technology is required for new CANDU power stations and is potentially valuable in many industrial situations.

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