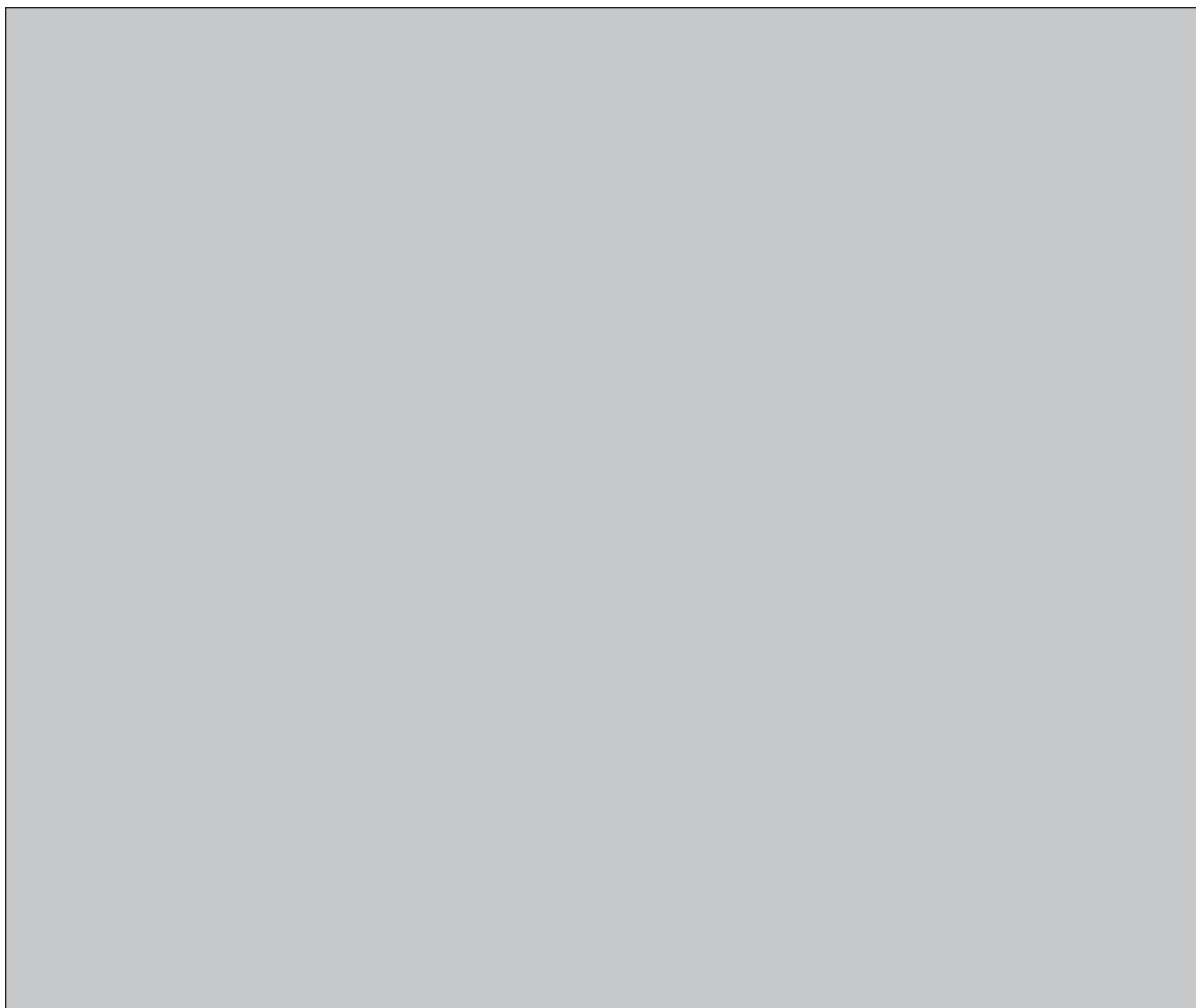


NWMO BACKGROUND PAPERS
4. SCIENCE AND ENVIRONMENT

4-4 THE CHEMICAL TOXICITY POTENTIAL OF CANDU SPENT FUEL

Don Hart & Don Lush, Stantec Consulting



NWMO Background Papers

NWMO has commissioned a series of background papers which present concepts and contextual information about the state of our knowledge on important topics related to the management of radioactive waste. The intent of these background papers is to provide input to defining possible approaches for the long-term management of used nuclear fuel and to contribute to an informed dialogue with the public and other stakeholders. The papers currently available are posted on NWMO's web site. Additional papers may be commissioned.

The topics of the background papers can be classified under the following broad headings:

1. **Guiding Concepts** – describe key concepts which can help guide an informed dialogue with the public and other stakeholders on the topic of radioactive waste management. They include perspectives on risk, security, the precautionary approach, adaptive management, traditional knowledge and sustainable development.
2. **Social and Ethical Dimensions** - provide perspectives on the social and ethical dimensions of radioactive waste management. They include background papers prepared for roundtable discussions.
3. **Health and Safety** – provide information on the status of relevant research, technologies, standards and procedures to reduce radiation and security risk associated with radioactive waste management.
4. **Science and Environment** – provide information on the current status of relevant research on ecosystem processes and environmental management issues. They include descriptions of the current efforts, as well as the status of research into our understanding of the biosphere and geosphere.
5. **Economic Factors** - provide insight into the economic factors and financial requirements for the long-term management of used nuclear fuel.
6. **Technical Methods** - provide general descriptions of the three methods for the long-term management of used nuclear fuel as defined in the NFWA, as well as other possible methods and related system requirements.
7. **Institutions and Governance** - outline the current relevant legal, administrative and institutional requirements that may be applicable to the long-term management of spent nuclear fuel in Canada, including legislation, regulations, guidelines, protocols, directives, policies and procedures of various jurisdictions.

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EXECUTIVE SUMMARY

The purpose of this background paper is to identify elements in CANDU spent fuel that should be included in environmental assessments when demonstrating “safety” with respect to chemical toxicity in long-term storage or disposal of spent fuel. It should be noted that previous assessments have demonstrated the safety of specific storage/disposal concepts with respect to radiotoxicity, and similar demonstrations can probably be made with respect to chemical toxicity. This paper is not intended to be a safety assessment. However, it is useful to develop a rationale by which such assessments can focus on the elements of greatest potential concern. The rationale presented herein involves very conservative assumptions such as rapid chemical release from fuel and unretarded transport to the biosphere. The resulting short list of chemicals of potential environmental concern provides a starting point for subsequent safety assessment, in that the onus is on the proponent to demonstrate why conditions in the long-term management facility and surrounding environment will be such that these chemical elements do not pose unacceptable environmental risk.

The screening process begins by a consideration of the total elemental composition of spent fuel approximately 10 years following its removal from the reactor core. Since most of all known elements are present at very trace quantities in the spent fuel, the first screen applied is a comparison of the concentration of a particular element in spent fuel with the comparable concentration in background rock (granite). Elements found in spent fuel in concentrations lower than that found in granite rock are excluded from further consideration. In addition, certain “elements of life” such as carbon, nitrogen, hydrogen, oxygen, etc., and other non-toxic elements such as noble gases, are excluded from further consideration.

The second step in the screening process is to make some very conservative assumptions concerning the degradation of the spent fuel and the release of the contents to the surrounding environment. Decay and ingrowth of new elements is also considered, as well as a minimal degree of dilution in various environmental media such as water, soil, sediment and air. The result of this process is a set of maximum concentrations of a wide range of the elements that could ever reasonably be expected to be encountered in the vicinity of a spent fuel management facility.

The third step in the screening process is to compare the concentrations of these elements to a number of toxicity-based environmental guidelines. If an element has a guideline concentration and it is exceeded, it is considered as an element of potential concern and recommended for evaluation in any safety assessment. If an element does not have a guideline or other benchmark because it is very rare and has not been studied, but if it is relatively abundant in spent fuel and soluble, it is identified as a candidate for toxicity studies.

The result of this screening process is a short list of elements present in spent fuel, either initially or as a result of radioactive decay and ingrowth through time, that will require consideration in the safety assessment to be carried out for any spent fuel long-term management facility.

The elements identified based on screening-level estimates of concentration in water (groundwater and/or surface water) included lead (Pb), nickel (Ni), uranium (U), molybdenum (Mo), antimony (Sb), cobalt (Co), cadmium (Cd), chromium (Cr) and zirconium (Zr). All of these elements were also identified based on estimates of concentration in soil, as well as sediment or air in some cases. Elements identified based only on estimates of concentration in soil included lanthanum (La), iodine (I), bromine (Br), tungsten (W), technetium (Tc), tin (Sn) and niobium (Nb). The soil and air estimates, by direct partitioning from undiluted groundwater, were considered to be particularly conservative.

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1.0 INTRODUCTION

The Canadian Nuclear Waste Management Organization has been mandated by the Parliament of Canada to consult with the Canadian public and to recommend to Parliament the best approach for Canada to take over the next several decades in order to manage spent fuel from Canada's nuclear power generators. The two generic options to be explored and evaluated include long-term surface storage or deep geological disposal. In addition to these two generic options, other technologies and approaches may be evaluated and discussed, with a final recommendation and implementation plans being made in late 2005. Long-term surface storage could be implemented at one or more existing nuclear stations or at a centralized facility. Deep geological disposal could be at one centralized or two or more locations. As part of the consultation with the Canadian public, a series of technical papers are being produced to provide factual information which will assist in framing the discussion.

In the past in Canada and internationally, the principal focus on the management of spent fuel has been on ensuring that the public and natural environment are adequately protected from the ionizing radiation given off by a wide range of radioactive elements contained in the spent fuel. This is indeed the proper focus, especially in the early years following the removal of the spent fuel from the reactor when the fuel is highly radioactive. Even after approximately 100,000 years when the level of radioactivity in spent fuel has decayed to a level similar to that which may be found in natural uranium minerals, it is still essential to consider the radiological risk that may be posed to humans and the natural environment. However, it is also necessary to recognize that spent fuel also contains stable or non-radioactive elements, which will never decay away. Also included in spent fuel are some radioactive materials such as U-238, which are more chemically toxic than radiotoxic. The question then arises as to whether or not a safety assessment of a long-term management concept for spent fuel must consider not only the potential radiological hazard that may be posed by the concept, but also any chemical hazard. It is the purpose of this paper is to address this question.

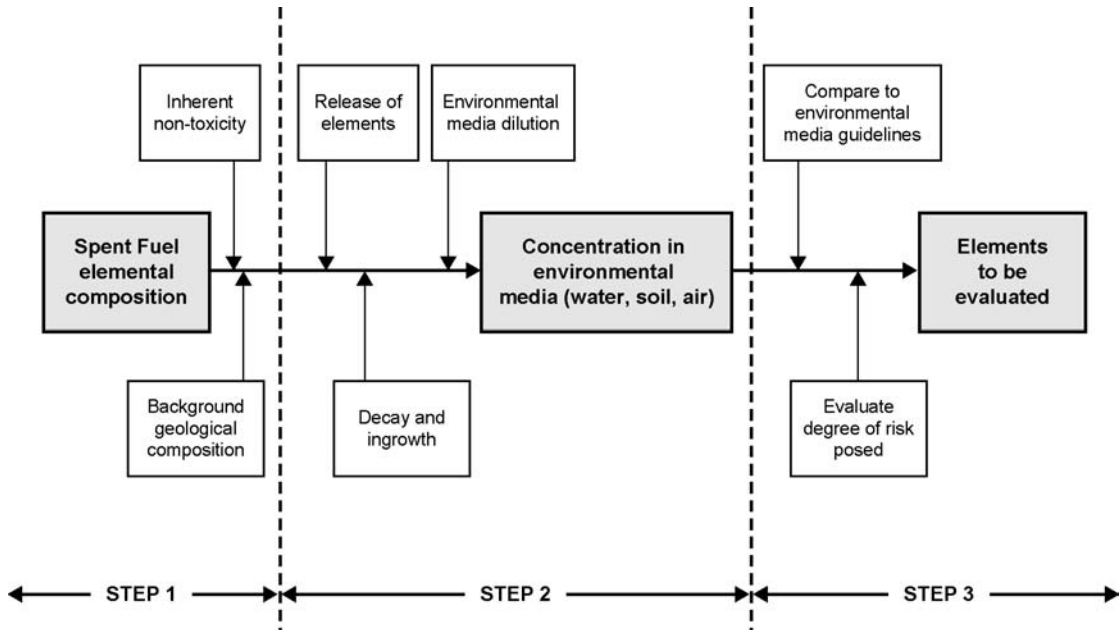
Over a long enough time, any waste material will eventually degrade and its constituent elements will migrate from the waste and enter the environment moving through long-term geochemical cycling processes. The time necessary for this to occur will be very dependent upon the form of the waste (its physical and chemical stability) and the nature, stability and consistency of the surrounding environment. Studies of natural uranium deposits, such as found at Oklo (see NWMO Background Paper on Natural and Anthropogenic Analogues), have functioned as natural nuclear reactors in the past. These studies have shown that, under the appropriate (stable) environmental conditions, the bulk of the "natural spent fuel" that was burned in these reactors can remain essentially intact for time periods in excess of 2 billion years. During this time however, some elements whose chemistry is different from that of the uranium still present in the ore body which "hosted" the natural reactor have migrated from the deposit and entered local and global geochemical cycles. Other

examples of ore bodies of many types have shown that, under different and fluctuating geochemical conditions, elements can be much more highly mobile and enter local and global cycles much more readily. The potential environmental risk posed by both radionuclides and stable nuclides of elements is related to the rate at which they enter the surrounding environment and the dilution they encounter in that environment. These two processes in turn lead to particular concentrations in the surrounding environment that can be compared to “benchmarks” to evaluate risk. The processes that control the rate of migration from a spent fuel a management facility to the surrounding environment and the resulting dilution encountered in that environment are site- and facility-specific, and these site specific aspects must be evaluated in any facility safety assessment. The purpose of this discussion paper is to evaluate, through the use of very conservative assumptions concerning the degradation of spent fuel and the release of its constituents to the surrounding environment, coupled with conservative assumptions about dilution in the receiving environment, which elements present in spent fuel if any may require a chemical toxicity evaluation (as opposed to radiotoxicity evaluation) in any safety assessment.

The purpose of this background paper is to identify elements in CANDU spent fuel that should be included in environmental assessments when demonstrating “safety” with respect to chemical toxicity in long-term storage or disposal of spent fuel. It should be noted that previous assessments have demonstrated the safety of specific storage/disposal concepts with respect to radiotoxicity, and similar demonstrations can probably be made with respect to chemical toxicity. This paper is not intended to be a safety assessment. However, it is useful to develop a rationale by which such assessments can focus on the elements of greatest potential concern. The rationale presented herein involves very conservative assumptions such as rapid chemical release from fuel and unretarded transport to the biosphere. The resulting short list of chemicals of potential environmental concern provides a starting point for subsequent safety assessment, in that the onus is on the proponent to demonstrate why conditions in the long-term management facility and surrounding environment will be such that these chemical elements do not pose unacceptable environmental risk.

The process used to screen for potential stable elements of concern in this document is illustrated in Figure 1.

FIGURE 1: SCREENING PROCESS TO IDENTIFY ELEMENTS OF POTENTIAL CONCERN

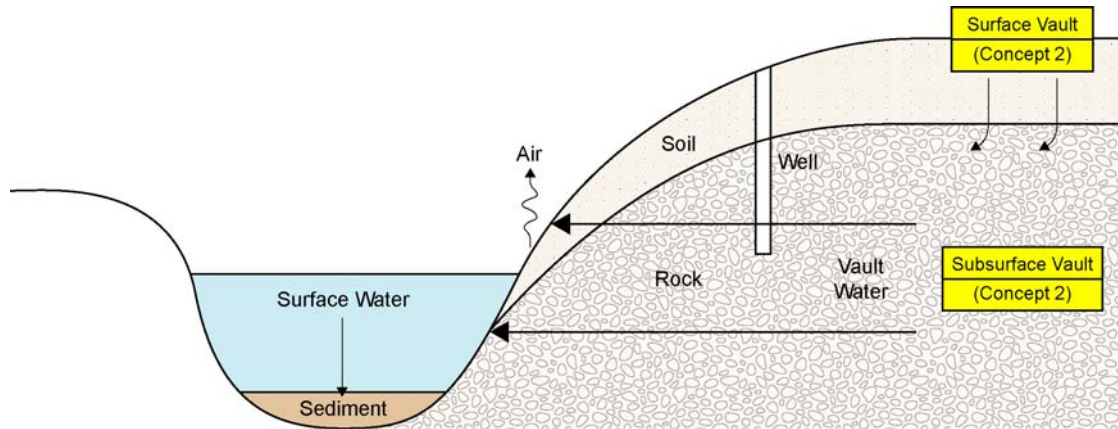


The screening process begins by a consideration of the total elemental composition of spent fuel approximately 10 years following its removal from the reactor core. Since most of all known elements are present at very trace quantities in the spent fuel, the first screen applied is a comparison of the concentration of a particular element in spent fuel with the comparable concentration in background rock (granite). Elements found in spent fuel in concentrations lower than that found in granite rock are excluded from further consideration. In addition, certain “elements of life” such as carbon, nitrogen, hydrogen, oxygen, etc., and other non-toxic elements such as noble gases, are excluded from further consideration.

The second step in the screening process is to make some very conservative assumptions concerning the degradation of the spent fuel, the release of chemical constituents to storage vault water, and transport/partitioning from vault water to environmental media. The conceptual model is illustrated in Figure 2. Decay and ingrowth of new elements is also considered. The result of this process is a set of maximum concentrations of a wide range of the elements that could ever reasonably be expected to be encountered in the vicinity of a spent fuel management facility.

The third step in the screening process is to compare the concentrations of these elements to a number of toxicity-based environmental guidelines. If an element has a guideline concentration and it is exceeded, it is considered as an element of potential concern and recommended for evaluation in any safety assessment. If an element does not have a guideline or other benchmark because it is very rare and has not been studied, but if it is relatively abundant in spent fuel and soluble, it is identified as a candidate for toxicity studies.

FIGURE 2: CONCEPTUAL MODEL OF CHEMICAL PARTITIONING FROM A SPENT FUEL STORAGE VAULT TO ENVIRONMENTAL MEDIA



The result of this screening process is a short list of elements present in spent fuel, either initially or as a result of radioactive decay and ingrowth through time, that will require consideration in the safety assessment to be carried out for any spent fuel long-term management facility.

2.0 TOXICITY CONCEPTS

The toxicity of a chemical is usually described in terms of the lowest concentration or dose that may be harmful to a particular class of organism or, conversely, the highest concentration or dose that may be considered safe. These exposure levels are respectively called Lowest Observed Adverse Effects Levels (LOAELs) and No Observed Adverse Effect Levels (NOAELs). The LOAEL and NOAEL concentrations are defined for different environmental media, such as water, sediment, air and soil, designed in each case to protect organisms that are typically exposed to these media. For birds and mammals, where a distinction is easily made between different routes of exposure (e.g., inhalation, ingestion), the toxicity of a chemical is often defined in terms of the LOAEL or NOAEL dose for each route (e.g., mg of chemical ingested per kg body weight per day). The LOAEL or NOAEL dose can be expressed in terms of a corresponding environmental concentration, based on knowledge of relevant exposure factors, such as organism body weight and rate of water or incidental soil ingestion.

Environmental quality guidelines are developed by regulatory agencies as environmental media concentrations, which are at or below the NOAEL value for sensitive organisms. Therefore, if a chemical is at or below its guideline value in a particular environmental medium (air, water, soil, etc.), adverse effects are not expected. In the context of human health protection, guidelines are based on a Reference Dose (RfD), which is an NOAEL dose divided by a safety or uncertainty factor (typically 10 to 1,000), in order to increase the confidence that no individual (including particularly sensitive individuals) will be harmed by exposure at the guideline level. For example, drinking water guidelines are derived in this manner to be protective of human health.

The NOAEL and RfD values that are used in developing environmental quality guidelines are based on long-term (chronic) exposure situations. While NOAELs for short-term (acute) exposure situations exist in the toxicity literature, they are usually higher than the values for chronic exposure situations. They are applicable only to short-term events, such as spills of non-persistent chemicals, where organisms cannot be exposed for prolonged periods. In order to be generally protective in all situations, environmental quality guidelines are usually based on assumptions of long-term and continuous exposure. As a further safety measure, the guidelines may be applied as concentrations not to be exceeded, even for short periods of time.

The adverse effects that are considered in defining the LOAEL and NOAEL values for a chemical should, and generally do, include the most limiting health effects, i.e., the effects that occur at the lowest exposure levels. For example, while ingested cadmium and mercury both may produce a variety of different adverse effects on human health, at different levels of exposure, the NOAEL based on kidney effects is limiting for cadmium, while the NOAEL based on neurological effects is limiting for mercury, because these are the effects that have been observed at the lowest levels of exposure.

For some chemicals, such as arsenic, which is a carcinogen, the limiting human health effect is cancer induction. For health protection purposes, as in radiation protection, it is usually assumed that these chemicals induce some probability of cancer at any exposure level, with a linear dose response and no threshold dose. For these chemicals, while we may identify a NOAEL or RfD for non-cancer effects, environmental quality guidelines are driven by a Risk-Specific Dose (RSD). This is the dose level that has been associated with an acceptably low lifetime risk of cancer induction, usually 10^{-6} , or 1 case in 1,000,000 people exposed. The acceptable risk target used for carcinogenic chemicals is substantially lower than the risk target implied by the 1 mSv/a public dose limit used in radiation protection. In some cases, the chemical target risk leads to environmental concentration limits well below background, in which case guidelines must be set near background.

Cancer induction is usually considered to be a relevant endpoint for protection of human health, but not for protection of non-human biota. The reason for this is that cancer tends to be a disease of later life. As such, it is important to quality of life (and death) for individuals, and we wish to protect human quality of life as much as possible. However, survival to the point of reproduction is the primary factor dictating the persistence of a wildlife population. From an anthropogenic point of view, ecological quality of life is a secondary consideration. Thus, environmental quality guidelines designed to protect plant and animal populations are focussed on toxic effects other than cancer.

Radioactive elements may be both chemically toxic and radiotoxic. Chemical toxicity is mediated by the chemical reactions that occur inside the body between the chemical and the body tissues. Radiotoxicity is mediated by the radiation emissions from the element, which may damage body tissues, whether they originate inside or outside the body. Either chemical toxicity or radiotoxicity may be the limiting health effect. For example, natural uranium contains radioactive isotopes, primarily U-238 by mass, which are somewhat radiotoxic when ingested or inhaled. However, it is the chemical toxicity effects that are limiting, because adverse effects on the kidney may occur at exposure levels that do not produce unacceptable radiation doses. Environmental quality guidelines for uranium are based on the chemical effect levels. On the other hand, cesium in used fuel, due to a substantial component initially of Cs-137, is primarily radiotoxic when ingested or inhaled. It is of little concern from a chemical toxicity perspective, and the only environmental quality guidelines that exist are based on limiting the radiation dose.

The toxicity of a chemical element may be highly dependent on its chemical form, which determines its bioavailability (ability to be absorbed by an organism). For example, soluble salts of uranium are more bioavailable than oxides, and therefore more toxic. Similarly, compounds containing hexavalent uranium (U^{+6}) tend to be more soluble and hence bioavailable than other uranium compounds. Most toxicity tests are performed using soluble forms of a specific material in order to maximize bioavailability. This represents a worst-case exposure situation. Environmental quality guidelines, while based on toxicity tests with bioavailable forms, are often

considered to be generally applicable to any form of the chemical. This is a practical approach, which avoids the need to routinely characterize the chemical speciation of an element in the environment. It recognizes that the chemical form of a material in the environment may change with time and changing environmental conditions. However, it will overstate the risk for less available chemical forms. By using this approach, implicitly we accept the tradeoff that environmental guidelines may be unnecessarily stringent in some situations where chemicals may actually be less bioavailable.

3.0 CHEMISTRY OF SPENT FUEL

The fuel used by CANDU reactors is natural uranium in the form of uranium dioxide (UO₂). Natural uranium consists primarily of U-238 by mass, with a small quantity of U-235 (0.711% by mass), and an even smaller quantity of U-234 (0.0054% by mass). Nuclear energy is obtained primarily from the fission (splitting) of U-235 atoms during “burnup” of the uranium fuel within the reactor. On completion of burnup, the “spent” fuel is still primarily UO₂, with U-238 still the main isotope of uranium by mass. However, the mass contribution of U-235 is reduced, depending upon the degree of burnup achieved, to approximately 0.2% (Tait *et al.*, 1989). This simple characterization of the fuel ignores the small quantities of trace elements that are present as impurities in the initial (fresh) fuel (Table 3.1), and the trace elements that are formed during burnup by fission and neutron activation.

TABLE 3.1: MAXIMUM LIKELY UO₂ FUEL IMPURITIES (from Tait *et al.*, 2000)

Element	µg/g U ¹	Element	µg/g U
Al	50	Fe	400
B	0.3	Mg	50
Cd	0.2	Mn	10
Ca	50	Mo	4
C	100	Ni	30
Cr	25	Si	60
Cu	20	Ag	1
Dy	0.15	Th	500
Gd	0.1		
O ²	134,454	N ₂	100

¹ Micrograms of element for each gram of uranium in spent fuel (parts per million); uranium comprises 87% of spent fuel.

² Atomic oxygen in UO₂ fuel.

The complete inventory of elements present in the spent fuel includes:

- fission products arising from the splitting of uranium and heavier elements, and subsequent radioactive decay of these primary fission products to other elements;
- neutron activation products arising from the absorption of a neutron by uranium and heavier elements (to give actinides) and subsequent radioactive decay of these actinides to other elements; and

- neutron activation products arising from the absorption of neutrons by impurities in the fuel, and subsequent radioactive decay of these activation products to other elements.

The UO_2 fuel is packaged for use in bundles, which are encased in a zircaloy cladding (Figure 3). Zircaloy is an alloy of zirconium and tin, with a variety of other elements present as impurities (Table 3.2). For every kg of initial uranium in fuel, there is 0.12 kg of zircaloy cladding (Goodwin and Mehta, 1994). Therefore, the inventory of elements in the spent fuel zircaloy cladding package includes:

- original zircaloy constituents;
- neutron activation products of these constituents; and
- isotopes arising from radioactive decay of these activation products.

FIGURE 3: NUCLEAR FUEL BUNDLE USED IN CANDU REACTORS



TABLE 3.2: MAXIMUM LIKELY IMPURITY LEVELS IN ZIRCALOY¹
(from Tait *et al.*, 2000)

Element	µg/g Zr	Element	µg/g Zr
Sn	17,000	Fe	2,400
Al	75	Mn	50
B	0.5	Mo	50
Cd	0.7	Ni	70
C	300	Nb	100
Co	20	N ₂	65
Cu	50	Si	120
Hf	100	Ta	200
H ₂	25	Ti	50
Pb	130	W	100
Mg	20	U	3.5
O ₂	1,500	V	50
		Cr	1,300

¹ Zircaloy-4 in fuel bundle, 0.12 kg/kg U.

Considering all the sources of elements in the spent fuel and zircaloy cladding, most of the periodic table is represented, at least in trace quantities, at the time of fuel discharge from the reactor. Many of these elements include radioactive isotopes, and some of these isotopes are very short-lived. As a consequence of radioactive decay, the exact composition of spent fuel changes through time, with some elements decreasing in mass, while others (decay products) may increase in mass.

The elemental composition of fresh nuclear fuel, as given in Table 3.1, does not indicate the chemical form of each element. However, as a sintered metal oxide, the chemical forms present cannot be readily soluble. Similarly, the elements in zircaloy cladding, as given in Table 3.2, are present in a metallic matrix and cannot be readily soluble. Any release of these elements from the waste forms to the surrounding environment will be limited by the slow processes of metal and metal oxide corrosion and dissolution.

Table 3.3 lists the elemental concentrations in spent fuel and zircaloy (as a package), based on burnup calculations by Tait *et al.* (1989) for a fuel that has a burn-up of 190 MWh/kg U and aged 10 years since discharge from the reactor. Due to high levels of radioactivity at the time of discharge and for some time thereafter, it is unlikely that spent fuel would be prepared sooner than this for long-term storage or disposal. The concentrations are expressed per kg of initial uranium in the fuel.

THE CHEMICAL TOXICITY POTENTIAL OF CANDU SPENT FUEL

TABLE 3.3: ELEMENT CONCENTRATIONS IN USED FUEL WASTE - 10 YEARS AFTER BURNUP TO 190 MWh/kg U

Radionuclide		Waste 10 Yr g/kgU ²	Average Granite g/kgGr ³	Radionuclide		Waste 10 Yr g/kgU ²	Average Granite g/kgGr ³	
Symbol	Name			Origin ¹	Symbol			Name
Ac	Actinium	AP	3.87E-12	Nb	Niobium	FP,FI,Z	1.19E-02	2.0E-02
Ag	Silver	FP,FI,Z	2.12E-02	Nd	Neodymium	FP	9.54E-01	4.4E-02
Al	Aluminum	FI,Z	4.50E-04	Ni	Nickel	FI,Z	3.74E-02	5.0E-04
Am	Americium	AP	8.98E-02	Np	Neptunium	AP	3.88E-02	
As	Arsenic	FP	2.99E-05	Os	Osmium	Z	6.77E-05	
At*	Astatine	AP	9.76E-25	P	Phosphorus	FI,Z	7.47E-07	7.0E-01
B	Boron	FI,Z	3.00E-04	Pa	Protactinium	AP	3.20E-08	
Ba	Barium	FP	3.76E-01	Pb	Lead	AP,Z	1.56E-02	2.4E-02
Be	Beryllium	FI,Z	2.51E-07	Pd	Palladium	FP,FI,Z	3.07E-01	5.0E-07
Bi	Bismuth	AP	5.33E-14	Pm*	Promethium	FP	5.88E-03	
Bk*	Berkelium	AP	2.00E-17	Po*	Polonium	AP,Z	1.32E-15	
Br	Bromine	FP	5.32E-03	Pr	Praseodymium	FP	2.69E-01	1.1E-02
Cd	Cadmium	FP,FI,Z	1.32E-02	Pt	Platinum	Z	1.22E-10	5.0E-07
Ce	Cerium	FP	5.76E-01	Pu	Plutonium	AP	3.99E+00	
Cf	Californium	AP	6.34E-14	Ra	Radium	AP	6.40E-11	7.2E-10
Cl	Chlorine	FI ⁺	4.34E-06	Rb	Rubidium	FP	8.03E-02	1.5E-01
Cm	Curium	AP	1.54E-04	Re	Rhenium	Z	5.29E-04	5.6E-07
Co	Cobalt	FI,Z	2.22E-03	Rh	Rhodium	FP,FI,Z	1.55E-01	2.0E-07
Cr	Chromium	FI,Z	1.81E-01	Ru	Ruthenium	FP,FI,Z	5.03E-01	1.0E-06
Cs	Cesium	FP	5.64E-01	S	Sulfur	FI,Z	2.08E-10	2.7E-01
Cu	Copper	FI,Z	2.57E-02	Sb	Antimony	FP,Z	2.20E-03	2.0E-04
Dy	Dysprosium	FP,FI	3.06E-04	Sc	Scandium	FI,Z	3.02E-06	6.9E-03
Er	Erbium	FP,FI	1.44E-05	Se	Selenium	FP	1.31E-02	5.0E-05
Eu	Europium	FP,FI	2.30E-02	Si	Silica	FI,Z	7.34E-02	3.4E+02
F	Fluorine	FI, Z	2.05E-07	Sm	Samarium	FP,FI	2.19E-01	8.5E-03
Fe	Iron	FI,Z	3.88E-01	Sn	Tin	FP,FI,Z	2.59E-01	3.5E-03
Fr*	Francium	AP	1.09E-19	Sr	Strontium	FP,FI,Z	1.81E-01	2.9E-01
Ga	Gallium	FI,Z	4.21E-13	Ta	Tantalum	Z	1.72E-01	3.5E-03
Gd	Gadolinium	FP,FI	1.62E-02	Tb	Terbium	FP,FI	5.31E-04	1.0E-03
Ge	Germanium	FP,FI,Z	9.89E-05	Tc	Technetium	FP,FI	2.05E-01	
Hf	Hafnium	Z	1.24E-02	Te	Tellurium	FP,Z	1.13E-01	5.0E-06
Hg	Mercury	Z	1.11E-20	Th	Thorium	AP	1.52E-06	2.3E-02
Ho	Holmium	FP,FI	4.86E-05	Ti	Titanium	FI,Z	6.00E-03	2.3E+00
I	Iodine	FP,Z	5.71E-02	Ti*	Thallium	AP,Z	2.24E-13	1.1E-03
In	Indium	FP,FI,Z	8.79E-04	Tm	Thulium	FI	9.51E-10	5.4E-04
Ir	Iridium	Z	5.51E-10	U	Uranium	F,AP	9.87E+02	4.4E-03
La	Lanthanum	FP	2.90E-01	V	Vanadium	FI,Z	6.23E-03	7.2E-02
Li	Lithium	FI,Z	4.67E-05	W	Tungsten	Z	1.50E-02	1.5E-03
Lu	Lutetium	Z	1.21E-05	Y	Yttrium	FP,FI,Z	1.06E-01	3.3E-02
Mn	Manganese	FI,Z	1.56E-02	Yb	Ytterbium	FI,Z	1.08E-10	3.3E-03
Mo	Molybdenum	FP,Z	8.03E-01	Zn	Zinc	FI,Z	1.33E-04	5.2E-02
Na	Sodium	FI,Z	3.35E-08	Zr	Zirconium	FP,FI,Z	1.18E+02	2.4E-01

* Greatest half life <10 years.

+ There may be additional Cl associated with zircaloy and activation of graphite on UO₂ pellets (Johnson and Tait, 1992).

¹ AP = activation product, FP = fission product, FI = fuel impurity, Z = zircaloy, bold = main source.

² Concentration in spent fuel waste (includes cladding) at 10 years (Tait et al., 1989).

³ Concentration in average granite (Bowen, 1979; Faure, 1998).

Example:

Aluminum is present in granite at about 74 grams per kilogram of granite (7.4E+01 g/kg Gr). The concentration present in the waste package is less than 1/100,000th of this. Therefore, replacing granite with the waste reduces the local concentration of aluminum.

More recent calculations by Tait *et al.* (2000) show spent fuel composition for a range of burnup rates. However, the average burnup rate over the 1987-1999 period for Ontario's power reactors (about 200 MWh/kg U) is very similar to the rate used in the earlier calculations (190 MWh/kg U). The new results for average burnup do not differ substantially from earlier data, except for the fact that Tait *et al.* (2000) have included a large number of "unspecified" elements such as fuel impurities. These are elements that have neither been detected in fuel nor listed in manufacturer's specifications, but are conservatively assumed to be present at upper limit concentrations based on natural abundance in source minerals.

It should be recognized that the trace elemental composition of spent fuel and associated cladding material will be dependant upon the chemical composition of the material used to contain the fuel (cladding) and its trace elemental composition as well as the degree of "burnup" achieved for the fuel. The nuclear power industry in striving for increased efficiency and safety is continually looking for ways to increase the power generated from each fuel bundle. As new reactor and fuel design improve efficiency and safety it is possible that the elemental composition of the spent fuel produced will change. Any safety assessment of a long term spent fuel management system must consider the level of burnup in the fuel to be managed as well as the composition of the cladding containing the spent fuel.

The element concentrations in the spent fuel waste produced by operation of CANDU reactors are compared to average concentrations of the same elements in granite (Bowen, 1979; Faure, 1998). It is reasonable to conclude that elements present in spent fuel waste at concentrations below those in natural granite are of little concern with respect to chemical toxicity. The waste forms are not expected to be more leachable than trace elements contained in granite, and the emplacement of the waste in granite rock, as may be carried out in a deep geological disposal context, or in concrete as may occur with long-term surface storage, will result in some level of dilution of available concentrations of these elements in nearby environmental media.

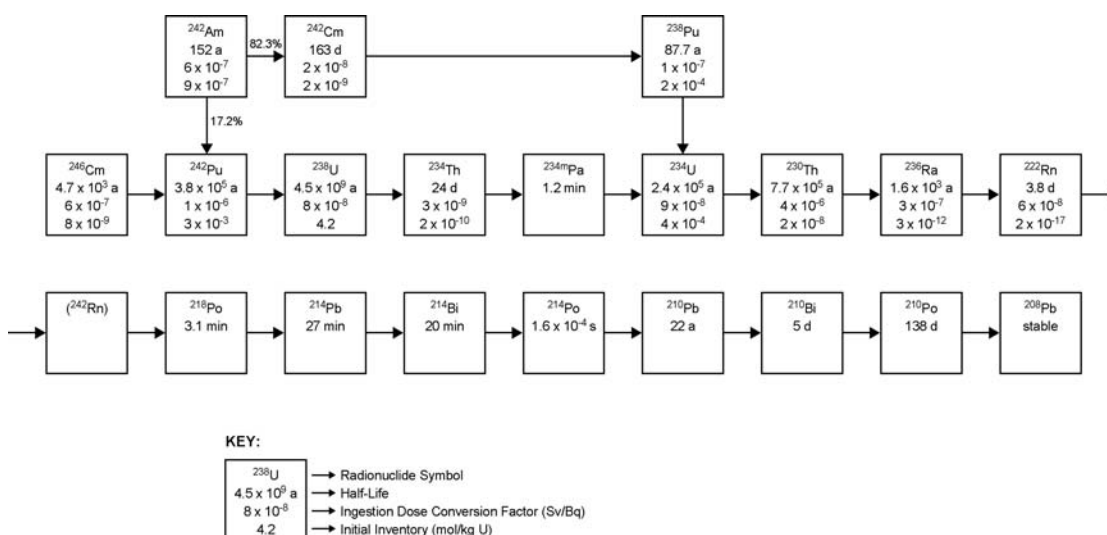
A number of elements present in spent fuel and/or zircaloy cladding are omitted from Table 3.3. These include noble gases, elements of life, and some common nutrients. The noble gases omitted are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). Because of their inert nature, these elements cannot react with body tissues and cannot produce chemical toxicity. The elements of life omitted are carbon (C), hydrogen (H), oxygen (O) and nitrogen (N). As the building blocks of biological tissue, abundant in the environment, it is most unlikely that these elements could be released from waste at harmful concentrations. The common nutrients omitted are calcium (Ca), potassium (K) and magnesium (Mg). These elements are abundant in biological tissues and the environment, and are integral to the biochemical processes of life. Again, it is most unlikely they could be released from waste at harmful concentrations.

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Some of the elements present in spent fuel and/or zircaloy cladding are present only as short-lived isotopes, with half-lives of less than 10 years. Groundwater transit

times from a deep geological repository to the surface environment and any significant release from a secure surface storage site are expected to be on the order of a minimum of hundreds of years. Therefore, isotopes with a half-life of ten years or less are unlikely to reach the surface environment, unless supported by ongoing ingrowth from parent isotopes that are also in transit. For example, polonium (Po-210) in the U-238 decay chain (Figure 4) has a half-life of 138 days. If separated from its long-lived parent (Pb-210), a quantity “x” of Po-210 will be reduced to 0.031 “x” after almost 2 years (5 half-lives) and to 1.1×10^{-8} “x” after 10 years.

FIGURE 4: RADIOACTIVE DECAY SERIES FOR U-238
(from Goodwin and Mehta, 1994)



Elements that are present only as short-lived isotopes (as defined above) include astatine (At), francium (Fr), polonium (Po), berkelium (Bk) and promethium (Pm). It is likely that any transport of these elements to the surface environment and resulting concentrations in environmental media would be limited by the mobility and concentration of parental isotopes in the surrounding environment. Short-lived elements that are unsupported by parents (e.g., Bk, Pm) are unlikely to persist long enough to ever be transported to the surface environment.

Most of the elements listed in Table 3.3, if their concentrations in waste change through time as a result of radioactive decay, will not increase in concentration beyond concentrations found in spent fuel 10 years after removal from the reactor. Many elements will decrease substantially through time. However, some will increase in concentration as a result of ingrowth from parental isotopes. The elements that are expected to substantially increase at source beyond 10 years after removal from the reactor are actinium (Ac), astatine (At), francium (Fr), polonium (Po), protactinium (Pa), lead (Pb), bismuth (Bi), radium (Ra), thorium (Th), thallium (Tl), niobium (Nb) and mercury (Hg). Most of these elements are involved in the

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decay chains of one or more uranium isotopes, and will grow in as a result of uranium decay. The end products of these decay chains are either stable lead (Pb) or bismuth (Bi). The vast majority of uranium present in fuel will decay eventually to stable lead. Niobium (Nb) is an end product of the decay of zirconium (Zr-93) and molybdenum (Mo-93). Its increase beyond 10 years is mainly due to zirconium decay. Mercury (Hg) increases through time by decay of trace activation products in zircaloy.

Table 3.4 shows the concentrations through time in spent fuel with zircaloy cladding, for the elements that increase beyond the ten-year timeframe. These concentrations are compared to the corresponding concentrations in typical granite (Bowen, 1979; Faure, 1998). The elements that did not exceed the granite background at Year 10, but do exceed later, include bismuth (Bi), lead (Pb), niobium (Nb), radium (Ra) and thorium (Th).

TABLE 3.4: CONCENTRATIONS THROUGH TIME FOR ELEMENTS THAT INCREASE IN USED FUEL WASTE

Radionuclide Symbol	Name	Origin ¹	Concentration in Waste at Time (g/kgU) ²					Average Granite g/kgGr ³
			10 Yr	10 ² Yr	10 ³ Yr	10 ⁴ Yr	10 ⁶ Yr	
Ac	Actinium	AP	3.87E-12	9.61E-11	1.28E-09	1.36E-08	1.43E-07	
At*	Astatine	AP	9.76E-25	4.58E-23	1.05E-20	1.63E-18	8.92E-17	
Bi	Bismuth	AP	5.33E-14	1.07E-12	1.96E-09	3.66E-06	5.14E-02	6.5E-05
Fr*	Francium	AP	1.09E-19	2.90E-18	1.28E-16	1.52E-14	8.14E-13	
Hg	Mercury	Z	1.11E-20	1.05E-19	1.04E-18	1.04E-17	1.04E-15	8.0E-05
Nb	Niobium	FP,FI,Z	1.19E-02	1.20E-02	1.21E-02	1.28E-02	7.97E-02	2.0E-02
Pa	Protactinium	AP	3.20E-08	2.08E-07	1.99E-06	2.08E-05	2.16E-04	
Pb	Lead	AP,Z	1.56E-02	1.56E-02	1.56E-02	1.56E-02	1.43E-01	2.4E-02
Po*	Polonium	AP,Z	1.32E-15	6.58E-13	1.11E-10	4.46E-09	7.51E-08	
Ra	Radium	AP	6.40E-11	5.39E-09	5.05E-07	2.03E-05	3.41E-04	7.2E-10
Th	Thorium	AP	1.52E-06	1.47E-05	1.56E-04	1.63E-03	6.83E-02	2.3E-02
Tl	Thallium	AP,Z	2.24E-13	2.16E-12	2.16E-11	2.16E-10	2.11E-08	1.1E-03

* Greatest half life <10 years.

¹ AP = activation product, FP = fission product, FI = fuel impurity, Z = zircaloy, bold = main source.

² Concentration in spent fuel waste at 10 years following a burnup to 190 MWh/kg U (Tait *et al.*, 1989).

³ Concentration in average granite (Bowen, 1979; Faure, 1998).

It is interesting to note that the ingrowth shown in Table 3.4 can be masked by assuming high levels of these elements to be initially present in fresh fuel. For example, when Tait *et al.* (2000) assume mercury (Hg) to be initially present in fuel at 1 g/kg U, the ingrowth of Hg to levels on the order of 10⁻¹⁵ g/kg U cannot be seen.

4.0 ASSESSING TOXICITY OF SPENT FUEL

Our concerns about toxicity are usually focussed on the surface environment (biosphere) where most life exists. This includes the surface waters, upper soil and sediment layers, and the atmosphere near ground level. It does not include the deeper geological environment (geosphere) where life is generally absent, with the possible exception of deep-dwelling microbial species.

The potential for toxicity in the surface environment, as a result of release from a spent fuel repository, can only be judged in terms of potential concentrations of constituent elements as they may appear in the surface environment at some time in the future. At a screening level, simple but very conservative approaches can be used to estimate upper limit concentrations that may potentially appear in the surface environment. These are hypothetical worst-case scenarios. These concentrations can then be compared to environmental guideline concentrations or benchmarks based on element toxicity. The overall screening assessment process is illustrated in Figure 1 and the conceptual model for estimating concentrations in environmental media is illustrated in Figure 2.

As a first step, we can estimate upper limit concentrations of each element in the groundwater of an underground vault, in the case of deep geological disposal, or in the groundwater that may underlie a long-term surface storage facility following a failure at some point in the future. In the case of deep geological disposal, the vault must fill with groundwater after work underground is completed. Based on a previous Environmental Impact Statement (AECL, 1994), a vault footprint of 2 km x 2 km, with a ceiling height of 9 to 10 m, was anticipated. Rock pillars left to support the vault ceiling would comprise 75% of the nominal volume. The vault would be backfilled with bentonite clay and possibly crushed rock following waste emplacement. Depending on the backfill mixture, average porosity might vary from 0.1 to 0.4. Assuming an average porosity of 0.3 for backfill material, the groundwater volume in this vault would be $40 \text{ million m}^3 \times 0.25 \times 0.3 = 3 \text{ million m}^3$. The vault was designed to contain up to 190 million kg of uranium. Therefore, an upper bound element concentration in groundwater can be estimated as concentration in waste (per kg U) $\times 200 \text{ million kg U} \div 3 \text{ million m}^3$ of groundwater. This imagines the total inventory to be dissolved in the vault groundwater, i.e., released faster than the groundwater transit time through the vault.

Conceptually, the same process could be considered for a surface storage repository where the structural integrity fails and there are extreme conditions, which result in dissolution of the constituents of the spent fuel and their leaching to the groundwater underlying the site. In this situation, we would anticipate lower source area concentrations due to higher groundwater flow volumes, but probably similar loadings of contaminants from groundwater to downgradient surface waters. Total inventory concentrations in groundwater are very conservative for either case.

For some less soluble elements, the concentration suggested by this approach would be virtually impossible to achieve. Goodwin *et al.* (1987) have estimated limits to solubility in groundwater based generally on assumptions of oxide or hydroxide solid phases. Generic molar solubilities were assumed for “very soluble” or “insoluble” elements where specific solubility data were lacking. We have also considered how much of the fuel or zircaloy matrix (U^{+4} or Zr^0) could conceivably be oxidized to a more soluble form (U^{+6} or Zr^{+4}) if the groundwater was initially rich in oxygen (say 10 mg/L O_2). All elements would then be released in proportion to U or Zr, depending on which matrix they are primarily found in. We imagine the groundwater source to be either at this “oxidation limit”, or at the assumed solubility limit (not to exceed the total inventory concentration), whichever concentration is higher. This assumption would also cover the case that may exist in waters infiltrating a degrading surface storage facility.

It is likely that the kinetics of chemical release from spent fuel waste would be so slow in relation to groundwater transit time through the vault that the assumed concentration limits would not be realized. However, site-specific factors must be considered to demonstrate that this is the case. We ignore the kinetics at this screening level, ensuring an evaluation that is conservative for all reasonable storage or disposal concepts.

In order to influence the surface environment, waste constituents must travel with the groundwater through the granite pore spaces and/or fractures, to a downgradient point of discharge or extraction, e.g., to a surface stream or a drinking water well. In reality, this must be a slow process, with considerable dispersion/dilution along the groundwater flow path. For a deep geological flow path, with groundwater transit times on the order of 10,000 years, many of the radioactive elements would decay substantially prior to reaching the surface. Different elements would travel at different rates according to their adsorptive properties. None could travel faster than groundwater, and many would travel much more slowly as a result of this differential retardation. Goodwin and Mehta (1994) have estimated retardation/decay factors for isotopes of each element, based on a conservatively assumed groundwater path length of 25 m. The actual concept for deep geologic disposal involves a vault depth that is more than ten times this distance whereas, for a degrading surface storage facility, a 25-m path length may be considered as conservatively reasonable.

For screening purposes in this assessment, we ignore dispersion, retardation and decay along the groundwater flow path, and imagine vault water, based on element inventory at any given time period, reaching a surface stream or well. The well (vault) water is compared to drinking water guidelines. A modest dilution is assumed in the surface stream, based on relative groundwater and stream flow volumes. Groundwater flow is estimated using a conservative velocity of 3×10^{-11} m/s x the vault footprint area (4 million m^2) x the pillar-free fraction of 0.25. This velocity value is suggested by Davison *et al.* (1994) as a maximum for sparsely fractured rock. Stream flow is estimated at 0.03 m^3/s , a minimum base flow for good trout stream habitat (Flint, 2003). The resulting dilution factor (groundwater flow/stream flow) is

approximately 1×10^{-3} , and is used to estimate concentrations in a stream from concentrations in vault water. The stream water is compared to surface water guidelines, which are designed to protect aquatic life.

Drinking water and surface water guideline values were taken where possible from the Canadian Council of Ministers of the Environment (CCME, 1999). Drinking water guidelines were also taken from the U.S. EPA (2003) Region III Risk-based Criteria tables. Surface water guidelines were also taken from the Ontario Ministry of Environment and Energy (MOEE, 1994), and from the Oak Ridge National Laboratory (ORNL) screening benchmarks for water (Suter and Tsao, 1996, Secondary Chronic Values). The latter are derived using conservative methods (safety factors) when the database of effect and no-effect levels is considered to be limited.

Element concentrations in soil and sediment were estimated from the assumed vault water concentrations, or surface water concentrations, using soil/water partition coefficients (K_d) from Sheppard *et al.* (1992) and Sheppard and Thibault (1990). The highest of the geometric mean values for clay or loam soil were used. Values for aquatic sediments were assumed to be ten times higher than terrestrial soil values. There is typically greater partitioning of contaminants to sediment solids as a result of the greater water content or lower solids concentration (O'Conner and Connolly, 1980). Where partitioning has been measured in sediments, differences of approximately an order of magnitude are suggested, as compared to soil values. Estimated concentrations in soil and sediment were compared to soil and sediment quality guidelines.

Soil and sediment quality guideline values were taken where possible from the CCME (1999). The uranium value for soil is a draft CCME guideline. Sediment quality guidelines were also taken from the Ontario MOEE (1993) Lowest Effect Levels. The cobalt value is a dredge spoil disposal guideline that has been considered to be an LEL (MOE, 1997). Both federal and provincial sediment guidelines are designed to be protective of bottom-dwelling aquatic organisms. Soil quality guidelines were also taken from the ORNL screening benchmarks for protection of soil organisms (Efroymsen *et al.*, 1997a,b), and from the Oregon Department of Environmental Quality (ODEQ, 1998). The CCME soil guidelines are based on protection of either human health or soil-dwelling organisms, whichever produces the lowest guideline.

Element concentrations in air were generally estimated from a Canadian average particulate concentration in air of $5.9 \times 10^{-8} \text{ kg/m}^3$ (Amiro, 1992) assuming that all this dust load is contaminated soil. The particulate concentrations at isolated Canadian Shield sites are typically about one-third of this value. A few elements of interest, based on molecular vapour pressure, are potentially released as gases (e.g., F, Cl, Br). However, these elements could not exist long as gases due to their high reactivity which favours the ionic form. Gaseous release of toxic chemicals from soil to air was not considered likely to occur.

Air quality guideline values were taken where possible from the MOE (2001) Ambient Air Quality Criteria (lowest values). These values are not to be exceeded by any 24-hr sample, except in the case of lead, where the lowest value is expressed as a 30-day average. The guidelines used are based on protection of human health or vegetation, whichever produces the lowest guideline. Air quality guidelines were also taken from the U.S. EPA (2003) Region III Risk-based Criteria tables, in some cases where the MOE has not defined a guideline based on chemical toxicity.

Based on these very conservative screening procedures, a number of elements in spent fuel waste can be recognized as potentially of concern from a chemical toxicity perspective. These are elements that may warrant further attention in the safety assessment for the spent fuel long-term management concept, based on more realistic evaluations incorporating site-specific and/or concept-specific information.

Table 4.1 shows the estimated environmental concentrations (including groundwater) in relation to relevant guideline values (Table 4.2), for all elements that are either more concentrated in spent fuel waste than in granite, or not known to be less concentrated (granite values are unavailable for some elements). The environmental concentrations shown are derived from 10-year-old spent fuel, except for elements that have higher concentrations based on older fuel as a consequence of decay of parent radionuclides. In these cases, the maximum concentrations for a 1,000,000-year timeframe are shown.

The elements of potential concern include uranium (U), zirconium (Zr), cadmium (Cd), chromium (Cr), molybdenum (Mo), antimony (Sb), cobalt (Co), nickel (Ni) and lead (Pb), based on groundwater and/or surface water concentrations. All these elements were also of potential concern based on soil concentrations, and some were of potential concern with respect to sediment or air concentrations. In addition, niobium (Nb), technetium (Tc), iodine (I), bromine (Br), tungsten (W), tin (Sn) and lanthanum (La) were identified, based only on soil exposure. Groundwater discharge directly to surface soil (rather than via water) is a particularly conservative scenario. If it occurs, it would be confined to seeps near a watercourse. Elements identified as a potential concern in air (via soil dust) included uranium (U), molybdenum (Mo), cobalt (Co), lead (Pb) and nickel (Ni). The screening assessment for air shares the conservatism inherent in the groundwater to soil scenario.

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TABLE 4.1: ESTIMATED ENVIRONMENTAL CONCENTRATIONS COMPARED TO GUIDELINE VALUES FOR ELEMENTS THAT EXCEED GEOLOGICAL BACKGROUND IN SPENT FUEL WASTE

Radionuclide Symb Name	Origin	Limit ¹ in Groundwater mg/L	Oxidation Limit ² mg/L	Surface Water ³ mg/L	Sediment Kd L/kg	Sediment Conc. ⁴ mg/kg	Soil Conc. ⁵ mg/kg	Air Conc. ⁶ mg/m ³	
Ac Actinium	AP	2.58E-07	**	2.16E-08	2.58E-10	24000	6.19E-06	6.19E-04	3.65E-11
Ag Silver	FP,FI,Z	2.16E-04		3.20E-03	3.20E-06	1800	5.75E-03	5.75E-01	3.39E-08
Am Americium	AP	4.86E-04		1.35E-02	1.35E-05	81000	1.10E+00	1.10E+02	6.47E-06
At Astatine	AP	6.51E-20	**	1.34E-17	1.34E-20	100	1.34E-18	1.34E-16	7.93E-24
Bi Bismuth	AP	3.55E-09	**	7.75E-03	7.75E-06	6000	4.65E-02	4.65E+00	2.74E-07
Bk Berkelium	AP	1.33E-12	*	3.01E-18	1.33E-15				
Br Bromine	FP	3.55E+02		8.02E-04	3.55E-01	750	2.66E+02	2.66E+04	1.57E-03
Cd Cadmium	FP,FI,Z	7.87E-01		1.98E-03	7.87E-04	5600	4.41E+00	4.41E+02	2.60E-05
Ce Cerium	FP	1.12E+04		8.68E-02	1.12E+01	200000	2.24E+06	2.24E+08	1.32E+01
Cf Californium	AP	4.23E-09	*	9.55E-15	4.23E-12				
Cm Curium	AP	1.03E+01	*	2.32E-05	1.03E-02	180000	1.85E+03	1.85E+05	1.09E-02
Co Cobalt	FI,Z	1.48E+02	*	5.36E-04	1.48E-01	13000	1.93E+03	1.93E+05	1.14E-02
Cr Chromium	FI,Z	5.20E-01		4.35E-02	5.20E-04	15000	7.80E+00	7.80E+02	4.60E-05
Cs Cesium	FP	3.76E+04	*	8.50E-02	3.76E+01	44000	1.65E+06	1.65E+08	9.76E+00
Cu Copper	FI,Z	2.54E-02		3.88E-03	2.54E-05	365	9.27E-03	9.27E-01	5.47E-08
Eu Europium	FP,FI	4.56E-01		3.47E-03	4.56E-04	6530	2.98E+00	2.98E+02	1.76E-05
Fr Francium	AP	7.27E-15	**	1.23E-13	1.23E-16	2450	3.01E-13	3.01E-11	1.77E-18
Gd Gadolinium	FP,FI	1.57E-01		2.44E-03	1.57E-04	5240	8.24E-01	8.24E+01	4.86E-06
Hf Hafnium	Z	7.14E-07		2.98E-03	2.98E-06	24000	7.15E-02	7.15E+00	4.22E-07
I Iodine	FP,Z	3.81E+03	*	8.61E-03	3.81E+00	45	1.71E+02	1.71E+04	1.01E-03
In Indium	FP,FI,Z	5.86E+01	*	1.33E-04	5.86E-02	14800	8.67E+02	8.67E+04	5.12E-03
La Lanthanum	FP	1.93E+04	*	4.37E-02	1.93E+01	8760	1.69E+05	1.69E+07	9.99E-01
Mo Molybdenum	FP,Z	5.35E+04	*	1.21E-01	5.35E+01	1250	6.69E+04	6.69E+06	3.95E-01
Nb Niobium	FP,FI,Z	9.29E-05	+	1.92E-02	1.92E-05	33000	6.34E-01	6.34E+01	3.74E-06
Nd Neodymium	FP	6.36E+04	*	1.44E-01	6.36E+01				
Ni Nickel	FI,Z	1.17E+03		5.64E-03	1.17E+00	6500	7.63E+03	7.63E+05	4.50E-02
Np Neptunium	AP	2.37E-05		5.85E-03	5.85E-06	550	3.22E-03	3.22E-01	1.90E-08
Os Osmium	Z	1.90E-04	+	1.63E-05	1.90E-07	4450	8.46E-04	8.46E-02	4.99E-09
Pa Protactinium	AP	2.31E-04	+	3.26E-05	2.31E-07	27000	6.24E-03	6.24E-01	3.68E-08
Pb Lead	AP,Z	2.07E+02		3.45E-02	2.07E-01	160000	3.32E+04	3.32E+06	1.96E-01
Pd Palladium	FP,FI,Z	1.06E-04		4.62E-02	4.62E-05	2700	1.25E-01	1.25E+01	7.36E-07
Pm Promethium	FP	3.92E+02	*	8.86E-04	3.92E-01	6530	2.56E+03	2.56E+05	1.51E-02
Po Polonium	AP,Z	8.80E-11	**	1.13E-08	1.13E-11	30000	3.40E-07	3.40E-05	2.00E-12
Pr Praseodymium	FP	4.23E+03		4.05E-02	4.23E+00	5540	2.34E+04	2.34E+06	1.38E-01
Pu Plutonium	AP	2.44E-04		6.01E-01	6.01E-04	49000	2.95E+01	2.95E+03	1.74E-04
Ra Radium	AP	1.13E-01	+	4.73E-05	1.13E-04	360000	4.07E+01	4.07E+03	2.40E-04
Re Rhenium	Z	3.53E+01	*	1.28E-04	3.53E-02	600	2.12E+01	2.12E+03	1.25E-04
Rh Rhodium	FP,FI,Z	1.03E-04		2.34E-02	2.34E-05	2260	5.28E-02	5.28E+00	3.11E-07
Ru Ruthenium	FP,FI,Z	1.01E-04		7.58E-02	7.58E-05	9900	7.50E-01	7.50E+01	4.43E-06
Sb Antimony	FP,Z	7.90E+00		3.32E-04	7.90E-03	2400	1.90E+01	1.90E+03	1.12E-04
Se Selenium	FP	7.90E-05		1.97E-03	1.97E-06	1500	2.95E-03	2.95E-01	1.74E-08
Sm Samarium	FP,FI	1.50E+00		3.29E-02	1.50E-03				
Sn Tin	FP,FI,Z	1.19E-04		6.24E-02	6.24E-05	6700	4.18E-01	4.18E+01	2.47E-06
Ta Tantalum	Z	1.81E-04		4.15E-02	4.15E-05	12000	4.98E-01	4.98E+01	2.94E-06
Tc Technetium	FP,FI	4.85E+00		3.09E-02	4.85E-03	12	5.82E-02	5.82E+00	3.43E-07
Te Tellurium	FP,Z	1.28E-03		1.70E-02	1.70E-05	7200	1.22E-01	1.22E+01	7.20E-07
Th Thorium	AP	6.96E-05	+	1.03E-02	1.03E-05	54000	5.56E-01	5.56E+01	3.28E-06
U Uranium	F,AP	2.38E-05		148.8	1.49E-01	15000	2.23E+03	2.23E+05	1.32E-02
W Tungsten	Z	1.00E+03	*	3.62E-03	1.00E+00	1480	1.48E+03	1.48E+05	8.73E-03
Y Yttrium	FP,FI,Z	7.07E+03	*	1.60E-02	7.07E+00	10000	7.07E+04	7.07E+06	4.17E-01
Zr Zirconium	FP,FI,Z	4.56E-06		28.5	2.85E-02	33000	9.41E+02	9.41E+04	5.55E-03

Exceeds relevant environmental guideline.

* Limit defined by vault inventory and volume, solubility limit is higher; + indicates million yr value.

¹ Limit based on solubility of oxide or hydroxide solids, or vault inventory and volume.

² Limit defined by oxidation of UO₂ or Zr, assuming 10mg/L O₂ in water.

³ Highest limit in groundwater, with conservative dilution factor.

⁴ Based on partitioning from surface water.

⁵ Based on partitioning from groundwater.

⁶ Based on dust levels in air.

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TABLE 4.2: ENVIRONMENTAL GUIDELINE VALUES USED IN SCREENING OF ESTIMATED ENVIRONMENTAL CONCENTRATIONS

Radionuclide Symbol	Name	Origin	Environmental Guideline Values ^{1, 2, 3, 4, 5, 6}				Air mg/m ³	
			S. Water mg/L	Drinking W. mg/L	Sediment mg/kg	Soil mg/kg		
Ac	Actinium	AP						
Ag	Silver	FP,FI,Z	0.0001	0.18 ⁺		20	0.001	H
Am	Americium	AP						
At	Astatine	AP						
Bi	Bismuth	AP				120000 ^x	E	
Bk	Berkelium	AP						
Br	Bromine	FP				10 ^x	E	0.02
Cd	Cadmium	FP,FI,Z	0.000017	0.005	0.6	1.4	H	0.002
Ce	Cerium	FP						
Cf	Californium	AP						
Cm	Curium	AP						
Co	Cobalt	FI,Z	0.05	0.73 ⁺	50 ⁺	40		0.0001
Cr	Chromium	FI,Z	0.0089	0.05	37.3	64	E	0.0015
Cs	Cesium	FP						
Cu	Copper	FI,Z	0.002	1	35.7	63	E	0.05
Eu	Europium	FP,FI						
Fr	Francium	AP						
Gd	Gadolinium	FP,FI						
Hf	Hafnium	Z						
I	Iodine	FP,Z				4 ^x	E	
In	Indium	FP,FI,Z						
La	Lanthanum	FP				50 ^x	E	
Mo	Molybdenum	FP,Z	.01-.05	0.18 ⁺		5		0.018 ⁺
Nb	Niobium	FP,FI,Z				10 ⁺	E	
Nd	Neodymium	FP						
Ni	Nickel	FI,Z	.025-.15	0.73 ⁺	16 ⁺	50	E	0.002
Np	Neptunium	AP						
Os	Osmium	Z						
Pa	Protactinium	AP						
Pb	Lead	AP,Z	.001-.007	0.01	35	70	E	0.0007
Pd	Palladium	FP,FI,Z						0.01
Pm	Promethium	FP						
Po	Polonium	AP,Z						
Pr	Praseodymium	FP						
Pu	Plutonium	AP						
Ra	Radium	AP						
Re	Rhenium	Z						
Rh	Rhodium	FP,FI,Z						
Ru	Ruthenium	FP,FI,Z						
Sb	Antimony	FP,Z	0.02 ⁺	0.006		20		0.025
Se	Selenium	FP	0.001	0.010		1	E	0.01
Sm	Samarium	FP,FI						
Sn	Tin	FP,FI,Z	0.073 ^x	22 ⁺		5		2.2 ⁺
Ta	Tantalum	Z						
Tc	Technetium	FP,FI				0.2 ^x	E	
Te	Tellurium	FP,Z				1440 ^x	E	0.01
Th	Thorium	AP						
U	Uranium	F,AP	0.01	0.02		10	H	0.00048
W	Tungsten	Z				400 ^x		
Y	Yttrium	FP,FI,Z						
Zr	Zirconium	FP,FI,Z	0.004 ⁺			11 ⁺	E	

¹ Surface water values from CCME, plus MOE (+) or ORNL (x).

² Drinking water values from CCME, plus EPA Region III (+).

³ Sediment values from CCME, plus MOE (+).

⁴ Soil values from CCME, plus ODEQ (+) or ORNL (x).

⁵ Air values from MOE, plus EPA Region III (+).

⁶ E = ecological, H = health, V = vegetation.

Chemical toxicity data were lacking for a number of elements potentially present at mg/L concentrations in vault water. These elements, including cesium (Cs), yttrium (Y), samarium (Sm), cerium (Ce), indium (In), tantalum (Ta), promethium (Pm), rhenium (Re), curium (Cm), praseodymium (Pr) and neodymium (Nd), may or may not be of concern with respect to chemical toxicity. Some of these elements (e.g., Cs) have been well studied but are considered to be primarily radiotoxic. Thus, benchmarks for chemical toxicity (as distinct from radiotoxicity) are not useful and would be difficult to define. Other elements (e.g., Pm) are present only as short-lived isotopes and are most unlikely to reach the biosphere. In other cases, toxicity studies might be useful.

5.0 SUMMARY AND CONCLUSIONS

The main conclusion that can be drawn from this high level screening assessment is that there are elements in spent nuclear fuel and zircaloy cladding that are of potential concern from a chemical toxicity perspective in a long-term storage or disposal scenario. This conclusion is based on a series of simple conservative assumptions, which are probably unrealistic (overly conservative) in the circumstances of a particular storage/disposal concept or plan. It will be important to demonstrate, through more detailed analyses, carried out as a part of the safety assessment of any particular proposal, whether there are realistic concerns regarding chemical toxicity and the specific nature of these concerns.

Table 5.1 shows the summary list of elements that should probably be addressed as to chemical toxicity in such a safety assessment. The elements are arranged here in priority classes, based on the degree to which our conservative estimates of exposure concentrations exceed relevant guideline values.

TABLE 5.1: ELEMENTS OF POTENTIAL ENVIRONMENTAL CONCERN TO BE CONSIDERED IN SAFETY ASSESSMENTS

Level of Priority	Drinking Water and/or Surface Water	Sediment Impacted by Surface Water	Soil at Point of Groundwater Discharge	Air at Point of Discharge to Soil
1	Molybdenum (Mo) Lead (Pb)	-	Molybdenum (Mo) Lanthanum (La) ² Lead (Pb) Uranium (U) Nickel (Ni)	-
2	Uranium (U) Nickel (Ni) Antimony (Sb) ¹	-	Zirconium (Zr) Cobalt (Co) Iodine (I) ² Bromine (Br) ²	-
3	Cobalt (Co) Cadmium (Cd)	Lead (Pb) Nickel (Ni)	Tungsten (W) ² Cadmium (Cd)	Lead (Pb) Cobalt (Co)
4	Chromium (Cr)	Chromium (Cr)	Antimony (Sb) Technetium (Tc) ² Chromium (Cr)	Uranium (U) Nickel (Ni) Molybdenum (Mo)
5	Zirconium (Zr)	Cadmium (Cd)	Tin (Sn) ² Niobium (Nb) ²	-

¹ Concern based only on use of undiluted groundwater as drinking water (not on impairment of surface water).

² Concern based only on soil contamination by groundwater; no concerns identified for other media.

The more site-specific and/or concept-specific data are available, the more realistic these fate and transport models can be. Geochemical and hydrogeological processes should be considered, and the spatial aspects of exposure in the surface environment may also be considered.

Given that the same processes are involved in transport of stable elements and radionuclides, that both may be chemically toxic, and that most of the mass of spent fuel waste (U-238) is more chemically toxic than radiotoxic, it may be expected that the level of effort devoted to assessment of chemical toxicity issues, especially over long time periods after significant radioactive decay has occurred, would be similar to the effort involved in assessment of radiotoxicity. Demonstration of radiological safety does not necessarily imply that there are no chemical toxicity issues.

6.0 REFERENCES

- Atomic Energy of Canada Limited (AECL). 1994. Environmental Impact Statement on the Concept for Disposal of Canada's Nuclear Fuel Waste. Atomic Energy of Canada Limited Report, AECL-10711, COG-93-1.
- Amiro, B.D. 1992. The Atmosphere Submodel for the Assessment of Canada's Nuclear Fuel Waste Management Concept. Atomic Energy of Canada Limited Report, AECL-9889, COG-91-199.
- Bowen, H.J. 1979. Environmental Chemistry of the Elements. Academic Press Inc., London.
- Canadian Council of Ministers of the Environment (CCME). 1999. Canadian Environmental Quality Guidelines.
- Davison, C.C., T. Chan, A. Brown, M. Gascoyne, D.C. Kamineni, G.S. Lohda, T.W. Melnyk, N.W. Scheier, N.M. Soonawala, F.W. Stanchell, D.R. Stevenson, G.A. Thorne, S.H. Whitaker, T.T. Vandergraaf and P. Vilks. 1994. The disposal of Canada's nuclear fuel waste: The geosphere model for postclosure assessment. Atomic Energy of Canada Limited Report, AECL-10719, COG-93-9.
- Efroymsen, R.A., M.E. Will and G.W. Suter, II. 1997a. Toxicological Benchmarks for Contaminants of Potential Concern for Effects on Soil and Litter Invertebrates and Heterotrophic Process: 1997 Revision. ES/ER/TM-126/R2. Report prepared for the U.S. Department of Energy.
- Efroymsen, R.A., M.E. Will, G.W. Suter, II and A.C. Wooten. 1997b. Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Terrestrial Plants: 1997 Revision. ES/ER/TM-85/R3. Report prepared for the U.S. Department of Energy.
- Faure, G. 1998. Principles and Applications of Geochemistry. 2nd Ed. Prentice Hall Inc., Upper Saddle River, New Jersey.
- Flint, S. 2003. Stream Health Index: an integrated streamflow and water quality index for small streams of the Assabet River watershed, Eastern Massachusetts.
- Goodwin, B.W. and K.K. Mehta. 1994. Identification of Contaminants of Concern for the Postclosure Assessment of the Concept for the Disposal of Canada's Nuclear Fuel Waste. Atomic Energy of Canada Limited Report, AECL-10901, COG-93-265.
- Goodwin, B.W., N.C. Garisto and J.W. Barnard. 1987. An Assessment of the Long-Term Impact of Chemically Toxic contaminants from the Disposal of Nuclear Fuel Waste. Atomic Energy of Canada Limited Report, AECL-8367.

- Johnson, L.H. and J.C. Tait. 1992. Source terms for ^{36}Cl in the assessment of used fuel disposal. *In*: Unpublished Documents Cited in the EIS and Primary References. Atomic Energy of Canada Limited Technical Record, TR-567, COG-92-27.
- O'Conner, D.J. and J.P. Connolly. 1980. The effect of concentration of adsorbing solids on the partition coefficient. *Water Res.* 14: 1517-1523.
- Ontario Ministry of the Environment (MOE). 1993. Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario.
- Ontario Ministry of the Environment (MOE). 1994. Water Management. Policies, Guidelines, Provincial Water Quality Objectives of the Ministry of Environment and Energy.
- Ontario Ministry of the Environment (MOE). 1997. Guideline for Use at Contaminated Sites in Ontario.
- Ontario Ministry of the Environment (MOE). 2001. Summary of Point of Impingement Standards, Point of Impingement Guidelines, and Ambient Air Quality Criteria (AAQCs).
- Oregon Department of Environmental Quality (ODEQ). 1998. Guidance for Ecological Risk Assessment.
- Sheppard, M.I. and D.H. Thibault. 1990. Default soil solid/liquid partition coefficients K_{ds} , for four major soil types: a compendium. *Health Physics* 59: 471-482.
- Sheppard, S.C., C. Gaudet, M.I. Sheppard, P.M. Cureton and M.P. Wong. 1992. The development of assessment and remediation guidelines for contaminated soils, a review of the science. *Can. J. Soil Sci.* 72: 359-394.
- Suter, G.W., II and C.L. Tsao. 1996. Toxicological Benchmarks for Screening Potential Contaminants of Concern for Effects on Aquatic Biota: 1996 Revision. Report prepared for the U.S. Department of Energy.
- Tait, J.C., I.C. Gauld and G.B. Wilkin. 1989. Derivation of Initial Radionuclide Inventories for the Safety Assessment of the Disposal of Used CANDU® Fuel. Atomic Energy of Canada Limited Report.
- Tait, J.C., H. Roman and C.A. Morrison. 2000. Characteristics and Radionuclide Inventories of Used Fuel from OPG Nuclear Generating Stations. OPG Report No. 06819-REP-01200-10029-R00.
- United States Environmental Protection Agency (U.S. EPA). 2003. Region III Risk-Based Criteria Tables. U.S. EPA, Region III, Philadelphia.