

5 Analysis and Fractionation of Isotopes

5.1 Introduction

The ability to measure extremely low concentrations of ions and other dissolved substances in the groundwater around a deep repository for used nuclear fuel is an essential requirement for future safety analysis. This concerns not only the measurement of total concentrations, but also the speciation and transport through the natural and technical barriers that will surround the copper capsules deposited in accordance with the KBS-3 concept. Of particular concern in these respects are the radionuclides, which are isotopes of the elements that decay, emitting electromagnetic or particulate radiation, and thus may be hazardous to the environment. Although many such isotopes occur naturally, it is quite conceivable that they could be released from nuclear waste deposits should the protective barriers fail to function as planned.

Since most radionuclides are more or less soluble in water, transport pathways will be dependent on the presence and the characteristics of the water in the repository environment.

Freely flowing water should, of course, be avoided, as this would facilitate rapid transport of dissolved species, as well as colloids. Colloids may consist of precipitated radionuclides or particles from the bentonite barrier together with adsorbed species.

However, transport of ions and neutral species will even occur in stagnant water, as a result of, e.g., diffusion. One of the driving forces for the latter process is known as chemical potential, which strives to eliminate differences in concentration. Consequently, ions or other mobile species flow from regions of high concentration to regions of low concentration. Capsule breach, followed by dissolution of exposed radionuclide compounds, presents such a scenario where diffusion would become operative.

There is also an additional array of chemical processes that affect transport, e.g., precipitation, dissolution, complex formation, oxidation/reduction and adsorption on surfaces in the local environment. All of these processes can interact with transport, the dominating mechanism depending on the chemical characteristics of the species, as well as water parameters such as pH, ionic strength, redox conditions and the presence of other dissolved substances or bacteria. Investigations concerning the analysis and transport of radionuclides therefore constitute prioritised areas of research for the Swedish Nuclear Fuel and Waste Management Company (SKB).

For these purposes, a variety of analytical techniques have been applied, ranging from simple measurements of electrical conductivity to diverse chromatographic methods. Atomic absorption spectrometry, as well as the more modern and more advanced technique of inductively coupled plasma mass spectrometry (ICP-MS), has also found application. The latter technique offers the distinct advantage of furnishing isotope-specific information. This enables its use in, e.g., determining the age and origin of groundwater, or tracing the sources of possible heavy metal and radioactive substance contamination.

Such measurements often assume that isotope ratios are constant, which has proven to be a rule with many exceptions. In fact, it has been observed that many, if not all, of the aforementioned processes lead to changes in the original isotopic composition, an effect termed fractionation. This is an important reason for KASAM to give an account of the current state of

knowledge about isotope analyses, and to give examples of processes leading to fractionation.

This chapter will begin with a general introduction to the elements and their isotopes, as well as a description of certain characteristics of the latter.

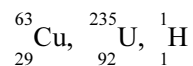
5.2 The elements, isotopes and mass numbers

Atoms of any given element are characterised by a specific number of protons in their nuclei, defining the atomic number, normally denoted by the letter Z . For example, pure copper consists entirely of atoms of atomic number 29. Each element has been assigned a name and a defined place in the periodic table; all atoms of the element have essentially identical properties.

Even though all atoms of a given element have a defined number of protons, the number of neutrons can vary, within certain limits. This leads to the occurrence of isotopes. One example is element 1, hydrogen, which besides containing a single proton in its nucleus, may also possess 0, 1 or 2 neutrons, i.e., hydrogen has three isotopes with atomic masses of 1, 2 or 3, denoted by the symbols H, D (or ^2H) and T (^3H), respectively.

Several important properties of the isotopes are, on closer inspection, dependent on mass number, which is the sum of the numbers of protons and neutrons, denoted A . The mass number gives an approximate value of the atomic mass of an isotope, whereas the atomic weight of an element is determined by the composition of the isotopic mixture in question.

To specify a certain isotope of an element, the quantities A and Z , in addition to the chemical symbol, are written in a defined fashion. As examples, the following notations



correspond to three specific isotopes of the elements copper,

uranium and hydrogen, namely copper-63, uranium-235 and hydrogen-1, or simply hydrogen.

5.2.1 What is fractionation?

Two different isotopes of the same element therefore have distinct mass numbers but essentially identical chemical properties since these are determined by the number of electrons. Certain chemical effects can, however, arise because of differences in mass number. Different isotopes may exhibit slightly different equilibrium constants for a given chemical reaction, which can result in so-called fractionation. The extent of this effect can be expressed in terms of the fractionation factor, α , also known as the separation factor or enrichment factor. α is defined by the quotient between isotope ratios describing the compositions of two different chemical compounds or phases, i.e.,

$$\alpha = \frac{\left({}^hN/{}^lN\right)_1}{\left({}^hN/{}^lN\right)_2}$$

where hN and lN are the abundances of the light and heavy isotopes, respectively, present in the two forms denoted by the subscripts 1 and 2.

To obtain more convenient numbers (with fewer decimal places) the following relationship is often used. The fractionations given in the rest of this chapter have been calculated using

$$\delta^{h,l}N = \left[\frac{\left({}^hN/{}^lN\right)_{\text{sample}}}{\left({}^hN/{}^lN\right)_{\text{standard}}} - 1 \right] \cdot 1000\text{‰}$$

yielding the relative change in an isotope ratio between two forms, in this case a sample and a reference, expressed in per mil units (‰). An example of an equilibrium reaction that results in

fractionation is the precipitation of calcium carbonate (CaCO_3) from an aqueous solution. ^{18}O is enriched, relative to the most common isotope, ^{16}O , in the precipitate by 25‰ (2.5% or $\alpha = 1.025$). The magnitude of the fractionation factor is temperature dependent, permitting measurement of oxygen isotope ratios in CaCO_3 to be used to determine the temperature of the water at the time of precipitation. This is the principle for the oxygen isotope geothermometer.

Photosynthesis is an example of a process where the lighter isotope, in this case ^{12}C , is enriched relative to the heavier ^{13}C . Cellulose and lignin in wood have in this way been enriched in ^{12}C by somewhere in the region of 2.5% (or $\delta^{13,12}\text{C} = -25\text{‰}$). This is actually an example where kinetic effects lead to fractionation, since the lighter carbon-12 isotope moves more rapidly through the processes of cellulose or lignin formation, thereby becoming enriched in the final products of the reactions.

Physical processes such as evaporation, condensation and diffusion can also result in pronounced fractionation. In this way the lighter oxygen isotope, ^{16}O , becomes enriched in water vapour from the oceans. At the same time, since the heavier ^{17}O and ^{18}O containing water molecules are enriched by condensation, atmospheric water vapour becomes even more depleted in these heavier isotopes. Through evaporation and condensation processes at the equator and poles, water deposited in Polar Regions is enriched in ^{16}O by up to about 5%.

The fissionable uranium isotope, ^{235}U , can be separated and enriched relative to the more abundant, non-fissile isotope ^{238}U , by virtue of minor differences in transport rates arising when gaseous $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ diffuse through porous barriers (see section 5.5).

5.2.2 Radioactive isotopes

Only a small fraction of all known isotopes are stable, whereas the vast majority changes spontaneously by radioactive decay. A

radionuclide decays ultimately to one or more stable isotopes with the release of energy. This may be exemplified by the radionuclide tritium (^3H or T, as mentioned previously), which always converts to helium-3, ^3He , by release of a β -particle, which is nothing more than an energy-rich electron.

Under normal conditions, each type of radioactive isotope decays at a well-defined and characteristic rate. This means that, in the absence of any new source of formation, it is only a matter of time until all radionuclides disappear. However, certain isotopes decay so slowly that they still persist on Earth some 4500 million years after their formation. Examples of long-lived radioactive isotopes are potassium-40, ^{40}K , rubidium-87, ^{87}Rb , neodymium-144, ^{144}Nd , thorium-232, ^{232}Th , uranium-235, ^{235}U , and uranium-238, ^{238}U .

It might therefore seem surprising that short-lived isotopes, such as radon-222, ^{222}Rn , and carbon-14, ^{14}C , are so common on Earth. The reason is that the amounts of these isotopes are continuously renewed by special nuclear reactions, ^{222}Rn by radioactive decay of uranium and ^{14}C by cosmic radiation. Nuclear weapons testing and nuclear power plants also give rise to a multitude of radioactive isotopes.

5.2.3 The isotopic composition of the elements

Since the end of the 1930's, geochemists, astrophysicists and nuclear physicists have combined talents in an attempt to explain the observed isotopic composition of different elements. Hydrogen and helium, the two lightest elements are now assumed to have been formed in the "Big Bang". The relatively rare isotopes with mass numbers 6-11 (lithium, beryllium and boron) have partly originated from the influence of cosmic radiation. The heavier elements are believed to derive from nuclear reactions occurring in stars, resulting in the isotopic composition of the elements known today. Consequently, practically all iron on

Earth and in meteorites has been shown to contain about 5.85% ^{54}Fe , 91.75% ^{56}Fe , 2.12% ^{57}Fe and 0.28% ^{58}Fe .

The fact that the isotopic composition of different elements is relatively constant has enabled the tabulation of average atomic weights. Atomic weights are of the utmost importance in all chemical calculations.

5.2.4 The properties of isotopes

Generally speaking, all differences between the properties of different isotopes of the same elements can be related to two factors – differences in mass or differences in nuclear structure. The first is usually called the isotope effect, whereas the second has various names depending on the nature of its effect.

Helium consists of two stable isotopes, ^3He and ^4He , both of which exist as gaseous atoms under normal conditions. At given temperature and pressure, ^4He will have 33% greater mass than the same volume of ^3He , thus conferring a greater density. If the hydrogen isotopes (H) are completely replaced by deuterium in water, the result is so called heavy water, with a density some 10% greater than that of normal water.

A further difference in properties, which also depends on isotopic mass, concerns the mobility of atoms. Gaseous ^3He atoms move with an average velocity some 15% greater than ^4He at the same temperature. Additional properties that depend on average velocities, and hence mass, include thermal conductivity and gaseous viscosity.

As mentioned above, certain properties are dependent on nuclear structure. Radioactivity is one of these, and is the result of an interaction between the forces acting on protons, neutrons and electrons. For example, ^6He is radioactive whereas ^4He is stable.

Nuclear spin is another property of the isotopes that depends on the number and structural arrangement of neutrons and protons in the atomic nucleus. This means that atomic nuclei

behave like minute magnets, which can, e.g., interact with electromagnetic radiation. This property is exploited in nuclear magnetic resonance (NMR) spectroscopy, which is employed in research, medicine and a range of technical applications.

The distribution of neutrons and protons in the nucleus also affects the surrounding electrons. The presence of an extra neutron in a certain isotope changes the distribution of protons and thus the shape of the atomic nucleus, in turn affecting the energies of electromagnetic radiation that can be absorbed or emitted by the electrons.

5.2.5 Fissionable isotopes

None of the elements with atomic numbers greater than 83 (bismuth), i.e., $Z > 83$, possess stable isotopes, and therefore are subject to radioactive decay. Those elements primarily of interest for application in the nuclear power industry are the actinides with $Z \geq 90$, since some of their isotopes are fissile.

Among the actinides are the only known fissionable isotopes with their enormous potential for energy production, but also with attendant, long-term risks for the environment. Uranium, with atomic number 92, has a pair of fissile isotopes, ^{233}U and ^{235}U . Plutonium, $Z=94$, also has two such isotopes of considerable importance, namely ^{239}Pu and ^{241}Pu . These are formed as unwanted bi-products in nuclear reactors from ^{238}U , itself non-fissile, via the capture of neutrons released during ^{235}U fission. ^{235}U is present at a relative abundance of only about 0.7 % in naturally occurring uranium ores, and must be enriched to concentrations in the vicinity of 2.8 % before a nuclear reaction can be initiated (Spiro & Stigliana, 2003a).

Heavier actinides, $Z > 94$, are mostly of scientific interest, although they have found some, albeit limited, application in cancer therapy. ^{232}Th has great potential economic value since it can be converted to ^{233}U , which is in turn fissionable.

Even though relatively few isotopes are actually fissile, considerably more are instable and radioactive. As a matter of fact, all elements have at least one radioactive isotope. As mentioned previously, the lightest of all elements, hydrogen, has three isotopes, of which the heaviest, tritium, is radioactive. More than 1,000 radioactive isotopes are currently known, about 50 being found naturally and the rest artificially synthesised. In excess of 500 radionuclides are produced in nuclear reactors.

Radioactive isotopes are utilised in a range of applications in medicine and technology: radioactive tracers for imaging and functional diagnostics, e.g. technetium (^{99}Tc) phosphate complexes for skeletal scintillography; further ^{99}Tc labelled substances for the diagnosis of heart, kidney, lung, etc. conditions; and ^{18}F labelled glucose for tumour diagnosis.

Radioactive formulations are also used for localised radiation therapy, e.g., ^{125}I and ^{192}Ir for tumour treatment. ^{60}Co is employed as a radiation source for cancer therapy and ^{131}I to locate brain tumours, whereas ^{14}C is utilised for studies of diabetes, gout, anaemia, etc.

^{241}Am has found application in fire alarms, ^3H in luminous evacuation signs, and both ^{210}Po and ^{238}Pu in batteries for the space industry.

5.3 Analytical methods and their limitations

5.3.1 Mass spectrometry

Mass spectrometry (MS) is the technique that has provided most of the experimental evidence on which our understanding of the nature and, indeed, the very existence of isotopes is based.

J. J. Thomson is credited with constructing the earliest form of instrument designed to separate atoms on the basis of their mass-to-charge ratios. Experiments with this instrument led to the discovery of the first two isotopes of any element, ^{20}Ne and ^{22}Ne of the noble gas neon in 1913 (Rouessac & Rouessac,

2000b). This work followed Thomson's receipt of the 1906 Nobel Prize in physics, for studies demonstrating the particulate properties of the electron.

A colleague of Thomson, F. W. Aston continued this pioneering work and discovered over 200 of the naturally occurring isotopes, including a third minor isotope of neon, ^{21}Ne . For his outstanding achievements, Aston was awarded the Nobel Prize for chemistry in 1922. Platzner (1997; Chapter 1) gives a brief historical account of the early development of MS in a recent book, which is also a good source of literature on the subject of isotope measurement in general.

Over the century since its conception, a plethora of instruments for MS has been designed (Platzner, 1997), certainly too numerous to describe in detail here. Therefore, we will confine ourselves at this point to a discussion of the magnetic sector type of instrument, as used in the original device constructed by Thomson, and still in use today. The basic premise in MS is that the motion of charged particles in a vacuum can be manipulated by application of magnetic or electric fields. As illustrated in *Figure 5.1*, ions having different mass-to-charge ratios will subscribe circular trajectories of differing radii in a magnetic field. Another important feature is that ions of different mass-to-charge ratios will be brought to focus along a plane. By positioning an array of detectors along this focal plane, it is therefore possible to simultaneously monitor a suite of ions and thus measure isotope ratios with very high levels of precision.

Once ions have been generated in a suitable source, *vide infra*, they are sampled by applying a large potential gradient, of opposite sign to the ionic charge, between the source and the mass spectrometer. In this way, the ions are accelerated to high velocities, preventing them from simply diffusing to surfaces inside the instrument where they would be neutralised.

A prerequisite for the technique is that the ions survive transport from the source of their production to the detector. Operating the mass spectrometer under vacuum conditions

facilitates their survival. As the pressure is lowered, collisions between particles become less and less frequent. Collisions are undesirable for two reasons, the first being that the ion may lose its charge by abstracting an electron from its collision partner. Uncharged particles cannot be detected and so collisions resulting in charge transfer will result in a reduction in the number of ions surviving transport to the detector. The second effect of collisions is to scatter ions, diverting them from the trajectory that leads to the detector, again resulting in losses before detection. (This latter effect can be visualised as a billiard ball grazing another ball on its way to the pocket. The collision will obviously cause the moving ball to change direction and the shot will be missed.) Scattered ions tend to collide with parts of the instrument, such as the magnet poles, where they are neutralised.

Most of the residual pressure in a mass spectrometer results from leakage of atmospheric gases into the instrument. These gases, mainly oxygen (O_2), nitrogen (N_2) and argon (Ar), are very light, i.e., have relatively low masses, and therefore tend to scatter lighter ions to a greater degree than heavier ions. (A stationary billiard ball will scatter a moving ping-pong ball much more effectively than a moving bowling ball.) Consequently, heavier ions are more likely to survive transport through a mass spectrometer than lighter ions, which means that the detection efficiency increases with mass. It should be noted that there are also other effects that tend to accentuate this problem, which is termed instrumental mass discrimination or mass bias. The result of this effect is that, when an isotope ratio is measured experimentally, it will not correspond to the true value actually present in the studied material. Experimental MS data must therefore always be corrected for instrumental mass discrimination. Correction is based on experimental measurement of the mass discrimination using a sample of known isotopic composition. However, herein lies the dilemma, since isotopic compositions are determined using MS! The key to overcoming this problem is to use synthetically prepared mixtures of pure isotopes.

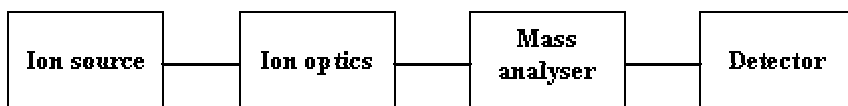
Although more efficient means for the isolation of pure isotopes are now available, MS itself can be used for this purpose. Historically, large sized mass spectrometers, known as calutrons, were developed for the electromagnetic separation of ^{235}U , the uranium isotope employed in the manufacture of the first atomic bomb in the Manhattan project (Rouessac & Rouessac, 2000b). Assuming that sufficiently pure samples of two or more isotopes are available, mixtures of known composition can be prepared. Comparison of measured (R_{meas}) with known or true (R_{true}) isotope ratios can then be used to calibrate the mass spectrometer, i.e., determine the instrumental mass discrimination correction factor (K):

$$R_{\text{true}} = R_{\text{meas}} \times K ; K = R_{\text{true}}/R_{\text{meas}}$$

It should be mentioned that K is dependent on mass, and must therefore be determined for each element, and perhaps even for each pair of isotopes under study (Woodhead, 2002). The functional form of the correction factor has also been the object of considerable investigation (Russell et al., 1978).

Since a complete mathematical treatment of mass discrimination awaits a more thorough understanding of the underlying physical phenomena, K remains a purely empirical correction factor, despite widespread reference to various “laws” in the literature. For this reason, there is a growing need to ensure that isotope ratios measured and corrected in one laboratory, can be reproduced elsewhere. This necessitates the availability of reference materials that can be used as international standards for the calibration of mass spectrometric measurements. Reference materials with certified isotopic compositions may be obtained from such authorities as the Institute for Reference Materials and Measurements, Geel, Belgium, and the National Institute of Standards and Technology, Gaithersburg, USA.

(a)



Vacuum system

(b)

$$m/z = \frac{B^2 \cdot r^2 \cdot q_e}{2 \cdot V}$$

m = mass of isotope (kg)

z = ionic charge (dimensionless)

B = magnetic field strength (T)

r = magnetic sector radius of curvature (m)

q_e = electronic charge (1.60×10^{-19} C)

V = accelerating potential (V)

(c)

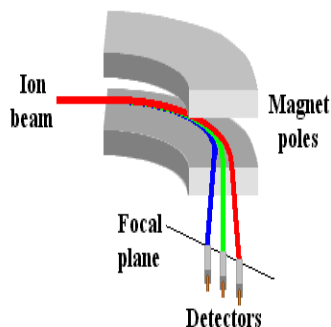


Figure 5.1. Schematic diagram showing: (a) The lay-out of a mass spectrometer; (b) The governing equation showing how mass separation is achieved. Ions generated in the ion source have characteristic mass to charge ratios (m/z). The ions are accelerated by a potential applied across the ion optics, and injected into the mass analyser. Since the magnetic sector has a fixed radius of curvature (r), ions of different m/z are brought to focus by varying either the accelerating potential (V) or the magnetic field strength (B). Increasing B or decreasing V will bring heavier ions to focus at a given point on the focal plane shown in (c); (c) A detail of the magnetic sector mass analyser, showing how ions of differing m/z are focused at different positions. The left (blue) beam represents the path of the lightest ions; the right (red) beam is that of the heaviest ions. Moveable detectors are positioned at intervals along the focal plane to permit simultaneous collection of several ion beams and determine isotope ratios.

5.3.2 Infrared spectroscopy

Although MS is undoubtedly the first choice of technique to use for the measurement of isotopic abundances, it is not the only one. The major advantage of MS in its various forms is that it is applicable to essentially all elements and compounds. On the other hand, as noted in the preceding paragraphs, mass discrimination can be a source of considerable error if not adequately corrected for. Thus there is an incentive to be able to measure isotope ratios by other techniques, as this provides an independent means of checking the data. One such independent technique is infrared (IR) spectroscopy.

As far as the measurement of isotopes is concerned, IR spectroscopy is still very much in its infancy. Unlike MS, which can measure isotopic compositions for samples in almost any form, IR spectroscopy is, at least at present, only applicable to compounds that can be introduced to the instrument as gases. Consequently, isotope ratio measurements by IR spectroscopy have found greatest application in the study of atmospheric gases, carbon dioxide (CO_2) being a popular choice (Becker et al., 1992; Esler et al., 2000). The greatest advantage of IR spectroscopy over MS, other than the lack of mass discrimination problems, is that the instrumentation is less expensive, simpler and portable. Therefore, atmospheric monitoring probably comprises the most important area of potential application.

Esler et al. (2000) have remarked that IR spectroscopy is capable of resolving the symmetry isotopomers of gases such as ozone (O_3) and nitrous oxide (N_2O) – a gas implicated in the environmental issues of global warming and the destruction of the stratospheric ozone layer (Spiro & Stigliani, 2003b). [Isotopomers are chemical compounds in which one or more of the constituent atoms may exist as a mixture of isotopes. Since there are two stable hydrogen isotopes, ^1H and ^2H , the simple molecular species hydrogen (H_2) exists in three isotopomeric forms ($^1\text{H}-^1\text{H}$, $^1\text{H}-^2\text{H}$ and $^2\text{H}-^2\text{H}$) representing all the possible

combinations of two hydrogen atoms.] In the case of N_2O , two such isotopomers, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, have identical molecular weights, since they contain equivalent isotopes, and thus cannot be distinguished by MS (Yung & Miller, 1997).

Considering how the atoms are connected provides the key to the resolution of this and other pairs of equal mass isotopomers by IR spectroscopy. Although mass discrimination is not of direct concern, IR spectroscopy still requires calibration in order to be able to convert instrumental signals to concentrations of isotopomers. For this reason, gas standards with known composition must be available for calibration purposes. Such standards are often analysed by MS (Esler et al., 2000). Fortunately, synthetic standards can also be prepared using isotopically enriched starting materials and purified products, thus relaxing the reliance on complementary measurements by MS.

It may come as some surprise to note that most car owners will unwittingly come into contact with IR spectroscopy, sooner or later (Rouessac & Rouessac, 2000a). Such instruments are namely used routinely to measure exhaust gas emissions of atmospheric pollutants such as carbon monoxide, unburnt fuel in the form of hydrocarbons, etc.

5.4 Applications of isotope ratio measurements

Isotope ratio measurements have numerous areas of application in a variety of scientific disciplines (Platzner, 1997). Two particularly relevant fields of study concern the dating of groundwater and the isotopic analysis of the actinides, especially uranium (U) and plutonium (Pu), as exemplified in the following paragraphs.

5.4.1 Dating of groundwater

Mass spectrometry has an important role to play in the selection of sites for nuclear waste storage.

One important criterion for the selection is that, in the event of leakage from the deposited capsules, the released radioactive material will be isolated by geological barriers and hindered from entering the biosphere (KASAM, 2001a). In effect, contaminated depository water should not be able to flow unrestricted into neighbouring water bodies. Injecting stable isotopes or long-lived, radioactive isotopic tracers and monitoring their progress through geological barriers and appearance in recipient water bodies can be used to investigate water flow patterns in boreholes. Changes in isotopic composition can then be employed to infer rates of transport through the bedrock. Such experiments have recently been initiated at the Äspö laboratory.

A more traditional and non-invasive means to assess the efficiency of the bedrock as a barrier to radioactive waste dispersion is provided by dating techniques. These are performed by measuring specific isotopes in water samples collected from boreholes at prospective repository sites. Certain radioactive isotopes are naturally produced by the interaction of cosmic rays with atoms present in the Earth's atmosphere. Such so-called cosmogenic radionuclides are distributed in the atmosphere, gradually being removed by rain and snow, thus entering water bodies at the Earth's surface. One chlorine radionuclide, ^{36}Cl , shows particular promise for groundwater dating (Faure, 1986). This isotope has a half-life of 3.08×10^5 years, and the chemical properties of the chloride ion largely ensure that deposited ^{36}Cl will remain dissolved. Therefore, losses of ^{36}Cl are only by radioactive decay (and not by precipitation reactions as may affect other cosmogenic radionuclides), the time-scale of which allows water that may be millions of years old to be dated.

Measurements of ^{36}Cl in modern Antarctic ice samples have shown that the concentration is about 2.5×10^6 atoms kg^{-1} ice. If a volume of water, or a block of ice, is isolated from further input of recently formed ^{36}Cl , the concentration will decay exponentially, as shown in *Figure 5.2*. From the known initial concentration present in water, and measurement of the current level in a sample collected from, e.g., a borehole, the age of the water can be calculated. For example, if the measured ^{36}Cl concentration is 1.25×10^6 atoms kg^{-1} (1.25 mega atoms per $\text{kg} = 1.25$ Matoms kg^{-1}), then one half-life has expired in the sample, i.e., the water is about 0.3 million years (0.3 Myear) old. If water sampled at a site has been isolated from the in-flow of younger, fresher water for extensive periods of time, then it is likely that the geological formations will also be able to limit the out-flow of any accidentally released radioactive material in the event of any of the capsules being breached.

Further examples of the use of radioactive isotopes in connection with the dating of groundwater and groundwater flows are given in Chapter 4.

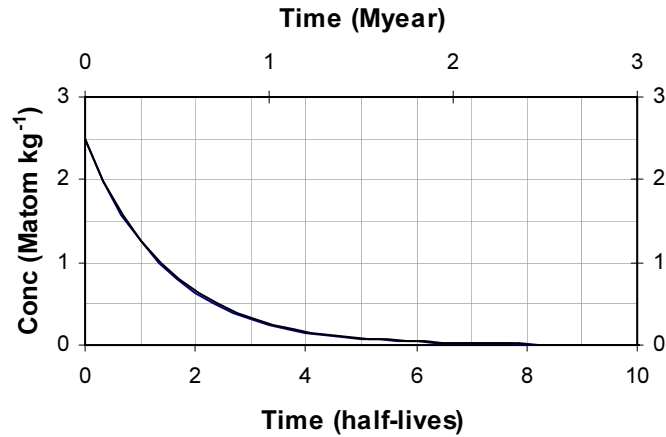


Figure 5.2. Change in the concentration of the cosmogenic radionuclide ^{36}Cl in groundwater as a function of time. It is assumed that the initial concentration is 2.5×10^6 atoms kg^{-1} , as has been measured in recent samples of Antarctic ice (Faure, 1986). After 3.08×10^5 years (one half-life), the initial concentration will have halved. Measurement of the ^{36}Cl concentration in groundwater by mass spectrometry therefore allows the age of the sample to be determined.

5.4.2 Tracing radioactive sources

The uranium found in all naturally occurring minerals has an essentially invariant isotopic composition, consisting of 0.005% ^{234}U , 0.720% ^{235}U and 99.275% ^{238}U (Richter et al., 1999; Desideri et al., 2002; Cobb et al., 2003).

The resultant ratio, $^{235}\text{U}/^{238}\text{U} \approx 7.25 \times 10^{-3}$, is therefore that expected in, e.g., biological tissues and body fluids collected from flora and fauna exposed only to natural, environmental sources of uranium. However, the isotopic composition is radically altered by industrial processes geared to the production

of enriched uranium suitable for nuclear-fuel or -weapons manufacture. Both applications require enrichment in the abundance of ^{235}U , although to rather different extents. For use as fuel in light-water nuclear reactors (the kind used in Sweden), the atomic abundance of ^{235}U must be at least 2.8%, whereas enrichment to some 93% is necessary to produce weapons-grade uranium (Spiro & Stigliani, 2003a). A by-product of the enrichment process is the infamous depleted uranium (DU).

In the wake of the Gulf War and the more recent Balkan conflict, concerns grew that exposure to DU-containing debris from spent armour-piercing ammunition could constitute a health hazard (Sandström, 2002). Some soil samples collected from Kosovo in the aftermath of the conflict revealed altered uranium isotope ratios, providing evidence for the contamination of the region by DU originating from munitions (Boulyga et al., 2001). Urine samples collected from inhabitants of a suspected DU contaminated urban area, on the other hand, exhibited uranium isotope ratios consistent with natural sources (Tresl et al., 2004), as illustrated in *Figure 5.3(a)*.

In 2001 a study was conducted on participants of the Swedish peace keeping force. Before departure for Kosovo, and again after six months of service, urine samples were acquired and analysed by MS. It was observed that the concentrations of uranium in urine were, on average, 10 times lower at the later date, as evident in *Figure 5.3(b)* (Sandström, 2002). Thus the application of MS contributed to dispelling fears concerning the exposure of Swedish servicemen to DU in Kosovo.

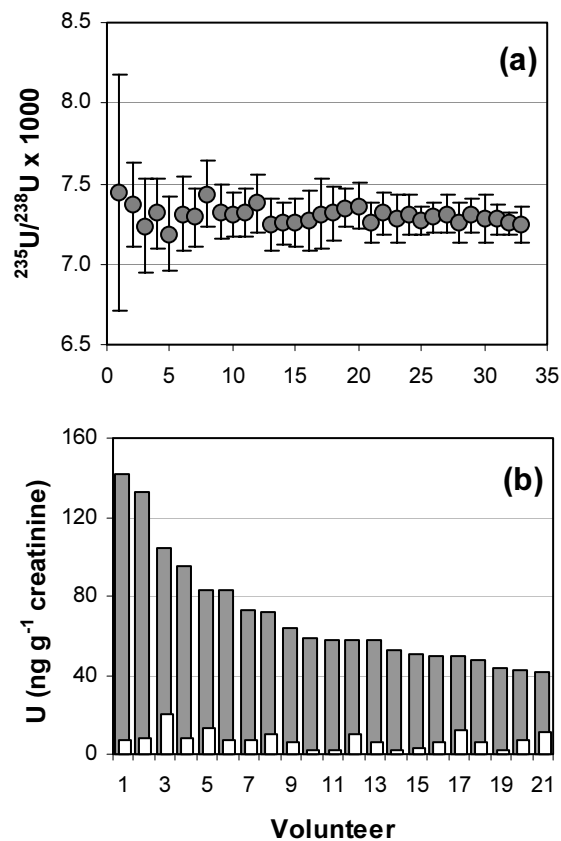


Figure 5.3. (a) Uranium isotope ratios measured in the urine of local inhabitants of an urban area suspected of being contaminated with depleted uranium. Uncertainty bars are drawn at a 95% confidence level; data have been gleaned from Tresl et al. (2004). (b) Uranium concentrations present in the urine of KFOR personnel before leaving Sweden (shaded bars) and after six months service in Kosovo (open bars). The data have been extracted from Sandström (2002).

It should be mentioned that spent fuel from nuclear reactors still contains ^{235}U . By reprocessing, this ^{235}U can be re-enriched up to about 4% and used to fuel a reactor (Desideri et al., 2002). However, during the chemical reprocessing of spent fuel, both the enriched uranium and the DU by-product are contaminated with artificial isotopes including ^{236}U , ^{239}Pu and ^{240}Pu .

Mass spectrometric analyses have provided irrefutable proof that the armour-piercing ammunition employed in the Balkans contained at least some DU derived from re-processed nuclear fuel, and thus spread artificial radioactive isotopes in the environment. On the other hand, the amounts of radionuclides actually released are considered to be insignificant in comparison to other sources, such as fallout from Chernobyl, and consequently, their toxicological effects are deemed negligible (Desideri et al., 2002).

Mass spectrometry also has an important role to play in differentiating the sources of nuclear contamination in the environment. During the latter half of the 20th century, nuclear weapons detonations in the stratosphere, conducted by the United States and the former Soviet Union, spread radioactive material across the face of the Earth, deposition reaching a maximum in the period 1963-1964.

This resulted in global fallout inventories in the range 50-100 Bq m⁻², expressed as the sum of the most prevalent isotopes, ^{239}Pu and ^{240}Pu , and denoted $^{239+240}\text{Pu}$. This may be augmented by local or regional sources, such as leakages or authorised discharges from nuclear power plants and fuel reprocessing facilities, as well as reactor or satellite accidents (Warneke et al., 2002). Although a local or regional source might conceivably be detectable on the basis of an elevated $^{239+240}\text{Pu}$ inventory, more definitive evidence can be obtained from isotope ratios, each source having a characteristic isotopic composition (Kelley et al., 1999; Warneke et al., 2002; Ketterer et al., 2004).

Note that the use of $^{239+240}\text{Pu}$ results from the common application of α -spectrometry to measure plutonium inventories in the environment. For most instruments, the energies of the α -

particles emitted by decay of ^{239}Pu and ^{240}Pu are too similar to be resolved, and so, in effect, the sum of the activities of both isotopes is measured (Mitchell et al., 1997).

Data for the plutonium isotopes are collected in Table 5.1, where it can be seen the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio differs greatly between sources, thus providing an excellent means of revealing the origins of environmental contamination. This possibility is exemplified by the data shown in *Figure 5.4* (adapted from Ketterer et al., 2004), where soil sampled from southern Poland is seen to be contaminated with plutonium from northern hemisphere fallout. Samples collected in north-eastern Poland, on the other hand, have also been subjected to pollution from the Chernobyl accident. The plutonium present in the latter samples therefore represents a mixture of material derived from these two different sources.

It is important to realise that isotope ratios will be altered over the projected time scale for nuclear waste storage in the deep repository, because of differences in the half-lives of the radionuclides, such as ^{239}Pu and ^{240}Pu , as evident from *Table 5.1(a)*. Nevertheless, differences between the isotopic signatures of the sources will be preserved, and thus isotope ratio measurements will continue to provide a means of identifying the origins of radionuclides in the environment, far into the future. However, in about 65,000 years time, i.e., after 10 half-lives of ^{240}Pu , the concentration of ^{240}Pu will be only 0.1% of the current level, and therefore extremely difficult to detect, at least with today's technology.

Table 5.1. (a) Half-lives (Kelley et al., 1999; Ketterer et al., 2002) and abundance ranges of Pu isotopes in weapons-grade plutonium (Mitchell et al., 1997). (b) Atomic abundance ratios of the two most common Pu isotopes originating from various sources.

(a) Isotope	Half-life (year)	Abundance (atom %)
²³⁸ Pu	87.74	<0.005 – 0.04
²³⁹ Pu	24 119 ± 27	93.3 – 97.0
²⁴⁰ Pu	6 564 ± 11	2.9 – 6.0
²⁴¹ Pu	14.33 ± 0.02	0.12 – 0.58
²⁴² Pu	376 000	–

(b) Source of Pu	²⁴⁰Pu/²³⁹Pu	Reference
Global fallout (northern hemisphere)	0.166 – 0.194	Kelley et al., 1999
Weapon production	0.01 – 0.07	Warneke et al., 2002
DU from nuclear fuel reprocessing	0.12	Desideri et al., 2002
Chernobyl accident	0.37 – 0.41	Muramatsu et al., 2000, Boulyga & Becker, 2002

5.5 Processes leading to isotopic fractionation

In the so called LTDE (long term diffusion experiment) project, SKB is currently assessing the extent of diffusion of radioactive species through bedrock. In the parallel LOT (long term test of buffer material) project, SKB is also studying the diffusion of radionuclides through the bentonite buffer material.

These projects, to study the transport of radionuclides through the bedrock at Äspö and bentonite, raise two potentially complicating factors for the interpretation of the results. As the groundwater flow rate through the bedrock at any finally selected site must be essentially zero, to prevent the spreading of any accidental radioactive waste leakage, transport of material will be driven by diffusion.

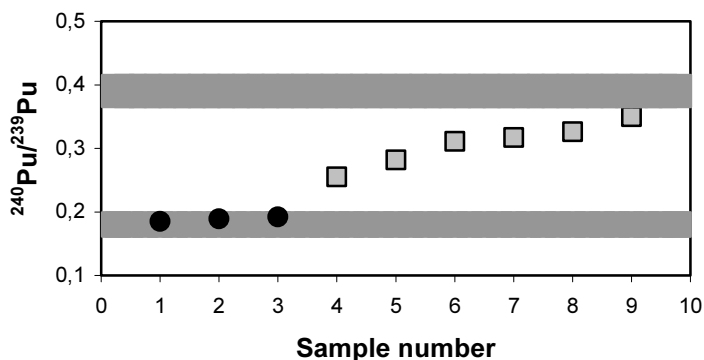


Figure 5.4. Plutonium isotope ratios in soil samples collected in Poland, illustrating the ability to discriminate between sources. The lower shaded region covers the range of $^{240}\text{Pu}/^{239}\text{Pu}$ typically found in northern hemisphere fallout. The Pu present in samples 1-3 collected in southern Poland (filled circles) clearly originates from this source. The upper shaded region encompasses the composition interval of Chernobyl-derived Pu. Samples 4-9, acquired in north-eastern Poland, exhibit isotope ratios that are characteristic of two-component mixing between northern hemisphere fallout and Chernobyl Pu. Data adapted from Ketterer et al. (2004).

The first question that follows is whether diffusion transports different isotopes of the same element in groundwater at the same rate or not. The second concerns the extent to which chemical reactions, such as precipitation and complex formation, might induce fractionation of isotopes in the deep repository environment.

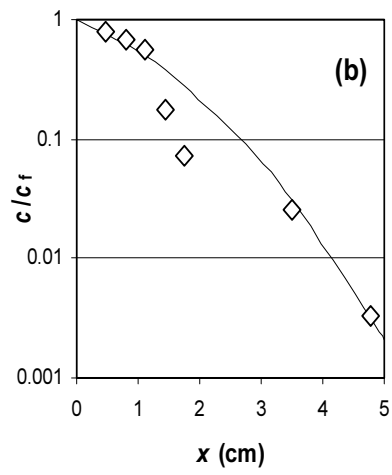
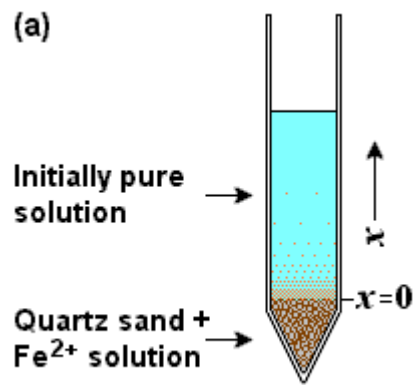
It is well known that, in the gas phase, lighter atoms and molecules diffuse faster, this principle being exploited for the enrichment of fissionable ^{235}U , as mentioned above. This process requires that uranium be converted into the volatile compound,

UF₆. On passing through each of a series of porous diffusion barriers, the gas becomes enriched in the lighter isotopomer, ²³⁵UF₆, by a factor equal to the square root of the ²³⁸UF₆/²³⁵UF₆ mass ratio. As each fluorine atom has a mass of 19, the factor is equal to $\sqrt{[(238 + 6 \times 19)/(235 + 6 \times 19)]} \approx 1.004$, so literally hundreds of diffusion barriers are required to enrich natural uranium, containing 0.720% ²³⁵U, to fuel-grade uranium, with at least 2.8% ²³⁵U (Spiro & Stigliani, 2003a).

Although isotopic separation by gas phase diffusion is a well-understood process, the question of whether similar effects might be observed in solution has only recently been addressed (Rodushkin et al., 2004).

As shown schematically in *Figure 5.5(a)*, when a solution containing dissolved iron (Fe²⁺ ions) is brought into contact with another, iron-free solution, Fe²⁺ will diffuse into the pure medium. Gradually, Fe²⁺ migrates deeper into the initially pure solution, causing a concentration gradient to develop, as illustrated in *Figure 5.5(b)*. The concentration of iron in the solution drops by factors of 10 and 100 at distances (x) of about 2.7 cm and 4.2 cm, respectively, from the boundary between the two solutions, located at x = 0. These observations are in perfect agreement with the behaviour expected according to theory (Noggle, 1996).

In *Figure 5.5(c)*, the effect of diffusion on the isotopic composition of the iron sampled at various distances from the initial boundary is depicted. After 72 h and about 5 cm from the initial boundary, a $\delta^{56,54}\text{Fe}$ -value of -0.4‰ (-0.04%) is observed, i.e., the solution has become enriched in the lighter isotope, consistent with ⁵⁴Fe-species diffusing more rapidly than the corresponding ⁵⁶Fe-containing ones. *Figure 5.5(d)* demonstrates that consistent behaviour is also obtained for a third iron isotope, ⁵⁷Fe.



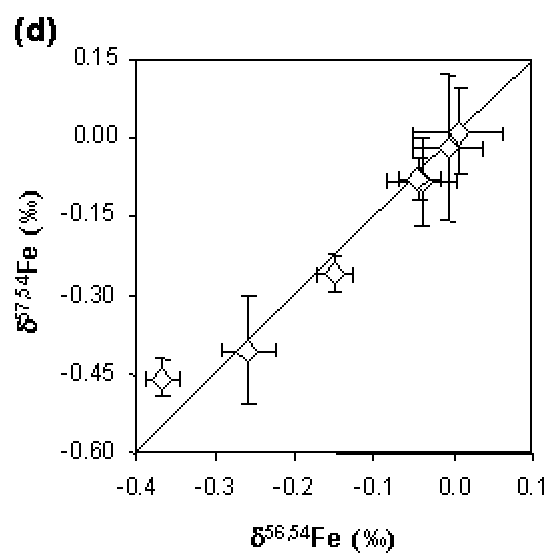
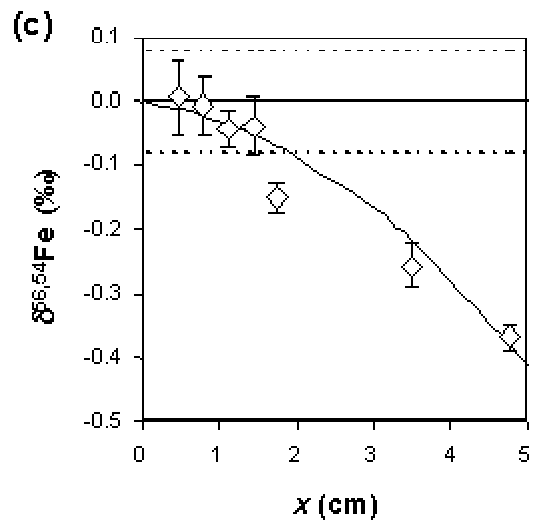


Figure 5.5. Effect of diffusion in solution on the concentration and isotopic composition of iron. (a) Experimental set-up with 1 ml iron solution covered by quartz sand to provide a mechanical barrier. After careful addition of 9 ml of pure, iron-free solution, the set-up was allowed to stand undisturbed for 72 h. Then the solution was removed, from the top, in portions of 0.5 to 1.0 ml. (b) With increasing distance (x) from the source of dissolved iron, the concentration drops in accordance with a pure diffusion model, illustrated by the solid line. The data are given as measured concentrations (c) divided by the final concentration (c_f) that would be reached once all iron has been uniformly distributed throughout the solution volume. (c) Changes in the isotopic composition of the iron measured at various distances from the source. The solid horizontal line shows the initial isotopic composition, the parallel dotted lines representing the range of uncertainty in the $^{56,54}\text{Fe}$ ratio. The data points (diamonds) with uncertainty bars trace the change in isotopic composition with distance. After about 1.5 cm, the isotopic composition has changed significantly from that of the iron source. The solid curve is a mathematical model of the effect of diffusion on the isotopic composition. (d) Three-isotope plot showing that the change in isotopic composition is dependent on the masses of the diffusing isotopes. As the mass differences between the isotope pairs $^{57}\text{Fe} - ^{54}\text{Fe}$ and $^{56}\text{Fe} - ^{54}\text{Fe}$ are 3 and 2 atomic mass units, respectively, the data points should plot on a line with a slope of about 3/2. Clearly, all but one of the data points fit the theoretical slope (solid line).

The latter is known as a three-isotope plot (Zhu et al., 2001), and provides a useful check on the consistency of experimental data. Considering the isotope pairs $^{57}\text{Fe} - ^{54}\text{Fe}$ and $^{56}\text{Fe} - ^{54}\text{Fe}$, the mass differences are 3 and 2 atomic mass units, respectively. Any mass-dependent process causing fractionation between $^{56}\text{Fe} - ^{54}\text{Fe}$ (*Figure 5.5(c)*) would be expected to induce a proportionately greater effect on the $^{57}\text{Fe} - ^{54}\text{Fe}$ isotope pair, by virtue of the greater mass difference. In the simplest terms, we expect that the ratio of δ -values, $(\delta^{57,54}\text{Fe})/(\delta^{56,54}\text{Fe})$, should be roughly equal to the ratio of the mass differences, 3/2, as verified by the results shown in *Figure 5.5(d)*. Analogous results have also been obtained for zinc isotopes in the same experimental set-up.

Clearly then, diffusion will cause fractionation of dissolved species in any environment, representing a potential source of error in the interpretation of isotopic measurements. On the other hand, the magnitude of the observed effect is very small as shown by *Figure 5.5(c)*, and thus should not have any significant effect on the safety analyses performed on the deep repository for nuclear waste. Pescatore (2002) has called for more careful consideration of the potential isotope fractionation effects that may occur in the setting of radioactive waste disposal. To this end, a new model accounting for the effects of chemical potential gradients as well as Brownian motion has been proposed (Pescatore, 2002).

It should be noted that based on the theory of Brownian motion, there is a simple relationship between the diffusion coefficient ($\text{D}/\text{cm}^2\text{s}^{-1}$) and the distance (x/cm) that an isotope (or any other diffusing species) will travel in a given time (t/s), as expressed by the Einstein-Smoluchowski equation (Atkins, 1990): $D = x^2/(2 t)$. If we assume a diffusion coefficient of $1.0 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, which corresponds to a somewhat lighter and faster moving species than iron ($D \approx 0.6 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$), the Einstein-Smoluchowski equation tells us that travelling average distances of 1, 10 and 1,000 m by diffusion alone would take 16, 1600 and 16 million years, respectively. Diffusion in solution is

evidently an extremely slow process, which is why you must stir your coffee or tea after adding a lump of sugar!

Regarding the second concern alluded to above, there is a growing body of evidence that fractionation is a rather commonplace accompaniment to chemical reactions in a diverse range of settings. Therefore, the discussion will be confined to some preliminary experimental results obtained following the addition of individual, transition metal solutions to fresh, powdered samples of bentonite clay (Forsling et al., 2004).

After standing overnight, samples of solution remaining above the swollen bentonite were taken for concentration measurement and isotopic analysis. The results are summarised in *Table 5.2*, and indicate that bentonite efficiently removes most of the dissolved metal ions from solution. This is one of the attractive features of bentonite as a technical barrier in the KBS-3 concept for nuclear waste storage (KASAM, 1998).

One interesting observation made during these experiments was that, during water (and metal ion) uptake, the degree of bentonite swelling was noticeably diminished by the presence of copper ions (Cu^{2+}) in solution. A similar effect has previously been noted for calcium ions (Ca^{2+}), i.e., the degree of swelling for sodium-bentonite is significantly greater than that of calcium-bentonite (Abdullah et al., 1999; Hoeks et al., 1987). During the repository lifetime, sodium-bentonite (the preferred barrier material in the KBS-3 concept) would be converted to the calcium form by ion exchange processes occurring following the influx of Ca^{2+} -rich groundwater (KASAM, 2001b).

Calcium-bentonite cannot adsorb as much water as the sodium form, and will therefore contract, possibly creating fissures in the material. This could potentially impair the efficiency of bentonite as a barrier to the dispersion of radioactive waste in the event of capsule damage. Corrosion of the copper cladding, and subsequent uptake of Cu^{2+} by the clay, might similarly compromise the integrity of the bentonite layer.

The % sorption results in *Table 5.2* show that the efficiency of copper uptake is lowered at the higher initial concentration,

suggesting that the bentonite buffers capacity to take up Cu^{2+} has been exceeded. This indicates that Cu^{2+} is very strongly bound to the surfaces of negatively charged bentonite particles, in turn causing inter-particle attraction and aggregation of the clay, effectively limiting the space available for water molecules to be accommodated (KASAM, 2001b). This interpretation explains the observation that dissolved copper reduces the degree of bentonite swelling, and is supported by the isotopic data presented in *Table 5.2*, as will become apparent below.

Table 5.2. Uptake of cadmium, copper and zinc from solution during the swelling of initially dry, powdered bentonite. The δ values are expressed as average values per atomic mass unit to facilitate comparison between isotopic pairs for different elements. The isotope ratios measured were $^{111}\text{Cd}/^{110}\text{Cd}$, $^{112}\text{Cd}/^{110}\text{Cd}$, $^{113}\text{Cd}/^{110}\text{Cd}$ and $^{114}\text{Cd}/^{110}\text{Cd}$ for cadmium, $^{65}\text{Cu}/^{63}\text{Cu}$ for copper and $^{66}\text{Zn}/^{64}\text{Zn}$, $^{67}\text{Zn}/^{64}\text{Zn}$ and $^{68}\text{Zn}/^{64}\text{Zn}$ for zinc.

Element	Concentration (mg l^{-1})		Sorption (%)	δ (‰ per amu)
	Initial	Final		
Cadmium	500	18.9	96.2	+0.02 ± 0.04
Cadmium	50	2.0	96.1	+0.13 ± 0.04
Copper	500	55.1	89.0	-0.06 ± 0.10
Copper	50	0.2	99.6	-1.64 ± 0.09
Zinc	50	0.35	99.3	+0.52 ± 0.14

First though, we must consider the processes occurring during hydration of bentonite clay. During water uptake, water molecules and dissolved metal ions interact with surfaces and diffuse into pores in the clay mineral particles. If diffusion to particle surfaces and within pores were the only processes taking place, then we would expect that the fraction of ions remaining in solution would be over-represented by heavier isotopes. As shown in *Figure 5.5(c)*, diffusion favours the lighter isotopes,

which would thus be able to migrate into pores more readily than their heavier counterparts, leaving the latter behind. This is what appears to happen in the cases of cadmium and zinc (*Table 5.2*). At both initial cadmium concentrations, the fractions sorbed are statistically identical. While this demonstrates that the capacity of bentonite for cadmium uptake has not been exceeded, it also indicates that the Cd^{2+} resides within water channels inside, and between particles, and is not strongly bound to surfaces like copper ions.

Other than transport phenomena, chemical reactions may occur during the hydration process. The products of reactions are the most stable compounds that can be formed from the given starting materials. Heavier isotopes form more stable bonds than lighter isotopes (Fujii et al., 2002; Schauble et al., 2001; Weston, 1999), thus chemical reactions may be an important source of fractionation. As copper is suspected of being strongly bound to bentonite particles, the reaction should lead to preferential removal of the heavier isotope (^{65}Cu) from solution. In other words, the $\delta^{65,63}\text{Cu}$ -value measured for the copper remaining in solution should be negative, as indeed is observed (*Table 5.2*). Isotopic measurements can therefore be used to shed light on processes occurring in the deep repository.

5.6 Conclusions

There are a variety of processes with the potential to disturb the natural isotopic compositions of different elements. Such changes, which can be documented by measuring isotope ratios, are termed fractionation effects.

Many of the processes inducing isotopic fractionation have been known for decades, such as those observed for oxygen and carbon in natural cycles or caused by radioactive decay. The fractionation occurring during natural cycling of the elements is, to a large extent, a result of differences in diffusion rates between isotopes in the gas phase.

This chapter demonstrates that there are additional chemical and physical processes that may cause fractionation, e.g., in aqueous solutions, and thereby affect the transport of radionuclides through natural and technical barriers in the deep repository. These processes include diffusion in solution, which favours transport of the lighter isotopes of a given element, whereas many chemical reactions, such as precipitation, complex formation and possibly adsorption as well, lead to enrichment of the heavier isotopes.

Measurements of the isotopic composition of a specific element have traditionally been used to trace pollution sources, but the fact that many chemical reactions along transport pathways may alter isotope ratios, suggests that such methods may provide ambiguous results.

As illustrated by our own experiments, changes in isotopic compositions resulting from various chemical and physical processes can be exploited in different ways. Clearly, careful measurements of isotope ratios can provide important information on the underlying mechanisms for transport of various elements in the deep repository.

This is a field that SKB should investigate further in the future.

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6 Copper Canisters – Fabrication, Sealing, Durability

6.1 Introduction

Based on available information on canister fabrication methods, strategies and industrial experience, this chapter provides an account of the fabrication processes, methods and techniques which are generally known in the industry and which are reliable with a broad base of experience. Processes, methods and techniques that are new or customised for this application will also be examined. A comparison between this fabrication project and other similar industrial manufacturing projects is conducted, particularly with respect to design, welding and residual stresses. Furthermore, requirements on methods for Non-Destructive Testing (NDT) are compared with other industrial applications. Metallurgical characteristics that arise as a result of varied manufacturing techniques are evaluated and the impact of these characteristics on the long-term properties of the repository is examined.

The sealing of the repository is examined by evaluating its long-term properties and by posing the question of whether there are any canister fabrication processes that could degrade mechanical properties or cause long-term corrosion. Methods, procedures and models that are usually applied in the industry to evaluate long-term corrosion or creep are discussed in a long-term perspective. Furthermore, the extent to which different models can predict phenomena such as corrosion and creep over very long timescales is treated.

According to the KBS-3 method, the canister, which comprises different parts (*Figure 6.1*), is an important barrier inside the repository, since the canister prevents groundwater from coming into contact with the radioactive spent nuclear fuel. The outside of the canister is a copper shell which covers a nodular cast iron insert – combining external resistance to corrosion with internal load bearing capacity. Both of these components are therefore important for isolating the spent nuclear fuel from the groundwater over very long timescales (>100,000 years), which is much longer than the lifetime of any other industrially fabricated product. To prevent radioactive substances from leaking out of the canister, the fabrication methods must allow a defect-free canister to be manufactured where the materials properties of the copper and cast iron are guaranteed and optimised against all relevant damage mechanisms, such as forms of corrosion, creep, rupture etc.

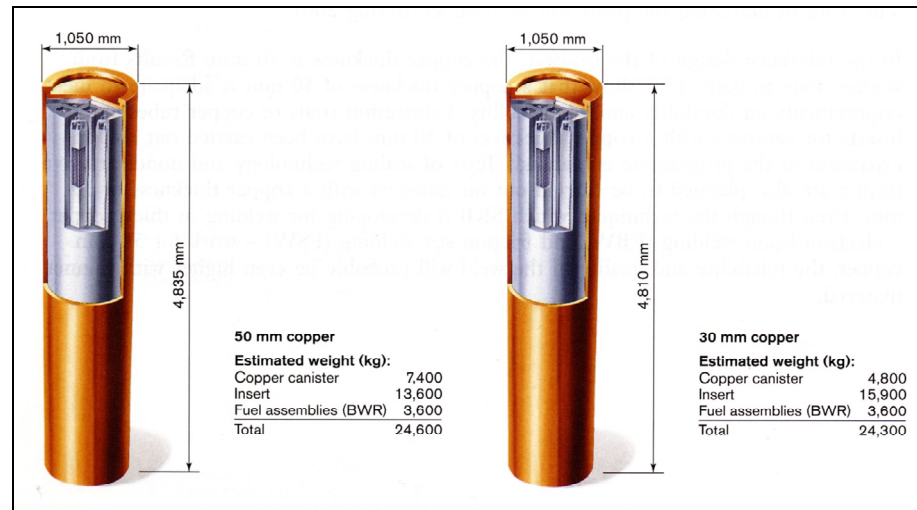


Figure 6.1. Dimensions and weights for canisters with wall thicknesses of 50 mm and 30 mm (RD&D Programme 2001). The

fuel from both boiling water reactors (BWRs) and pressurised water reactors (PWRs) will be deposited in the repository. The total quantity of spent nuclear fuel to be deposited depends on the total number of reactor operating years. For example, in a scenario with 40 years of reactor operation, the quantity of BWR fuel from Swedish reactors is estimated at about 7,000 tonnes and the quantity of PWR fuel at about 2,300 tonnes. In addition to this, 23 tonnes of MOX fuel and 20 tonnes of fuel from the Ågesta reactor will be deposited. The hypothetical repository is designed for 8,000 tonnes of BWR fuel, which corresponds to 4,000 canisters in Sweden. The canisters weigh about 25 tonnes each when filled with four PWR or twelve BWR fuel elements. This means that one canister can hold about two tonnes of spent fuel. (RD&D Programme 2001)

In Finland, three different canister models are needed, one each for BWR fuel, VVER 440 fuel and OL3 fuel. After 50 to 60 years of reactor operation, the quantity of spent BWR and VVER 440 fuel is estimated at 6,000 tonnes, which corresponds to 3,000 canisters in Finland. The current estimate of spent OL3 fuel is about 2,000 tonnes, which corresponds to 1,000 canisters. (TKS-2003)

The copper shell (50 mm wall thickness) protects the spent nuclear fuel against corrosion. From the standpoint of fabrication, a thinner wall thickness (30 mm) would be better, but the wall thickness must be acceptable from the corrosion standpoint, especially from the perspective of local corrosion. A 30 mm wall thickness facilitates Non-Destructive Testing (NDT). With thinner material, finer grain sizes are also achieved and the canister microstructure is easier to control.

It is expected that the canister will be fabricated either from drawn seamless tubes or by welding together two tube halves of rolled plate. A bottom will be welded to the copper tube either through electron beam welding or Friction Stir Welding (FSW).



Figure 6.2. Example of fabricated canister components and objects (RD&D Programme 2001).

After the fuel has been placed in the canister, the insert is sealed with a lid that is screwed. The lid is then welded onto the copper shell and leaktightness testing is then conducted using NDT methods. The quantity of copper needed for the finished canisters is about 40,000 – 60,000 tonnes in Sweden and about 25,000-30,000 tonnes in Finland.

The copper material must first and foremost meet the requirements in accordance with the ASM UNS C101000 (Cu-OFE) or EN133/63:1994 Cu-OF1 standards. Other requirements besides these are: O<5 ppm, P 40-60 ppm (in the future, possibly 30-70 ppm), H<0.6 ppm, S<8 ppm and the grain size <360 μm in all conditions after fabrication. See *Table 6.1* for the quality requirements for copper (Andersson, 2002).

The fuel channels in the insert are fabricated in the form of an array (cassette) of square tubes. The walls and bottom of the

insert are then manufactured by casting nodular cast iron around the channel array. The cast iron must comply with the requirements of the EN-GJS-400-15U standard. The insert is the heaviest component of the canister.

Table 6.1. Requirements on materials composition and comments on different properties of the copper canister material (Andersson, 2002; Appendix 2, Technical Specification no. KTS001).

Property	Specification	Comments
Weldability	O < 5 ppm	Higher levels give a reduced weldability.
Ductility	H < 0,6 ppm	Higher levels give reduced mechanical properties. (Hydrogen embrittlement).
Tensile strength, ductility	S < 8 ppm	Higher levels give reduced mechanical properties caused by non-dissolved sulphur which will be concentrated to grain boundaries.
Creep ductility	P 40 – 60 ppm	A phosphorus content of this order reduces the influence of sulphur impurities, increases creep ductility, increases recrystallisation temperature and has a minor influence on the weldability.
Microstructure	Grain size < 360 µm (Hot formed material)	This grain size gives a resolution at ultrasonic testing comparable to X-ray testing of 50 mm thick copper.
Ductility	Elongation > 40% RT – 100°C (Hot formed material)	The canister will be deformed 4% in final repository.
Creep ductility	Elongation at creep-rupture > 10% RT – 100°C (Hot formed material)	Same comment as above.

Three methods of NDT are used for the canister. X-ray radiography allows pore defects to be detected while ultrasound inspection allows defects that do not occupy volume to be detected, such as incomplete penetration, and eddy-current testing allows near-surface defects to be detected. Since the weld surface must withstand corrosion, it is important that the

finished canister should not have any surface defects. Acceptance criteria will be established in the future for all of the parts of the canister, including the welds. The other destructive test methods make it possible to determine whether the test criteria are fulfilled by the NDT methods.

6.2 Fabrication

6.2.1 Copper Shell

Forging

The forging of copper tubes is a possible alternative to canister manufacturing. However, this process has not been completely investigated and developed. A large number of lids and copper bottoms have been manufactured through hot forging of continuous cast parent material. Homogeneous and defect-free material has been obtained for the finished components. The structure of the material is more coarse-grained than the material in extruded or pierce and draw processed copper tubes but meets the grain size requirement of the Swedish Nuclear Fuel and Waste Management Co's (SKB) specification (360 μm), see *Table 6.1*. Further development work is needed to optimise the forging process with respect to materials microstructure and usage.

Roll Forming

By roll forming 12 full-scale copper tubes have been longitudinally welded with electron beam welding for SKB. The weld technique has been improved and the weld quality has increased with time. Consequently, the method can probably be further developed, especially for thinner (30 mm) wall thicknesses, as a suitable alternative for tube manufacturing.

Extrusion and Pierce and Draw Processing

Extrusion and pierce and draw processing are two different methods for the manufacturing of drawn or seamless tubes. Both methods are currently suitable for canister fabrication. At least 14 seamless tubes have been manufactured, 11 by extrusion and three by pierce and draw processing, for SKB. 5 tubes have been fabricated for Posiva in Finland.

Hot Isostatic Pressing (HIP)

The HIP process is currently only a theoretical possibility since the largest HIP furnaces are only 3 m high. The HIP process can provide a small and even grain size compared with the other manufacturing methods, although the properties can only be moderately improved due to the absorption of oxygen during the process.

6.2.2 Cast Iron Insert

Many attempts (over 20 in Sweden and two in Finland) have been made to cast full-scale inserts. Since the mechanical properties of the cast iron are highly dependent on the dimensions of the body of casting, the materials testing must be conducted on the finished inserts. So far, these studies have shown a wide scatter in tensile testing results. This has been caused by both casting defects and microstructural inhomogeneity. The probability of obtaining a defect of a critical size increases with the size of the component and under the assumption that the greatest defect determines the canister's load-bearing capacity, the maximum permitted load – the size effect – in large components decreases. The casting process and the specification of the cast iron, EN-GJS-400-15U (EN 1563), (see also Andersson, 2001), must be optimised due to the above

investigations of inserts. For the cast iron insert, reliable materials data are required as input data in connection with final mechanical strength calculations.

The canister with its cast iron insert must withstand considerable stresses under the hydrostatic pressure that can occur in a deep repository, for example, the groundwater pressure at a depth of more than 500 m in the rock, the pressure from the swollen bentonite buffer surrounding the canister and from a 3 km thick ice sheet (glaciation). Altogether, there might be a maximum pressure of about 45 MPa (450 bar) on the canister. In a recently conducted test, the model canister – with a cast iron insert with defects – managed a hydrostatic pressure that was three times as high, 130 MPa. Investigations of deformations and possible canister cracking are underway. On the basis of these studies, it will be possible to state, with a high degree of certainty, whether the canister will meet the requirements with an adequate margin (Nilsson and Burström, 2004).

The cast iron insert must be manufactured with high tolerance requirements as must the copper tube for the canister. Copper tubes manufactured by roll forming and longitudinal welding require more material for the final machining than the other manufacturing methods.

6.2.3 Lid Welding

Electron Beam Welding

Electron beam welding is a fusion welding method which in a vacuum (or under low pressure) with a strong electron beam melts the material through local heating. The method has several advantages: thick objects can be welded without consumables and weld parameters are programmable and reproducible. The weld has the same composition as the parent metal, but the oxygen concentration in the copper, in particular, has a negative impact on the weldability and the oxygen concentration must

therefore be controlled. Even with a high-energy method, such as electron beam welding, the welding of copper is difficult to conduct due to the high thermal conductivity of the material and the low viscosity of the melt. Therefore, the electron beam welding method needs to be further developed with respect to equipment and welding parameters in order to achieve a stable process with high reliability (Claesson & Ronnetag, 2003). In particular, the seal weld must meet the requirements on long-term properties and durability.

Friction Stir Welding (FSW)

The principle for Friction Stir Welding is relatively simple. A rotating tool is pressed into the joint between the parts that are to be welded. The copper around the tool is heated up by the friction to over 800°C and becomes soft. The tool is then moved in the direction of the joint and the two metal parts are joined together. The fundamental difference, compared with electron beam welding is that the material does not melt during welding. A new large welding machine for FSW has been taken into operation at SKB's Canister Laboratory in Oskarshamn in 2003. The design is such that the welding head rotates during the process around the stationary canister. When the FSW technique is developed, both the lid and the base are welded to the tube and the copper tube can also be manufactured of two halves of roll-formed plate, especially if 30 mm thick copper is to be used. The development of the tool, together with the optimisation of the design is particularly necessary in order for the technique to function reliably. When full-scale welding is conducted on a 50 mm thick copper canister (3.3 m long weld) with a welding speed of about 100 mm/min, the welding time is up to an hour for the entire canister circumference. The welding temperature can be up to 950°C and the welding forces are high (Andersson *et al.*, 1999; 2000; Cederquist, 2003).

Narrow Gap (NG) Welding

Narrow Gap (NG) TIG welding is currently used to a large extent for the manufacturing of nuclear power components of steel. For several different reasons, for example, the fact that the thermal diffusivity of the copper is 10 to 100 times higher compared with steel and nickel-based alloys, this technique cannot be applied to thick-walled copper products since the heat transfer must be very high and the welding speed becomes slow (Pohja et.al., 2003).

6.2.4 Residual Stresses

After all manufacturing stages, with forming, machining and welding, residual stresses will occur in the material. These residual stresses must be measured and modelled. The residual stresses have a major impact on creep and stress corrosion. The highest permitted value for the residual stresses, which should be below half of the yield point, must be determined. Furthermore, the need for different techniques to reduce the residual stresses, for example, through stress relief annealing or mechanical surface treatment methods, must be evaluated.

6.2.5 Non-Destructive Testing (NDT)

The copper canister has defects after manufacturing, but only a few (0.1 %) of the canisters are allowed to have greater defects than those allowed by the acceptance criteria for the NDT (RD&D Programme 2001). The acceptance criteria have not yet been specified. One assumption is that these unacceptable defects can cause water leaks in the canister in 100,000 years' time. Bowyer (2000) has compiled an overview of all possible materials or manufacturing related defects and residual stresses that can occur in copper canisters and in cast iron inserts. Above

all, defects in the canister lid weld are important. From the standpoint of corrosion, it is important to minimise the occurrence of fabrication-related defects. Therefore, it is essential that the size and form of various initial defects can be measured as accurately as possible. The requirements on the maximum grain size are important to facilitate ultrasonic testing. The acceptance criteria for initial defects must be based on the best available NDT methods. The sensitivity of the NDT methods must be verified with the help of metallography and microscopic investigations of defects and POD (probability of detection) diagrams for defects of different sizes, forms and positions must be generated. Further qualification of the NDT methods that will be used in the final process during the manufacturing and sealing of canisters must be conducted.

6.2.6 Encapsulation Plant

Trial manufacturing of thirteen full-scale canisters with cast iron inserts has so far been completed (Andersson, 2002). Five of these have already been used in different research projects.

The layout of the canister manufacturing plant was planned in Sweden (Andersson, 2001). The plant is expected to produce more than 200 canisters per year and contains equipment for machining canister shells and lids, welding of copper bottoms, machining of cast iron inserts, quality control and the final assembly of canisters. Finally, the finished canisters are delivered to the encapsulation plant. The handling of the canisters during manufacturing, transport and emplacement in the repository is critical for the subsequent corrosion behaviour of the canisters. Manufacturing methods, equipment and organisation still have to be established in order for canister manufacturing to be conducted as required to achieve a high level of productivity and quality in manufacturing. Further investigations concerning choice of method are needed with respect to welding processes and copper cylinder machining, in particular.

6.3 Durability

6.3.1 Corrosion Properties

The copper canisters will be affected by both general and different types of local corrosion in the complex chemical, microbial and mechanical environment of the repository, which varies in time and space. The probability of corrosion penetration in the canister should be very low in a 100,000-year perspective. During the first hundred or two hundred years, the copper shell will be deformed under compression. During the same time, oxidising corrosion conditions will occur in the repository. The risk of stress corrosion during this stage must be thoroughly evaluated. The threshold for the initiation and crack propagation of stress corrosion in copper must be measured in the repository environment under different modes of loading. There is a considerably better understanding of other corrosion mechanisms, both with respect to general and local corrosion (pitting and crevice corrosion), due to laboratory investigations and experience from marine and archeological copper discoveries. Considerable progress has also been made with respect to the modelling of these corrosion forms. However, a fundamental problem is the fact that the corrosion rates are based on short-term experiments. Therefore, it is uncertain whether these results are relevant to very long timescales. All known corrosion mechanisms with respect to copper have been summarised in a state-of-the-art report (King *et al.*, 2002). The corrosion properties of weld metals, where the microstructures vary and are quite different compared with the base metal, have been investigated to a limited extent.

When the copper shell has been penetrated due to some corrosion and rupture mechanism, the water will penetrate into the damaged canister and into the gap between the copper shell and the cast iron insert. The copper and cast iron are in contact with each other and galvanic corrosion occurs in the cast iron which causes hydrogen gas to form and leads to increased

pressure inside the canister. Under anaerobic conditions, the rate of cast iron corrosion is still very low, less than $1 \mu\text{m}/\text{year}$. The galvanic contact with copper in oxygen-free water will only cause a marginal increase in the corrosion rate. Verified experiments should still be conducted to show that galvanic corrosion is not probable in a repository environment for the canister configuration in question. After some time, water will come into contact with the spent nuclear fuel and tube material of zirconium and the actual fuel material will also be attacked by corrosion. At this stage, a number of corrosion mechanisms are active and modelling must be based on many different assumptions (e.g. Shoesmith, 2000). Due to the complexity and the possible interaction between different mechanisms, in order to better model how corrosion damage evolves in the damaged canister, empirical studies must also be conducted under realistic conditions in the future.

6.3.2 Creep Properties

After manufacturing, there is a gap of about two mm between the copper shell and the cast iron insert (depending on tolerances). This means that the copper must be capable of deforming about 4-5 % in the repository. Slow deformation, in the temperature range of 75 to 90°C, which occurs in the repository under residual stresses together with the hydrostatic pressure and the pressure caused by the swelling of the bentonite buffer, generates creep in the copper shell. The copper which is used must have a creep ductility (maximum strain before rupture) of at least 10 % even after long timescales, both in the base metal and the weld metal. The importance of the phosphorus alloying (50 ppm) in the base metal for the creep-rupture strength and creep ductility of pure copper must be explained mechanistically. Information is also needed about the mechanisms for the long-term extrapolation of available data. It is important to explain the creep properties of weld metals, both

for the electron beam and FSW welding, which have very different creep properties compared with the parent metal due to their highly variable grain size, which is of importance to creep. When the creep data for all of the canister materials is available, it is possible to carry out a Finite Element Modelling of the deformation of the entire canister.

6.4 Summary

The canister design has already been specified with high precision and the design principles can be considered to be good. However, flexibility must be maintained when ultimately selecting the manufacturing methods, such as lid welding. Full-scale manufacturing is probably easier with extrusion and draw and pierce processing compared with roll forming and longitudinal welding, which cause greater residual stresses in the canister. When selecting the manufacturing method, economic factors should not only be taken into account but also, for example, the long-term properties of the canister. The above-mentioned methods are known in the steel industry on a large scale, but have not been previously used for copper products. As a result, a very small number of companies are expected to be adept at these techniques on a large scale for copper.

The insert, which is of nodular cast iron, has not yet shown such acceptable mechanical properties and, therefore, the casting process must be analysed and better controlled or some other type of cast iron must be used. Casting defects must be more thoroughly analysed. Casting simulation can be a support when planning improvements in casting processes and for the design of different forms of casting. Also, a more accurate specification of the casting process (downhill or uphill) and requirements for the insert are necessary.

Welding methods, electron beam welding and FSW are potentially acceptable for high quality welding of canisters. Both methods, especially FSW, should be further developed. Electron

beam welding is known to be suitable for steel products on a large scale and FSW has been previously applied to thick aluminium structures. FSW is a completely new technique which has never before been used for welding 50 mm thick copper. These methods should be further studied since both methods may be needed, especially for repair welding. Under all circumstances, a very deep understanding of the mechanisms that cause weld defects must be developed and the planning of repair welding must be started at an early stage. For this, different NDT methods are required in order to detect defects and to verify the quality of the canisters. It is also very important that no macro-defects, which can rapidly penetrate the canister, should occur during manufacturing and remain undetected. It is necessary to thoroughly follow the development of new NDT methods and to determine their limitations for different defects (Stepinski *et al.* 2004).

More research work, focusing on the long-term properties of the copper canisters with different manufacturing methods and conditions, is required to better predict future scenarios. More corrosion research is necessary, especially focusing on stress corrosion and microbial corrosion of the copper canister; at an initial stage, under laboratory conditions but also over a longer timescale and, if possible, also *in situ* in the actual repository.

To guarantee reliability throughout the canister manufacturing process and the final disposal period, acceptance criteria for all of the components of the canister, including welds, must be developed. These criteria should take into account material properties and defects, both surface defects and defects inside the material, in the copper shell and in the cast iron insert. Altogether, consequence analyses must be performed in order to predict possible processes when the canister does not meet the requirements that have been established. It is also important that the acceptance criteria can be verified by NDT methods and that a quality system for canister fabrication will be formulated.

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7 An Attempt at a Comparable Classification of Radioactive Waste and Hazardous Chemical Waste

7.1 Introduction

The quantification and classification of risks are currently being conducted in different ways for different activities. This means that the risks to which human beings are exposed are difficult to compare and the overall situation is difficult to evaluate. From the standpoint of society, it is desirable to obtain as many comparable assessments as possible. This chapter attempts to compare the risks of radioactive waste with the risks of hazardous chemical waste.

Waste is material that is considered to have too low a value to justify further use and must therefore be disposed of in some way. Waste therefore imposes an economic burden on the producer and society. However, it cannot be excluded that the waste could have a value in some other application than that where it was produced or in a future activity. Waste, which contains toxic substances, either in the form of radionuclides (radioactive substances) or toxic chemicals, is created by many human activities. Waste can arise as a result of the increased availability and concentration of natural substances and materials (mining activities, petroleum extraction, uranium extraction), industrial activities (melting facilities, metal industry, chemical industry, pharmaceutical industry), agriculture (weed killers, plant protection agents) or in households (batteries, fire detectors, electronics, medicines).

Many of the most important radioactive substances, from the standpoint of waste, are heavy metals and have chemical pro-

perties that are similar to those of non-radioactive (stable) heavy metals. They are non-volatile and less soluble in water than several other pollutants. It is also important to remember that radioactive substances with long physical half-lives can be more chemically toxic than radiotoxic. This applies, for example, to natural uranium in human beings and, probably also to radioactive iodine, ^{129}I , in soil.

Unlike organic pollutants – and like metals – radionuclides cannot be destroyed or degraded. Therefore, waste management is based on methods such as separation, concentration, volume reduction, fixation and isolation.

Radionuclides have the advantage over stable heavy metals that the amount of a radioactive substance is reduced through radioactive decay, even if the process occurs slowly in some cases.

Over the years, radioactive and chemical waste have come to be viewed differently. Classification systems and regulations are currently strongly associated with the source of the waste.

The difference in views has meant that the public often judges radioactive waste as hazardous while planners often have the view that safety margins are large with respect to radioactive substances. Similar risk-based classification systems and regulations for radioactive substances and chemically toxic substances would simplify environmental impact statements. For environmental and economic reasons, society would gain from a harmonised view based on evaluations that are made on principles that are as similar as possible. Such an approach would also broaden the perspective in the debate on a repository for spent nuclear fuel and would bring to the fore the need for a corresponding repository for heavy metals, such as mercury (SOU, 2001).

7.2 Proposal for a Comparable Classification of Radioactive and Chemical Waste

The National Council on Radiation Protection (NCRP, 2002) in the USA has recently proposed a system for classifying all types of waste containing either radioactive or chemically toxic substances. This chapter describes the proposal and discusses it in the light of the current system, which is different for radioactive substances and toxic chemicals. The proposed system is interesting in principle, since it provides the necessary basis for making the above-described similar evaluations of different types of waste.

In Europe, limited activities are conducted in the area within the OECD/NEA and within the European Union's Fifth Framework Programme (www.riskgov.org).

The system proposed by NCRP:

- can be used for each type of waste that contains radio-nuclides, hazardous chemicals or a mixture of these,
- has a classification that is based on a determination of the health hazards to the population resulting from the waste,
- has an exemption class for waste that involves such a low risk that it can be handled as non-hazardous waste.

The system comprises 3 waste classes:

High-level hazardous waste
Low-level hazardous waste
Non-hazardous waste

The system is based on the following principles:

- A linear dose-effect relationship without a threshold for cancer-inducing substances and with a threshold for non-cancer-inducing substances.
- The term "dose" should be given a uniform meaning. "Dose" currently means different things for radioactive substances

and for hazardous chemicals. In the case of radiation and radioactive substances, the “dose” is the absorbed dose (often average absorbed dose to the entire specified organ or tissue) or effective dose. The biological effect can be assessed from such dose data. The “dose” in the case of toxic chemicals (as for pharmaceuticals) is the amount of substance taken in.

- A uniform risk concept. The risk figures that have so far been used for ionising radiation and radioactive substances refers to the number of cancer fatalities while, for chemically carcinogenic substances, the number of cancer cases (incidence) is usually cited.
- The way of estimating health hazards is also different in the case of radionuclides and hazardous chemicals through the varying degree of caution that is incorporated into the postulated probabilities for undesirable health effects per dose unit and through taking into account different numbers of risk organs in the body.
- A number of exposure scenarios are assumed when estimating the risk that human beings are exposed to (exposure situations that can be used for each waste repository).

7.3 Designations for Risks to Individuals

For ionising radiation, the following risk assessments are often made

- *Unacceptable risk*, which must be reduced, regardless of cost or other conditions. This assessment is made if the radiation caused the extra risk of dying of cancer during the rest of the individual’s life to be greater than an “acceptable” level (often a value in the range of 0.1-0.001 or greater or, in other words, between 10 % and 0.1 % or greater; where in the range it is, often depends on the exposure situation).

- *Acceptable risk* (risks under unacceptable levels as well as ALARA – “as low as reasonably achievable”). Risks just below unacceptable levels are considered to be just about acceptable and should be considerably reduced by applying the ALARA principle.
- *Negligible risk* is considered to be so low that further effort to reduce the risk (in accordance with ALARA) is not justified. This risk usually comprises an extra fatal cancer risk of 0.0001-0.000001 (0.01-0.0001 %) or less for the rest of the individual’s life.

What we currently call “acceptable” risks or doses in the case of toxic chemicals corresponds to what is called “negligible” risk in the case of radionuclides, while “acceptable” risks or doses in the case of radionuclides may be far above negligible levels, providing that they are ALARA. In the case of hazardous chemicals, “unacceptable” is essentially the same as “non-hazardous”. In the case of radionuclides, “unacceptable” refers to doses and risks that are far above negligible levels that cannot be tolerated under normal conditions.

Table 7.1. Differences in the interpretation of “acceptable” and “unacceptable” risk (dose) for radionuclides and hazardous chemicals

<i>Risk description</i>	<i>Interpretation for radionuclides</i>	<i>Interpretation for hazardous chemicals</i>
"Unacceptable"	Intolerable risk. This risk must be reduced, regardless of cost.	The risk exceeds negligible levels. Risk reduction must be considered but is only required to an appropriate extent.
"Acceptable"	Risk below intolerable levels and ALARA.	The risk is negligible. Further risk reduction is not necessary.

Risk, in the case of radioactive substances, is considered to be unacceptable even if it is below unacceptable levels, but not ALARA. This difference in interpretation between toxic chemicals and radioactive substances in risk assessment causes considerable difficulties for decision-makers and the general public as well as for those who have to provide information to these groups.

7.4 Proposed Risk Index for Waste Classification (NCRP)

“Risk” generally refers to the probability of damage occurring combined with the degree of severity of the damage (for example, death, reduced life expectancy, reduced kidney, liver or thyroid function).

For waste, the NCRP normally states the risk as the probability that something will happen to an individual or as the frequency of events in a population group. The following are required in order to calculate the risk

1. The probability of events resulting in a radioactive release
2. The probability that the individual or population group will be exposed to the release
3. The probability that exposure will result in damage

The risk from a repository/landfill can be expressed as a dimensionless risk index (RI). The risk index for the i th hazardous substance (R_i) is defined as the risk that arises from the disposal of the substance in question relative to a determined allowable risk for an assumed waste system.

$$RI_i = F_i \frac{(\text{risk due to disposal})}{(\text{allowable risk})}$$

F_i is a modifying factor for substance i and may depend on the design of the waste facility, the packaging of the waste, the uncertainty in the risk assessment etc.

For each substance where the risk can be assumed to be proportional to the dose (substance quantity/activity quantity) without a threshold, RI_i can be written as follows:

$$RI_i = F_i \frac{(\text{dose due to disposal})}{(\text{allowable dose})}$$

The difference in the meaning of “dose” for radionuclides and chemicals is uninteresting as long as the same meaning is applied to a given substance in the numerator and the denominator.

If we assume that the risk from an individual source is additive, the following is required

$$\sum_i RI_i < 1$$

namely, that the sum of all contributions may not exceed the permissible dose (or risk).

Adding the risks for non-carcinogenic substances requires caution, bearing in mind the fact that the dose-effect relationship does not have to be linear and that interacting (multiplicative) factors between different chemical substances cannot be excluded.

The advantage of the proposed risk index is that all toxic substances are treated in a similar manner.

7.5 A Risk-based Waste Classification System

The NCRP proposes that all types of waste should be classified into three classes.

I Waste Excluded from the Regulations

For non-carcinogenic toxic chemicals, the NCRP recommends that a negligible dose should be defined as a small fraction (for example, 10 %) of a certain threshold value for deterministic (predictable) effects in human beings. For radionuclides, it is recommended that an annual effective dose of 0.01 mSv should be considered to be a negligible individual dose. This dose corresponds to an estimated lifetime risk of cancer mortality of about $4 \cdot 10^{-5}$ (0.004 %) for an assumed exposure time of 70 years (5 % per Sv). This dose is also the dose that the IAEA uses to define an exemption class for radioactive waste.

What is meant by negligible risks or doses for radionuclides and chemical carcinogens can also be discussed in relation to risks from natural background radiation (1 mSv/year) that cannot be avoided. Since the lifetime risk from exposure to natural background radiation and the natural occurrence of chemical cancer-inducing substances is about 1 %, a negligible risk could be determined as a part of this average background risk (for example 1 % of 1 %). In the long-term, such a “negligible risk” would be less than the variation in background risk, which arises as a result of differences in living habits.

II Low Risk Waste

Low risk waste can be deposited in a special landfill for hazardous waste. It should be possible to derive the limit for concentrations of hazardous substances by establishing that the risk or dose for an unintentional intrusion should not exceed acceptable (just tolerable) levels.

Acceptable (barely Tolerable) Risks or Doses

For non-carcinogenic toxic chemicals, an acceptable dose should be established at the threshold for the deterministic effect on humans or just below the threshold (for example, by a factor of 2 or 3) if an additional safety margin is desired.

For radionuclides, the limit for the annual effective dose to individuals among the general public is 1 mSv, which corresponds to an estimated risk of dying of cancer during the remaining lifetime of about 4×10^{-3} or 0.4 % (for an assumed exposure time of 70 years). This can be compared to the risk of dying of cancer from causes other than radiation which is just over 20 % or a little more than one out of every five people. Acceptable risk or doses can, as above, also be related to the unavoidable risk from the natural background.

III High-risk Waste

This waste cannot be deposited in landfills but must be deposited beneath the surface of the earth. Geological repositories have so far been the solution for high-level radioactive waste. This type of disposal is also now recommended for mercury (SOU, 2001).

7.6 Risk Estimates and Risk Comparisons

It is possible to, at least theoretically, estimate the risk from low radiation doses (ICRP, 1991). It is of course necessary to discuss this risk in the light of the risk that we accept, without further thought, in our daily lives, for example, risk from natural background radiation. On the other hand, the existence of other risks does not entitle exposure to additional radiation. However, the risk that we have previously accepted provides a framework

for gaining a perspective on the risk of an additional exposure to radiation from radioactive waste.

Another way of gaining a perspective on the radiation doses to which we are exposed is to compare the hazards of radionuclides with the hazards of chemicals. There is a basic difference between radioactive substances (ionising radiation) and chemicals with respect to dose-response calculations. The dose-response calculations for radiation can be based on an estimated absorbed dose to organs and tissue in the body. Furthermore, the relationship between the dose and the response which was obtained from studies of groups of individuals exposed to radiation is applied to all radionuclides and most exposure situations. Thus, separate studies do not have to be conducted for each individual radionuclide as is required for each individual chemical. In the case of chemicals, the situation becomes more complex because there are about 30,000 substances, of which perhaps 20-25 % may cause cancer, damage to the embryo/foetus and genetic effects (Bengtsson, 2002). For toxic chemicals, no units have yet been defined that correspond to the absorbed dose or equivalent dose, even if much work is currently being done to develop a "dose measure" (Törnqvist and Ehrenberg, 2001). The dose response relationship for specific toxic chemicals must therefore be based on studies of the specific substance.

Predictable (Deterministic) Tissue Effects

A basic principle in protection work is to prevent predictable (deterministic) tissue effects (for radiation: skin damage, cataracts; for chemicals: kidney and liver damage, neurological effects etc.) occur both as a result of radioactive substances and chemicals. For chemicals and radiation, the dose-effect curve is expected to have a threshold for deterministic effects. For each substance, the assumed threshold value is based on data for the most sensitive organ or tissue. However, there are important

differences between radioactive substances and toxic chemicals in the way these threshold values are calculated and then applied for radiation protection work.

In radiation protection, dose limits for predictable effects (skin damage, cataracts) are only based on data from human beings and are normally established at a factor of 10 below the assumed threshold values. This safety factor is intended to ensure that deterministic effects are excluded for practically all individuals, including those who could be unusually sensitive to radiation. With respect to toxic chemicals, an even more conservative approach (which probably overestimates rather than underestimates the risk) is used. This is partly due to the fact that the toxicity of the substances has only been studied in animal experiments. Limits for acceptable doses are often defined by “reference doses”, which are usually derived from the lower value of the uncertainty range for the assumed threshold values in the way that they are represented by the NOAELS (No Observed Adverse Effect Level) or lower confidence limits, for the benchmark dose (the dose where 10 % of the tested animals show an effect) by adding a great number of safety and uncertainty factors, most often of a minimum of a factor of 100, in order to obtain a reference dose. These safety factors can be as high as 5000 for some substances.

The reference doses for toxic chemicals therefore probably most often give a significantly greater safety margin than the dose limits for radiation-induced predictable effects.

Random (Stochastic) Effects

The basic principle for protection against both radioactive substances and toxic chemicals is that the probability for random effects, primarily cancer, should be limited to an acceptable level for the individual and society, seen in the light of the advantages that the activity generates or has generated. For each substance that causes random effects, a linear dose-response relationship

without a threshold is generally postulated for health effects. This approach is well established in radiation protection and is gaining increasing acceptance with respect to estimating the risk of cancer from carcinogenic chemicals in the environment (Bengtsson, 1998; Granath and Ehrenberg, 1997; Duggan and Lambert, 1998; Granath et al., 1998; Törnquist and Ehrenberg, 2001).

The specified probability values for radioactive substances and chemicals that result in stochastic effects differ in two important respects. Firstly, the dose-response relationship for radiation and associated probability coefficients is based on the best possible estimates. On the other hand, as far as chemicals causing stochastic effects are concerned, the corresponding data are often intended to provide an upper boundary (the upper boundary in the uncertainty interval). In animal data, such a value can be 5 to 100 times greater than the best estimate. Secondly, the primary measure of random effects of exposure to radiation and radioactive substances has been the number of fatalities for the rest of life. On the other hand, in the case of chemicals, the measure has been the incidence, namely the proportion of those becoming ill or injured in a population as a result of exposure to a carcinogenic substance, which is explained by the fact that, in the latter case, the estimate is based on animal testing.

There is another difference between radiation and chemicals. Radiation is a more general carcinogen which can result in cancer in many more organs and tissues than chemicals. In radiation protection, the effective dose measure takes this into consideration. In the case of most of the toxic chemicals, only a single risk organ or tissue is taken into consideration and the rest of the body is ignored. The development of biokinetic models for toxic chemicals provides a corresponding possibility. However, such models have not yet been prepared to any great extent.

7.7 Calculation of Risk Figures

Different measures of cancer risk are established for radionuclides/radiation and chemicals. In order to classify radioactive waste, the risk figure of 0.05 per Sv (5 % per Sv) can be used, which is the figure that is normally used for the radiation protection of the public (ICRP, 1991). This figure has been derived from the best adaptation to epidemiological data for high doses, above all from Hiroshima and Nagasaki, and has then been further adapted for low radiation doses and dose rates (factor: 0.5). For chemical carcinogenic substances, the risk figures come from the upper value of the uncertainty interval for observed effects at high doses (mainly from animal studies). In several studies, the adjustment at the upper boundary of the uncertainty interval is 10 times higher than that obtained with the best possible adjustment.

For risk estimates, the risk figure mentioned above is applied to the effective dose. The risk figures for chemical carcinogenic substances are based on the observed effects on an individual organ or on a special tissue (often in animals). Attention is seldom paid to the possibility of effects on several organs. Risk figures for low doses of carcinogenic chemicals are more conservative (it is more probable that the risk is overestimated) than the risk figures for radioactive substances.

For radionuclides, the dose constraint at an effective dose of 1 mSv limits the deterministic effects. In the case of toxic non-carcinogenic chemicals the threshold for deterministic effects on humans is estimated from benchmark doses which, to an increasing extent, are used to obtain values for permissible doses of non-carcinogens. A benchmark dose is, as has already been mentioned, a dose that belongs to a specified effect level in a population that is studied (for example, a 10 % increase in the effect). The lower boundary of the uncertainty interval for the benchmark dose (which belongs to the 10 % increase) is then used as a basis for obtaining the permissible dose. In order to obtain a dose that will provide a safe protection for all human

beings, it is recommended that a dose that is 10 times lower than the lower confidence level should be used for the “benchmark” dose which is obtained in connection with a well-conducted study of human beings and 100 times lower than the lower confidence level for a benchmark dose that is obtained in connection with a well-conducted study on animals.

In order for the proposed standardised classification system to be usable, risk figures for a very large number of chemicals must be obtained. The limited availability of such risk figures currently limits the applicability of the proposed system.

7.8 Examples of Comparative Limits for Radiation, Asbestos and Nickel

In this section, the limits that have been obtained for exposure to radiation, asbestos fibres and nickel compounds are compared (Schneider et al., 2000). Both epidemiological studies and animal experiments have clearly shown that asbestos fibres and certain nickel compounds can cause cancer in the same way as radiation. Epidemiological studies have shown that there is a relationship between relatively high exposure levels and an extra incidence of cancer. There is also cause for a linear, no-threshold relationship to be assumed between exposure and risk. The comparison between risk and permissible levels is based on the rules applied in France (which, at least with respect to radiation, are the same as in Sweden) and are illustrated in *Table 7.2*.

Table 7.2. Comparisons between risk estimates and permissible exposure levels for ionising radiation, asbestos and nickel. In this comparison, an exposure time of 40 years has been used.

	<i>Extra risk of mortality during the expected remaining lifetime</i>	<i>Permissible exposure level</i>	<i>Risk in connection with permissible exposure level for 40 years</i>
Ionising radiation, occupationally exposed persons	4 % per Sv	100 mSv/5 years	3 %
Asbestos, occupationally exposed persons	0.04 % per fibre/ml years	0.1 fibre/ml	0.16 %
Ionising radiation, public	5 % per Sv	1 mSv/year	0.2 %
Nickel, public	14 % 10^{-6} per ng/m ³ year	Tens of ng/m ³	0.01 %

The dose limits for ionising radiation, asbestos and nickel are based on extrapolations from known dose-risk relations at high exposure levels. In order to arrive at permissible exposure levels, a comparison with the risk of mortality in other occupations considered to be safe has been conducted for occupationally exposed persons. For the public, comparisons with natural background radiation have been conducted.

7.9 Consequences of the Proposed Classification System

The proposed classification system is applicable to every type of waste containing radioactive substances, toxic chemicals or a mixture of these two types of waste. The system is based on an assessment of the health risks to the public as a result of waste disposal. The system contains an exemption class, which contains waste which entails a very low risk and which can be

handled as non-hazardous material. The other two classes are low-risk waste (can be stored in near surface facilities) and high-risk waste (requires an underground repository in bedrock).

In future work, the limits between the different waste classes can be quantified in terms of limits for concentrations of different substances so that the exemption group will contain such as low concentrations that the substances do not entail more than a negligible risk for a hypothetical "intruder" into a waste repository. The low-risk facility may not cause more than an acceptable risk for an intruder. Waste with a higher content than can be dealt with the two types of near surface facilities mentioned are classified as high-risk waste and need to be deposited in the bedrock.

The fact that considerable quantities of waste that contain small amounts of radionuclides or toxic chemicals can be excluded from the regulations simplifies handling and makes it cheaper. The high-risk waste will mostly comprise high-level radioactive waste, transuranic waste and long-lived radioactive waste with a lower activity. Chemical waste containing high concentrations of heavy metals (lead, cadmium, mercury) belongs to the same group. The current classification system for chemical waste does not contain such a class. It is assumed that the proposed system will be advantageous compared to the current system. It is simple and easy to understand. The clear connection between the classification and the requirements of protecting the public health will hopefully increase public confidence in waste management and disposal. The system has obvious advantages when it comes to handling mixed waste. The system provides the necessary conditions for a more just assessment of the hazard of different types of waste than the current system.

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