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INORGANIC CHEMISTRY | REVIEW ARTICLE

An introduction to serious nuclear accident chemistry

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Abstract: A review of the chemistry occurring inside a nuclear power plant during a serious reactor accident is presented. This includes some aspects of the behavior of nuclear fuel, its cladding, cesium and iodine. This review concentrates on the chemistry of an accident in a water-cooled reactor loaded with uranium dioxide or mixed metal oxide fuel.

Subjects: Chemistry; Environmental Chemistry; Inorganic Chemistry

Keywords: iodine; cesium; Chernobyl; Fukushima; serious reactor accidents; uranium; tellurium; niobium; fallout; radioactivity

1. Introduction

Regardless of how in favor or how opposed to the use of nuclear technology you or your government is, the possibility of serious nuclear accidents is relevant; either a nuclear plant in your own country or one in another state could malfunction and release radioactivity. What happens after a nuclear or radioactivity accident is often misunderstood; it is important to avoid falling into one of two equally bad traps. One is to dismiss such events as having no ability to cause harm, while the other is to assume any release of radioactivity will result in an adverse outcome such as cancer, impaired fertility, or even the acute radiation syndrome (commonly known as radiation sickness). Both extreme assumptions are equally wrong; the chemistry of the event will control the size of the release into the environment, the mobility of the radioactivity, and how it behaves when it finally reaches humans, animals, and plants. Another snare to avoid is the belief that it is impossible for anyone outside either the expert population, in either the nuclear sector or antinuclear movement, can ever be able to understand the event. The last trap is that the ordinary chemist, physicist, or physician is able to understand such an event with no additional education or training beyond that normally delivered during their bachelor's degree. It is sad that many professionals believe that they are incapable of obtaining an understanding of these events, while others stray into areas which they know nothing about while proclaiming a mastery of these areas. This review of some areas of serious nuclear reactor accidents will inform the reader and act as an antidote to these snares.

ABOUT THE AUTHOR

Foreman is an associate professor in Chemical and Biological Engineering at Chalmers University of Technology, Sweden. His research covers both nuclear chemistry and industrial materials recycling. Much of his work is centered on the recycling of polymers, metals, and other materials while also evaluating practices surrounding the safe and sustainable (environmental, social, and financial) management of hazardous wastes. Additionally, Foreman's work focuses on the chemistry of serious reactor accidents, the organic chemistry of low/intermediate radioactive wastes, and new separations for the nuclear fuel cycle.

PUBLIC INTEREST STATEMENT

While many nations use nuclear power to deliver the electrical energy they need, the disadvantages of nuclear power include the production of hazardous waste and the possibility of a serious reactor accident. The radiation dose due to a serious nuclear accident to the public is influenced by the chemical properties of a series of materials both inside the plant and elsewhere. This paper is a review of some of the important chemical processes which are either part of a nuclear reactor accident or associated with the accident.

2. Review

In April 1986 a safety experiment at Chernobyl went horribly wrong, while in March 2011 an earthquake and flooding caused a long-lasting loss of electrical power (station blackout) which resulted in serious damage to the cores of three nuclear reactors. These two large accidents have some features in common, but many differences exist between them. It is important to understand that chemistry controls the progression of a reactor accident and the release of radioactivity. I have chosen to write about these events in April as it is around the anniversary of both events. I will restrict myself to that which is verifiable and well proven.

The Chernobyl accident was a large surge in the rate of the nuclear fission process caused by a combination of poor reactor design, failures by regulatory bodies, and operator error. Here, the neutron poisoning caused by ^{135}Xe ($t_{1/2} = 9.2$ h) which is formed by the beta decay rate of ^{135}I ($t_{1/2} = 6.6$ h) suppressed the reactivity of the core. The operators tried to maintain the core at a low power by withdrawing almost all of the control rods, then as they started the test the rapid consumption of ^{135}Xe by neutron capture combined with some other effects (such as the void effect) caused the reactivity rate to increase greatly. The operators were unable to reinsert the control rods sufficiently quickly to maintain control of the reactor, and a steam explosion (boiling liquid expanding vapor explosion) occurred which blew the reactor apart. Equation 1 can predict the amount of ^{135}Xe in a reactor if we assume the whole reactor has the same neutron flux (ϕ).

$$N_{\text{Xe}} = \left\{ \phi \gamma I \sigma_{\text{fission}} N_{\text{U}} \lambda_{\text{I}} \left(\frac{1}{\lambda_{\text{I}} K_{\text{Xe}}} \right) + \left[\frac{(e^{-\lambda_{\text{I}} t})}{(-\lambda_{\text{I}} / \{ (K_{\text{Xe}} - \lambda_{\text{I}}) \})} + \frac{(e^{-K_{\text{Xe}} t})}{(-K_{\text{Xe}} / \{ \lambda_{\text{I}} - K_{\text{Xe}} \})} \right] \right\} + \left[\lambda_{\text{I}} N_{\text{I}}^0 / (\lambda_{\text{Xe}} - \lambda_{\text{I}}) \right] \cdot (e^{-\lambda_{\text{I}} t} - e^{-\lambda_{\text{Xe}} t}) + (N_{\text{Xe}}^0 \cdot e^{-\lambda_{\text{Xe}} t}) \quad (1)$$

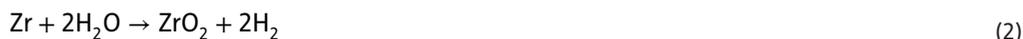
where K_{Xe} is $(\lambda_{\text{Xe}} + \phi \sigma_{\text{Xe}})$, N_{U} is the number of ^{235}U atoms, λ are the decay constants, and σ are the neutron cross sections. While the kinetics of the xenon poisoning effect might appear to be complex, the Bateman equations can explain it (Bateman, 1910). These equations allow a prediction of the amounts of different nuclides in a decay chain; these allow a series of first-order reactions to be modeled.

While at Fukushima the damage was not caused by a power surge, in contrast to the Chernobyl accident, the three damaged cores at Fukushima boiled dry and slowly heated up over hours until the fuel melted. The Fukushima reactors were SCRAMed by the earthquake, so in common with the Three Mile Island accident the damaged reactors were in a shutdown state. The term for an emergency or unplanned shutdown of a nuclear reactor is Safety Control Rod Axe Man (SCRAM); the origins of this term are not clear. A man with an axe was near the first man-made nuclear reactor (Chicago Pile). In the event of an uncontrollable nuclear reaction, his duty was to cut a rope thus causing control rods to reinsert into the reactor. A range of different methods exists for SCRAMing nuclear reactors, for instance at the Torness nuclear power plant is to inject nitrogen gas into the carbon dioxide-cooled core. It is noteworthy that in common with any area of endeavor, the nuclear/radioactivity field has its own lexicon; to avoid confusing the reader, this review is written in plain English. However, to educate the reader, sometimes a nuclear word will be included in brackets after plain English phrase.

The molten fuel slumped to the bottom of the reactor pressure vessels before melting a hole through the bottom of at least one pressure vessel. The gradual fuel melting at Fukushima was similar but worse than the fuel melting and core damage that occurred in 1979 during the Three Mile Island accident.

During the Fukushima accident, a series of explosions occurred; these were hydrogen/air explosions; we should consider where did the hydrogen come from. One of the key reactions forming hydrogen was the reaction of zirconium alloy (zircaloy) with water. As all chemists should understand, the more electropositive metals (sodium, potassium, magnesium, and calcium) react with water. In common

with aluminum and titanium, an oxide coating normally protects the surface of zirconium. This oxide layer protects the metal from air and water. Because of intense heating, the metal can start to react with oxidants such as air, water, and other metal oxides. Here, the protective effect of the oxide has been defeated. As nuclear fuel overheats in steam, the water will react with the hot zircaloy to form zirconium dioxide and hydrogen gas in an exothermic reaction according to Equation 2:



I imagine that many of my readers will be aware of the thermite reaction; the classic thermite is a mixture of aluminum powder and iron(III) oxide. This mixture requires heating to a high temperature; then a vigorous reaction forming iron metal and aluminum oxide occurs. As oxide nuclear fuel is heated up, it can start to react with the cladding according to Equation 3; this reaction releases further heat and can also lower the melting point of the fuel in the reaction zone:



Near the Chernobyl accident site, evidence of a layered structure was found. Here, on the surface of uranium oxide was found a layer of a zirconium-doped uranium dioxide, a mixed uranium/zirconium oxide, and finally zirconium bearing a thin layer of the oxide (Ushakov, Burakov, Shabalev, & Anderson, 1997) (Figure 1).

The western plume of radioactivity from the Chernobyl reactor included particles with a mixed zirconium uranium oxide; this indicates that uranium dioxide reacted in the absence of air with zirconium metal. The fact that air inhibits this reaction clearly indicates that the fuel reached at least 2,600°C before the reactor disintegrated during the first explosion (Burakov et al., 1997). One alternative to zircaloy would be to use silicon carbide as a fuel cladding in light water reactors, together with other accident-tolerant claddings and fuels; these are reviewed elsewhere (Youinou & Sen, 2014). A further similar heat-producing reaction is that of boron carbide with metals; (B₄C) reacts with many transition metals to form borides (Mirsalehi & Hadian, 2010). This reaction is exothermic, while the use of boron-containing steels might appear to be attractive. Inside control rods, a large amount of helium is generated according to Equation 4:



Helium bubbles can form inside the metal after neutron irradiation; in one recent paper, both helium and lithium have been detected in voids in neutron-irradiated boron-loaded steel (Klimenkov, Möslang, & Materna-Morris, 2013). Helium production in the metal can cause stainless steel to become brittle (Materna-Morris, Möslang, Rolli, & Schneider, 2009). To avoid this degradation of control rods, it is common to use boron carbide. Boron carbide has some advantages; the control rods do not become intensely radioactive. In recent years, I visited a small power reactor (Ågesta), which was shut down in the 1970s. This reactor used another type of control rod; these rods over 30 years later were still very radioactive.

Overheated nuclear fuel will release radioactivity; the volatility of the element in question has a very strong effect on the fraction of an element that is released. For example, if we look at the releases of radioactivity from the fuel into the water pools (Nishihara et al., 2015) at the Fukushima accidents, it is clear that the fraction of the elements released from the fuel varied greatly between both the units and the elements (Table 1).

Figure 1. Fuel cladding interaction during overheating.



Table 1. Release of different elements into water pools at Fukushima

Nuclide	Release into water pools (%)		
	Unit 1	Unit 2	Unit 3
¹³¹ I	6.9	52	27
¹³⁴ Cs	6.8	33	17
¹³⁶ Cs	7.0	27	14
¹³⁷ Cs	6.2	34	17
¹⁴⁰ Ba	-	1	0.7
¹⁴⁰ La	-	0.5	0.1
³ H	5.9	57	67
⁸⁹ Sr	-	1.6	1.5
⁹⁰ Sr	-	2.4	2.2

It is clear that more of cesium and iodine than strontium and barium was released from the fuel. One of the main reasons for this difference is the difference in the boiling points of the elements. Much of the iodine in the used nuclear fuel is present as cesium iodide. Because of the temperature gradients which exist in nuclear fuel pellets during normal use, the volatile fission products tend to migrate into the gap between the pellets and the cladding.

What tends to happen is that during the fission process, the majority of the nuclei with a mass of 133 amu are in the form of ¹³³Xe ($t_{1/2} = 5.2$ days); this gives these atoms plenty of time to diffuse through the fuel pellets into the colder gap between the cladding and the pellet. It is also important to note that more fission occurs in the rim of a pellet rather than the core of the pellet. This is because the thermal neutron flux is highest near the edge of the pellet; the core of the pellet is shielded by the outer layers of the pellet from thermal neutrons. As a result, plenty of ¹³³Xe is in the rim and gap where it decays to stable cesium (¹³³Cs). This stable cesium tends to combine with iodine to form cesium iodide in this area of fuel pins. The precursors (¹³⁵I $t_{1/2} = 6.6$ h and ¹³⁷Xe $t_{1/2} = 3.8$ min) for the other important cesium isotopes have half-lives of hours or minutes which helps these cesiums appear in the gap and rim.

While we normally do not think of cesium iodide (bp = 1,280°C) as being volatile, the melting points of zirconium metal (1,860°C) and uranium dioxide (2,900°C) so when the fuel cladding melts and then uranium dioxide melts then cesium iodide will evaporate. This is the reason why cesium is so mobile during a nuclear accident when compared with the fission products which tend to either stay in the uranium dioxide matrix or form perovskite phases (such as BaZrO₃). As a result, both cesium and iodine escape from the damaged fuel as cesium iodide; we will return to these elements later, but please allow me to digress for a moment.

As I commented before, the Fukushima accident was a slower and gentler accident than the Chernobyl accident. A kitchen analogy between the two would be flinging an egg across the kitchen into a frying pan that is then allowed to heat up on the stove (Chernobyl), while the other is more like leaving a frying pan with an egg on the stove too long. In the latter case, the volatiles from the overheated egg will create a stink in the kitchen, while in the case of the former the volatiles will again create a stink, but also the splatter from the impact of the egg will spread around the kitchen. Even while Fukushima might have been simpler than Chernobyl, it is still not an event which is fully understood. The radionuclide signature of debris from different parts of the reactor site is not the same, suggesting that the different sources of contamination were not all the same (Tanaka et al., 2014).

During the accident, the levels of ⁹⁵Nb, ^{110m}Ag, ^{129m}Te, ¹³¹I, ¹³²Te, ¹³⁴Cs, ¹³⁶Cs, and ¹³⁷Cs in aerosols were measured in Japan (Kanai, 2015). Rather than the ⁹⁵Nb activity divided by the ¹³⁷Cs activity decreasing as the ⁹⁵Nb ($t_{1/2} = 35$ days) and its parent ⁹⁵Zr ($t_{1/2} = 64$ days) decayed away, the ⁹⁵Nb:¹³⁷Cs

changed in the other direction. This suggested that some unknown process had favoured the release of niobium and/or zirconium. One possibility was that volatile metal compounds such as zirconium(IV) chloride (bp = 331°C, sublimes) or niobium(V) chloride (bp = 254°C) had formed during the accident as a result of addition of sea water to the reactors. The idea of a release of zirconium or its daughter is at first glance worrying, as zirconium(IV) oxide is a mimic of plutonium(IV) oxide which is the most likely oxidation state of the plutonium in the fuel. While zirconium(IV) (Krebs, 1970) and hafnium(IV) (Niewa & Jacobs, 1995) chlorides are coordination polymers with six coordinate metal atoms with the same crystal structures the actinide chlorides have different structures (Figure 2).

The tetrachlorides of uranium (Taylor & Wilson, 1973) and neptunium (Zachariasen, 1949) have different and more cross-linked structures which suggest that their melting and boiling points should be higher. Also plutonium(IV) chloride has never been observed in the solid state. Instead, plutonium(III) chloride is well known in the solid state (Burns, Peterson, & Stevenson, 1975); this is a solid which is highly cross-linked as it has nine coordinate plutonium atoms. Plutonium(III) chloride has much higher melting and boiling points than zirconium tetrachloride. The moral of this story is that if a stable element is used as a surrogate for a radioactive element, then it is important to make sure that the two elements have the same (or similar) chemistry under the conditions which are relevant. We will conclude this matter by pointing out that niobium forms a volatile oxychloride (NbOCl_3), the crystal structure of which suggests that it exists as $\text{Nb}_2\text{O}_2\text{Cl}_6$ molecules linked into chains (Sands, Zalkin, & Elson, 1959). By dissociation of the long oxygen niobium bonds, the solid can break up into $\text{Nb}_2\text{O}_2\text{Cl}_6$ molecules which in turn can dissociate into NbOCl_3 molecules (Figure 3).

The paper which reported the release of ^{95}Nb used gamma spectroscopy, as ^{95}Nb emits photons at 766 keV; then it is likely that the same gamma spectrometer which was also used to measure ^{137}Cs (662 keV), ^{134}Cs (605 and 796 keV), and other gamma emitters would also be able to record the 724- and 757-keV photons from ^{95}Zr . As a result, their failure to detect ^{95}Zr is unlikely to be due to the gamma spectrometer being unable to measure photons from the zirconium nuclide. The reason for this apparently high mobility of niobium should be the subject of investigation by the scientific community.

Figure 2. Solid-state structure of zirconium(IV) chloride.

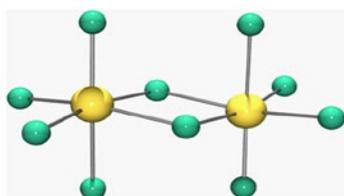
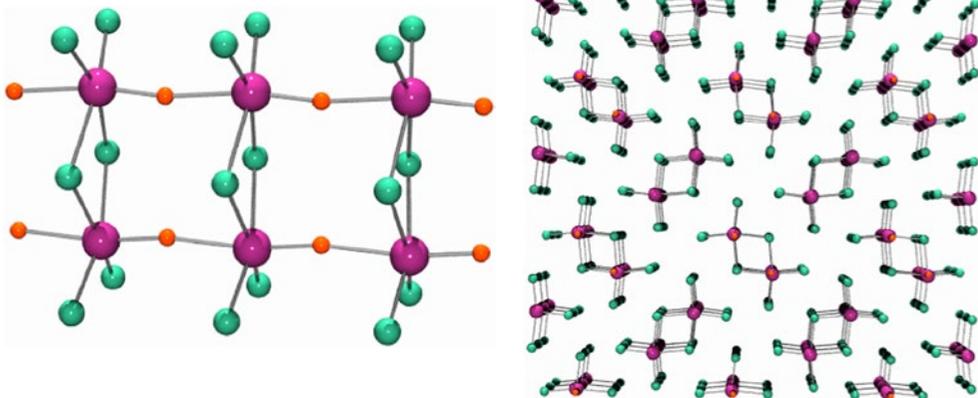


Figure 3. Solid-state structure of niobium oxytrichloride.



A chain of $\text{Nb}_2\text{O}_2\text{Cl}_6$ units

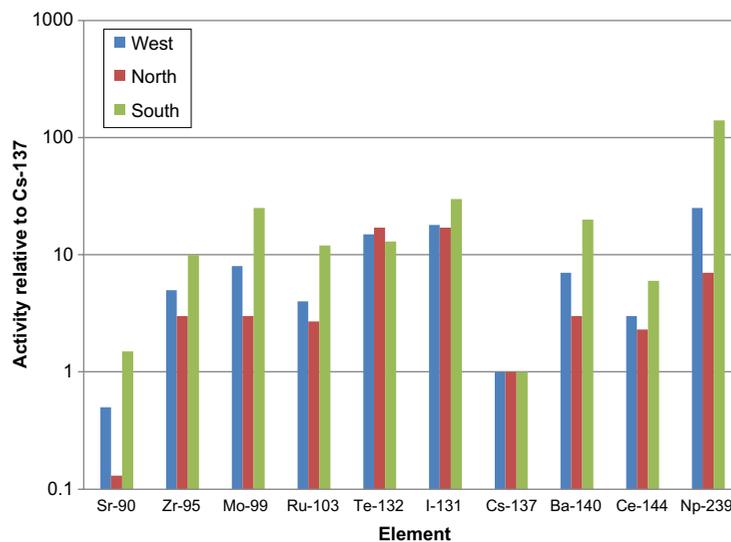
The crystal structure

While the Fukushima was a relatively simple overheating event, the Chernobyl event was a combination of overheating, steam explosion, and oxidation of the fuel. All three mechanisms released radioactivity in different forms from the damaged core. It was interesting to see that the radioactive signatures of the different plumes from the damaged reactor were different. If we compare ^{90}Sr , ^{95}Zr , ^{99}Mo , ^{103}Ru , ^{132}Te , ^{131}I , ^{137}Cs , ^{140}Ba , ^{144}Ce , and ^{239}Np between the western, northern, and southern plumes close to the reactor, then the ratio of the radionuclides on surfaces differs greatly (United Nations Scientific Committee on the Effects of Atomic Radiation, 2000) (Figure 4).

The first plume (to the west) is of the radioactivity released during the explosion on the first day; the wind then changed direction to the north as the core started to heat up further after the accident. After the explosion, the fuel was cooling as it melted the steel, concrete, sand, and other structural materials in the reactor building. During this time, the silicate melt which appeared later in the form of an elephant's foot started to form. The majority of the reactor fuel (71%) is now in the form of these lava-like fuel-containing materials (Borovoi & Sich, 1995). The lava flows are far from homogenous. The lava flows contain uranium fuel (90 tons), some steel (<20 tons), concrete (610 tons), zirconium (45 tons), cavity-filling materials (280 tons), and a serpentinite mixture (160 tons) (Bogatov et al., 2008). The gaps between the tubes and other parts above and below the reactor were filled with serpentinite, while the cavity between the walls of the reactor vault and the reactor was occupied with water tanks and sand. Even now, radioactivity is still being leached out of the lava flows and the other solids inside the wrecked plant by the water which is present in the building.

As the fuel was being heated up in air, uranium dioxide was oxidized to a higher oxidation state oxide such as U_3O_8 . Microscopic X-ray diffraction and $\mu\text{-XANES}$ indicate that the fuel particles collected from the north of the accident site consist of a UO_2 core with a $\text{U}_2\text{O}_5/\text{U}_3\text{O}_8$ coating (Salbu et al., 2001). In contrast, the fuel particles to the west had a UO_2 core and a reduced surface. One of the modern developments in nuclear reprocessing is to repeatedly oxidize and reduce used nuclear fuel; this is a process which converts pellets into a fine powder and also releases tritium (^3H), ^{14}C , and ^{85}Kr from the fuel (Song, Park, Lee, Park, & Yang, 2008). These redox reactions are accompanied by volume changes; as a result, the fuel is further fragmented increasing its surface area. These volume changes caused by oxidation will also increase the releases of radioactivity from the core. Also the oxidized fuel particles release their radioactivity with greater ease during leaching experiments; real undamaged fuel recovered from the Chernobyl site was either crushed or crushed and then heated in air (400°C). The heated fuel was found to release more radioactivity in leaching experiments (Kashparov et al., 2000). This observation is paralleled in nuclear fuel leaching experiments performed under the

Figure 4. Different radionuclides in the three plumes released from the Chernobyl plant; this is for fallout from close to the reactor site.



conditions expected in the Swedish repository conditions; in these experiments, the lower the oxygen content of the water in an autoclave, the lower the rate at which uranium dioxide dissolves (A. Odegaard-Jensen, Private Communication). While used, uranium dioxide fuel is a more complex solid than pure uranium dioxide; it is possible to exert better control over its corrosion. Uranium dioxide is a semiconductor; its conductivity is increased by lanthanide fission products. The solid contains many small metallic particles (Mo/Ru/Pd alloy); at these particles, hydrogen can undergo an anodic reaction. This reaction can lower the corrosion potential of uranium dioxide, thus slowing down the corrosion rate (Broczkowski, Noël, & Shoesmith, 2005). Broczkowski et al. (2005) showed that when a simulated used uranium dioxide (SIMFUEL) pellet was immersed in potassium chloride solution, the corrosion potential changed when the electrolyte was bubbled with different gases. The corrosion potential became more cathodic when the air was replaced with argon and then even more cathodic when the argon was replaced with a mixture of hydrogen and argon.

During the Fukushima crisis, TEPCO did sometimes add hydrazine to the water that they used in ponds; this addition was done to lower the amount of dissolved oxygen in water. It is noteworthy that in aqueous chloride solutions hydrazine is less effective as a deoxygenating agent (Motooka, Sato, & Yamamoto, 2013). I hold the view that the key message is that during an accident, it is important to keep the fuel in an anaerobic and cool environment. It is also important to bear in mind that the chemistry of irradiated water is far from simple; the addition of oxygen will cause the water to form predominantly oxidizing radicals, while the addition of a reducing agent will cause the water to form predominantly reducing radicals.

The wreckage from the Chernobyl core then heated up further as the wind blew south. While little difference exists between the Te:Cs and I:Cs ratios in the different plumes, it is clear that in the explosion (western plume) the less volatile elements (Sr, Zr, Mo, Ba, and Np) were more represented in the radioactivity emitted than they were in the heating up phase of the accident. During the explosion, the fuel fragments ejected from the plant would have carried the non-volatile elements out of the plant, while when the fuel was at its hottest, the releases of the non-volatile elements relative to cesium increased again.

During this hottest time the final lava was formed the Zr-U-O phase reacted with the silicate melt forming the high uranium zircon (Zr,U)SiO₄ also during this time ruthenium and molybdenum also started to separate out from the molten fuel. During the Chernobyl accident, a large number of hot particles were released from the reactor site; some of these were found on the clothing of travellers returning to the west after the accident (Van der Veen, Van der Wijk, Mook, & De Meijer, 1986). While some of the radioactive particles were fuel fragments, some had very high radioactivity levels but only contained a few radionuclides (Sandalls, Sagal, & Victorova, 1993). One of the important radionuclides in these particles was ¹⁰³Ru; this is a fission product which was not emitted in large amounts during the Fukushima accident. A series of theories existed as to why it was released at Chernobyl; in the paper by Sandalls these are summarized as:

- (1) Mechanical emission of molten matter which cools into solid particles.
- (2) Liquid droplets formed by cooling a vapor which in turn changes into solid particles.
- (3) Water condensed onto existing aerosols which then form droplets which then dry out again.
- (4) The particles existed before the accident as epsilon particles in fuel.
- (5) Ruthenium deposited onto surfaces and existing particles.

The chemistry of ruthenium tetroxide (RuO₄) under the conditions of a nuclear accident was reviewed by Mun, Cantrel, and Madic (2006). The fourth hypothesis can be discounted as the ruthenium particles also contain ⁶³Ni and ⁶⁰Co from the stainless steel which was associated with the reactor (Kleszcz & Mietelski, 2010). If the particles were epsilon particles in the fuel, then as nickel/cobalt is not found in zirconium-clad uranium dioxide fuel, these activation products would be absent from these ruthenium particles. The last possibility that ruthenium formed the volatile tetroxide which

then deposited onto surfaces and existing particles thus forming the hot particles is likely to be true (Kashparov et al., 1996).

Within a year, most of the ruthenium radioactivity decayed away, which left behind ^{90}Sr and ^{137}Cs in the Chernobyl fallout. These nuclides ($t_{1/2}$ ca. 30 years) have plenty of time to pass through food chains, internally contaminate humans, and to disrupt farming. An examination of a soil sample from near the Iitate village (Fukushima) indicated that cesium was absorbed into microscopic clay particles (Mukai et al., 2014), which suggests that cesium was released in a form which dissolves with ease in water. However, some cesium was found in the form of spheres of a silicate glass which were released during the Fukushima event; these spheres will release their cesium slowly (Abe et al., 2014). The slow leaching of cesium will decrease its availability to plants. A key message is that the chemical form of the accident fallout has an effect on the transfer of these radionuclides into plants. The transfer into plants is the first stage of the journey of the element through the food chain which ends with a human or some other important animal.

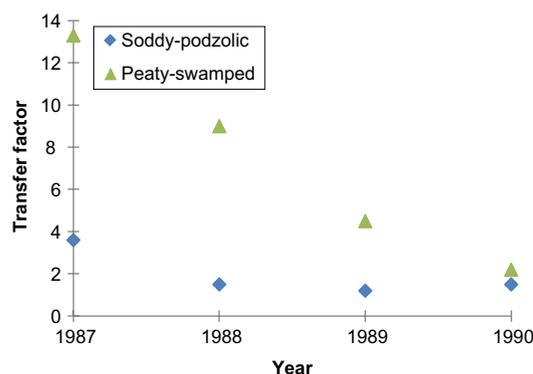
The degree of transfer of cesium or any other element from soil into plants will depend on many factors. My own view is that the prophet of doom who exaggerates the health effects of pollution is morally equivalent to the prophet of false reassurance who deliberately downplays the health effects of the same pollution. Rather than taking either politically motivated extreme position, I reason it is better to make a judgement based on the evidence.

We need to know the transfer factor; this is the ratio between the radioactivity of the soil and the radioactivity of the plants. It can be expressed in several different ways. One method is to divide the radioactivity (Bq kg^{-1}) of the plants by the contamination level (Bq m^{-2}) of the soil. This has the advantage of being a useful value which can be used to make predictions for farming with great ease, but it has a scientific weakness. If the contamination spreads deeper into the soil, then it might either become more or less available to the roots of the plants. In some ways, a transfer factor expressed as contamination of the plant matter expressed as Bq kg^{-1} divided by the contamination level of the soil also expressed as Bq kg^{-1} is better. But we can still do some useful work with either, or some other version of the transfer factor.

The first thing we need to consider is the soil type: if we look at data from the former Soviet Union for ^{137}Cs transfer into grass at sites between 15 and 50 km from the Chernobyl plant, in the following graph it is clear that with time the cesium transfer factor decreases (Sanzharova et al., 1994). Also the transfer factor for the swampy peat soils is much higher than the soddy podzolic soil. The latter soil type is a mixture of humus, iron/aluminum oxides, and clay. It is likely that the clay is responsible for preventing the entry of cesium into plants (Figure 5).

With increasing time, the Chernobyl cesium becomes strongly fixed by the soil minerals; soil samples taken at different times during the first eight years after the accident were taken from a site within the 30-km restricted zone around the Chernobyl accident site. ^{137}Cs becomes more strongly

Figure 5. Change in cesium transfer factor for grass with time for two different soils close to the Chernobyl plant.



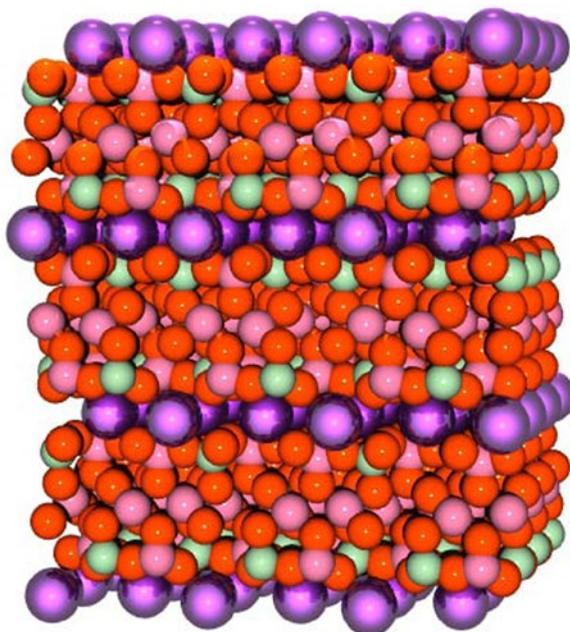
fixed to the soil (Krouglov, Kurinov, & Alexakhin, 1998); the soil sample was subject to a sequential digestion similar to that in the Tessier method. This decrease in the fraction of cesium which can be leached with mild reagents from the soil suggests that the cesium content in the soil water will decrease with time; as a result, the transfer of cesium to plants will decrease. On the other hand, ^{90}Sr , ^{103}Ru , and ^{144}Ce were becoming more available for plants to absorb. This increase in the mobility of these other elements is likely to be due to the dissolution of fuel particles.

Rather than waiting for cesium to bind more tightly to the soil minerals, an alternative is to take action, while it is possible to remove cesium by scarping off the top layer where the majority of cesium in this method of remediation will generate vast amounts of waste and will also damage the environment. Alternatives include the triple digging method (Roed et al., 1999). This is a remediation method which places the radioactivity below the surface out of reach of the roots of shallow plants. The top layer is cut out and inverted; it is placed at the bottom of a nearby hole. The bottom layer is placed on top of the inverted top layer and lastly the middle layer is placed on top to finish off the surface. Another alternative is to add potassium to the soil; in the case of the islands where the US hydrogen bombs such as Castle Bravo were tested, the soil contains very little potassium or clay. As a result, cesium is transferred into plants such as coconut trees with great ease; but by applying potassium chloride or another water-soluble potassium fertilizer to the soil, the transfer of ^{137}Cs into coconuts can be greatly reduced (Robison et al., 2009).

The reader can be forgiven for asking why cesium binds to soil minerals so tightly, while the other elements are not so tightly bonded to the soil. Many clay-containing soils include clay minerals which are able to act as ion exchange materials; these typically can release potassium cations (Gualtieri et al., 2008) (which form the jam) between the anionic aluminosilicate slices (which look like bread). Figure 6 shows a picture of part of an illite lattice; you should be able to see that it has the layers of potassium atoms (purple) between the aluminosilicate layers.

Even if cesium is able to enter a green plant and thus the food chain, it is still possible to intervene using chemistry. When a person ingests ^{134}Cs or ^{137}Cs in their diet, then cesium will be distributed throughout their body. Again the Bateman equations can be used to model the amount of cesium inside a person after either a single dose or a constant intake of cesium. The biological half-life of

Figure 6. Crystal structure of illite.



cesium in mammals is in the range of 1–4 months; this biological half-life can be combined in Equation 5 with the physical (radioactive) half-life to calculate the effective half-life of cesium in an animal:

$$t_{1/2}^{\text{effective}} = 1 / \left\{ \left(1/t_{1/2}^{\text{physical}} \right) + \left(1/t_{1/2}^{\text{biological}} \right) \right\} \quad (5)$$

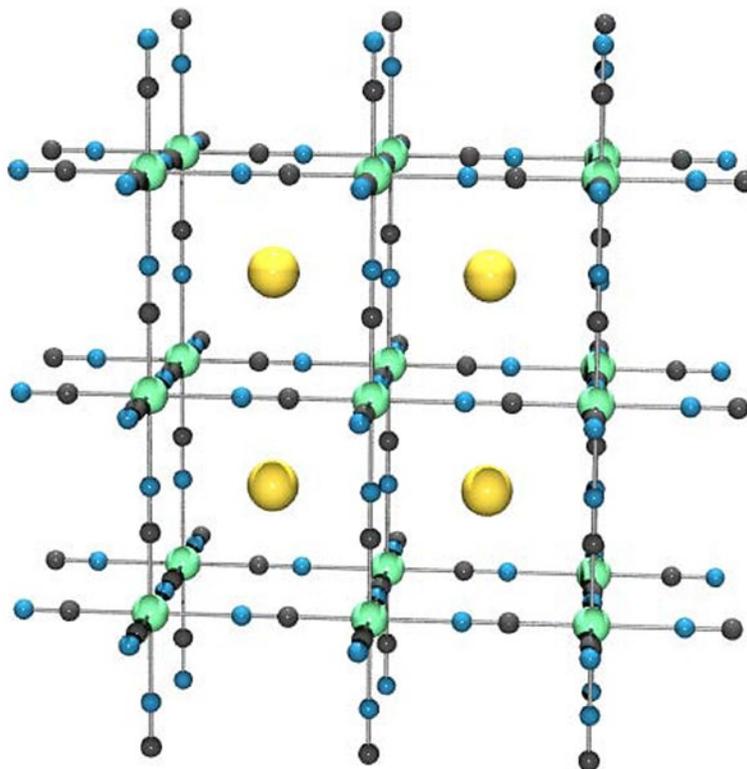
While in the case of iodine it is possible to reduce the uptake of iodine into the thyroid gland by ingesting stable iodine as potassium iodide, in the case of cesium it has been shown in pigs that it is not possible to decrease the biological half-life by supplementation with stable cesium (Prochazka et al., 1991). I would also like to point out that the oral consumption of large amounts of cesium salts is both expensive and harmful. One alternative cancer cure is to swallow grams of cesium salts each day in the misplaced hope that it will make one's body alkaline and thus cure cancer; sadly, in large amounts, cesium is cardiotoxic (Chan et al., 2009; Melnikov & Zanoni, 2010). While discussing cardiac issues, it is interesting to note that a lot of work has been done on the non-cancer effects of radiation exposure; in some populations such as the Estonian men who worked as Chernobyl clean-up works, it has not been possible to observe any obvious non-cancer health effects with the possible exception of some thyroid effects (Rahu et al., 2014), while a study of men who worked at Sellafield found that a possible link exists between radiation exposure and circulatory system disease (McGeoghegan, Binks, Gillies, Jones, & Whaley, 2008). Claims have been made that radioactivity from Chernobyl has damaged the hearts of children in the former USSR. It should be understood that it has been found that the hearts of women who have been treated with radiation for breast cancer can tolerate 2.7-Gy (270 rads) doses of gamma rays, while a 6-Gy dose to the heart does increase the incidence of some forms of heart disease (McGale et al., 2011). Tondel, Arynchyn, Jönsson, Persson, and Tagesson (2005) reported that a population of Belarusian children who in 1999 were exposed to Chernobyl fallout has an annual radiation dose of 1.8 mSv (0.18 rem); this yearly dose is very small when compared with the dose which has been shown that adult female hearts can tolerate. They also found that the level in urine of a marker for DNA damage (8-hydroxydeoxyguanosine) in radiation-exposed rural children was lower (8.5 nmol dm⁻³) than its level (18.8 nmol dm⁻³) in urban children whose annual radiation dose (0.25 mSv, 0.025 rem) is lower. They concluded that urban living had a greater effect on the oxidative stress level in children than the small radiation dose that rural children get as a result of the radioactivity released by Chernobyl years ago.

Nevertheless, back to radioactive cesium in humans, one method of removing cesium (and thallium) from humans and other animals is to add some Prussian blue to their diet. Prussian blue is a set of coordination polymers of cyanide with iron where the iron atoms have two oxidation states. Prussian blue is a pigment that has been used for many years; Vincent Van Gogh is known to have used Prussian blue in some of his paintings, but now back to the chemistry.

One great problem is that at least four different forms of Prussian blue exist and the ion exchange properties of the solid do vary as a function of the particle size; Josef Novosad once told me how every batch of Prussian blue which he made when he worked on cesium in farmyard animals was different to the last. He also found that supplementation with stable cesium (1 mg per kilogram body mass) does not increase the rate at which radioactive cesium is lost from an animal (Prochazka et al., 1991). While a vast daily dose of stable cesium might be able to promote the loss of cesium radioactivity from a person, a danger exists that this vast amount of cesium might affect the heart.

Prussian blue is very difficult to characterize by X-ray crystallography; some other closely related solids have been characterized using crystallography. For example, a version of Prussian blue with sodium ions has been used in a sodium ion cell (Pramudita et al., 2014), while another analog has been reported. Figure 7 shows the crystal structure of the sodium form of a mixed manganese/iron analog of Prussian blue (Long, Feng, Lu, & Gao, 2006). You will see how this solid contains yellow sodium ions which are present as guests in the solid; in common with the potassium ions in the clay these can be exchanged for cesium ions. What happens in an animal is that Prussian blue

Figure 7. Crystal structure of a Prussian blue analog.



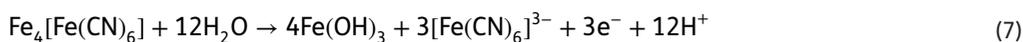
passes unchanged through the acidic stomach before entering the intestines; here it acts as an ion exchange material releasing potassium ions as it absorbs cesium. Cesium-loaded Prussian blue then comes out in the feces.

I have to admit that I did make some cosmetic adjustments to the crystal structure; I did remove the disorder of the cyanide groups by removing half of the carbon and nitrogen atoms. Disorder is when different unit cells have two or more arrangements of atoms; rather than being something wrong with the work of the crystallographer, this is simply a fact of life that sometimes in a crystal two or more arrangements of atoms have similar energies.

In some ways Prussian blue is a wonder substance; if the medical grade ($3\text{--}30\text{ g day}^{-1}$) is fed to a human, then the rate of loss of cesium excretion becomes much larger. It is possible to greatly reduce the biological half-life in a person; this can greatly reduce the radiation dose to a person caused by internal exposure. I hold the view that Prussian blue should be regarded as the gold standard against which other cesium-removal drugs should be compared. For example, apple pectin was suggested by Nesterenko, Nesterenko, Babenko, Yerkovich, and Babenko (2004) as a means of removing cesium from humans; however, this study could not be reproduced in rats. In the later study in rats, apple pectin was found to have no effect, while Prussian blue increased the rate of cesium removal (LeGall, Taran, Renault, Wilk, & Ansoborlo, 2006). While the medical-grade Prussian blue is effective as a cesium-removal agent, often pigment-grade Prussian blue is not effective. The stability of Prussian blue in soil depends on the pH of the soil water; in anaerobic alkaline soils one form can decompose according to the reaction in Equation 6 (Meeussen, van Riemsdijk, & van der Zee, 1995):



while in aerobic soils it can decompose according to the reaction in Equation 7:



While Prussian blue can dissolve under alkaline conditions, this is reported to often require decades; as a result Prussian blue can survive long enough to prevent cesium quickly re-entering green plants. If cesium can be sequestered for years or decades, then it will give it time for at least ^{134}Cs to decay away. Even the longer lived ^{137}Cs will undergo some decay over the decades.

While I have written about a long-term threat, I want to discuss a short-lived threat; this is the vast amount of radioactive iodine which is inside the core of a nuclear reactor shortly after shut-down. If we consider radioactive iodine, then we should bear in mind the following. Firstly, iodine can exist in several volatile and mobile chemical forms; secondly, the radioactive yield of iodine in the days after nuclear fission is high; and lastly, iodine in a mammal is reconcentrated in a small but vital organ. This combination of attributes causes radioactive iodine to pose a particularly large threat to the general public. It is interesting that large doses of I (3.7–22 GBq range) can be used to cure some forms of thyroid cancer (Durante et al., 2006).

Both in some areas of the former USSR and on islands close to where the atmospheric hydrogen bomb tests occurred, it is possible to observe an increase in the incidence of thyroid cancer as a result of the Chernobyl accident (Astakhova et al., 1998) and the bomb tests. This can be understood as proof that radioactive iodine causes thyroid cancer; however, in a Swedish study, Holm et al. (1988) were unable to find an excess of thyroid cancer in a large population which had been exposed to moderate amounts of ^{131}I during thyroid scans; Holm suggested that this might be due to either a deviation from the linear no threshold model. A second explanation offered by Holm is that due to the fact that ^{131}I ($t_{1/2} = 8$ days) has a much lower beta energy than the shorter lived iodines, it is a much weaker carcinogen. As the time at Chernobyl and the bomb tests between the end of the criticality and the release was short, so could some of the short-lived iodines ($^{132},^{133},^{134},^{135}\text{I}$) have been released during these events?

While an explosion released fuel particles on day one at Chernobyl, 60% of ^{131}I was released on later days (Métivier, 2002); this slow release of iodine from the reactor core is important. As a result, the shortest lived iodines ^{134}I ($t_{1/2} = 53$ min) and ^{135}I ($t_{1/2} = 6.6$ h) would have largely decayed away almost totally inside the reactor. Also much of ^{133}I ($t_{1/2} = 20.8$ h) in the core would have decayed away before having had a chance to be released. As a longer time between the end of the criticality and the start of the release of iodine elapsed during the Fukushima accident, it is reasonable to expect that even less of the short-lived radioactive iodines were released during the accident in Japan. One great problem during a serious accident such as Fukushima is that the collection of detailed data is a lower priority than accident mitigation work; while some data will be collected at the reactor site, the data collected in the early stages of the accident will be often limited. The earliest high-resolution gamma spectra that I have found for the Fukushima fallout was collected almost one week after the earthquake on 17 March in Fukushima city. In these spectra, ^{131}I and ^{132}I were observed; but by the time the data collection was started, the shorter lived iodines (^{133}I , ^{134}I , and ^{135}I) which lack a longer lived precursor (such as ^{132}Te , $t_{1/2} = 78$ h) would have decayed away (Takada & Suzuki, 2013). Table 2 lists the fractions of the different iodines which are thought to have escaped from the damaged reactor.

Table 2. Releases of radioactive iodine and tellurium-132 from Chernobyl

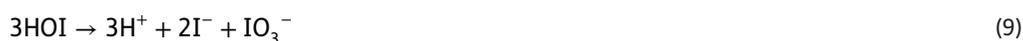
Nuclide	Chernobyl release	
	PBq	Inventory (%)
^{131}I	1,760	42
$^{132}\text{Te}/^{132}\text{I}$	1,040	25
^{133}I	910	19
^{134}I	25	1.2
^{135}I	250	8.6

Much of the thyroid exposure in the former USSR was due to the consumption of contaminated dairy products (Drozdovitch et al., 2010); as radioactive iodine would need some time to pass through the dairy cow and the milk distribution network, the shorter lived iodines ($^{132,133,134,135}\text{I}$) had time to decay away. But the same paper commented that in a study of people evacuated from Pripyat it was found that 30% of their thyroid dose was due to $^{132/133}\text{I}$ and ^{132}Te . This population is different as their exposure was inhalation only; for those people who were within 30 km of the reactor site who inhaled iodine directly, the short-lived iodines could have been important.

It might come as a surprise to many that iodine can exist in many different chemical forms which include both inorganic iodine (such as I_2 and IO_x) and organic iodine (such as methyl iodide). When radioactive iodine from Chernobyl reached Japan, it was found to be a mixture of I_2 (5%), HOI (6%), aerosols (19%), and organic compounds (70%) (Noguchi & Murata, 1988). One of the great problems in nuclear accident research is that with small experiments it is possible to control the conditions well and repeat the experiment again and again with different conditions, but with real accidents while all the different systems will be able to interact with each other, it is impossible to repeat an accident under slightly different conditions and often many key parameters are poorly defined or not measured. The small experiments suffer from the problem that only a small part of the nuclear accident can be examined in the experiment; here, it is not possible to study the interactions between one part and another. The larger experiments are part-way between the small experiments and the accidents; while these experiments may contain many of the parts of a nuclear power plant and can be repeated, they are very expensive.

In recent years in France, a series of exciting experiments with the code name PHEBUS have been conducted (Clément & Zeyen, 2013); these used a scale model of a PWR reactor. In the experiments, real nuclear fuel was placed inside a special nuclear reactor. While the coolant flow for most of the reactor (the driver core) was maintained normally, the flow for the experimental channel could be stopped or replaced with steam. The output of this experimental channel was fed through a pipe into a model of a steam generator and then into a tank which is used as a model of the containment. During these tests, iodine was found in multiple forms (Girault et al., 2012), thus confirming that the iodine chemistry during such an event is complex.

As I have already commented, as the fuel heats up, cesium iodide is vaporized from the fuel; this carries plenty of iodine into the containment. Once it arrives there, it can be chemically modified. One of the key processes is the oxidation of iodide into elemental iodine. Even if no air is present when the water in the containment is irradiated, then it will generate oxidants such as hydrogen peroxide and hydroxyl radicals. The pH of the water is very important. If the water is alkaline, then any elemental iodine will tend to disproportionate into iodide and iodate according to the reactions in Equations 8 and 9:



I have written out these equations assuming that the water at the end of the reactions is neutral; the pKa values of HI, HOI, and HIO_3 are -10, 11, and 0.8, respectively. When the pH is high the forward reactions are all favored, but when the pH is low then the reverse reactions are favored. The rate at which equilibrium is reached is controlled by the rate of formation of IO_2^- (Truesdale, Luther, & Greenwood, 2003). In a nuclear reactor containment after an accident, a large concentration of ^{133}Xe and ^{135}Xe will be in the air or the nitrogen used in many containments. By irradiation of air or water containing nitrogen, it is possible to form nitric acid; an additional source of acid is the degradation of the electrical cables. In a BWR, a vast number of cables are present under the core; these cables are required to operate the control rod mechanism. Both PVC and chlorosulfonated polyethylene have been used in nuclear reactor containments; both of these plastics can release hydrogen

chloride when they are heated (Auvinen, Zilliacus, & Jokiniemi, 2005). Hydrogen chloride can dissolve in water thus forming hydrochloric acid; this hydrochloric acid will then alter the chemical equilibria for iodine. Therefore, the partitioning of iodine between the water and the gas phase will change.

If we assume that some of the iodine remains in the gas phase as I_2 , then we need to consider the oxidation of iodine by ozone and the other radiolysis products of air. Iodine reacts in the gas phase with ozone to form iodine oxide aerosols (Funke et al., 2012; Vikis & MacFarlane, 1985). These solid particles of iodine oxides are hygroscopic and can react with water to form aqueous solutions (Dickinson et al., 2014).

As mentioned above, a large fraction of iodine from a nuclear accident can be in the form of organic iodine compounds. One problem is that during a real-life nuclear accident, no one has ever set up a GC machine to collect the organic iodine compounds to allow their radioactivity to be measured. However, some time ago at Hanford, volatile organic radioactive iodine emissions were examined. Radioactive methyl, ethyl, propyl and butyl iodides, and some other compounds were emitted (Haller & Perkins, 1967). Despite this observation of a range of alkyl iodides, it is typical in nuclear research to use methyl iodide to represent the organic iodine fraction. It would be better if instead of concentrating on a single alkyl iodide, a range of organic iodine compounds were used to test the sampling and mitigation systems that are intended to capture radioactive organic iodine after an accident. It is possible that the iodine release from the Windscale reactor fire was underestimated because the early sampling filters were unable to retain the organic iodides such as methyl iodide which may have undermined dose estimates (Garland & Wakeford, 2007). Even if a sampling or mitigation system is shown to retain the radioactivity in methyl iodide, it may not be possible to extrapolate these results to other organic iodine compounds. These systems if they have been shown to work well with other organic iodine compounds would be more trustworthy.

The relative yields of the different alkyl iodides formed from alkanes are a function of the structure of the hydrocarbon (Schuler & Wojnarovits, 2003; Wojnarovits & Schuler, 2000). In studies at both Chalmers (Tietze, Foreman, & Ekberg, 2013) and elsewhere (Taghipour & Evans, 2000), it has been shown that alkyl iodides other than methyl iodide can form from paint solvents and that different paint solvents form different alkyl iodides. One common event when matter is irradiated is the ejection of an electron from a molecule or atom to form a radical cationic center; these electrons can move around and in some cases react with electron-accepting molecules. For example, when a polychlorobiphenyl (PCB) (Mincher, Arbon, Knighton, & Meikrantz, 1994) or DDT (Evans, Nesyto, Radlowski, & Sherman, 1971) in an alcohol is irradiated, the solvated electrons react with the organic molecule to form a chloride anion and a carbon-centered free radical. For example, dichloromethane can react with the solvated electron to form a chloromethyl radical. These organic radicals are well known to react with elemental iodine to form organic iodine compounds; in his seminal book, Swallow (1960) wrote at length about the use of elemental iodine as a radical trap. Elemental iodine reacts with carbon-centered radicals to form organoiodine compounds and a relatively stable radical (an iodine atom) which is unable to abstract a hydrogen atom from another organic molecule. As a result, no halogenation chain reactions occur; such reactions would obscure organic iodine formed from the original radicals.

In this way, dichloromethane can react with solvated electrons to form chloromethyl radicals which in turn are trapped as chloriodomethane by elemental iodine as shown in Equations 10 and 11:



An alternative radical-forming reaction is the recombination of solvated electrons with the radical cationic molecule from which the electron was ejected from by the radiation. Here, the radiation first ejects an electron forming the solvated electron and the cation as shown in Equation 12:



The electron then loses energy and becomes solvated; next the electron is attracted back to the cation. The two recombine to form an excited state of the original molecule; this excited state can then fragment into radicals and other reactive species as shown in Equation 13:



As before the radicals can react with iodine to form organic iodine compounds; one enduring problem which I envisage is the fact that the nature of the radicals depends on the organic compounds and the nature of the organic compounds used inside nuclear plants is changing. A need exists for the paint chemistry used in the nuclear industry to be kept under surveillance. Already together with a co-worker at Manchester at Chalmers, samples of old and new paints from nuclear sites have been compared (Tietze, Foreman, Ekberg, & van Dongen, 2013). This paper documented how the older alkyd paint used at the now defunct Barsebäck nuclear power plant differs from modern paints such as emulsion and epoxy paints which are used in modern nuclear sites. While this paper compares the past with the present, it is impossible to predict with certainty the type of paint that will be used in the future. As a result, a future need will exist for paint in nuclear sites to be re-evaluated.

I would like to end this review by pointing something out: chemistry offers a bridge between physics and biology. Also through a better understanding of the chemistry of a serious accident, we can better understand the processes by which radioactivity escapes from a damaged plant and then be able to expose humans to radiation; while we should strive to make nuclear reactor accidents a thing of the past, we should still make sure that we are better informed and better prepared in case another one occurs.

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