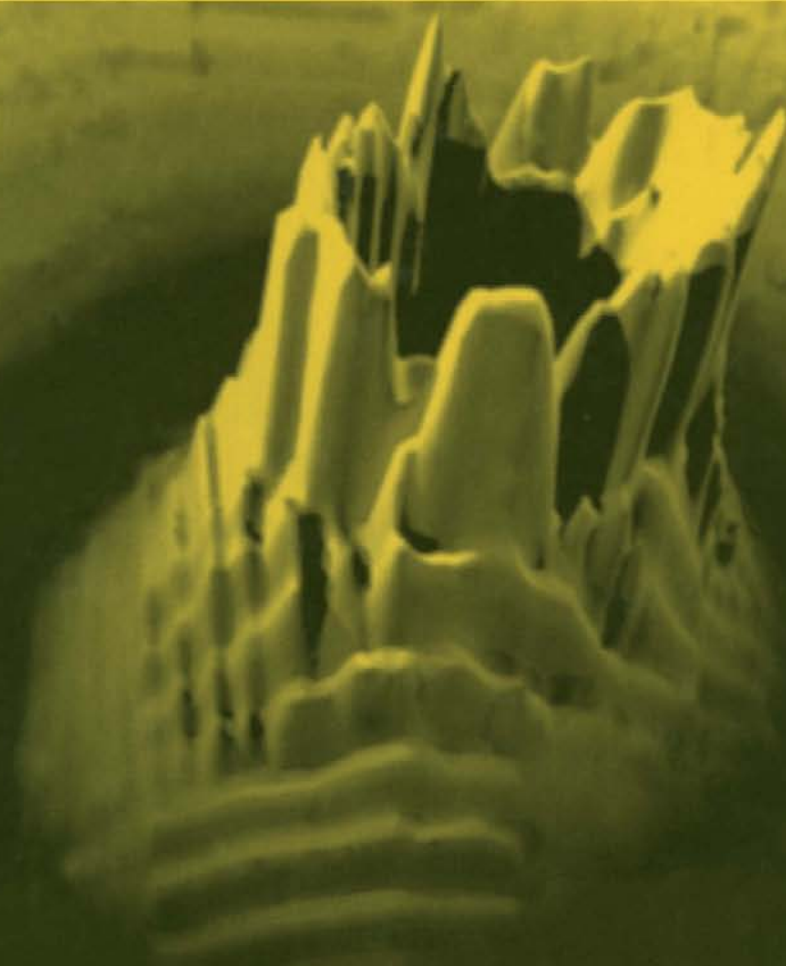


CORROSION INDUCED BY LOW-ENERGY RADIONUCLIDES

MODELING OF TRITIUM AND ITS RADIOLYTIC AND
DECAY PRODUCTS FORMED IN NUCLEAR INSTALLATIONS



G. BELLANGER

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Formed in Nuclear Installations**

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**Modeling of Tritium and Its Radiolytic and Decay Products
Formed in Nuclear Installations**

Gilbert Bellanger

Selongey, France

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Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam
The Netherlands

ELSEVIER Ltd
The Boulevard, Langford Lane
Kidlington, Oxford OX5 1GB
UK

ELSEVIER Inc.
525 B Street, Suite 1900
San Diego, CA 92101-4495
USA

ELSEVIER Ltd
84 Theobalds Road
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PREFACE

Nuclear power plants produce radionuclides emitting radiation and particles with a range of energies. Energy deposition on and in the materials can therefore be very different depending on the type of emitter. Gamma rays and neutrons have the highest energies and penetrate the interior of metals by breaking the metal bonds, thus leading to their degradation. They have been the origin of one of the problems in the construction of nuclear power plants and consequently their effects have been studied widely and discussed in numerous scientific publications in order to select the most suitable alloy. This is not the case for the low energy nuclide environment. Here the β^- particle can be taken as a model and although it has a low energy, it will be the source of problems that are both different and appreciable. These are degradation of the passive oxide layers protecting the metals. Without this protective layer, the metals are easily corroded. Particular charge transfers result in excitation by β^- particles giving birth to special electrochemical reactions in the oxide. However, while the reactions are in generally classical the particular effects are produced in conditions energetically favored by the energy brought by the radiation. Excitation creates holes in the oxide lattice leading to broken valence bond between two neighbor atoms. Moreover, electrons move out and become holes that lead to unoccupied orbitals that can receive an electron from a neighbor atom. It can be also noted for constant β^- particles flow that the equilibrium state is not obtained, but a stationary state can be established. This is characterized by a charge carrier density different from that obtained in the unexcited state. Among the low energy radionuclides present in nuclear power stations, tritium is of major importance due to its physical-chemical properties. Tritium is also found at different concentrations in plants for fuel reprocessing and military and civilian applications. Moreover, very large amounts of this low decay energy element is used in controlled fusion reactors. Due to its properties it can be substituted for the bound hydrogen in the molecules. This characteristic makes it possible to elucidate more easily the different types of corrosion of oxide layers than with another low energy nuclide, which is why tritium was chosen. In discussing tritium we must also discuss tritiated water since it is not possible to have tritium without tritiated water in such installations. The tritium in tritiated water always causes difficulties in these installations, including equipment corrosion. Moreover, with tritiated water there are, in addition, the radiolytic products. Special emphasis is given to aqueous corrosion which is the most important. The discussions include comments on tritiated water, radiolytic products and decay helium using aqueous corrosion models and

a model taking account of metal embrittlement. With regard to tritium installations, there were too many errors made to render it possible to exploit them. This is due to the fact that in most cases, persons in charge lacked solid knowledge of fluid flow, heat exchange, gas diffusion in materials and of materials resistance. In order to avoid these problems courses should be given, or books written, in these fields. Until the present there has not been a book devoted to corrosion by low energy radionuclides and consequently, there was a need to fill this vacancy concentrating on the effects of tritium and tritiated water. This book does not provide a course on corrosion, but is aimed at the specialists working in the nuclear field and scientists in electrochemistry and corrosion. This book is a reference tool of interest to post-graduates because of the concise examples treated in different chapters. Equipment manufacturers also may be interested by the choice of alloys and their characteristics.

In common with my previous publications and my conferences, this book has required support from individuals and organizations from different continents to whom I am very grateful. These include my friend, Professor Jean Jacques Rameau (University of Grenoble, France), who has motivated me to publish my results. He was there whenever I needed scientific help and advice. There are researchers who have unfailingly supported my conferences. Most particularly, I would like to thank the President of the International Society of Electrochemistry, previously Member of the Executive Committee and Officer of the Scientific Division of Corrosion: Professor Kálmán (Academy of Sciences, Budapest, Hungary). Special thanks also are due to the Officer of the Scientific Division of Industrial Electrochemistry and Electrochemical Engineering, Professor Matsunaga (Kyushu Institute of Technology, Kitakyusu, Japan), who sustained my project for the ISE Meeting in Japan, and also to the French Secretaries: Dr. Deslouis (University of Jussieu, Paris, France) and Professor Savall (University of Toulouse, France). I would like to thank Professor Ali Ben Bachir Hassani (University of Mohammed V, Rabat, Morocco), who is also Scientific Adviser in the Moroccan Government for his support in Marrakech. I would like to thank Professor Ives (Mc Master University, Hamilton, Canada) and Professor Savadogo (Ecole Polytechnique de Montréal, Canada) and especially to the Managers of UKAEA JET (United Kingdom Atomic Energy Authority—Joint European Torus) for their proposal to work as a consultant testing equipment. Thanks are also due to Professor Su-Il Pyun (Korea Advanced Institute of Science and Technology, Daejon, South Korea) and Dr. Varga (Department of Radiochemistry, University of Veszprém, Hungary) for their proposal in scientific collaboration in nuclear corrosion. I would also like to express my gratitude to many expert friends who helped me during the Meetings of The Electrochemical Society (USA) and those of EuroCorr (European Community of Anti-corrosion). My writing was guided step by step by my friend, Allan William Boyd, who helped to turn the scientific English style into intelligible and engaging literature. Without his tireless efforts my publications would not have seen the light of day. Most of all, I must give my sincerest thanks to my wife Marie Claude and I dedicate this book to her patience and understanding in accepting the financial outlay, making it all possible.

The book is supported by the accompanying CD-ROM, which contains the pdf, slides files and 3D views for the appreciation of the text and figures as a reference source. It makes possible interlaced interactive links (more than 5000) acting on the figures, photographs, tables, bibliography...

About the Author

Dr. Bellanger obtained an engineering diploma in Electrochemistry and Engineering of Nuclear Materials from the Conservatoire National des Arts et Métiers in Paris, having studied the retreatment of tritiated water by diffusion metal electrodes. Following this, Dr. Bellanger received a Doctorate in Electrochemistry and Engineering of Nuclear Materials. His studies for this degree involved the decontamination of metals by electrochemistry.

His early contributions in research were in the development of isotopic separation of uranium hexafluoride by gaseous diffusion, on which he worked from 1962 to 1965. From 1965 to 1985, he headed the Plutonium Analysis Laboratory at the Commissariat à l'Énergie Atomique and he has been responsible for the analysis of impurities present in aqueous solutions and plutonium metal. He has over 20 years of solid experience in physical chemistry analysis to his credit. He has also worked on the diffusion of radioactive tritium in metals and the decontamination of tritiated steels by isotopic exchange with electrolytic hydrogen.

Dr. Bellanger has been the Director of the Materials and Corrosion Laboratory since 1985. Within the past ten years he has authored approximately 65 technical papers and articles published in international journals such as *Fusion Technology*, the *Journal of Nuclear Materials*, the *Journal of Materials Science*, *Corrosion Science*, the *Canadian Journal of Chemical Engineering* and *Electrochimica Acta*, and in the proceedings of international conferences held in Europe, Japan and North America. He has published two chapters of a book on the passivity of metals and holds two international patents concerning the retreatment of radioactive water and decontamination of steels. His published work mainly concerns the effects of tritiated water on metal corrosion that is induced by released energy. Dr. Bellanger has studied the effects of radiolytic species on the corrosion of super-alloys and has over 10 years of experience in materials, corrosion and electrochemistry; he has carried out research and written extensively in these subject areas.

Dr. Bellanger was elected the member responsible for corrosion conferences for the scientific committee of the Electrochemistry Days Meeting held at Strasbourg, Montréal and Toulouse. He served in this position for 6 years, until the year 2000, organizing 450 people at each meeting. He has also been a guest speaker several times at present plenary and thematic conferences, and chair of several international conferences organized in foreign countries. He has also been a member of several international scientific societies, including the International Society of Electrochemistry, the Electrochemical Society Inc., the Institute of Corrosion, and Nace International Corrosion. Dr. Bellanger is now a senior consultant for a number of companies.

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INTRODUCTION

Aspects for understanding corrosion induced by low energy nuclide—modeling to tritium and tritiated water

The tritiated media are very reactive and their properties are extremely interesting. Tritium decays as follows:



A positively charged ${}^3\text{He}$, β^- particle and the antineutrino, ν_e are formed. Table 1 gives the nuclear data for tritium decay. Electrons of 18.6 keV per atom have sufficient low energy deposition to induce radiolysis phenomena in the hydrated oxide and in tritiated water leading to a blue luminescence (chapter 25 and Fig. 1). Radiolysis of the oxide, i.e. damage of an ionic lattice by β^- radiation, results in an increase in defects as free electrons, anion holes and vacancies. This increase has a direct impact on the oxidation kinetics if the limiting step in the oxidation process involves the mobility of the O^{2-} vacancies or electrons. In addition, water radiolysis induces the formation of unstable radical or molecular species at high concentrations such as O^3H^* , ${}^3\text{H}^*$, ${}^3\text{H}_2\text{O}_2$ [1–3], modifying the oxidizing character of this medium and is thus able to influence the oxidation kinetics of steels or stainless steel alloys.

Due to its unfilled electron shell, tritium reacts with almost all chemical species by ionic or covalent bonds. However, its reactivity is not limited to this behavior; it can replace hydrogen atoms in various chemical bonds by isotopic exchange. As tritium has extremely high mobility, and if the chemical compound is not stable enough to resist the low energy released with the β^- particle, chemical bonds are broken along the chains during its transit, first giving transient chemical species then stable compounds over a wide concentration

Table 1. Characteristic data of tritium

Radiation	β^-
Half-life ($\tau_{1/2}$)	12.3 yr.
Decay product	${}^3\text{He}$ and ν_e
Maximum β^- energy	18.6 keV
Energy produced by tritium decay	$1.95 \text{ W mol}^{-1} {}^3\text{H}_2$
Activity per mole of tritium	1075 TBq

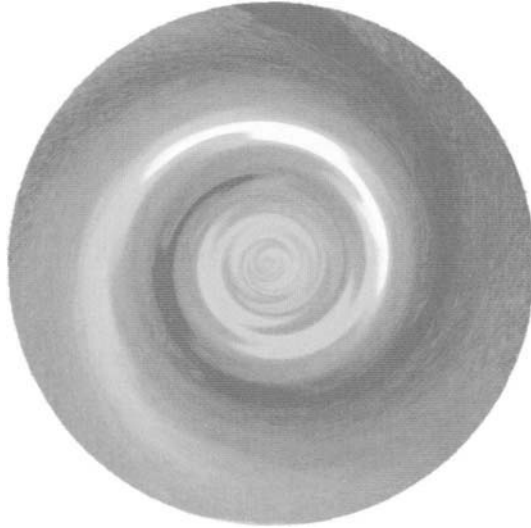


Figure 1. Spatial blue luminescence of tritiated water due to the presence of unstable free radicals on a disk electrode during convective stirring. The blue spiral pattern is representative for the displacement of radiolytic products and tritium at the surface of metal indicating thereby dynamic corrosion.

range. Chloride, fluoride, carbonate and nitrate are formed with pH modification by degradation of organic materials [1–3]. The transient species and stable compounds will react in various ways with the metal oxide layers thus producing corrosion.

In contrast to tritium, helium atoms are very stable and helium forms only a limited number of compounds. Therefore, other chemical species do not bond to it. Moreover, its recoil energy of about 0.4 eV is negligible as is the radiation due to the antineutrino. Therefore, due to its stability, helium is not involved in corrosion in the same way. It has extremely low solubility and can be easily trapped in metals, and as a result it and tritium induce metal embrittlement.

The damaging action of tritiated water and tritium on the corrosion resistance of the stainless steels is a very real problem. As these attacks lead to severe damage of metals, it is essential to know the effects of this complex medium in order to interpret the mechanisms in passivation or localized corrosion. To avoid these attacks, the corrosion tests must make it possible:

- to analyze tritiated water and tritium for its radiolytic and decaying species,
- to study the initiation and evolution of corrosion phenomena in the presence of tritium, tritiated water and various radiolytic species,
- to identify defects on the passivating oxide layers,
- to understand their behavior,
- to select the best adapted materials.

Table 2. Composition of gases above and dissolved in tritiated water

Radiolytic gas	O ₂	³ He	H ₂	² H ₂	³ H ₂
mmol gas above 1 dm ³ ³ H ₂ O	50	150	10	8	0.8
mmol gas dissolved in 1 dm ³ ³ H ₂ O	1	1.5	1	0.5	0.05

Table 3. Composition of radiolytic species and corrosion species dissolved in tritiated water

Aqueous species	O, ³ H ₂ O ₂	NO ₃ ⁻	CO ₃ ²⁻	Cl ⁻	F ⁻	³ H ⁺	Fe ³⁺ , Fe ²⁺	Ni ²⁺	Cr ³⁺ , Cr ⁶⁺
mmol dm ⁻³ ³ H ₂ O	6	70	50	50	5	1	1.5	1	0.3

First of all, for a good understanding of corrosion phenomena, we need to know what there is in tritiated water and in tritium, i.e. their composition. Analysis of various tritiated water samples include determination of the tritium content and identification of the radiolytic species and their respective concentrations. The radiolytic gases dissolved in and above tritiated water (Table 2) were analyzed by mass spectrometry. The tritium and the low energy discharged in tritiated water were determined by calorimetric measurements. The radiolytic species and corroded metals were analyzed by laboratory methods (Table 3). These species will be considered together or separately to ascertain their mutual influence on corrosion.

Corrosion tests must also meet the selection criteria for new materials. These concern laboratory examinations of new super-alloys or stainless steels such as super-austenitic and Duplex stainless steels and nickel and/or cobalt base super-alloys, hardened or ductile stainless steels, or the exotic alloys of zirconium or titanium. Materials selection is a difficult, complex but essential process, and many problems are caused by an inappropriate choice leading to corrosion-related failures. To carry out this study in a hot laboratory, we have essentially made use of the results of cyclic voltammetry, electrochemical impedance spectroscopy, Dispersive X-ray and Scanning Electron Microscopy, autoradiography and the scanning Reference Electrode Technique. To quantify the potential influences of tritiated water and radiolysis on oxides and the oxidation process, the electrochemical cell and analyzer chambers were arranged in a glove box in order to ensure the protection against tritium contamination. The presence of transients influences the results and can drastically modify them, making the results difficult to analyze. Thus, the results are based on these research methods with the use of rotating disk electrodes that are very sensitive for determining the effects of the transients formed in tritiated water. These measurements provide information in real time on corrosion systems to investigate the processes and the research techniques are also employed for studying passive oxide layers. Finally, the corrosion parameters obtained are then used to provide the required information for improving corrosion resistance of metals and determining the most suitable alloy.

Before discussing the corrosion problems, it is necessary to describe the operation of fusion reactors and the preparation of tritium and its processing in current operations. This is extremely useful because the technology now employed in tritium plants is directly applicable to recycling tritium in future reactors because the basic principles of both processes are identical and, since the technologies are identical, there are no problems in

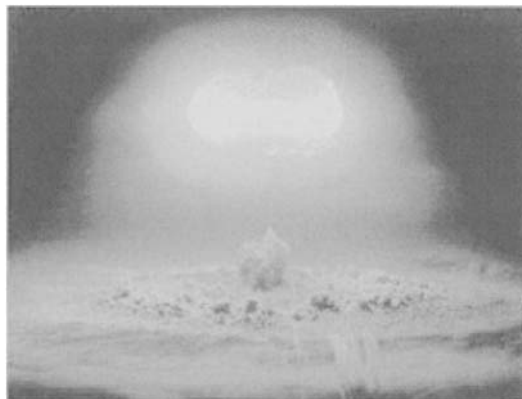


Figure 2. Thermonuclear fusion weapon fireball resulting in the formation of an extremely hot incandescent mass of gas (U.S. Army photograph, Marshall Islands).

applying the same anti-corrosion measures. Man-made tritium is generated on the industrial scale by bombarding lithium with neutrons, which also produces helium-4 generating α particles.

Tritium is also important in research and industry in the following applications: in producing luminous paint, in cancer treatment with the indirect generation of neutrons, in physico-chemical analysis and recently for ceramic electrolytes in hydrogen isotope separation as shown by Mukundan et al. [4]. The increasing amount of man-made tritium for consumer products and nuclear reactors requires more research into the techniques of analysis, disposal and recycling of tritium. For example, in analysis helium-4 and tritium can be easily detected using high sensitivity mass spectrometers and ionization chambers, respectively. The detection limit for tritium is far lower than that for hydrogen or deuterium due to tritium's radioactive decay. Tritium is thus employed as a label and tracer for hydrogen by nuclear-physical methods, and is the most versatile β^- -emitting radionuclide for use in chemical and biological research. Due to this large range of uses, high purity tritium is industrially available in large quantities. The half-life for tritium decay is twenty years. This signifies that five years after preparation of nuclear weapon, helium 3 content is large and there remains about 80–85% of tritium. In this condition, detonating does not work and therefore nuclear weapons must be recycled. Moreover, the nuclear weapons are made of three charges: tritium, plutonium 239 and uranium 235. In addition to this composition, lithium-6 compounds (deuteride or deuterio-tritide) in a warhead avoid the necessity of replacing tritium periodically. The presence of lithium and neutrons during predetonation increase the quantity of available tritium and boost the primary and secondary stages and the nuclear fireball (Fig. 2). Lithium-6 is a critical material and does not require the use of liquid deuterium and tritium liable for corrosion. Plutonium can be fissioned with slow neutrons. Because this material is fissionable, careful planning must be exercised in its handling and machining. The critical mass of plutonium varies over a wide range depend-

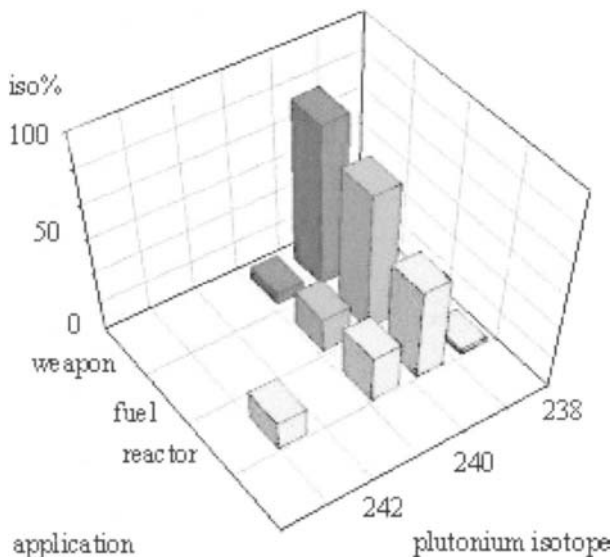


Figure 3. Isotopic composition of plutonium according to its use.

ing on such factors as geometry, reflectors (beryllium), material mass or density, neutron absorbers (boron-10) and the effect of diluents. Plutonium metal in the form of a powder or when finely divided is pyrophoric. Therefore, machining and manufacturing are usually conducted in a dry inert gas atmosphere. The isotopic composition of plutonium furnished by the manufacturer depends on its use (Fig. 3). A nuclear weapon needs more than 93% plutonium 239.

After several years of storage, the proportion of plutonium 239 decreases through decay, whereas that of plutonium 241 is increasing (about 12–15% for 5 years). Plutonium 241 is transmuted into americium 241 which produces gamma rays used in metal radiography for determining cracks and internal geometry in three dimensions. This ray is dangerous to humans, provoking burning and cancer. Moreover, this radiation destroys sensitive materials such as electronic components and organic materials. Consequently, plutonium 239 must also be periodically recycled to eliminate americium 241. The properties of unalloyed plutonium are a function of the six allotropes it forms during cooling from the melt (640°C) to room temperature.

Plutonium has electrons residing in the 7s, 6d and 5f states. Migration from the outer electron shells to the inner 5f causes contraction of the atom. Moreover, most of the phase transformations result in large volume changes and produce crystal structures that have different physical properties. These unusual characteristics have made the metallurgy of plutonium and its alloys particularly challenging. For example, the mechanical properties of plutonium indicate marked changes ranging from high strength, extremely brittle properties of the low temperature α -phase (monoclinic and martensitic) to the low strength,

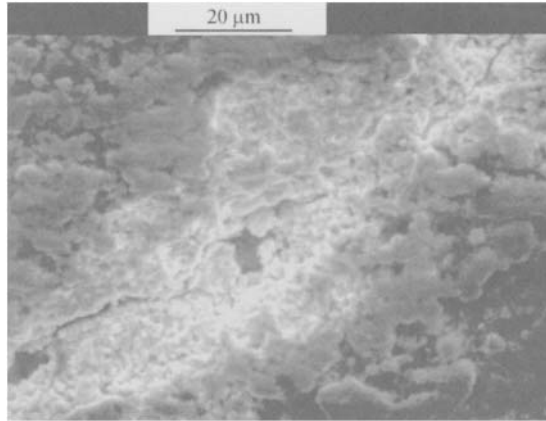


Figure 4. Embrittlement accompanied by cracking of pure plutonium.

high ductility properties exhibited by the δ -phase at temperatures 320 to 450°C. Thus the α -phase is a strong brittle phase due to the large volume reductions produced during cooling from the melt, and does not often attain the full density of 19.8 g cm^{-3} . This is caused by microcracking due to transformation by stresses (stress corrosion, Fig. 4). Cracks are formed, firstly in the body of the metal then progresses to the surface (Fig. 5). Fabrication of unalloyed α -phase plutonium to complex shapes also presents difficulties due to residual amounts of high temperature phases which make engineering tolerances difficult to achieve and to maintain over long periods. These high temperature phases tend to be retained by small amounts of impurity elements. The addition of 2 at.% Ga stabilizes the face-centered cubic δ structure, a phase with superior mechanical properties when compared to the α -phase (Fig. 6). Other elements can act as δ stabilizers, but the Pu-Ga system has been studied in much more detail than others.

The δ -phase alloys exhibited properties more suitable to fabrication techniques, exhibiting ductility and good forming properties that permitted the metal to be rolled into sheet and formed and machined in a conventional way. One of the key issues in understanding the phase stability of Pu-2 at.% Ga alloy is the solid-state microsegregation that occurs during cooling from the melt. This process results in a microstructure consisting of δ -phase grains with Ga-rich cores and Ga-poor edges. Alloys produced by casting or during cold working are not homogeneous. To ensure a uniform gallium content across the grains, heat treatment is undertaken to cause gallium diffusion and to achieve complete δ -phase stabilization. This needs to be performed below the $\delta \rightarrow \epsilon$ transformation boundary; the coring being produced at this interface originally during the cooling period. Employing extended homogenization treatments makes it possible to stabilize Pu-Ga alloys for long periods at room temperature. These alloys are relatively easy to cast as the liquid is more dense than the δ -phase.

Aging has significant impact on the nuclear weapons programs and weapon systems need to remain in service for very large periods. Plutonium itself suffers internal degen-

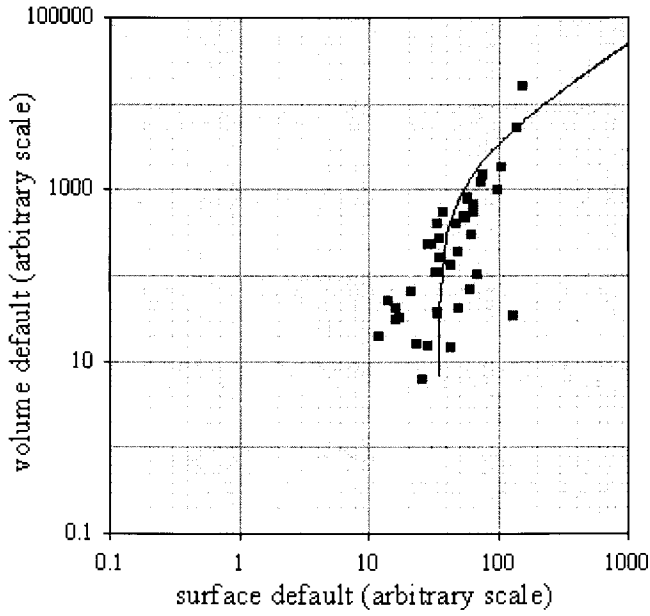


Figure 5. Cracking evolution in the bulk and at the surface of pure plutonium.

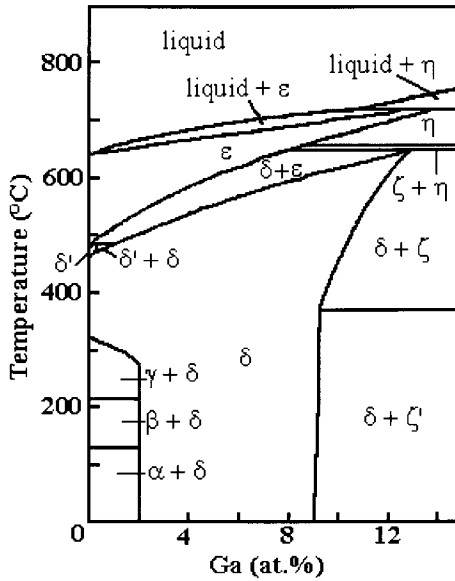


Figure 6. Gallium-plutonium alloy diagram showing the different allotropic domains.

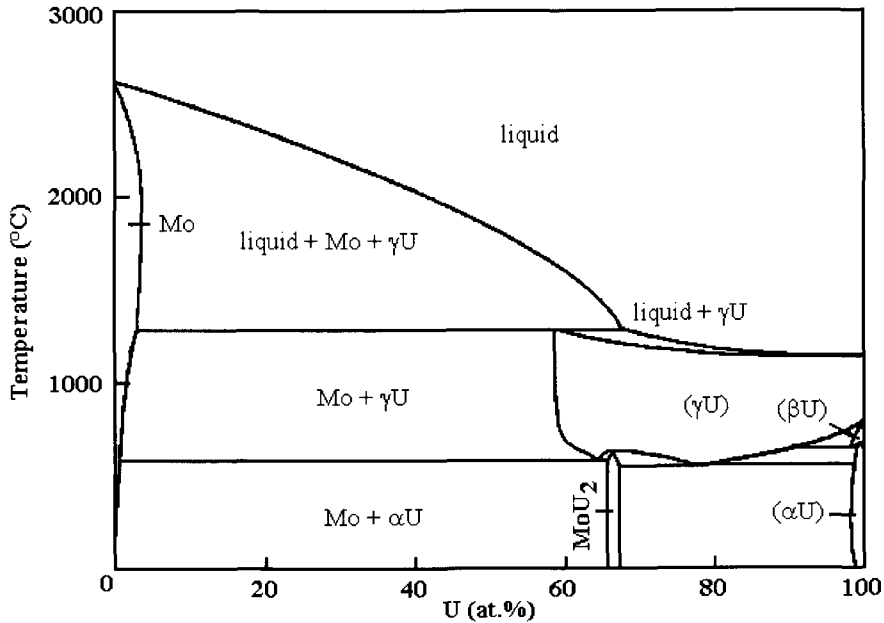


Figure 7. Molybdenum-uranium alloy diagram showing the different allotropic domains.

eration due to radioactive decay. The recoiling uranium nucleus and the smaller He ion cause considerable damage in the immediate area. The 'cannon ball' of the uranium nucleus causes about 2500 Pu atoms to be displaced and creates a large number of residual and interstitial vacancies at the periphery of its damage spike to such an extent that it can be calculated that statistically in 10 years time all the Pu atoms will have been forced from their original sites. Likewise, the He ion, having captured two electrons from the plutonium, comes to rest in the lattice as a helium atom with the potential for it to diffuse to create bubbles of helium in the metal, reducing the density, increasing the strength, and having significant effects on the implosion performance.

For implosion, subcritical masses of ^{235}U (and body-centered-cubic γ -phase Mo- ^{235}U and Ta- ^{235}U alloys) and ^{239}Pu are compressed to produce a mass capable of supporting a supercritical chain reaction. These uranium alloys are stabilized in the γ -phase (Fig. 7) by rapid cooling and are less sensitive to classical and stress corrosion and their mechanical properties are enhanced.

One obstacle to recycling uranium is that repeated casting with graphite crucible causes an accumulation of carbon in ingots which has a deleterious effect on casting properties. The procedure used to reduce carbon content before electrorefining is that of adding trace amounts of niobium that combines with the carbon. The resulting carbide is less dense than is the liquid uranium. Buoyancy forces would tend to transport it toward the top of the casting where, after solidification, the carbon-rich portion could be removed. Furthermore,

alloying niobium prevents oxidation and causes change in crystalline structure making the alloy brittle.

The compression is achieved by the detonation of specially designed high explosives surrounding a subcritical sphere of fissionable material. When the high explosive is detonated, an inwardly directed implosion wave is produced. This wave compresses the sphere of fissionable material. The decrease in surface to volume ratio of compressed mass and the increased density are such as to make the mass supercritical for a nuclear explosion. Boosting fission and predetonation are essential. This is done by insertion of a thin beryllium reflector and a neutron emitter of sufficient strength. Consider a spherical implosion, where Δ represents the change in system dimension (i.e. size of radius) along the axes of compression in three dimensions, then the compression C achieved by the implosion is represented in the simplified equation:

$$C = \left(\frac{r_0}{r_0 - \Delta} \right)^3 \quad (0.2)$$

Agglomeration and bubble formation lead to significant dilation of aged plutonium. Not only can the helium atoms agglomerate but the vacancies produced at the periphery of the damage spikes can diffuse and form voids. These voids could grow at an accelerated rate. Thus the original δ -plutonium alloy is continually changing, He content is increasing with time and then has an impact on phase stability, density, and strength of the δ -phase material. In addition other isotopes of plutonium, namely ^{241}Pu , are decaying to americium at a rate concomitant with a half-life of 13 years. This has significant implications for phase stability and also enhanced γ radiation output which will affect radiation dose levels to operations during the process. Finally, plutonium is rapidly corroded in moist atmospheres containing relatively small amounts of oxygen. In aqueous solutions, plutonium may exist in all four valency states (3, 4, 5 and +6) depending on radiolysis. The +4 valency is the most stable oxidation state.

Tritium is a crucial component of thermonuclear weapons in enhancing their explosive yield. A typical thermonuclear device consists of two stages, a primary where the explosion is initiated and focused to the inner by plutonium and uranium fission trigger (X-rays), and a secondary where the main thermonuclear explosion takes place (fusion) to form helium. The yield of the primary stage, and its effectiveness in driving the secondary to explode, is aided (boosted) by tritium gas which undergoes a nuclear reaction with deuterium, and generates a large amount of high-speed neutrons to 'boost' the nuclear burn-up of the plutonium or highly enriched uranium. Instant fusion reactions will not begin until the nuclei involved have been heated to very high temperatures, and pressures, by fission reactions. The reason is that the nuclei are positively charged (strong electrical repulsion) and repel one another strongly up until the moment they stick, collide and fuse, thereby releasing enormous amounts of energy and radiation. Incidentally, it is puzzling why a full and small palladium ball cathode using pure tritiated water, as made in the 'Cold Fusion' is not used to charge the tritium. Hyperconcentrated tritium in the ball center should release a few neutrons.

An optimally efficient fission explosion requires the implosion of the fissile core in a very short time (hundreds of nanoseconds) from shock waves produced by explosive when the neutron multiplication rate is at a maximum. Creating a symmetric implosion wave requires close synchronization in firing the detonators, because only they can be fired by very powerful and fast current surges. The normal method of providing the power supply for the detonator system is to discharge a high capacitance very rapidly at high voltage. The capacitor must be matched with a switch that can handle high voltages and currents without adding undue inductance to the circuit. A variety of technologies are available: triggered spark gaps, krytrons and thyatrons. More recently, laser detonating systems have been developed. These use a high power solid state laser to deliver sufficient energy in the form of a short optical pulse to initiate a primary or booster explosive. The laser energy is conducted to the detonator by a fiber optic cable. Finally, a miniature linear particle accelerator called a 'pulse neutron tube' can provoke collisions between deuterium and tritium nuclei to generate high energy neutrons through a fusion reaction. The tube has an ion source at one end, and an ion target at the other. The target contains one of the hydrogen isotopes adsorbed on its surface as a titanium hydride. When a current surge is applied to the ion source, an electrical arc creates a dense plasma of hydrogen isotope ions. This cloud of ions is then extracted from the source, and accelerated to an energy of 100–170 KeV by the potential gradient created by a high voltage acceleration electrode. Slamming into the target, a certain percentage of the ions fuse to release a burst of 14.1 MeV neutrons. These neutrons do not form a beam but are emitted isotropically. High explosives are designed to compress the core. To create a spherical implosion wave, inward facing explosive ring lenses need to be arranged on the surface of the sphere assembly so that the convergent spherical segments produced merge into one wave. It is a substantial advantage to use lenses with a small thickness to produce a wave with a smaller curvature. Powerful shock waves can dissipate significant amounts of energy in entropic heating. Energy that contributes to entropy increase is lost in compression. This problem can be overcome by using a shock buffer; this is a layer of low impedance or low density material that separates two denser layers. When a shock is driven into the buffer from one of the dense layers, a weaker shock of low pressure (but higher velocity) is created. This shock is reflected at the opposite interface, driving a shock of increased pressure into the second dense layer. This shock is weaker than the original and dissipates much less entropy. Two likely low density materials for use as buffers are graphite and beryllium. The term 'tamper' has long been used to refer both to the effects of hydrodynamic confinement in assembling and to neutron reflection. One must be careful to distinguish between these effects. The term 'tamper' refers exclusively to the confinement of the expanding fissile mass. Tamping is provided by a layer adjacent to the fissile mass. This layer dramatically reduces the rate at which the heated core material can expand by limiting its velocity to that of a high pressure shock wave. Two physical properties are required to accomplish this role: high mass density, and optical opacity to the thermal radiation emitted by core. High mass density requires both a high atomic mass and a high atomic density. Dense materials for use as tampers are natural or depleted uranium, tantalum and tungsten carbide. Any neutron that reaches the surface of the core is lost for ever to the reaction. A reflector around the core scatters

the neutrons to force some fraction of them to re-enter the surrounded fissile mass. Ideally the reflector is a layer of low-Z material. Beryllium and graphite are excellent neutron reflectors.

Safety is a serious problem with high yield fission weapons. Since several critical masses are present, simply collapsing the hollow space inside the core can render it highly supercritical. This does not require accurate implosion. Any accidental detonation of the explosive layer would squash a hollow core like a squashed tennis ball, and could lead to a very powerful explosion. Much milder accidents could also create serious criticality events such as a local region of criticality in the sphere. Several approaches are available to reduce these problems:

- keep the weapon core partially disassembled, with the fissile material brought into its ‘implosion ready’ configuration shortly before detonation,
- fill the hollow core with something that will prevent its collapse, then remove the material as part of the arming sequence,
- fill the core cavity with tritium and deuterium as part of the arming sequence,
- fill the core cavity with a good fast neutron absorber (i.e. something containing boron-10) to provide an additional margin of critical safety before arming,
- insert a continuous neutron emitter of sufficient strength to guarantee early predetonation,
- use locking mechanisms requiring special keys or codes,
- employ sophisticated fuzing systems to detonate the device at the proper place and time,
- resist malicious tampering, human error, component or systems failure (either inside or outside the weapon) and accidental damage,
- avoid inappropriate activation of the weapon’s firing system and detonation of the high explosives by means other than the firing system (e.g. physical damage through fire or impact),
- use multiple and redundant safety systems requiring cooperation by more than one person to complete weapon arming.

After this brief description of tritium and nuclides used with it and their military applications, we will describe the organization of this book that is in three parts.

- In chapter 1 general aspects of fusion reactors using tritium are given. Chapter 2 describes methods for preparing tritium from lithium blankets. A variety of techniques for tritium handling and processing of highly tritiated wastes are described in chapter 3.
- In chapter 4 and chapter 5 we present the strategy for controlling corrosion in tritium-tritiated water, theoretical recall of characteristics of super-alloys and stainless steels and typical corrosion examples in installations in various parts of the world.
- Finally, results obtained in our laboratory are discussed and analyzed in the next chapters. Chapters 6 to 9 and chapter 23 describe the corrosion obtained directly from discharged low energy, tritiated water, tritium and helium. Corrosion by the primary aqueous radiolytic products (peroxides) and the effects of changes in pH are detailed in chapters 10 to 12. The corrosion problems due to the indirect radiolytic species (Cl^- , F^- , CO_3^{2-} , NO_3^- and $^2\text{H}_2\text{O}$) are presented in chapters 13 to 21. Chapter 22 deals with

temperature effects. Finally, chapter 24 summarizes the findings and gives practical applications. In the annexe, 3D surface topographies show aspect of corroded metals in tritiated media (chapter 25) and fractal representation shows the modification of tritiated oxide layers leading to breakdown (chapter 26). These views of corrosion problems are significant and show the usefulness of this book. Because the book contains an unusually large number of corrosion terms a glossary is presented in the introductory material.

GLOSSARY

a = constant

abs = absorbed species

ads = adsorbed species

aq = aqueous solution

A = electrode surface (cm^2)

A = constant phase element (CPE)

B = rate coefficient for oxide layer corrosion or constant

b = constant

C = species concentration (mol dm^{-3}) or capacitance ($\mu\text{F cm}^{-2}$)

C = parameter depending on excitation and ionization in oxide or weapon compression factor

C_{ox} = oxide capacitance ($\mu\text{F cm}^{-2}$)

C_{dl} = double layer capacitance ($\mu\text{F cm}^{-2}$)

C_{p} = pore capacitance ($\mu\text{F cm}^{-2}$)

C_{hl} = Helmholtz layer capacitance ($\mu\text{F cm}^{-2}$)

$C_{\text{V}_{\text{O}^{2-}}}$ = concentration of O^{2-} vacancy

$C_{\text{V}_{\text{Me}^{n+}}}$ = concentration of Me^{n+} vacancy

{oxide- $^3\text{H}_2\text{O}$ } = interface $^3\text{H}_2\text{O}$ -oxide

D = diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)

d = depth of weld (mm)

d = oxide layer thickness (nm)

$d_{k,l}$ = deformation reaction of a metal to twinning

e = electron charge ($1.602 \times 10^{-19} \text{ C}$)

$e_{i,k}^{\text{p}}$ = irreversible part of a strain rate tensor where the subscript p is for elastic and plastic parts

E = electrochemical potential (V)

E_{a} = activation energy (J)

E_{corr} = corrosion potential (V)

E_{rep} = repassivation potential (V)

E_{pit} = pitting potential (V)

$E_{\text{breakdown}}$ = breakdown potential (V)

$E_{\text{n...}}$ = energy released in oxide by β^- particle

- f, f = frequency (Hz)
 F = Faraday constant (96 500 C)
 F = free energy correlated to martensitic transformation
 i = current (A cm^{-2})
 $i_{a,c}$ = anodic or cathodic current (A cm^{-2})
 i_{corr} = corrosion current (A cm^{-2})
 i_p = peak current (A cm^{-2})
 i_{passive} = passivity current (A cm^{-2})
 I = ionization energy in oxide
 j = imaginary operator
 J_0 = parameter depending on thermodynamic constant
 J_m = rate of submergence of the metal cation vacancy
 K_w = dissociation constant
 k = Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$) or rate constant
 k = interaction parameter
 $k_a, k_{c...}$ = rate constant of a reaction ($\text{mol cm}^{-2} \text{ s}$)
 l = cavity radius
 L = inductance (H)
 M = oxide mean molecular weight (g)
 Me = metal
 m = mass of β^- particle
 n = neutron
 n = number of electrons transferred in an electrochemical reaction
 n_d = donor density (n cm^{-3})
 n_i = number of impacts in oxide by tritium decay
 of = oxide layer formation
 om = oxide layer modification
 pd = primary depassivation
 sd = secondary depassivation
 p = pressure (Pa)
 P_s = entropy production, positive for stable phases and negative for unstable phases
 Q = electrical charge (C)
 r = adsorption site
 r = roughness factor or radius of the weapon-grade fissile material
 \bar{r} = corrosion rate ($\mu\text{m yr}^{-1}$)
 R = molar gas constant ($8.314 \text{ J mol}^{-1} \text{ K}$)
 $R_{1,2...}$ = resistance ($\Omega \text{ cm}^2$)
 R_{ct} = charge transfer resistance ($\Omega \text{ cm}^2$)
 R_{el} = electrolyte resistance ($\Omega \text{ cm}^2$)
 R_{ox} = oxide resistance ($\Omega \text{ cm}^2$)
 R_{pit} = pitting resistance ($\Omega \text{ cm}^2$)
 R_p = polarization resistance ($\Omega \text{ cm}^2$)
 R_{lc} = localized corrosion resistance ($\Omega \text{ cm}^2$)

- R_{im} = imaginary resistance ($\Omega \text{ cm}^2$)
 R_{real} = real resistance ($\Omega \text{ cm}^2$)
 R_{D} = diffusion resistance ($\Omega \text{ cm}^2$)
 s = Laplace operator
 $s_{i,k}$ = independent thermodynamic variable
 t, T = time (s)
 $\tau_{1/2}$ = half life for tritium (yr.)
 T = temperature (K: Kelvin degree, C: Celsius degree)
 V_{m} = measured potential (V)
 V_{fb} = flatband potential (V)
 $V_{\text{O}^{2-}}$ = oxygen vacancy
 $V_{\text{Me}^{n+}}$ = metal vacancy
 V = helium atom volume
 v = scan rate (V/s)
 ν = electrochemical reaction order
 \bar{v} = travel speed during welding (cm min^{-1})
 V_{fb} = flatband potential (V)
 w = width of weld (mm)
 w = equivalent weight of metal (g)
 W = Warburg impedance (Ω)
 W = energy carried out during welding (W)
 X^- = halide
 x = angular frequency or adsorbate or numerical value
 y = numerical value
 Z = atomic number of element
 Z = impedance (Ω)
 Z_{r} = real impedance (Ω)
 Z_{i} = imaginary impedance (Ω)
 Z_{ou} = outer oxide impedance (Ω)
 Z_{in} = inner oxide impedance (Ω)
 Z_{D} = diffusion impedance (Ω)
 Z_{L} = Laplace impedance (Ω)
 Z_{CPE} = constant phase element impedance (Ω)
 Z_{F} = faradaic impedance (Ω)
 $|Z|$ = impedance modulus ($|\Omega|$)
 ΔG = standard Gibbs energy (J)
 $\Delta \Phi$ = potential drop into oxide (V)
 $\alpha, (1\alpha)$ = symmetry factors
 α = constant
 β^- = negative particle emitted during tritium decay
 γ = surface tension on wall
 ν_{e} = antineutrino particle emitted during tritium decay
 φ = parameter

- Υ = dynamic viscosity (P)
 δ = diffusion-layer thickness (μm)
 Δ = change in dimension of the weapon-grade fissile material
 ε = relative dielectric constant
 ε_0 = permittivity of free space ($8.854 \times 10^{-14} \text{ F cm}^{-1}$)
 θ = fractional surface coverage or t/T (stepped potentials) or phase angle ($^\circ$)
 κ = conductivity (S cm^{-1}), or parameter depending on energy absorbed in oxide
 σ = Warburg coefficient ($\Omega^{-1} \text{ cm}^{-1}$)
 $\sigma_{i,k}$ = macroscopic stress tensor
 η = overpotential (V)
 Φ = electrical field inside an oxide layer (V)
 $\bar{\mu}$ = shear modulus
 ρ = solid density (g cm^{-3})
 ω = angular frequency (rad) or electrode rotation rate (n min^{-1})
 Ψ = function related to fractal polynomial
 v = parameter of β^- particle
 ζ = parameter of β^- particle
 Γ = concentration of adsorbed species
rpm = rotation per minute
* = excited species

Part I

THE ROLE OF TRITIUM IN THE NUCLEAR INDUSTRY

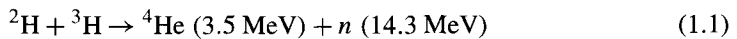
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THERMONUCLEAR FUSION REACTOR

1. Thermonuclear fusion reactor overview

Controlled nuclear fusion can be defined as the process by which tritium and deuterium nuclei combine at very high temperatures to produce ${}^4\text{He}$ and fast neutrons releasing a large amount of energy that can be recuperated as electrical power. The latest experimental machine, which is a joint undertaking of the European Union, Japan, the Russian Federation and the USA, is known as ITER (International Thermonuclear Experimental Reactor). The overall view of ITER is given in Fig. 1.1, as shown by Rebut and Keen [5]. The facility consists essentially of a vacuum and plasma vessel containing tritium and deuterium and magnetic field generators to confine the nuclei. In the reactor, the ignition of ${}^2\text{H}$ - ${}^3\text{H}$ must be maintained in the plasma over long pulse times during the thermonuclear reaction for the stationary state.

Here the deuterium-tritium nuclear reaction is:



Scientific aspects of thermonuclear reactors have been detailed by Dautray [6] and Dautray and Watteau [7]. As seen in the equation above large amounts of energy are released. To make this ignition reaction take place in a nuclear fusion reactor, the ${}^2\text{H}$ and ${}^3\text{H}$ ion fuel must be fused. This is achieved under the action of electromagnetic forces and extremely high temperatures overcoming the electrostatic Coulomb repulsion between positively-charged nuclei and bringing them close enough together for fusion to occur at a sufficient rate. For this, a temperature of around 10^7 °C and an ordered magnetic field of ten Tesla are needed in the plasma core of the reactor. At this temperature, the gas is a plasma and the ions and electrons form a macroscopically neutral fluid. Also, using magnetic confinement fields makes it possible to keep the plasma thermally insulated in the core. The fusion energy in this device would amount to several gigawatts. In practice, the confined radioactive ${}^4\text{He}$, formed in eq. (1.1), would heat, during its removal, the fresh fuel and then, once it has cooled, would be extracted from the core for its eventual sale. A 1000 MW fusion reactor will require about 3×10^{20} fusion reactions per second and produce about 10^{19} 14.3 MeV neutrons/s and would require several kilograms of tritium per year, equivalent to a fuel burn-up of about 3.6 g of deuterium and 5.4 g tritium per hour. This shows that tritium is

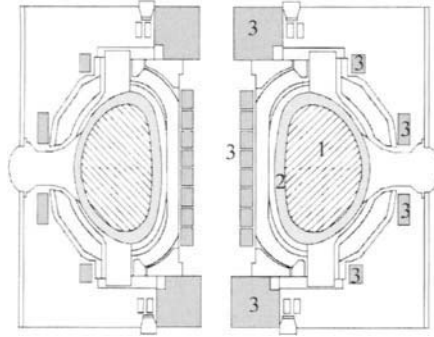


Figure 1.1. Cross-sectional view of the International Thermonuclear Experimental Reactor, 1: ${}^2\text{H}$ - ${}^3\text{H}$ plasma torus, 2: vacuum vessel, 3: magnetic field generators (coils, transformers).

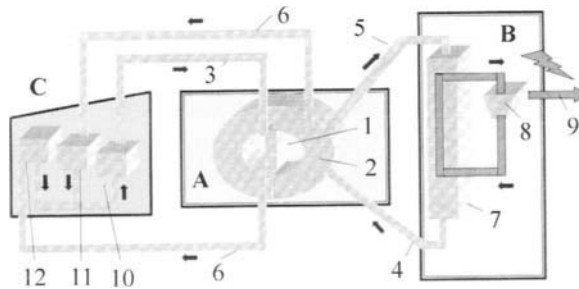
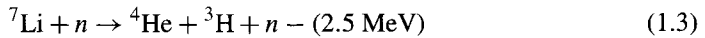


Figure 1.2. Schematic of the elements of the Fusion Energy Power Plant, A—fusion reactor, 1: torus, 2: blanket, 3: ${}^2\text{H}$ - ${}^3\text{H}$ fuelling, 4: coolant inlet, 5: coolant outlet, 6: ${}^3\text{H}$ outlet tritium. B—electrical power, 7: steam generator, 8: turbine, 9: electric output, C—tritium recycling, 10: ${}^2\text{H}$ - ${}^3\text{H}$ fuel preparation, 11: recovery, 12: clean up and recovery.

needed to keep the plasma burning. The major tritium inventories will be in the plasma, impurity processing, lithium blanket, isotope separation, fuel storage as metal tritides and tritiated water recycling. Since tritium and deuterium are such important components, their supply for the nuclear reactor must be anticipated (Fig. 1.2).

Deuterium is abundant in the Earth, but tritium is radioactive, with a half-life of 12.3 years and therefore does not occur naturally. It has to be manufactured, and breeding tritium in situ is an interesting possibility. In meeting this objective, some fast neutrons are used to breed enough tritium from a lithium blanket material adjacent to the nuclear reactor. For this process, 14.3 MeV neutrons pass through the nuclear reactor wall then interact with the lithium in the reactor blanket before being transported to a conventional power plant.





The basic material for this reaction, natural lithium, consisting of 92.5% ${}^7\text{Li}$ and 7.5% ${}^6\text{Li}$ is found in large quantities in the earth. Primary 14.3-MeV neutrons from the fusion plasma are slowed down in the blanket that must be sufficiently thick to generate a large quantity of tritium and slow neutrons. Slowing the neutrons heats the blanket and a coolant flowing through it and so the blanket in the fusion reactor serves a second function, i.e. it converts the released energy into useful heat.

In practice there are several options. Due to its low melting point the liquid lithium-breeding blanket can be used as coolant, as in the Phoenix type super-generators, to thermalize the neutrons. In this case, the bred tritium is transported with the liquid lithium stream and is separated externally. The blanket design can include, to be more efficient, the addition of beryllium to lithium for neutron multiplication; however, the compatibility of beryllium with the other materials and the coolant medium is a sensitive issue. Moreover, multiplied neutrons have lower energies. A second choice has been made between burning more lithium and the greater recuperation of energy for heating the blanket. In using solid lithium, three options have been examined for the blanket-support: lithium-ceramic (solid breeder), lithium-salts (aqueous salt) and lithium-lead eutectic. Key design issues for the lithium-ceramic are to maintain the breeder material at a temperature high enough in the presence of hydrogen to enhance tritium release at 400–1000 °C, while having a low temperature water-cooled steel structure. The bred tritium contains O^3H^- ions, LiO^3H and $\text{H}^3\text{HO}-^3\text{H}_2\text{O}$ moisture. Tritium recovery is strongly dependent upon the activity of these species. The key issue for the lithium-salt option is the corrosion of the coolant channels. Lithium-lead alloys such as $\text{Li}_{17}\text{Pb}_{83}$ with a melting point at 235 °C and a high breeding rate due to the neutron multiplying element, lead, have been also studied. The key property of the lithium-lead eutectic is the extremely low solubility of tritium in it leading to chemical reactions and high permeation through the hot stainless steel walls inducing material damage.

Moreover, the thermonuclear fusion reactor has specific advantages and disadvantages:

- a runaway fusion reaction is intrinsically impossible. Furthermore, once the supply of fresh fuel is cut off the reactor can continue operating for only a few tens of seconds and no melting of critical components would occur. In addition, major explosions similar to nuclear explosions cannot occur in fusion reactors because the total amount of reacting fuel in the plasma is unable to maintain full power operation for more than a few tens of seconds and any disturbance leads to loss of plasma confinement and hence terminates the fusion reaction,
- there are radioactive wastes, unburnt tritium and tritiated water to be treated in the tritium processing installations. Structural components of the nuclear reactor which have become radioactive through exposure to the neutrons will have to be stored for a long time.

2. Requirements for controlled nuclear fusion

Nuclear reactors produce a large amount of energy at very high temperatures and require, paradoxically, the provision of external energy. To control the energy balance, the conditions must be such that the thermonuclear fusion reaction delivers more energy by confinement than it consumes. Also, in a nuclear reactor burning a ${}^2\text{H}$ - ${}^3\text{H}$ fuel, the reaction can be partially self-sustaining by the 4.5-MeV kinetic energy to maintain the combustion temperature. The best performance obtained for a ${}^2\text{H}$ -11% ${}^3\text{H}$ combustion expressed by $Q_i \tau_E n^{-1}$ is $9 \times 10^5 \text{ EeV s m}^{-3}$ where Q_i is the ignition energy in the center of the plasma, τ_E energy confinement time and n the density of the ${}^2\text{H}$ - ${}^3\text{H}$ fuel contained in the plasma. To obtain this performance, the reactor specifications including reactor vessel toroid (made of stainless steel) must be taken into account. According to the specifications, the ignition chamber steel underwent various treatments where surface cleanliness was at a premium. Baking to 500°C took place under vacuum-removed gas and impurities adsorbed on the inner wall surface were removed. This made it possible to achieve the specified vacuum of about 10^{-7} Pa required for correct fusion operation with the ${}^2\text{H}$ -11% ${}^3\text{H}$ mixture without the presence of impurities. As the stainless steel vessel which is several tens of centimeters thick is the primary containment for plasma where there are high radiation levels, corrosion fatigue tests have been made. These verify that the stainless steel used meets the specifications of the loads both for fusion operation and also for accident conditions where there could be irradiation. To avoid tritium leakage and external contamination, double containment is provided between the plasma vacuum chamber and the external torus wall. It is clear that the vessel assembly due to its complexity and thickness is subjected to mechanical stresses that can lead to plastic deformation mechanisms and rupture following the cracking of the steel. This is an additional reason for carrying out these corrosion fatigue tests in a Pressurized Water Reactor.

The other components within the vacuum vessel are also subject to fatigue stress by irradiation. Since components have limited lifetimes, it must be possible to replace them quickly. In addition, the layout of the cooling pipes was designed to reduce the number of welds to a minimum in the most vulnerable regions where localized stresses, ruptures and induced corrosion can occur.

The best energy balances, plasma density, ignition temperature and pulse time have been obtained after applying these specifications and after applying the tests in selecting materials. The energy obtained by fusion of ${}^2\text{H}$ -11% ${}^3\text{H}$ is about 10.5 MW. It is hoped that, in the future, break even will be reached with ${}^2\text{H}$ -50% ${}^3\text{H}$.

It is foreseen that in this thermonuclear fusion the tritium is not completely consumed. Its inventory is thus important for following the recuperation and recycling operations. The recycling of tritium is well understood and controlled in specialized tritium-handling plants that use methods such as tritium isotope cryodistillation, uranium storage beds, gas chromatography and metal diffusion membranes for purifying the tritium gas to maintain tritium at a high standard of purity in the torus and annex facilities. Recycling will be discussed in the chapter that describes tritium processing.

3. Plasma confinement

Plasma confinement is necessary and is achieved by magnetic fields. Other modes for confinement are possible such as the inertial thermonuclear fusion confinement by laser beams. In confinement, a fuel capsule is heated and highly compressed to obtain a very high liquid density until ignition occurs in the center by implosion, then the explosion carries the energy outside the reactor for recuperation in the power plant. Ignition lasts as long as the fuel remains confined by its own inertia. This technology is not yet optimized and will not be described further. Nevertheless, if it is adopted in the future, the same lithium blanket, tritium reprocessing or recycling will be applied and so the tritium processing problems will be the same.

In the absence of magnetic confinement, the ^2H and ^3H ions in hot plasma tend to spread and fill the space available because of the collisions between ions. The plasma in this condition is not confined and the thermonuclear reaction cannot occur. If a linear, perpendicular magnetic field is applied, ^2H and ^3H ions move in helical paths around the magnetic field lines and thus remain radially confined and the hot plasma forms a magnetic trap for the ^2H and ^3H ions. The stationary burn is thus possible for as long as the magnetic confinement is maintained. The particles of plasma cannot reach the side walls of vessel, but they will strike the ends of the vessel and thermonuclear fusion is limited. To prevent the particles coming into contact with the ends of the vessel, toroidal configurations have been realized. In these configurations, a toroidal field has the perpendicular poloidal field superimposed upon it. The ^2H and ^3H ions trajectories thus take spiral paths along and around the plasma. The toroidal field magnet includes several water-cooled coils to maintain the necessary toroidal trajectory. The shape of these is chosen to reduce mechanical stresses because they are subjected to the forces due to magnetic pressure and control of the mechanical stresses is important to avoid stainless steel cracking and tritium leakage. The poloidal field coils are the primary windings of a transformer, and their main role is to induce the current flowing through the plasma. They create field components that control the equilibrium, position and shape of the plasma.

Three types of system produce a spiral path:

- the Tokamak consists of a series of coils spaced around the torus to generate the toroidal magnetic field with the transformer to produce an electric current flowing through the plasma creating the poloidal field. The transformer also serves to heat the plasma resistively. The transformer improves the magnetic coupling between the primary windings and the secondary plasma to create a demagnetizing effect. This produces the required voltage for gas breakdown in the vessel and maintains the plasma current to heat it ohmically. The values of the toroidal field and plasma current are about 3.45 T and 4.8 MA, respectively. An important parameter of the machine is the ratio of the major radius to the minor radius of the torus. Theoretical studies and experiments have shown that a ratio of about 1.5 provides the best plasma performance.
- the Stellarator is formed by a series of external coils to produce the spiral magnetic field lines. No current is induced in the plasma. The Stellarator can operate continuously

avoiding disruptions responsible for mechanical stresses in the stainless steel structures and walls.

- the Reversed Field Pinch device has the toroidal and poloidal configuration with a very high current so that the direction of the toroidal field at a certain radius within the plasma is reversed.

4. Plasma heating

In Tokamak devices, the current flowing through the plasma also serves to heat the plasma by the Joule effect until a high temperature is reached. Beyond this point the resistivity of the plasma is too low so that additional heating systems are needed to bring the plasma to the temperatures required for thermonuclear fusion.

In the case of Stellarators, these heating systems have to supply all the energy needed since there are no current flows induced within the plasma. The main methods of additional heating selected for controlled thermonuclear fusion systems are essentially injection of high-energy neutral beams, dissipation of radiofrequency waves in the plasma, adiabatic compression and the use of electrical transformers.

- neutral injection heating is achieved by injecting an intense beam of energetic neutral atoms across the confining magnetic field into the plasma. There, the neutral particles are ionized and confined by the magnetic field. The resulting energetic ions give up their energy to the bulk plasma via collisions, thus increasing its temperature. The beams are generated by the electrostatic acceleration of positive ions, which subsequently are neutralized in a gas cell since charged particles are unable to penetrate the magnetic fields of the torus. The neutralization efficiency is quite low and the remaining ion beams are deflected and dumped.
- additional radiofrequency generators dissipate energy which is absorbed by the plasma, and thus heating occurs for a long time.
- adiabatic compression of the plasma involves the plasma moving and changing shape from a region affected by a weak magnetic field towards a region where there is a strong magnetic field. In this method, heating occurs during all thermonuclear fusion time.
- transformers induce a heating inductive current on the plasma for only a short time.

THE PREPARATION OF TRITIUM

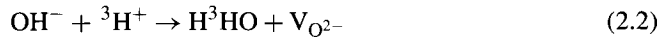
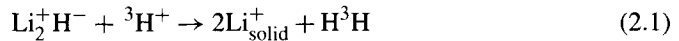
Obtaining background information for the industrial production of tritium by a lithium blanket is an important point for its use in a fusion reactor. Tritium is prepared by neutron activation of ${}^7\text{Li}$ -7.5% ${}^6\text{Li}$. Neutrons with sufficiently high energy activate ${}^6\text{Li}$, whereas ${}^7\text{Li}$ requires more energy for activation. Due to the fact that ${}^6\text{Li}$ has a low concentration, a larger fraction of the neutron trajectories will encounter ${}^7\text{Li}$ and therefore, neutrons with energies well above 2.9 MeV are required. In previous studies as reported by Johnson [8], it has been seen that tritium breeding materials are attractive because of their overall excellent tritium release, chemical inertness and thermophysical and thermomechanical properties with a stable phase under irradiation. Li_2O , Li_2AlO_2 , Li_2TiO_3 , Li_2ZrO_3 have been selected from a choice of several ceramics.

The work done has shown that the rate-limiting mechanism for tritium transport into the ceramic and its release must be known. A full understanding of processes is critical for achieving an efficient production of tritium fuel to sustain the fusion reaction. In fact, the mechanisms are complex and involve tritium diffusion and trapping in the ceramic grain, grain boundary diffusion, adsorption reactions on the grain surface, tritium desorption, gas-solid equilibration by bulk solubility and molecular diffusion in the gas phase. Diffusion should be the rate-limiting mechanism. However, it was shown that the rate-controlling step changed from diffusion to surface phenomena as the ceramic grain size decreased and/or temperature increased.

Also, oxygen activity controls the released oxidized and reduced tritium forms, the amount of tritium retained in the condensed phase, and the amount of blanket transported as $\text{LiO}^1\text{H}/\text{LiO}^3\text{H}$ vapor. If oxygen activity is reduced sufficiently, it is possible for tritide dissolved in the bulk to become an important species in the condensed phase and tritium release is slow. The result will be an increase in the tritium inventory in the blanket that is unacceptable from both an economic and safety viewpoint. For this, oxygen activity depends on the used ceramic type. Recent tests indicated excellent tritium release behavior of Li_2ZrO_3 and Li_2TiO_3 ceramics over the temperature range of 350–1100°C. Insensitivity to moisture or vapor for Li_2ZrO_3 ceramic was also observed. Fortunately for safety, activation by radiation of zirconium-ceramic is small in comparison with that from currently used structural steel materials. Postirradiation examination of the Li_2ZrO_3 pebble bed showed very low tritium inventory, about 0.05 ppm, and excellent release comparable with that of Li_2TiO_3 pebbles.

Helium-4 generated in ceramic breeder materials during neutron irradiation has also a significant impact on the durability of materials by its diffusion in the grains and release from the surface. Data indicate that helium-4 release is much lower than tritium and, therefore, can cause a blanket swelling problem if helium gas does not escape from the ceramic. Ceramics in small grain form do not represent too great a problem, and no fractures have been observed in the breeder Li_2ZrO_3 ceramic.

In the process, tritium outgassing from the ceramic compounds will be transported from the blanket in a helium or argon-stream and recovered externally. It has been noted that tritium release is very much easier with about 1000 vpm hydrogen. This particularity has been used in tritium-piles for several years. However, the addition of hydrogen to the purge gas imposes a multiple-stage tritium purification for isotope separation. Also, the species released have been found in two forms, H^3H and H^3HO , so that the tritiated water must be separated from the tritium-hydrogen mixture by alumina-ceramic desiccating beds. The presence of tritiated water in these beds could be a source of equipment corrosion. In addition, using hydrogen requires understanding of the tritium processes in the lithium ceramic. For this, the surface-to-volume ratio of the ceramic grains is an important parameter for diffusion and desorption. With large grains, the bulk diffusion will determine the release rate. For smaller grains, the surface reaction becomes important with respect to the role that hydrogen plays. For tritium release, there are two mathematical formulations depending on whether hydrogen is present or not. Irradiation of lithium by neutrons with no hydrogen in the helium purge gas creates tritium in the form of $^3\text{H}^+$ inside the ceramic at a few tens of ppm. The probability of forming $^3\text{H}_2$ or $^3\text{H}_2\text{O}$ is very small, and the release rate is proportional to the square of the low molecular tritium concentration in the lithium-based solid breeder ceramic. With hydrogen present, there is chemisorption of OH^- and Li_2^+H^- on the lithium ceramic surfaces and two possible reactions with $^3\text{H}^+$:



where $\text{V}_{\text{O}^{2-}}$ indicates oxygen vacancy. Tritium release rates are proportional to the product of the surface coverage of the chemisorbed hydrogen and the tritium concentration; the former is usually much larger than the latter. Therefore, in the second mathematical formulation, the tritium release rate is directly proportional to the tritium concentration and not to its square, as is the case in the absence of hydrogen. This is the basic reason that the addition of hydrogen to the purge gas leads to an enhancement of the tritium release rate. The model thus suggests that the tritium release rate should be enhanced by increasing hydrogen concentrations in the helium purge gas. But experiments have shown that majority of the surface sites are not available for hydrogen chemisorption with only a small number of sites such as step ledges and point defects being favorable. Once these sites are all occupied, further increases in the hydrogen concentrations would not be useful.

As a final point, the ceramic Li_2ZrO_3 is thermally stable and has satisfactory behavior under neutron irradiation. However, the consumption of lithium in the irradiation that can

reach 10 to 20% will lead to a two-phase ceramic made up of both zirconia, ZrO_2 , and zirconate, Li_2ZrO_3 . The appearance of zirconia is liable to embrittle this ceramic by degrading the grain cohesion. As shown by Abraham et al. [9], it is of interest to note that the introduction of copper in this substance as a solid solution makes it possible to conserve the lithium zirconate structure in the consumption of lithium by the creation of cationic vacancies favoring ion mobility. This presence of copper in the ceramic structure also enables improvement of its tritium release capacity by lowering the temperature at which it is produced. The resulting ceramic has the formula $Li_2ZrCu_yO_{3+y}$ with $0 < y \leq 0.06$.

The experimental campaign of ITER involves the introduction of tritium in torus. For reasons of safety, both the gas introduction system and gas collection system are confined inside ventilated enclosures. The cleaning system by ventilated air depends on the flow rate in each enclosure, the cross-section for blowing or extraction in pipes, the velocity rate for extraction or blowing, and the depression in regard to the atmospheric pressure.

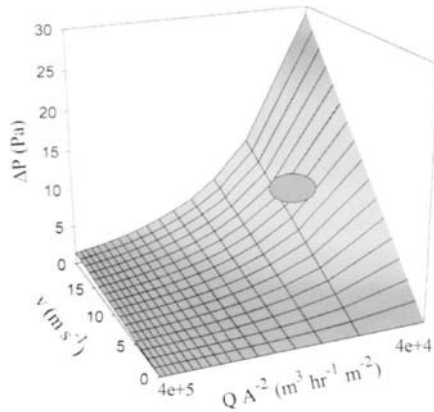


Figure 2.1. Mutual effects between depression, velocity rate and flow rate with the cross-section to eliminate tritium by ventilation.

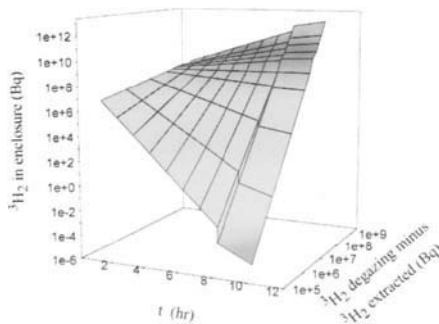


Figure 2.2. Air decontamination by extraction and blowing in force in regard to time.

Each parameter is dependent on others (Fig. 2.1). Good cleaning is obtained for a velocity rate of 10 m s^{-1} , a depression of 15 Pa and an air flow of $4500 \text{ m}^3 \text{ h}^{-1}$. Extraction in force can be also used up to $50000 \text{ m}^3 \text{ h}^{-1}$ to decontaminate a particular area. Decontamination is effective after several hours (Fig. 2.2).

TRITIUM RECYCLING

According to Hircq [10], in the thermonuclear fusion excess tritium will not be burned and will be present in addition to the pure tritium that is supplied continuously. A gas clean up exhaust system working by pulses will remove the excess tritium isotopes with radioactive ^4He into a gaseous stream. For this, the gases containing about 2% of unburned tritium will have to be processed for each pulse of about 5000 dm^3 . Moreover, this clean up exhaust will also be used to process tritiated gases produced during maintenance of the torus. The design of the tritium pulsing system is based on a daily processing by pumping the gases. High pumping speeds can be obtained with cryosorption and turbomolecular pumps. Fusion reactions also produce gaseous impurities such as CO_2 , N_2 , O_2 , H_2 , N^3H_3 and C^3H_4 . Therefore, in addition to their excellent pumping properties, cryopumps can be also used to partially separate the gases. For this, all gases are condensed in the cryopump, with the exception of helium. The cryosorption pump releases the free pure helium with a minimum of tritium carry-over. At 20 K the tritium and deuterium gases are separated from the other impurities by freezing. Tritium and deuterium are subsequently separated in a gas chromatography or cryodistillation unit in the tritium plant for recycling. Gaseous impurities still containing a little tritium are processed in another unit of the tritium plant. A disadvantage of the cryopumps is that the tritium inventory is large and requires periodic removal of the trapped gases. With turbomolecular pumps, the tritium gas is in contact with the lubricating oil and may undergo isotope exchange reactions with the H atoms in the oil. Due to the radiation, the viscosity of the oil and the operating life-time of the pump change. Moreover, there is tritiated water formed by cracking of the oil and chlorides from the breaking of the carbon chains of oil constituents. This is an example, among others, showing the necessity of a better understanding of tritium chemistry in order to improve the technology. Improving the technology for extracting tritium from the torus has required studies including those of corrosion to ascertain the compatibility of any form of new materials with tritium and tritiated water containing impurities. The difficulties inherent in selecting new materials are directly related to the β^- emission which includes intrinsic energy. These difficulties are due to:

- helium-4 and -3 generation permanently modifying the gas composition and pressure as well as thermodynamic and physico-chemical properties of the medium,
- tritium oxidation leading to tritiated water and organic effluents that exhibit radiolysis phenomena depending on the β^- density responsible for corrosion,

- isotopic exchanges with hydrogenated molecules,
- degradation of organic materials that have a complex radical chemistry making them incompatible with tritium.

In addition, tritium exhibits the general properties of hydrogen including permeation through metals for the first containment leading to consequences on several levels:

- tritium leakage and safety and tritium recovery problems,
- helium-3 and -4 in confinement materials leading to metal embrittlement and weldability problems resulting from coalescing,
- tritium in materials leading to contaminated wastes that are to be stored, degassed and eventually to be processed.

Therefore, tritium recuperated from the gas clean up exhaust system is recycled by the tritium plant processes in making allowance for the difficulties inherent to tritium. The primary function of the tritium plant is to purify and separate hydrogen isotopes for recycling and store them. Also, considering the large amounts hydrogen isotopes of circulating in the torus, high capacity tritide storage systems are needed. The second function of the tritium plant is to treat depleted tritiated gaseous, rich and depleted tritiated liquid and solid wastes to minimize tritium release and to recycle it. Tritiated water will undoubtedly be present in all parts of this plant. Considering its high activity level compared to tritium gas, its radiolysis properties and its corrosion effects on materials highly concentrated tritiated water must be processed.

Tritium treatments require the use of numerous processes with all their components, such as transfer pumps, absorbent beds and purification catalysts for satisfactory operation. Consequently, the materials of tritium processes have to be tritium compatible and keep their functional integrity under all operational conditions during aging and retain their physico-chemical and thermodynamical properties. Also, compatibility studies are required for materials, such as stainless steels for which tritium permeation, embrittlement by ^3He and weldability can represent severe problems. Aged steel with ^3He generation showed helium coalescence along the welding bead. Moreover, independently of work undertaken for gas process optimization, studies of material corrosion have been made with the same objective; one such was to test the super-alloys and stainless steels.

The basic operations for tritium treatments are represented by the diagram, Fig. 3.1. These include removal of impurities, hydrogen isotope separation, metal tritide storage and tritium recovery from tritiated water. As can be seen, numerous processes are involved.

1. Production of pure tritium and its storage

The tritium facility's mission is first to produce pure tritium gas. Due to the decay of the tritium to ^3He , to successive improvements, over the years, in the manufacturing process and to equipment maintenance and waste processing, concentrated tritium gas quantities are gradually being depleted or mixed with impurities in a broad concentration range. Separation is defined here as the process of removing unwanted gas from hydrogen isotopes.

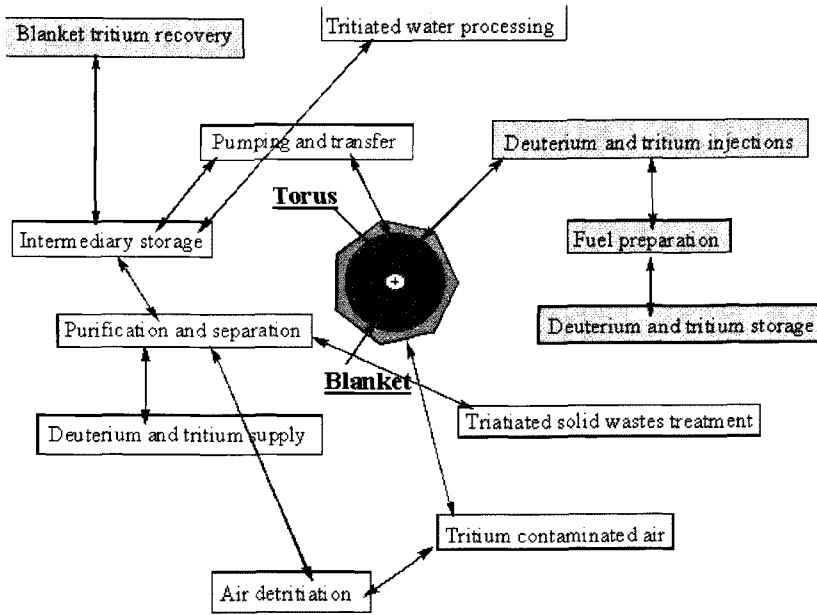


Figure 3.1. Overall tritium handling schematic.

The technologies used to accomplish this mission are divided into three main sectors as shown by Chabot et al. [11]:

- gaseous impurities separation,
- hydrogen isotope separation,
- tritium storage on tritide metals before reusing.

1.1. Impurity processing loops

Purification of tritium-deuterium gas is realized by permeation through 100 μm thickness palladium-silver membranes at high temperature as shown in Fig. 3.2 and [12]. Separation of 10^5 vpm of O_2 , N_2 , N^3H_3 , C^3H_4 , CO_2 impurities from tritium gas at low pressure showed no poisoning effect. For a high flow rate, the permeation module includes numerous hollow pins of Pd-25% Ag alloy. This module can supply about $700 \text{ dm}^3/\text{h}$ of pure deuterium-tritium gas for a continuous process. After purification, hydrogen isotopes are transferred by cryotransfer pump to the isotopic separation loop.

Tritium-deuterium gas can also be purified by absorption of impurities in hot uranium beds between 500 and 900°C . After absorption, an accumulation panel pumps all impurities by cryocondensation at a temperature ($< 100 \text{ K}$) while helium is trapped on activated

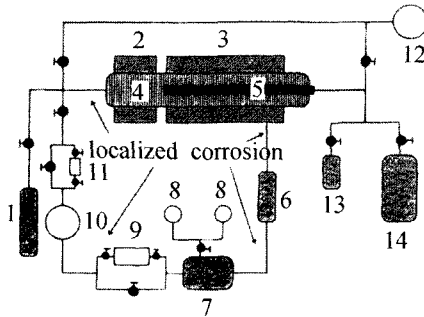


Figure 3.2. Schematic of thermal diffusion-purification loop process, 1: gas supply, 2: preheater, 3: furnace, 4: permeation cell, 5: Pd-Ag membrane, 6: cooler, 7: reservoir tank, 8: thermometer and manometer, 9: chromatograph analyzer, 10: circulator pump, 11: flow meter, 12: vacuum pump, 13: mass spectrometer, 14: reservoir tank.

charcoal at 4 K. The level of the resulting purification is altogether satisfactory (< 1 vpm starting from 1 vol% for each impurity such as O_2 , N_2 , N^3H_3 , C^3H_4 , CO_2).

After these processes, the recovered impurities still contain a little tritium; this trace level tritium is oxidized to tritiated water for storage.

1.2. Hydrogen isotope separation

Once the impurities of the plasma exhaust have been removed, it is necessary to separate deuterium and tritium in the pure gas stream. One possibility is hydrogen isotope separation by cryogenic distillation using the difference in the boiling points of these gases. The least volatile gas is 3H_2 with a boiling point of 25 K, whereas the most volatile gas is H_2 with a boiling point of 20 K. Thus, the more volatile isotope can be obtained at the head of the separation column, whereas the less volatile isotope can be obtained at the bottom of the column. The cryodistillation unit is designed for reprocessing the large tritium-deuterium amounts that are produced.

Another technique is gas chromatographic separation (Fig. 3.3). The purification process involves taking the hydrogen isotope stream and separating these, i.e. tritium, deuterium and hydrogen. This is carried out by a thermal cycle adsorption process using palladium hydride grains to perform the gas chromatography separation as reported by Botter et al. [13]. Depending on the composition of the gas phase in equilibrium (H^3H , $^2H^3H$, H^2H , H , 2H and 3H) with the hydride phase in solution, several equilibria are taken into account to obtain the appropriate isotopic separation. Also, the operating parameters (i.e. column capacity, column temperature, displacement velocity, pressure, hydrogen supply and eluent gas, etc.) must be correctly selected for separating pure tritium. This method is effective and gives separation levels above 99%. A disadvantage of this method is that a carrier gas, such as He, Ne or Ar, must be used and the hydrogen eluent makes it more difficult to separate small amounts of an isotope in the mixture.