NEWSLETTER 4

The nature and effects of the processes and events used to assess the safety of a geological disposal facility must be considered for timescales of hundreds of thousands of years. One of the main issues is the ability to assess these events and processes with sufficient confidence over these long timescales. Confidence depends on the quality and presentation of the research executed. This newsletter is one of a series of newsletters which are intended to inform stakeholders with a general interest in the CAST project.

CAST (Carbon-14 Source Term) is a research project that aims to develop understanding of the potential release of carbon-14 from radioactive waste materials under conditions relevant to waste packaging and disposal to underground geological disposal facilities. The project focusses on the release of carbon-14 as dissolved and gaseous species from irradiated metals (steels, Zircaloys), irradiated graphite and spent ion-exchange resins.

The CAST consortium brings together 33 organisations from 14 countries in the EU, Switzerland, Ukraine and Japan. The involvement of waste management organisations ensures that the project is aligned to European geological disposal programmes and that end results are of use in the safety assessments.

The progress of CAST is visualised in a digital growing tree and continuously updated on the website of CAST www.projectcast.eu

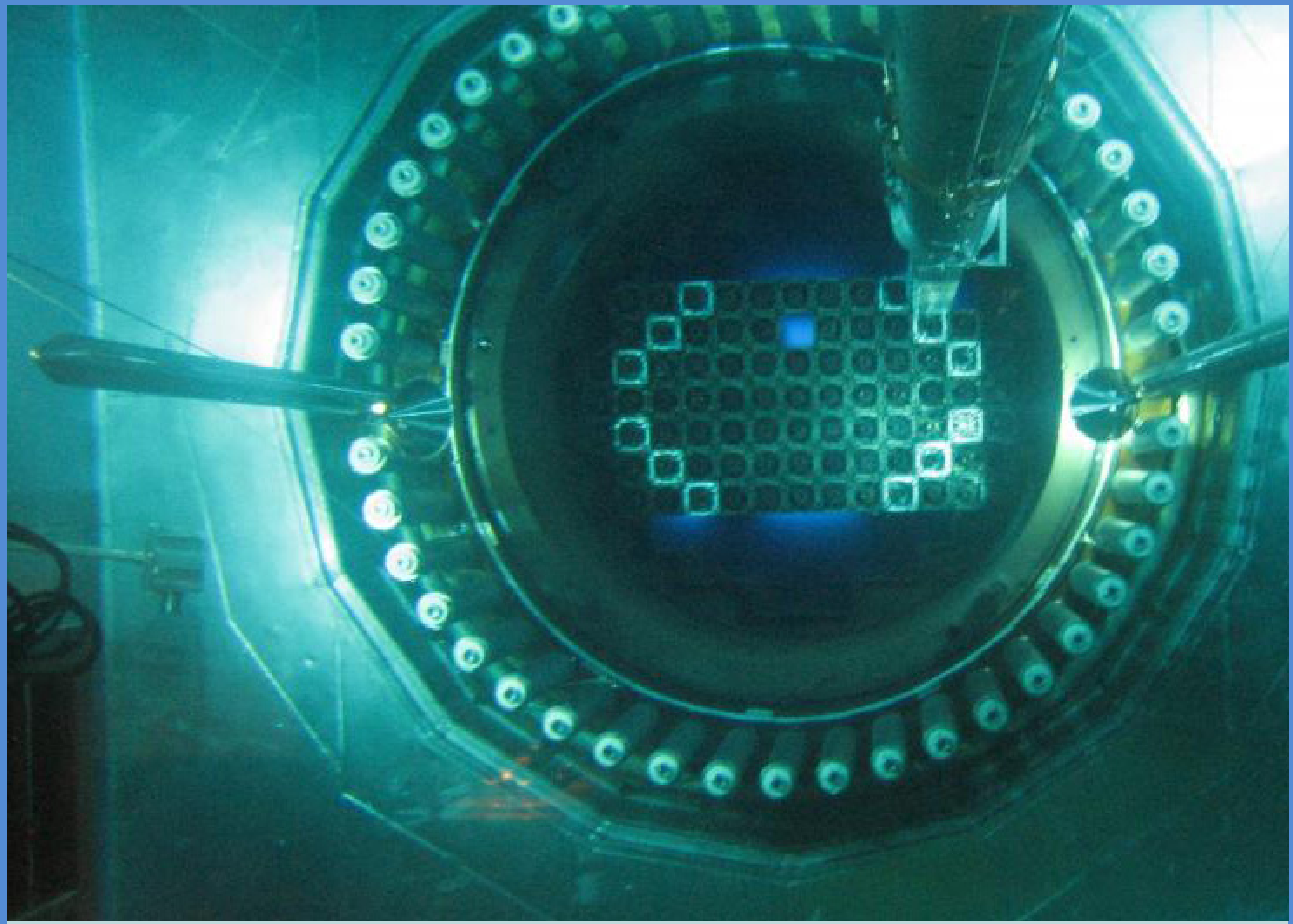
Carbon-14

Carbon-14 is a natural radioactive substance (radionuclide) that is continuously generated in our atmospshere and in nuclear reactors. In our atmosphere, carbon-14 is oxidized to carbon dioxide ($^{14}CO_2$). $^{14}CO_2$ is incorporated by plants and trees. When a tree dies, the incorporation of cosmogenically generated carbon-14 stops and its content decreases by decay.

Carbon-14 in neutron irradiated materials can be released as $^{14}CO_2$ but when these materials are processed with cementitious materials, this potential gaseous release is retarded by dissolution in concrete pore water and precipitation of calcium carbonate ($^{14}CaCO_3$). The majority of carbon-14 can then be decayed within the waste packages. Carbon-14 can also be released in organic form as a gaseous species that is assumed not to be retarded within cementitious materials. Of all radionuclides present in radioactive waste, carbon-14 is calculated to reach our living environment first, if released as organic species.

The presence of carbon-14 within materials, potential catalytic processes, the environmental conditions to which materials are exposed and radiolysis can have an impact on the carbon-14 speciation released at disposal. In this Newsletter, we describe the carbon-14 species that are expected or measured to be released from irradiated materials (steels, Zircaloys, graphite) and spent ion exchange resins.

What is the expected or measured chemical form of carbon-14 at disposal?



Irradiated steels

Carbon-14 is measured to be released as carboxylic acids

The photo above is taken during periodic maintenance of a Pressurized Water Reactor (PWR) in which fuel assemblies are relocated. New fuel assemblies have a shiny look, spent fuel assemblies have lost this look due to the formation of a very thin iron-oxide (magnetite) layer on the iron surfaces. This layer prevents iron to work as a catalyst for example to reduce, with available hydrogen, inorganic and organic carbon compounds into gaseous organic molecules. The high pH of cement pore water preserves this iron-oxide layer and therefore catalytic processes at disposal conditions are not foreseen. Catalytic reactions can have an impact on the measured carbon speciation if this iron-oxide layer is removed, for example during acid digestion to determine the carbon-14 content in steel.

In CAST, steel specimens are exposed to cementitious pore water at reducing conditions to investigate the potential release at disposal. The measurement of carbon-14 species during corrosion is challenging due to the small corrosion rates at these chemical conditions. A chemical analogue for carbon-14 release is carbon release of non-radioactive carbon present in steel that is available in a higher amount than radioactive carbon. The solubility of nitrogen and carbon in iron can be derived from thermodynamic phase diagrams. As collected in the beginning of the CAST project, the solubility supersedes the nitrogen and carbon content in steel. Carbon-14 is therefore expected to be dissolved within iron grains. The majority of carbon species measured in the Swiss programme by PSI at alkaline, reducing conditions were carboxylic acids. The gamma-radiation emitted by other radionuclides in neutron irradiated steel can cause dissociation of water molecules present in concrete pore water but also carbon species released during corrosion of steel. Carbon-14 has been measured to be released as gasesous species, carboxylic acids but also dissolved inorganic carbon.

CAST report D2.5: Rates of steel corrosion and carbon-14 release from irradiated steels - state of the art review; Latest results are presented at the CAST Final symposium, Final CAST reports are in progress.

Irradiated Zircaloy

Carbon-14 is precipitate as a species in Zircaloy

In water-cooled nuclear power plants, zirconium based (hafnium-free) cladding is preferred due to its transparancy for neutrons. In addition, Zircaloy has a better corrosion resistance than stainless steel and therefore Zircaloy is preferred to limit cladding failure. As collected in the beginning of the CAST project, nitrogen is soluble in zirconium up to 4%, which is much higher than the level at which it is controlled as an impurity so all nitrogen should be in solid solution with zirconium. The solubility of carbon is 100 ppm i.e. smaller than the usual carbon content in Zircaloy. It is expected that carbon-14 will precipitate in Zircaloy after neutron activation of nitrogen. The measurement of carbon-14 species at disposal conditions is more challenging than stainless steel due to the smaller corrosion rate and smaller carbon-14 content. Determination of non-radioactive carbon is still in progress.

CAST report D3.5: State of the art of 14C in Zircaloy and Zr alloys - 14C release from zirconium alloy hulls

Irradiated Graphite

Carbon-14 generated by neutron activation of nitrogen is loosely bound

The chemical content of nitrogen before graphite was neutron irradiated is usually not known. An impurity level as small as 15 ppm nitrogen is sufficient to be the main contributor to the carbon-14 inventory if it assumed that no carbon-14 release takes place in the operating nuclear plant. Nitrogen activated carbon-14 is present on graphite surfaces such as grain boundaries or bound to intergranular pores. The operating temperature and oxidizing conditions determine whether carbon-14 is released as ^{14}CO or $^{14}CO_2$.

CAST report D5.5: Review of understanding of inventory and release of C14 from irradiated graphite

Spent ion exchange resins

Carbon-14 is present as an anion in ion exchange resins

Ion exchange resins have functional groups that are to be exchanged with dissolved radionuclides as a cation or anion. Carbon species in aqueous fluids can be present as dissolved gas, uncharged species and as an anion but only as an anion, carbon-14 can be concentrated by ion exchange resins. Possible organic species are carboxylic groups or carboxylic acids for example acetate (CH_3COO^-) from acetic acid and oxalate ($C_2O_4^{2-}$) from oxalic acid. The chemical conditions of the moderator in PWRs are controlled i.e. reducing conditions are made to limit corrosion of metals (steel, Zircaloy) in the plant. In CAST, organic carbon has been measured to be contained by spent ion exchange resins (SIERs) that were used to clean aqueous fluids from PWRs. No control of redox in water chemistry is performed for Boiling Water Reactors (BWRs) and the oxidising conditions allow only inorganic carbon species such as CO_3^{2-} and HCO_3^- to be concentrated by ion exchange resins. In CAST, only inorganic carbon is measured to be contained by SIERs that were used to clean aqueous fluids from a BWR.

Resin beads have been investigated in CAST. The photo below shows these beads embedded in cementitious material. Carbon-14 has not been measured to be released for SIERs exposed to cementititous pore water. Only inorganic and organic carbon in anionic form are expected to be released based on the presence of carbon-14 in these resins.

CAST report D4.7: Final report on leaching and desorption experiments of ^{14}C from spent ion exchange resins
CAST report D4.8: Compilation and comparison of data on 14C from spent ion exchange resins

Final symposium

The last General Assembly meeting has been held as the CAST Final Cast symposium in Lyon in January 2018 to disseminate the outcomes of the CAST project and to act as a forum for related discussions. There was also the opportunity for relevant research not undertaken in CAST to be presented. Fifteen EU countries out of the 16 EU countries with operational nuclear power plants participated in this symposium. Also EU countries plans with plans to build nuclear power reactors or have closed nuclear power plants, Japan, Canada and Switzerland were present. Almost 80 persons attended this symposium.

The presentations held in the CAST Final Symposium and lectures in the training course are published on www.projectcast.eu.

Past training course

The second course was organised by COVRA. Dutch, Croatian, Hungarian, Lithuanian and English students were taught in monitoring carbon-14 from nuclear facilities, dismantling of nuclear plants and associated waste with Difficult To Measure Radionuclides such as carbon-14 and visited the storage facilities that contained the waste investigated in CAST. One day was devoted to modelling disposal of carbon-14 containing waste.

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