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Progress report on corrosion tests in the hot cell-experimental setup (D3.4)

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EURATOM

CAST – Project Overview

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

The CAST consortium brings together 33 partners with a range of skills and competencies in the management of radioactive wastes containing carbon-14, geological disposal research, safety case development and experimental work on gas generation. The consortium consists of national waste management organisations, research institutes, universities and commercial organisations.

The objectives of the CAST project are to gain new scientific understanding of the rate of release of carbon-14 from the corrosion of irradiated steels and Zircaloys and from the leaching of ion-exchange resins and irradiated graphites under geological disposal conditions, its speciation and how these relate to carbon-14 inventory and aqueous conditions. These results will be evaluated in the context of national safety assessments and disseminated to interested stakeholders. The new understanding should be of relevance to national safety assessment stakeholders and will also provide an opportunity for training for early career researchers.

For more information, please visit the CAST website at:
http://www.projectcast.eu

CAST		
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Document title
Progress report on corrosion tests in the hot cell-experimental setup

Executive Summary

This document gives an overview on the corrosion activities being done or planned to be done in hot cell facilities. Four project partners (INR, RWMC, JRC-ITU and SCK•CEN) use or consider using hot cells for the corrosion related experiments in WP 3.

RWMC performs tests in a glove box but a hot cell might be desired for more active samples in the future.

SCK•CEN plans to use hot cells for performing the leaching experiments and the accelerated corrosion tests in hot cells. After sampling the gaseous and liquid phase these samples would be transported outside the hot cell and analysed at a radiochemistry lab.

INR will perform polarisation measurements as well as weight loss measurements to determine the corrosion rates of Zircaloy in $Ca(OH)_2$ solution.

JRC-ITU will be performing experiments in hot cells on irradiated materials. They concern leaching studies, corrosion and total carbon determination experiments.

The details of hot cell corrosion experiments still need to be worked out and this is a part of the future tasks within the CAST project.

Contents

1 Experiments at INR

1.1 Introduction

Up to now, no corrosion tests have been performed on the irradiated Zy-4 fuel claddings from the Cernavoda NPP. INR has experience in corrosion testing of zirconium alloys (Zy-4, Zr-2.5%Nb) used as structural materials for fuel claddings and pressure tubes in CANDU reactor. The previous studies were related to oxidation and hydriding of zirconium alloys as a function of material characteristics in conditions simulating those of the primary circuit of CANDU reactor.

To determine the corrosion rates of Zy-4 in simulated repository environment, electrochemical accelerated tests (potentiodynamic polarization scans) and long term corrosion tests will be performed both on un-irradiated and irradiated Zy-4 samples.

1.2 Accelerated and long-term corrosion tests on un-irradiated and irradiated Zy-4 samples

Un-irradiated (oxidized and non-oxidized Zy-4) and irradiated Zy-4 samples of known dimensions will be immersed for long periods in anoxic alkaline environment (solution saturated in $Ca(OH)_2$ at pH12.5), and after different intervals of immersion, polarization scans will be performed. The non-irradiated and irradiated Zy-4 samples will be cut as 5 mm long pieces inside the hot cell after surface analysis using scanning electron microscopy (SEM).

The device is a potentiostat / galvanostat PAR STAT 2273 (**Figure 1**) connected to an electrochemical cell containing three electrodes.

The corrosion tests on irradiated Zy-4 hulls will be performed at room temperature, while those on non-irradiated hulls will be carried out at both room temperature and 80 °C.

Silver reference electrode and platinum counter electrodes will be used. All electrodes (reference, working, counter) and the gas bubbling tube will be introduced through a vessel lid with 5 openings and will be made gastight by adding resin or glue into the openings.

The anaerobic conditions will be maintained by bubbling argon gas (for 2 hours prior to introducing the sample and throughout the duration of the test). The polarization resistance measurement will be performed by scanning through a potential range very close to the corrosion potential E_{corr} . So, at the begining of the test the sample will be kept for 10 minutes in simple contact with the solution (without electrical connection) to attain a steady state. Following this, the specimen current will be measured. The potential imposed will be in the range of ± 25 mV versus E_{corr} . Using this narrow potential range, the method (Polarization resistance measurement) is a rapid procedure for determining corrosion rates. At a scan rate of 0.05 mV/sec, a potential range of 50 mV requires about 16 minutes. Since the applied potential is close to the corrosion potential, the surface of the specimen will not be materially affected by the experiment.

Calculation of corrosion rates from polarization resistance measurement will be carried out (ASTM G102/2004). The conversion of corrosion curent values into mass loss rates or penetration rates is based on Faraday's law.

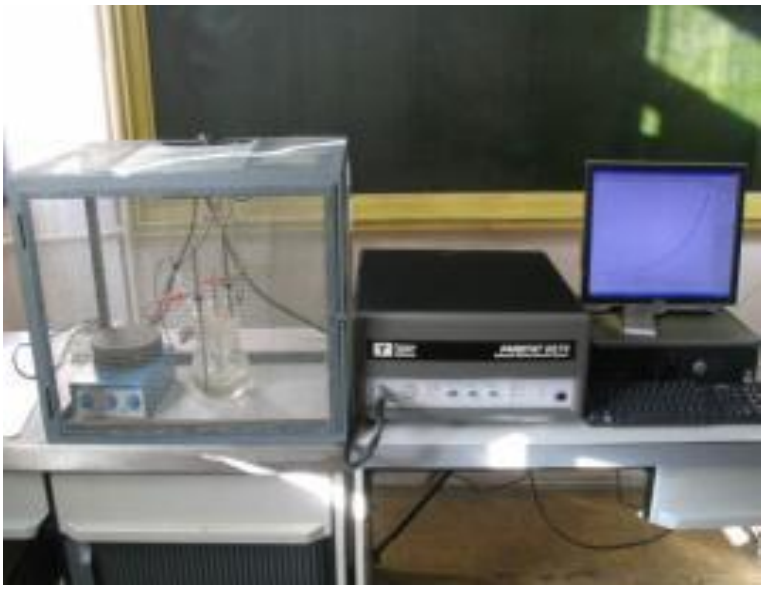

Figure 1: Electrochemical device PAR STAT 2273.

1.3 Long-term corrosion test on non- irradiated and irradiated samples

Some samples will be immersed in a solution of $Ca(OH)_2$ at pH=12.5 under anaerobic conditions.

Gravimetric analysis will be performed after different intervals (every 3 months during one year) to determine the corrosion rate (ASTM G31). The weight loss determinations will be correlated to the corrosion rates determined by electrochemical polarization measurements.

1.4 Determination of the corrosion rate from C-14 measurements

At the same moments as the Zy-4 samples are weighed to assess the weight loss, the $Ca(OH)_2$ solution will be sampled for the C-14 content to try to correlate the corrosion rate with C-14 release rate (if enough C-14 will be released to be able to measure by ultra low level LSC). Also when the polarization resistance measurement will be performed, the solution will be sampled for C-14 content. Collecting the gases released and measuring the C-14 released in the gas phase is under consideration at INR.

2 Experiments at EC-JRC-ITU

2.1. *Test material*

2.1.1. Chemical/µ-structural information availability

The test material is a standard Zry-4 from a high burn-up LWR fuel.

There is no further information for the claddings other than the manufacturer's specifications. Impurity levels (eg: C, N, O) can be measured. ITU can use a standard specification limit of Zircaloy 4 if no other value is available (ie. 80 ppm N) although this will be an overestimate. If a value measured for a similar fuel is available this could be used. For stainless steel cladding, cladding from a fast reactor fuel project NIMPHE 1 & 2 will be used. These were 25% Pu-U nitride and carbide fuels that were irradiated in the Phoenix reactor. Metallography of the cladding of the selected NIMPHE 2 carbide fuel of approximately 55GWd/tHM burn-up is available.

Regarding the activation/irradiation history, the total burn-up (probably local BU) and irradiation data will be available for the NIMPHE 2 fuel and for the high burn-up fuel with Zircaloy 4 cladding. The C-14 content could be estimated from burn-up and C, N specifications. Measurements are unlikely to be available.

2.1.2. Specimen preparation

The samples will be cut as 5mm long rings:

a) Some at fuel height i.e will need fuel removing but higher burn-up/C-14 content or,

b) Some above fuel height which is clean but will have a lower irradiation and C-14 content.

One will be mounted for metallography; others will go to total C content determination.

The remainder will go for leach testing in the autoclave (see D3.2 report).

The outer surface of the cladding will be visually inspected for any defects and the surface oxide condition. Thereafter a sample will be mounted and polished to determine the oxide thickness and its condition. SEM & EDX analyses of the surface oxide may be performed if the machine is repaired. The analysis of the surface oxide for trace elements by the SIMS technique is not available easily as there is a long waiting time.

2.2. Leaching experiments

The leaching experiment is presented in the D3.2. In this report, only the corrosion measurements that will be performed on samples from the leaching experiment are presented.

The corrosion estimates will be made using analysis of the solute at the end of the experiment (probably by ICP-MS) or by H_2 determination of the gaseous phase by mass spectroscopy. Sample weighing could be undertaken, but is likely to be too small to be reliable.

3 Experiments at RWMC

3.1 Irradiated Zircaloy cladding Leaching test/Corrosion rate measurements

So far, most of the leaching tests have been done in glove box at RWMC. However, these corrosion experiments may have to be run in hot cells as well.

Leaching experiment is described in detail in the D3.2 and the analytical procedure and results for C-14 measurements are described in the D3.3. When comparing the immersion test result of an irradiated cladding with the corrosion test result of a non-irradiated cladding, it is assumed that:

(1) C-14 is homogeneously distributed over the specimen;
(2) C-14 is released from the inner and outer surface of the specimen;
(3) The thickness of a sample is assumed to be 800 μm and 540 μm for BWR and PWR, respectively.

The equivalent corrosion rate was calculated by Equation 1:

Equation 1 $$R_C = \frac{R_A}{T} \times t,$$

Where,

- R_C (μm year^{-1}) is the equivalent corrosion rate,
- R_A is C-14 leaching fraction,
- T is test time (year),
- t is thickness of specimen(μm).

The results of the leaching tests (see D3.2 report) are shown in **Table 1**.

Total C-14 analysis and inorganic/organic C-14 analysis were carried out two times respectively only with the liquid phase for two-year immersion. C-14 was detected in the gaseous phase at 0.5 and 0.75 years. Remaining C-14 in the container could not be detected. In analysis of the liquid phase, the results of the samples immersed for two years showed a wide variation. This tendency will be checked using longer-term test data.

Table 1: Results of leaching test

Sample No	Hull weight / g	Test period / year	Quantity of nuclide leaching / Bq						C-14 analysis method
			C-14			Sb-125	Co-60	Cs-137	
			Gas	Liquid	Container				
1	5.8763	0.5	1.62x 10^{-1}	1.96 x 10^{-1}	ND	3.10 x 10^{1}	2.12 x 10^{0}	1.45 x 10^{2}	Total C-14
				1.29 x 10^{-1} (IC 39%, OC 61%)					IC / OC
2	5.8060	0.75	1.76 x 10^{-1}	1.82 x 10^{-1}	ND	2.91 x 10^{1}	1.97 x 10^{1}	6.58 x 10^{1}	Total C-14
				1.51 x 10^{-1} (IC 36%, OC 64%)					IC / OC
3	5.8415	1.0	ND	1.36 x 10^{-1}	ND	5.06 x 10^{1}	1.63 x 10^{1}	7.37 x 10^{2}	Total C-14
				1.26 x 10^{-1} (IC 72%, OC 28%)					IC / OC
4	5.7924	2.0	ND	2.35 x 10^{0}	ND	9.30 x 10^{0}	7.19 x 10^{0}	2.93 x 10^{2}	Total C-14
				3.41 x 10^{0}					
				7.12 x 10^{-1} (IC 19%, OC 81%)					IC / OC
				6.64 x 10^{-1} (IC 20%, OC 80%)					

IC: Inorganic carbon; OC: Organic carbon; ND: not detectable

The test results were compared with the results obtained with a Zry-4 cladding from PWR (Yamaguchi, et al., 1999). Up to one-year immersion, the BWR samples showed a lower C-14 release fraction than the PWR samples. The PWR cladding used for the leaching test had a thicker oxide film compared to the BWR cladding, and corrosion may have been accelerated under the influence of neutron irradiation and/or hydrogen absorption in a reactor.

The BWR samples showed a lower corrosion rate based on the C-14 release rate than the non-irradiated Zry-2 samples. The largest difference between these samples was whether or not they had been subjected to neutron irradiation. Neutron irradiation has various effects on the corrosion resistance of materials (Cheng, et al., 1994; Etoh et al., 1992), including both improvement and deterioration of corrosion resistance, and it is thought that the corrosion resistance was greatly improved by neutron irradiation in our tests. According to Etoh (Etoh et al., 1992), the corrosion resistance of Zry-2 is improved with a small dose of fast neutrons because precipitates that exist in Zry-2, such as Fe, Cr, and Ni, are dissolved into the Zr grains by neutron irradiation. However, the C-14 release rates of the samples immersed for two years showed a large variation, and the average value was almost equivalent to the results of the non-irradiated Zry corrosion test. To explain this behaviour, further investigation based on longer-term test results will be needed. The glove box is presented in **Figure 2**.

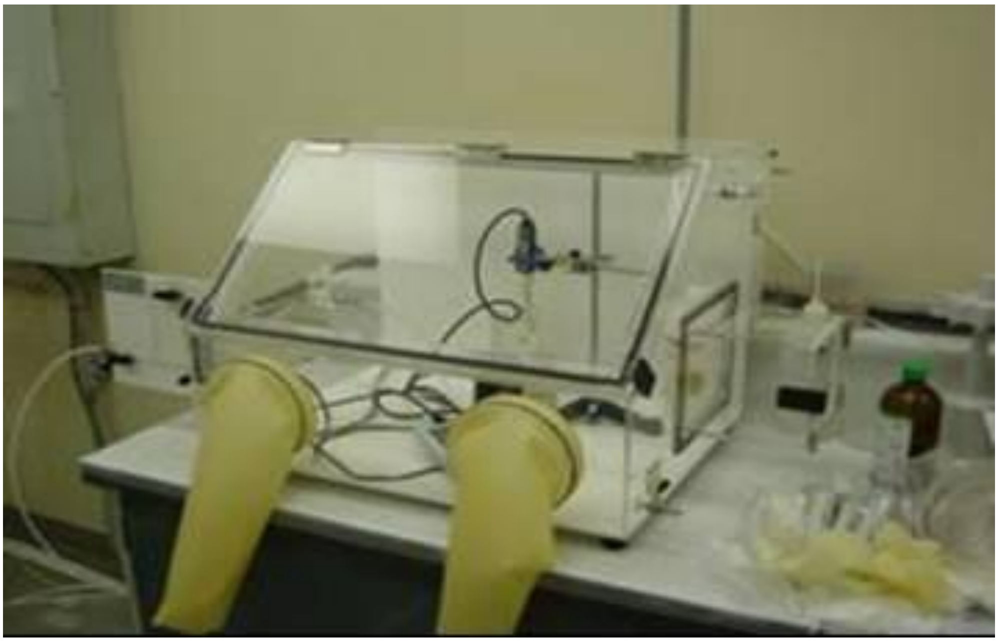

Figure 2: Special designed glove box at RWMC

3.2 Experiments at RWMC: non- irradiated Zircaloy cladding

3.2.1 Corrosion experimental setup

Corrosion behavior is a key issue in the assessment of disposal performance for activated waste such as spent fuel assemblies (i.e., hulls and end-pieces) because corrosion is expected to initiate radionuclide (e.g., C-14) leaching from such waste. Because the anticipated corrosion rate is extremely low, understanding and modeling Zircaloy (Zry) corrosion behavior under geological disposal conditions is important in predicting very long-term corrosion. Corrosion models applicable in the higher temperature ranges of nuclear reactors have been proposed based on considerable testing in the 523-633 K temperature range.

In this study, corrosion tests were carried out to confirm the applicability of such existing models to the low temperature range of geological disposal, and to examine the influence of material, environmental, and other factors on corrosion rates under geological disposal conditions.

The method to evaluate low-temperature corrosion in a geological repository (GR) is shown in Figure 3 (Tanabe et al., 2014). Corrosion tests were carried out to confirm the applicability of high-temperature corrosion models to the lower temperature range of geological disposal, and to examine the influence of various factors on corrosion rates.

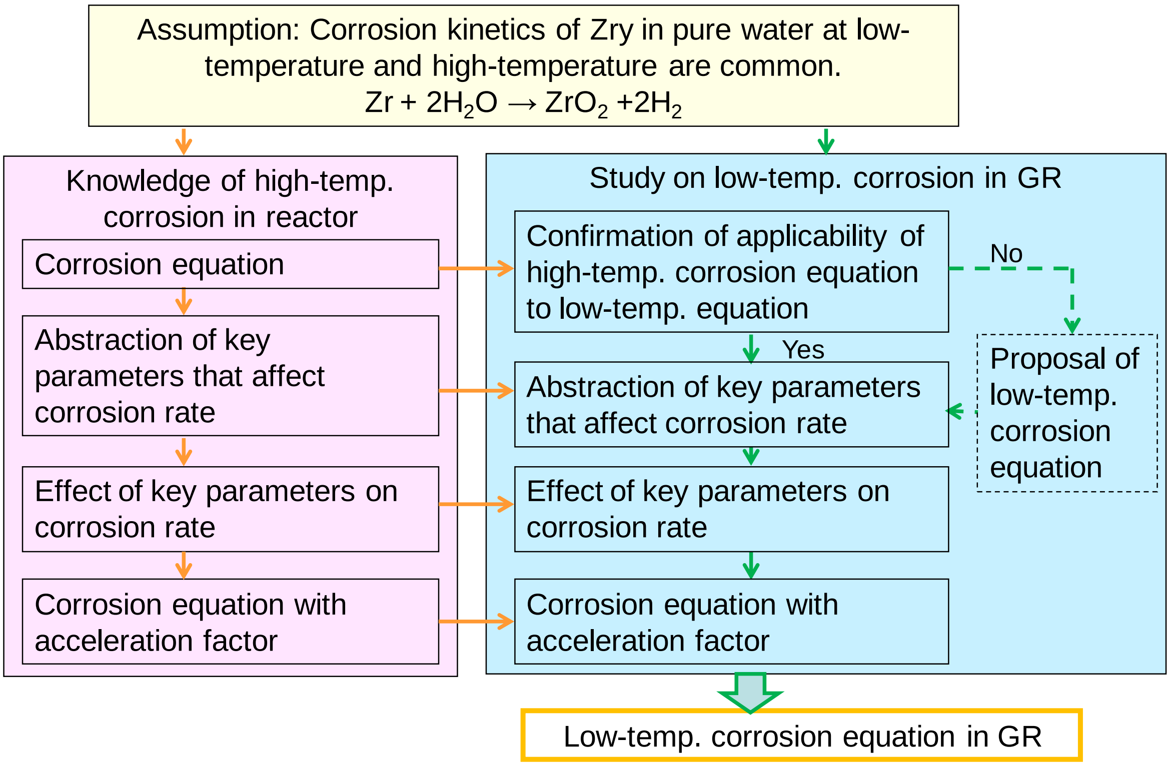

Figure 3: Method to evaluate low-temperature corrosion based on knowledge of high-temperature corrosion.

3.2.2 Sample pretreatment

Material

The Zry-4 and Zry-2 foils with a thickness of 2.0 mm (obtained from CEZUS Co., Ltd) were used for the corrosion test specimens. The chemical compositions of Zry foils supplied by CEZUS are shown in Table 2.

Table 2: Chemical compositions of Zry foils (weight%).

	Sn	Fe	Cr	Ni	O	H	N
Zry-4	1.29	0.21	0.11	0.001	0.13	0.0018	0.0027
Zry-2	1.26	0.17	0.11	0.034	0.12	0.0011	0.0035

<u>Pretreatment</u> (Figure 4)

The hydrogen concentration of Zry specimen before corrosion test must be reduced to distinguish from absorbed one during corrosion test. Pretreatment procedure of Zry specimens for corrosion tests is shown Figure 2. Zry foils with a thickness of 2.0 mm underwent four sets of cold-rolling, and each time vacuum annealing (< 10^{-2} Pa at 873 K for 1 h) to remove the processing strain. Then the thickness of Zry foils became 0.2 mm. Next, vacuum annealing (< 10^{-4} Pa at 1023 K for 10 h) was performed to the Zry foils to remove the hydrogen absorbed during cold-rolling. Furthermore cold-rolling and vacuum annealing (< 10^{-2} Pa at 873 K for 1 h) were performed to produce specimens with a thickness of 0.1 mm.

One set of 0.1 mm thick Zry specimens was cut into 3 mm×90 mm×0.1 mm after alumina powder polishing (0.02 mm). The other set of 0.05 mm thick Zry specimens was produced by abrasion, vacuum annealing (< 10^{-4} Pa at 873 K for 10 h) and alumina powder polishing (0.02 mm). The surface oxide thickness was approximately 5 nm.

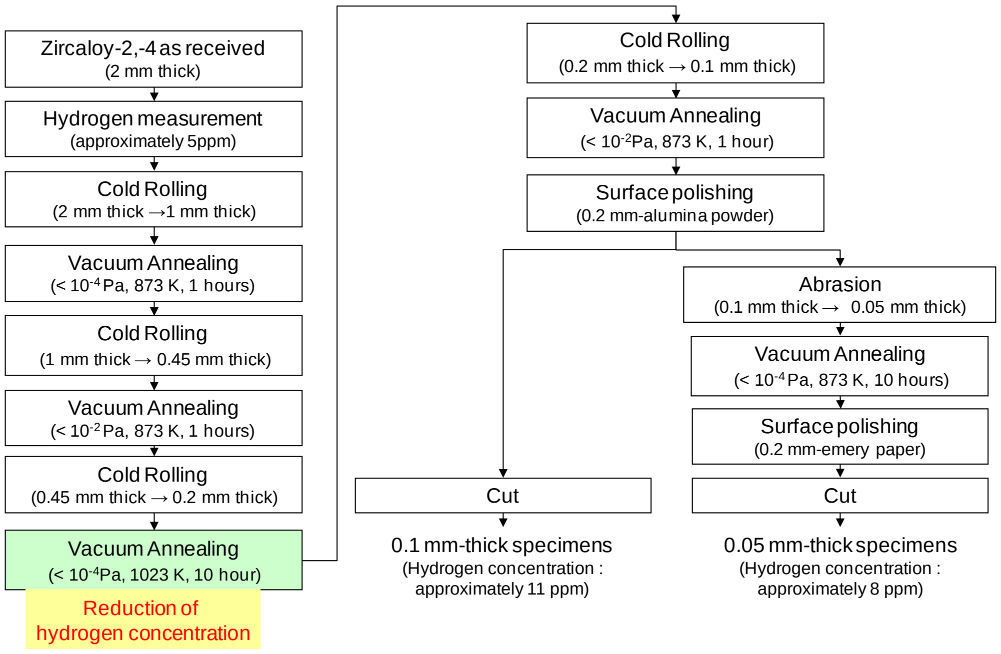

Figure 4: Pretreatment procedure of Zry for corrosion tests combined with hydrogen measurements of the specimens.

Chemical composition of Zry specimen used in corrosion tests measured after pretreatment are shown. The surface oxide thickness was approximately 5 nm after pretreatment.

Table 3: Chemical composition of Zry specimen used in corrosion tests measured after pretreatment (weight%).

		Sn	**Fe**	**Cr**	**Ni**	**O**	**H**	**N**
Zry-4	Specification	1.20 - 1.70	0.18 - 0.24	0.07 – 0.13	<0.0070	-	<0.0025	<0.008
	Measurements	1.24	0.18	0.10	<0.006	0.15	0.0010(0.1mm^{t}) 0.0009(0.05mm^{t})	0.028
Zry-2	Specification	1.20 - 1.70	0.07 - 0.20	0.05 – 0.15	0.03 – 0.08	-	<0.0025	<0.008
	Measurements	1.23	0.13	0.10	0.04	0.13	0.0007(0.1mm^{t}) 0.0006(0.05mm^{t})	0.032

3.2.3 Corrosion conditions

The corrosion tests are carried out by using ampoule batch experiment which is performed according to the methods described by Honda (Honda et al., 1999), and test procedure is presented in **Figure 5**. Zry specimens (21 pieces; 3 mm×90 mm×0.1 mm, 2 pieces; 3 mm×50 mm×0.05 mm surface area of 1.2×10^{-2} m^2) are placed in glass ampoules. A stop-cock is attached, then the ampoule is filled with the solution and the stop-cock closed. This enclosure procedure is performed in a glove box that had been purged by nitrogen gas with oxygen concentration below 0.1 ppm (**Figure 5**). The ampoules are moved outside the glove box and sealed by heating.

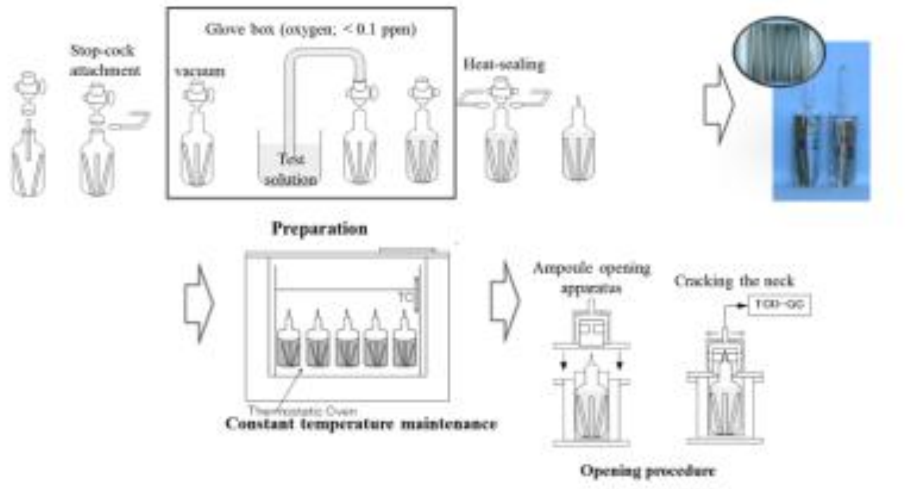

Figure 5: Corrosion test procedure of Zry.

The corrosion tests were carried out under the following conditions:

1) Applicability of high-temperature corrosion equations to low-temperature corrosion
    a) Zry corrosion rate in pure water and changes over time in lower temperature range
        - 303K, 323K, 353K, ~ two years
    b) Influence of differences in corrosion rate measurement methods (hydrogen measurement technique at low temperatures, weight gain measurement technique at high temperatures)
        - 353K and 433K, 150days
    c) Influence of annealing condition differences in actual Zry tube and test specimen
    d) Influence of composition differences in actual Zry tube and test specimen
    e) Properties of the oxide film forming at low temperatures
        - Evaluation of thickness of the oxide films by TEM-EDX, Crystal Structure by electron diffraction

2) Key parameters possibly affecting corrosion rate
    2-1) Material factor
    a) Type of Zry : Zry-4, Zry-2,
    2-2) Environmental factors
    a) Temperature: 303K, 323K, 353K, 433K
    b) pH: 7~8(pure water), 12.5, 13.5
    c) Cations: Na(NaOH), Ca($Ca(OH)_2$), K(KOH)
    d) Chemical species of groundwater (chloride, sulfate, carbonate, cement-equilibrium, seawater-derived groundwater, etc.)

The simulated groundwater (SGW) was prepared by the same method as previous study (Yamaguchi, et al., 1999), and its composition is presented in **Table 4**.

Table 4: The composition of simulated cement-equilibrated sea water derived ground-water.

Component	**Na^+**	**Ca^{2+}**	**SiO_2**	**Al^{3+}**	**Cl^-**	**SO_4^{2-}**	**HCO_3^- /CO_3^{2-}**	**pH**
Conc. /mol·dm^{-3}	6.0×10^{-1}	2.8×10^{-2}	3.0×10^{-5}	7.7×10^{-6}	6.0×10^{-1}	2.4×10^{-4}	1.4×10^{-5}	12.5

3.2.4 Hydrogen measurement technique applied on non-irradiated sample

Corrosion test have been performed on non-irradiated Zircaloy claddings. The experimental setup is described in detail in §4.2 of the D3.2 report. Hereafter, the analytical procedure applied to determine the corrosion rate is explained.

After a corrosion test, the ampoule was set on the ampoule opening apparatus with a vacuum gas collecting system connected with a gas chromatograph (Shimadzu GC1400).

Hydrogen absorbed into the specimen was measured with an inert gas melting system coupled with a gas chromatograph (LECO RH-404).

The total amount of generated hydrogen by anaerobic corrosion reaction is calculated by summing released hydrogen and absorbed hydrogen.

3.2.5 Calculation of equivalent corrosion rate

Zry weight gain was measured using a hydrogen measurement technique to measure the hydrogen generated by the anaerobic corrosion reaction between Zry and the solution as shown in Equation 2. The part of hydrogen generated by corrosion was released as gas and the rest was absorbed in Zry.

Equation 2 $$Zr + 2H_2O \rightarrow ZrO_2 + 4H$$

(4H → gas released ($2H_2$) or absorbed in Zry)

The equivalent corrosion rate, R_{total} (μm/y), which represents Zry corrosion by oxidation and hydrogenation according to the stoichiometry in Equation 2, can be obtained from the ***Equation 3***. The equivalent corrosion rates by released hydrogen gas, R_{gas} (µm/y), and by absorbed hydrogen, R_{abs} (µm/y), were calculated using ***Equation 4*** and ***Equation 5*** respectively, and the equivalent corrosion rate, R_{total}, is the sum of these two. The hydrogen pick-up ratio, $R_{\mathrm{abs/total}}$ (-) is also calculated by *Equation 6*.

$$R_{\mathrm{total}} = R_{\mathrm{gas}} + R_{\mathrm{abs}} \qquad \textit{Equation 3}$$

$$R_{\mathrm{gas}} = \frac{V \times 10^{-3} \times M \times 365}{2 \times Vm \times S \times \rho \times T} \qquad \textit{Equation 4}$$

$$R_{\mathrm{abs}} = \frac{C \times 10^{-6} \times W \times M \times 365}{4 \times S \times \rho \times T} \qquad \textit{Equation 5}$$

$$R_{\mathrm{abs/total}} = \frac{R_{\mathrm{abs}}}{R_{\mathrm{total}}} \qquad \textit{Equation 6}$$

where,

- R_{gas}:Equivalent corrosion rate by released hydrogen,
- R_{abs}:Equivalent corrosion rate by absorbed hydrogen,
- V:Volume of released hydrogen gas (cm^3),
- C:Hydrogen concentration absorbed into the specimen (mass ppm),
- M:Atomic weight of zirconium (= 91.22),
- Vm: Molar volume(=22.4 dm^3/mol),
- W: Weight of Zry specimen(g),
- S:Specimen surface area (m^2),
- ρ: Density of Zry (=6.5g/cm^3),
- T:Test time (day),
- $R_{\mathrm{abs/total}}$: Hydrogen pick-up ratio (-)

The relation between equivalent weight gain and Zry metal corrosion is 14.9 mg/dm^2 of weight gain = 0.66 µm of metal consumed.

The equivalent corrosion rate evaluated from weight gain measurement, the hydrogen measurement and oxide thickness measurement were in agreement within a 10% range of error.

3.2.6 Characteristics of oxide

The oxide films after the corrosion test were analysed with TEM (Transmission Electron Microscope), EDX (Energy Dispersive X-ray spectrometer), and XPS (X-ray Photoelectron Spectrometer). To view cross sections of the oxide film thickness, specimens were prepared with FIB (Focused Ion Beam) system. XPS was applied to analyse concentration distribution and quality in the depth profile of the oxide film. Analytical instruments and analysis conditions are shown below.

- TEM: JEOL JEM-2010F
  Accelerating Voltage:200 keV
- EDX: Noran Vantage EDX
- FIB: Hitachi FB2000A
  Beam Ion:Ga^+, Accelerating Voltage: 30 keV
- XPS: Physical Electronics Quantera SXM
- X-ray: Al *Ka* , Beam Diameter: 0.2 mm, X-ray Power:25 W, Sputtering: Ar^+ (1keV)

This research is part of "Research and development of processing and disposal technique for TRU waste (FY2013)" financed by the Agency of Natural Resources and Energy of the Ministry of Economy, Trade and Industry of Japan.

4 Experiments at SCK•CEN

The main objective of this task is to design an alternative test setup for corrosion experiments where highly irradiated metal specimens, with contact dose rate > 2 mSv/h, will be handled. On the one hand, for handling this kind of radioactive materials hot cell offers a safe option not only from gamma radiation point of view but there is also an emission probability of gaseous radioactive compounds during the tests. On the other hand, performing tests in hot cell makes manipulations more difficult and there is limited access to the sample too. For this reason works are preferably done in glove boxes but there will be certain cases where hot cell is the only option.

As far as the sample radioactivity is concerned experiments are planned on two different kinds of materials: non-irradiated and irradiated samples. Non-irradiated samples are used to find optimal experimental conditions and to see the behaviour of the materials in the proposed experimental conditions.

After having the optimal experimental conditions established, experiments with irradiated samples will be started. Before beginning any experiments with them, as much information as possible on their physical - chemical state and their irradiation history have to be obtained. A preliminary radiometric analysis is desirable to have information (1) on the radioactivity level, (2) ^{14}C interfering beta particle emitting radionuclides in the material and last but not least (3) the potential radiation risks. Static and accelerated corrosion tests will be run; therefore two different setups had to be designed.

4.1 Zircaloy samples

SCK•CEN has at its disposal both non irradiated and irradiated Zircaloy samples (Zircaloy-2/4 and M5™, which is the current reference cladding for AREVA fuel). The irradiated materials are representative for end-of-life conditions in nuclear power plants and thus offer the advantage of a realistic input of ^{14}C release into the national safety cases (WP6).

At the moment of drafting this report (04/07/2014) the approval of using M5™ material from AREVA was missing. For this reason no preliminary experiments have been performed on this material, but only on Zircaloy-4. These Zircaloy-4 specimens originate from two Belgian nuclear reactors (Tihange and Doel) and are ready for gamma ray spectrometry analysis.

The initial chemical composition of the SCK•CEN samples is available in their material quality control certificate. The chemical composition of a non-irradiated Zircaloy specimen is detailed in **Table 5**.

Table 5: Chemical composition of a non-irradiated Zry-4 specimen available at SCK•CEN*.

wt %			ppm						
Sn	Cr	Fe	C	Hf	Si	W	O	N	Zr
1.2-1.7	0.07-0.13	0.18-0.24	270	100	120	100	1000-1400	**< 50**	Bal.

**Reference: Material quality control certificate.*

A non-irradiated Zircaloy specimen is displayed in **Figure 6**.

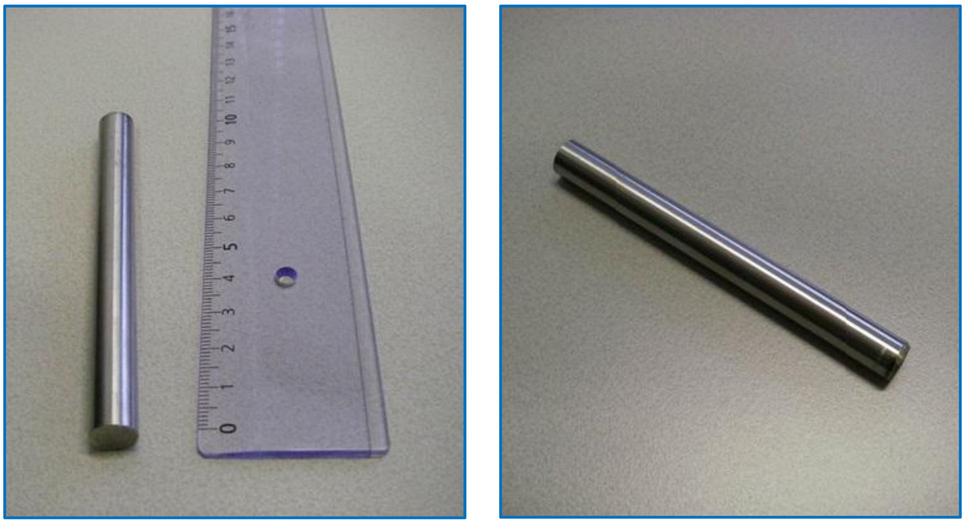

Figure 6: A non-irradiated Zry-4 specimen before cutting.

The burnup of the candidate CAST specimens has been estimated between 50-60 MWd/kgHM based on the reactor power history and the calculated power mapping across the core. More accurate burnup data will be presented after having more details on the irradiation history and campaign. The dose rate at different distances is measured for two Zircaloy specimens and the values are presented in **Table 6**.

Table 6: Dose rate from irradiated Zircaloy samples at 10 cm distance (measured on 01/07/2014 with Automess 6150 AD5 counter).

Sample code	at 10cm
D05	10 mSv/h
E14	3.5 mSv/h

4.2 Proposed electrochemical experiments

Static long term leaching and accelerated corrosion tests are planned for non-irradiated and irradiated metal samples under anaerobic alkaline conditions. The amount of released ^{14}C will be measured and the organic/inorganic ratio determined if amounts are sufficient.

There was a proposal to use a saturated Portlandite solution for the electrochemical experiments: $Ca(OH)_2$, pH ~ 12.5. This was concluded from the expected evolution of a cement system to be a representative pore solution. It has to be emphasized that in this case there are restrictions due to a possible precipitation of $CaCO_3$ from the Portlandite solution and CO_2.

As described in the CAST project proposal document, the typical scenario for most of the experiments is the corrosion of irradiated metals in a reducing highly alkaline cementitious environment for which a reference solution will be established. Two parameters will be varied to aid process understanding. pH will influence corrosion rate and possibly speciation of released ^{14}C. The availability of oxygen can significantly influence the inorganic or organic forms of ^{14}C.

Sample mass to electrolyte volume should be optimized and kept as high as possible to increase the ^{14}C concentration levels in the electrolyte but still to limit the matrix effect and the cost for discharging the potentially contaminated solutions (e.g. 1 g steel in few mL of electrolyte; mass to liquid ratio of 1:5-1:20).

It is assumed that uniform corrosion occurs during leaching and the accelerated corrosion tests. For uniform corrosion, the corrosion rate is usually expressed as the reduction in thickness of a particular metallic sample in millimetres per year (Bosch and Bogaerts, 2010). From previous experiments the corrosion rate for steels was found to be 0.1 µm/y under alkali conditions (pH > 12.5) (Kursten et al., 2013). It is already a very low corrosion rate which results in slow release of corrosion products in the solution within the scheduled timeframe. Therefore, to increase the concentration of corrosion products and carbon species, the corrosion rate has to be accelerated externally. The accelerated corrosion tests could consist in imposing a pre-determined potential to the samples that would result in accelerated active corrosion of the sample. To determine this potential, polarisation measurements should be performed to determine the E-i behaviour of the sample in the tested environment.

4.3 Proposed analytical experiments

The sequence of the proposed manipulations and sample analyses are presented in the flow chart (see **Figure 7**). Before manipulating the material the contact dose rate has to be measured first then the ^{14}C inventory will be determined. The total ^{14}C analysis is planned to be performed in glove box, this test needs a small piece of metal. Details will be presented in separate reports.

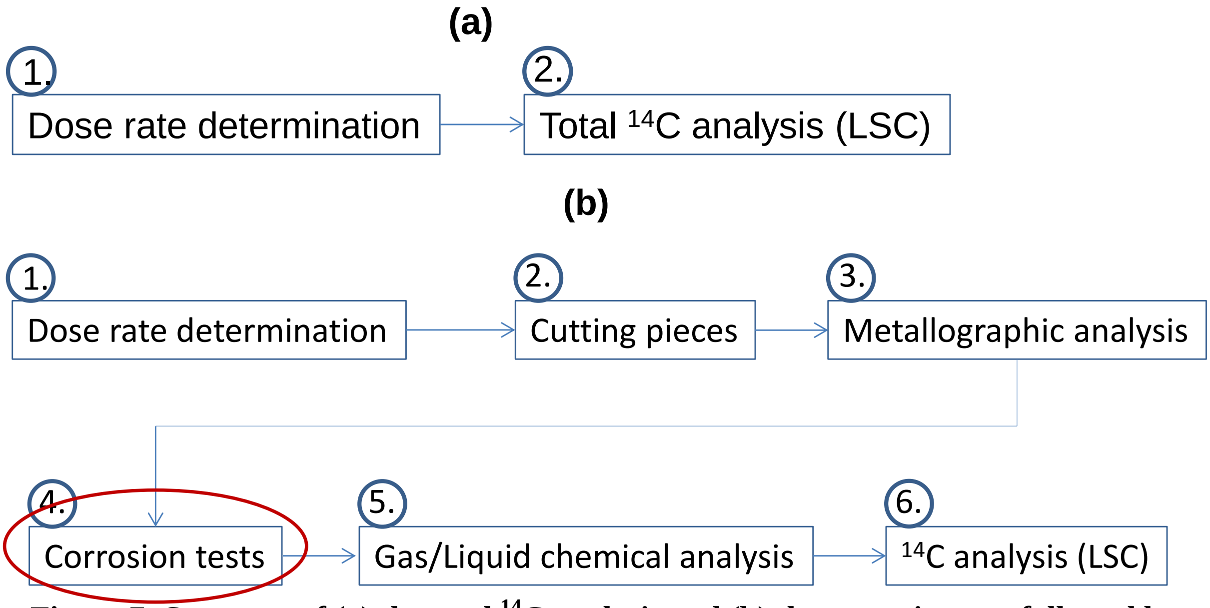

Figure 7: Sequence of (a) the total ^{14}C analysis and (b) the corrosion test followed by carbon speciation analysis.

The dose rate determination, the cutting, metallographic analyses and some of the corrosion tests will be performed in hot cells. An aliquot of aqueous and gaseous sample will be taken inside the hot cell and analysed outside the hot cell. These materials will be carefully checked by the SCK•CEN`s radiation protection officer for dose rate and external contamination of the transport container.

A metallographic examination of the material could be beneficial for determining the grain size and different phases which can play role in the carbon release process.

The corrosion rate of carbon steels and zirconium alloys are very low under alkali conditions due to a passive oxide layer formation on the surface of these metals (Kursten et al., 2013). By imposing a pre-determined potential to the samples the corrosion rate, and hence the release of carbon species, can be accelerated.

4.4 Corrosion test designs for carbon release experiments

Static and accelerated corrosion tests are planned therefore two different setups were drafted. Both test setups have to be placed either in a hot cell or glove box depending on the surface dose rate of the Zircaloy specimens (see D3.2 report). The atmosphere in the test cell has to be oxygen free, for this reason the hot cell/glove box itself should be also under anoxic atmosphere if technically possible. In the hot cell technical adjustments are necessary to maintain anoxic atmosphere. During the experiment an anoxic atmosphere will be maintained by continuous flow of argon, and the oxygen level will be monitored. The gas tightness of the test cells will be checked before starting the experiments. These measures help us to reduce the risk of having oxygen inside the test cells even when there is a leak of the cell.

Leaching experiments will be done in an airtight small volume ($\leq 100\ cm^3$) container with possibilities for sampling without opening the vials. The cell will be equipped with a gas inlet for the purging gas (argon), a gas outlet for the GC system and an outlet for the liquid phase sampling which is connected to a GC or ion chromatography (e.g. HPLC) unit.

Experiments were planned at two different temperatures. One experiment was planned at ambient temperature (t = 20-30 ^oC) and another at a higher temperature of 80 ^oC to mimic the heat evolution during the first phase of the nuclear waste storage. However, in the long term safety case the most representative temperature is estimated to be between 20-30 ^oC (Weetjens, 2009; Kursten et al., 2013), therefore temperature within this range will be applied for our experiments.

The following pore water is planned to be used for the leaching/corrosion tests: de-gassed $Ca(OH)_2$ (pH ~12.5). The pore water will be prepared in a glove box under anaerobic conditions and degassed with (nitrogen or argon) before the preparation of $Ca(OH)_2$ solution to reduce the risk of any traces of environmental origin $^{14}CO_2$ absorbed in the solution.
The layout and the description of the two experimental setups for static and accelerated leaching tests are presented in the D3.2 report. More details are given for the accelerated leaching/corrosion test in the following section.

4.4.1 Accelerated corrosion test

The accelerated corrosion tests could consist in imposing a pre-determined potential to the samples that would result in accelerated active corrosion of the sample. To determine this potential, polarisation measurements should be performed to determine the E-i behaviour of the sample in the tested environment. Depending on the active corrosion rate, we assume that a single accelerated experiment can last from a few days to several weeks.

The metal samples are first polished and then either embedded in a radiation resistant resin or just simply immersed into the electrolyte after point welding a wire to the back of the sample which serves as an electric connection. Silver reference and platinum counter electrodes will be used. The electrodes will be introduced through the cell cap but these holes will be made gas tight by adding resin or glue into them. The experiment will be stopped after dissolving sufficiently enough material. For the accelerated leaching test, one sample will be taken at the end of the experiment. After disassembling of the test cell, another sampling will be done and the liquid and solid radioactive waste will be collected separately. The experimental setup is drafted in **Figure 8** .

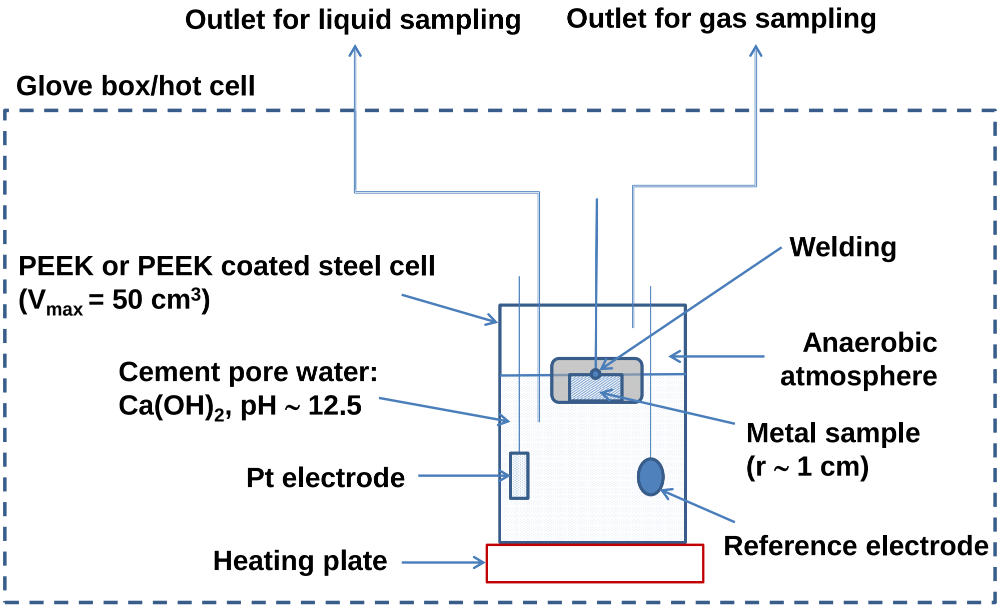

Figure 8: Proposed layout of the accelerated leaching test setup in glove box/hot cell under reducing atmosphere.

4.4.2 Estimated dissolution of metals during corrosion

A calculation was made to estimate the mass of the released metals and total ^{14}C due to uniform corrosion. It has to be noted that the carbon release may be not in linear relationship with the corrosion rate as discussed during the CAST WP2 and WP3 technical meeting in Paris (01-03/07/2014). For this calculation the following parameters were used:

For this calculation the following parameters were used:

- Φ, corrosion rate: 0.1 µm y^{-1},
- A, contact surface: 1 cm^2,
- ρ, density of Zircaloy-4: 6.56 g cm^{-3}.

The annual dissolved mass of Zr-4 (m_a) is calculated as follows:

$$\mathbf{m_a} = \Phi \times A \times \rho = 10^{-7}\ cm^3\ y^{-1} \times 6.56\ g\ cm^{-3} = 6.56 \times 10^{-7}\ g\ y^{-1} \cong \mathbf{0.7\ \mu g\ y^{-1}} \qquad (1)$$

Approximately 0.7 µg Zircaloy is dissolved in a year from 1 cm^2 surface.

4.5 Schedule of the experiments

Despite the large number of hot cells at SCK•CEN there are only few ones where chemical experiments can be done. Therefore reservation is needed well in advance before. We anticipate beginning hot cell experiments in 2015 as presented in **Table 7**. After the first tests with irradiated materials adjustment of experimental parameters may be needed. The schedule is tentative for this work phase. These tests will start in 2015 and run as long as the CAST project lasts.

Table 7: Proposed schedule for the experiments at SCK•CEN.

	2015						
	Jan	Feb	Mar	Apr	May	Jun	Jul
corrosion-leaching test	🟩	🟩	🟩	🟩	🟩	🟩	🟩
first carbon speciation analyses			🟩	🟩	🟩	🟩	🟩
adjusting the experimental parameters					🟩	🟩	🟩

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