Experimental investigation on the impact of cable fire products from flame-retardant cables on catalysts used in passive auto-catalytic recombiners

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Abstract

Cable fires in nuclear power plants have a significant probability to occur at any time in the course of a severe accident or may as well be the initiating event of a severe accident sequence. During the combustion process, enormous amounts of aerosols alongside specific combustion gases (e.g. CO, CO_2) can be released. Both nature and amount of the cable fire products depend on the combustion conditions. The effect of cable fire products distributing inside the containment and getting in contact with the catalyst surfaces of passive auto-catalytic recombiners (PARs) is of vital interest for safety analyses, in order to assess the hydrogen mitigation efficiency under these conditions.

The newly built REKO-Fire facility at Forschungszentrum Jülich combines a flow tube reactor for catalyst investigation with a steady-state tube furnace for the constant generation of cable fire products at varying combustion conditions. That way, simultaneous exposure of 5 x 5 cm² catalyst samples to cable fire products and hydrogen/air mixtures is possible, enabling to quantify the influence of gaseous and particulate components on the catalysts' start-up behavior. The installation has been used in the present study to investigate the effect of cable fire products obtained from flame-retardant power cables under three different fire conditions on the start-up of two types of catalysts for hydrogen recombination.

For well-ventilated cable fire, neither gaseous nor particulate (mainly soot) cable fire products seem to affect the onset of the catalytic H_2 conversion for both Pt and Pd-based catalysts. In under-ventilated fire conditions, the Pt-based catalyst is significantly deactivated, while the only impairment for the Pd-based catalyst is observed at very low hydrogen concentrations. For cable fire products generated from oxidative pyrolysis, the overall picture is ambiguous. On the one side it is obvious that deactivation and start-up delay occur for both catalyst types. However, no clear conclusion can be taken from the experimental data concerning the effect of exposure time. The presence of carbon monoxide in the atmosphere as well as particulate depositions from cable pyrolysis seem to be the most relevant mechanisms for catalyst deactivation and deserve further investigation.

Keywords: Severe accident, cable fire, hydrogen, carbon monoxide, passive auto-catalytic recombiner (PAR)

1. Introduction

Fires in nuclear power plants (NPPs) constitute a real and significant risk to nuclear safety (Aulamo and Contri, 2006). As identified in risk analyses, hydrogen for turbine cooling, lubricating oil and cable materials are essential fire materials. Cable fires (power cables, control cables and instrumentation cables) are of particular safety relevance, since their combustion can lead not only to the release of enormous amounts of aerosols, but also to failures, malfunctions or false indications of connected units (Allelein et al., 2009). Even smaller fire events including cables are considered to be potential precursors to more serious accident developments (Keski-Rahkonen et al., 2002). In this context, PVC cables still play a central role inside as well as outside of the containment. International research projects such as CAROLFIRE (Nowlen and Wyant, 2008) or PRISME (Audouin et al., 2013) focus on cable fire related open issues.

Cable fire products (CFPs) are physically a mixture of solid, liquid and gaseous components. Released particles are on the one hand smallest drops of condensed, organic substances and on the other hand carbon-rich agglomerates of hundreds up to many thousands of nearly spherical primary particles (Butler and Mulholland, 2004). Being very mobile aerosols, they can easily distribute inside the containment and get in contact with the catalyst surfaces of passive auto-catalytic recombiners (PARs). In the early days of PAR deployment, several investigations have been carried out by the manufacturers and independent test centers as part of the qualification program for commercial recombiners for use in NPP containments. No abnormalities were found in connection with the operating behavior of recombiners during the application of massive oil and cable fire products (EPRI, 1997). However, two cases have become known from practice in which fire products played a role. On the one hand, a study was able to show that organic residues of diesel exhaust led to functional failures during recurrent tests (Kelm et al., 2009). Secondly, after a plastic fire in the Swedish NPP Ringhals 2, severe contamination of the catalyst sheets with soot and significant corrosion damage has been observed (Ringhals AB, 2011).

2. State of the art

The combustion products generated in cable fires depend on the decomposition conditions, which are defined by the availability of oxygen (level of ventilation) and temperature. In real fires, these parameters may vary locally and over time. The conditions are classified as well-ventilated combustion, where the fire is small compared to the room and the fuel is controlled; under-ventilated combustion, where the fire is large in relation to the room and the ventilation is limited; and flameless combustion that is divided into self-sustaining fire, oxidative pyrolysis and anaerobic pyrolysis (Table 1).

Table 1: Classification of fire conditions based on ISO TS 19706, cited in (Stec and Hull, 2010)

Fire type or phase		**Temperature**	**Environment**	**Exhaust gas**	
		Fuel [°C]	**O_2 [vol.%]**	**O_2 [vol.%]**	**CO_2/CO ratio**
1 Flameless combustion					
(a)	Self-sustaining smoldering fire	450 - 800	20	0 - 20	1 - 10
(b)	oxidative pyrolysis	300 - 600	20	20	
(c)	(Anaerobic) Pyrolysis	100 - 500	0	0	
2 Well ventilated combustion (small fire in relation to the room, fuel controlled)		350 - 650	< 20	0 - 20	> 20
3 Under-ventilated combustion (large fire in relation to the room, ventilation controlled)					
(a)	Small impaired fire in enclosed spaces	300 - 600	15 - 20	5 - 10	2.5 - 5
(b)	Fading fires in large or open spaces	350 - 650	< 15	< 5	2.5 - 10

The amount of oxygen and fuel in a closed space is limited; consequently, the consumption of oxygen and fuel has an impact on the course of the fire. There are different phases during a fire in closed rooms. After ignition, flammable material is heated and the fire spreads. The room temperature is increased during the propagation phase and then the rise of the temperature is replaced by strong acceleration of fire propagation, leading to a full fire (i.e. an uncontrolled fire that affects an entire object). The full fire continues while there are still combustion conditions. When oxygen or fuel is consumed, the fire becomes extinct and the temperature decreases.

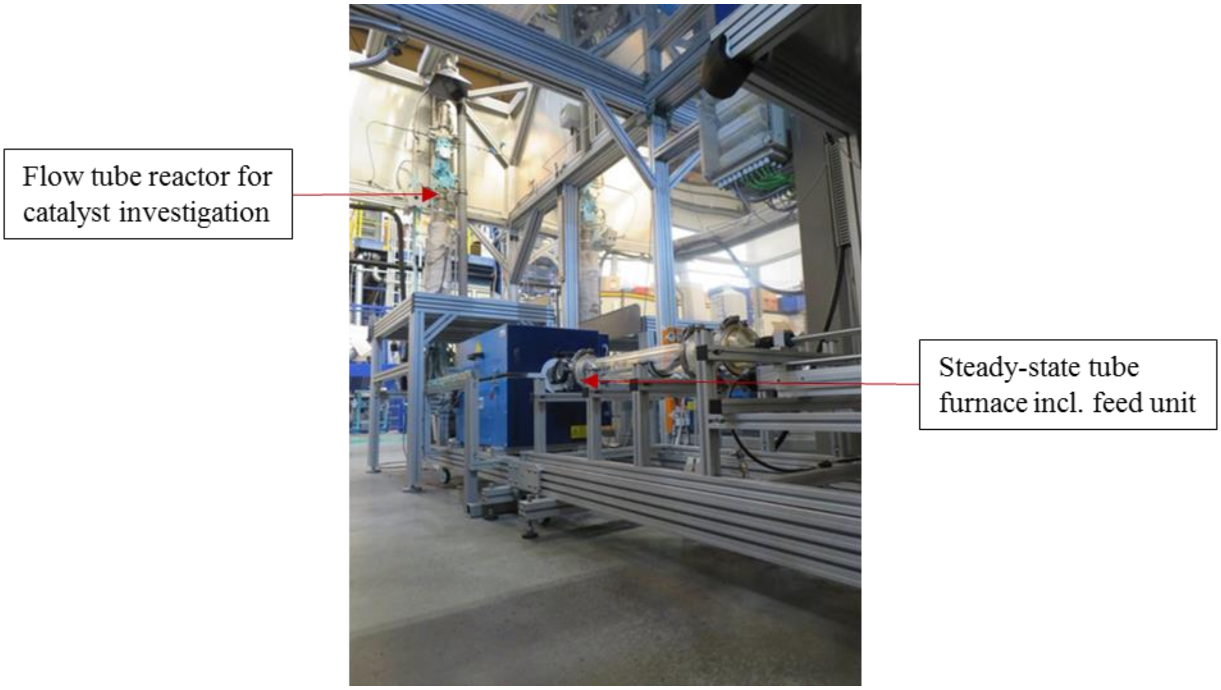
The main differences in the CFP properties are due to different formation mechanisms of the fire products in the gas phase or the polymer surface (Butler and Mulholland, 2004). Pyrolysis occurs as a consequence of increased temperatures at the polymer surface. Long-chain macromolecules are endothermically decomposed into monomers or short-chain volatile fragments. The formation of pyrolysis products precedes combustion. The diffusion of oxygen into the pyrolysis vapours leads to the formation of flammable mixtures in the gas phase that can cause combustion in case there is sufficient ignition energy. The pyrolysis gases are reduced to products of incomplete combustion in the lean oxygen areas and the corresponding products oxide with emission of light and heat in areas with higher oxygen concentrations. The higher oxygen concentration results in higher flame temperatures and larger combustion zone. The formation of soot happens in hot fuel-rich flames zones.

In the framework of an orienting study on the influence of cable fire products on catalytic surfaces performed in 2013/2014, a variation of catalyst samples was exposed to cable fire tests (PVC cables) in the DIVA facility in Cadarache. The soot deposition on the 5 x 5 cm² catalyst sheets was in the range of 9.5 – 13.1 mg. The subsequent functional tests of the catalyst samples showed a considerable delay in the start-up compared to reference measurements (Reinecke et al., 2016). In order to better quantify the impact of cable fire products and to assess the relevance for severe accident scenarios, a cable fire product generator has been established at Forschungszentrum Jülich in order to generate cable fire products under well-defined boundary conditions. The results of a test series with a commercial Flame Retardant Non-Corrosive (FRNC) cable indicated that start-up delay is possible especially due to the impact of pyrolysis products (14-27 mg per catalyst sample) while pure soot deposition (5-15 mg per catalyst sample) seemed to be of minor impact (Allelein et al., 2017). However, a drawback of these investigations was the fact that the generation of cable fire products and the functional testing of the catalyst samples were taking place in different facilities which made the transport of the catalyst specimen in between necessary. By this, gaseous and volatile compounds might have been disappearing and were no longer deposited during the start-up tests.

The present investigation is aiming to overcome this deficiency by combining a flow tube reactor for catalyst investigation with a steady-state tube furnace for the continuous generation of CFPs at well-defined combustion conditions. That way, simultaneous exposure of the catalyst to CFPs as well as hydrogen is possible, enabling to study the influence of volatile components on the catalysts' start-up behavior.

3. Facility description

The REKO-Fire facility (Figs. 1 and 2) was established at Forschungszentrum Jülich since late 2019 to investigate the impact of cable fire products on the hydrogen recombination on catalyst samples. For this purpose, catalyst samples are placed inside a vertical cylindrical reaction tube (1). The tube is connected with 3 feed lines: cable fire product generator (2), hydrogen/air mixture and steam generator (3), and dilution air (4). The reaction tube outlet is connected to the off-gas treatment system.



Flow tube reactor for catalyst investigation

Steady-state tube furnace incl. feed unit

Figure 1: REKO-Fire facility

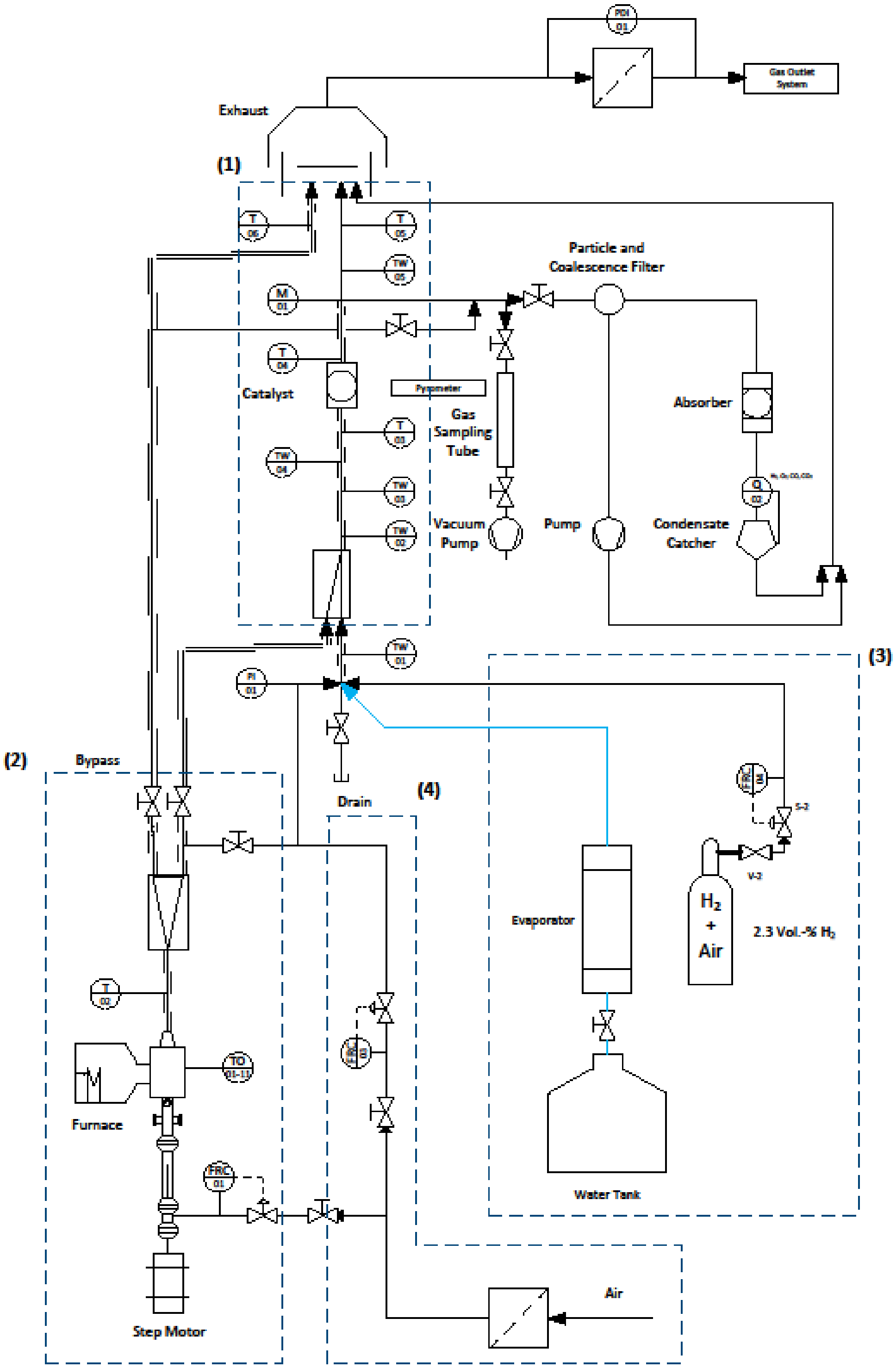


Figure 2: Flow chart of the REKO-Fire facility

3.1 Reaction tube

The reaction tube (Fig. 3, left) is approx. 180 cm long with an inner diameter of 6.7 cm. The tube contains gas temperature measurements by means of thermocouples (TCs) at the inlet and outlet of the tube. Several heating elements allow to heat the tube in order to reduce heat losses, condensation effects and the deposition of fire products on the inner tube wall. The temperature area of the channel in front of the catalyst is controlled by a heating collar. Above the catalyst, the temperature is controlled by several heating tapes.

The catalyst sample is mounted in approx. 1 m height inside the tube with a specific holder which was designed to keep the catalyst sheet in central position of the tube and to minimize contact with structures to avoid heat losses (Fig. 3, right). A TC located above the catalyst sample serves as indicator for the light-off of the catalytic reaction.

Figure 3: Vertical reaction tube (left), catalyst holder with sample (right)

3.2 Cable fire product generator

The concept of the cable fire product generation system is based on the "steady state tube furnace" described in ISO/TC 19700. It provides temporally constant and reproducible cable fire products from representative cable material avoiding "artificial" by-products, such as those produced by ignition using a gas burner. In addition to the composition of the cable material, the prevailing fire conditions are decisive for the extent and properties of the resulting products.

The system essentially consists of a feed unit which continuously moves a quartz glass slide inside a reactor tube into a tube furnace (Fig. 4). Due to the integrated combustion furnace and sample feeding by means of a stepper motor, the system is capable of burning cable samples under well-controlled and reproducible boundary conditions. The furnace by GERO Carbolite Company is operated at a constant internal temperature of between 30 and 3000 °C. The sample cable is placed on a quartz glass sample tray, which is transported by a stepper motor coupled to a linear drive at a feed rate of approx. 10 mm/s through a quartz glass channel into the furnace. The glass channel is coupled to the reaction tube by means of a specifically manufactured coupling in order to minimize mechanical loads on the quartz glass.

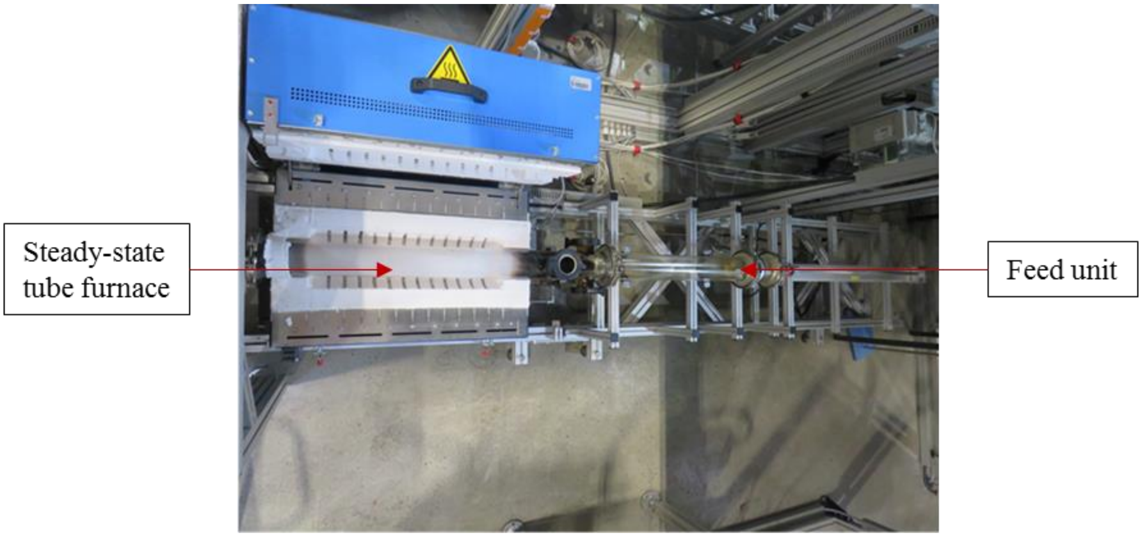


Figure 4: Steady-state tube furnace (top view)

3.3 Gas supply and off-gas treatment system

A total flow of approx. 160 L/min can be set via the mass flow controllers for gases (FRC 01: combustion air, FRC 02: nitrogen, FRC 03: dilution air, FRC 04: hydrogen/air mixture, see Fig. 2). Additionally, for experiments to be performed at elevated humidity, a direct evaporator of the ATHMOS series (Fa ADROP) supplies up to 10 kg/h of water vapor.

The exhaust gas filter system mainly consists of a radial fan connected to a cartridge filter (compact dust extractor with jet cleaning function) and additional filter elements that are suitable for separating particles. For toxic substances contained inside the exhaust gas from the cable fire, optional additional technical measures are available, e.g. carbon filters, scrubbers, etc.

3.4 Instrumentation

The recorded temperatures can be grouped into gas and wall temperatures. Gas temperatures are measured by Ni-CrNi thermocouples (type K) immediately upstream and downstream of the catalyst specimen inside the reaction tube. The thermocouples are each located in the center of the flow tube cross-section. Ni-CrNi thermocouples are also used to determine wall temperatures at several points at the outer side of the channel.

An Emerson gas analyzer system continuously extracts a gas sample via a probe in the tube, which is then analyzed in four serially coupled measuring cells. To analyze the sample gas, a partial flow of approx. 35 (max. 60) L/h is continuously fed to the analytical instruments via a sample gas pump through a heated sample gas hose. In the process, the sample gas is cleaned of possible particles by filters, and the water vapor is removed via a cooler. Measurement cells are available to determine oxygen, hydrogen, carbon monoxide and carbon dioxide concentrations. While the oxygen analyzer uses a paramagnetic sensor, the hydrogen content of the gas mixture is determined via an integrated thermal conductivity sensor. The combustion gases CO and CO_2 are measured within the gas analyzer using infrared sensors. The accuracy of the gas analyzer used is specified by the manufacturer as 1% of the full-scale value of each gas.

All measuring signals are processed by the process control system (Emerson DeltaV, Figure 5).

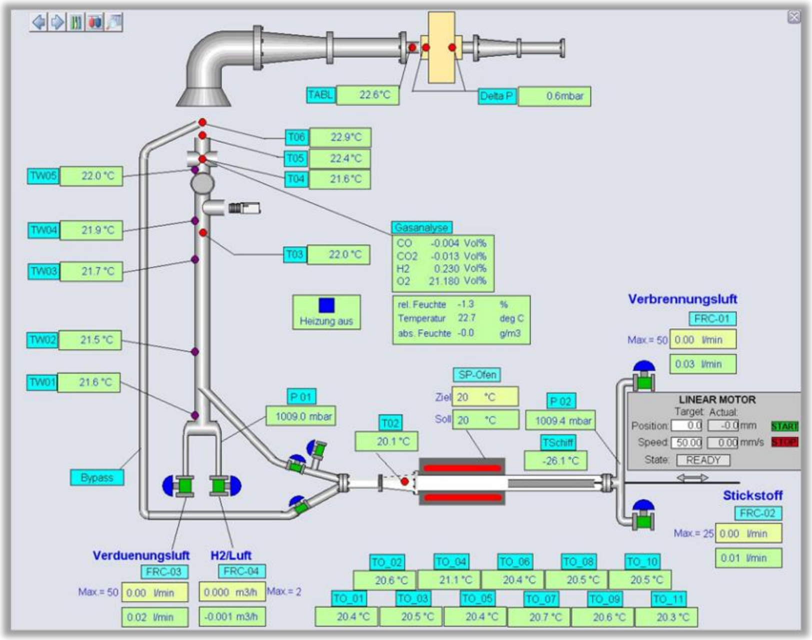

TABL 22.6°C
Delta P 0.6mbar
T06 22.9°C
T05 22.4°C
T04 21.6°C
T03 22.0 °C
TW05 22.0 °C
TW04 21.9 °C
TW03 21.7 °C
TW02 21.5 °C
TW01 21.6 °C
Gasanalyse
CO -0.004 Vol%
CO2 -0.013 Vol%
H2 0.230 Vol%
O2 21.180 Vol%
rel. Feuchte -1.3 %
Temperatur 22.7 deg C
abs. Feuchte -0.0 g/m3
Heizung aus
P 01 1009.0 mbar
T02 20.1 °C
SP-Ofen
Ziel 20 °C
Soll 20 °C
P 02 1009.4 mbar
TSchiff -26.1 °C
Verbrennungsluft
FRC-01
Max.= 50 0.00 l/min
0.03 l/min
LINEAR MOTOR
Target: Actual:
Position: 0.0 -0.0 mm
Speed: 50.00 0.00 mm/s
State: READY
Stickstoff
FRC-02
Max.= 25 0.00 l/min
0.01 l/min
Bypass
Verduenungsluft
FRC-03
Max.= 50 0.00 l/min
0.02 l/min
H2/Luft
FRC-04
0.000 m3/h Max.= 2
-0.001 m3/h
TO_01 20.4 °C
TO_02 20.6 °C
TO_03 20.5 °C
TO_04 21.1 °C
TO_05 20.4 °C
TO_06 20.4 °C
TO_07 20.7 °C
TO_08 20.5 °C
TO_09 20.6 °C
TO_10 20.5 °C
TO_11 20.3 °C

Figure 5: System control Graphical User Interface

4. Experimental program

Generally, cables consist of conductors, insulation, filling material and cable sheathing. The cables used in the experiments are of the type FRNC-BX 4 x 2.5 mm² (i.e. four wires with 2.5 mm² cross section each), a representative power cable for German Convoi-type NPPs, manufactured by company Prysmian Kabel und Systeme GmbH. To improve the continuity of the combustion process, the cable is pressed before being placed inside the carriage (Fig. 6). Pressing is necessary to override the physical fire protection properties of the cable sheath by uniformly violating its integrity and to facilitate the insertion of the flexible cable into the straight sledge.

Figure 6: Flame retardant non-corrosive (FRNC) power cable sample (left), pressed cable sample (right)

The catalyst samples used in this test series are thin sheets with a size of 5 x 5 cm² (Fig. 7) which have been manufactured by company Chemical Consulting Dornseiffer. The supporting material is a thin sheet of stainless steel with a thickness of 50 µm. The ceramic washcoat consists of 4 mg/cm² γ-Al_2O_3. The amount of active catalytic material (platinum or palladium) is 1 mg/cm².

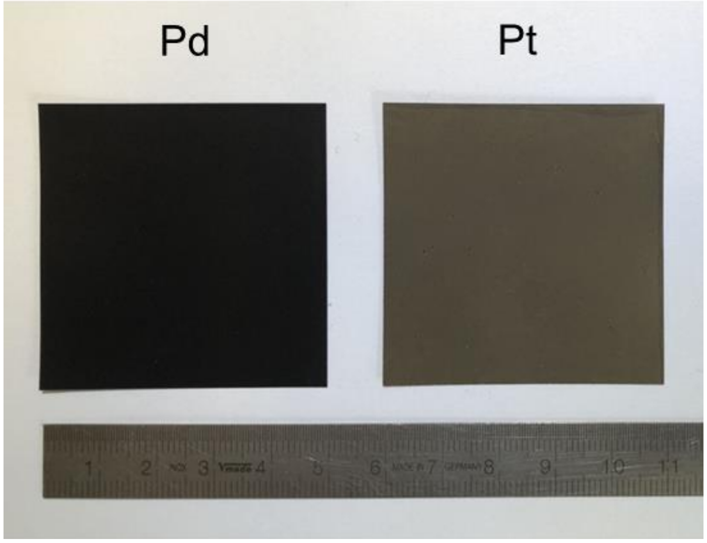
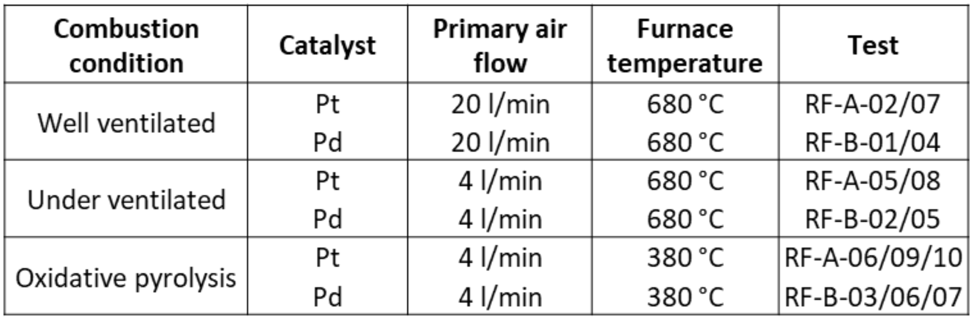


Figure 7: Catalyst samples (left: platinum, right: palladium)

This work focuses on cable fire products generated in well-ventilated combustion, under-ventilated combustion and oxidative pyrolysis. Tests under well-ventilated and under-ventilated conditions were repeated once. In case of oxidative pyrolysis, each test has been repeated twice. Table 2 shows the test matrix with the basic boundary conditions.

Table 2: Test matrix



Combustion condition	Catalyst	Primary air flow	Furnace temperature	Test
Well ventilated	Pt	20 l/min	680 °C	RF-A-02/07
	Pd	20 l/min	680 °C	RF-B-01/04
Under ventilated	Pt	4 l/min	680 °C	RF-A-05/08
	Pd	4 l/min	680 °C	RF-B-02/05
Oxidative pyrolysis	Pt	4 l/min	380 °C	RF-A-06/09/10
	Pd	4 l/min	380 °C	RF-B-03/06/07

A typical test sequence starts with the cable fire which is led into the bypass. Meanwhile, the walls of the reaction tube are heated to approx. 130°C in order to avoid condensation effects and to reduce particle deposition due to thermophoresis. After steady-state conditions are achieved, the CFPs are led through the reaction channel.

Fig. 8 gives an impression of the cable deformation after the different fire conditions.

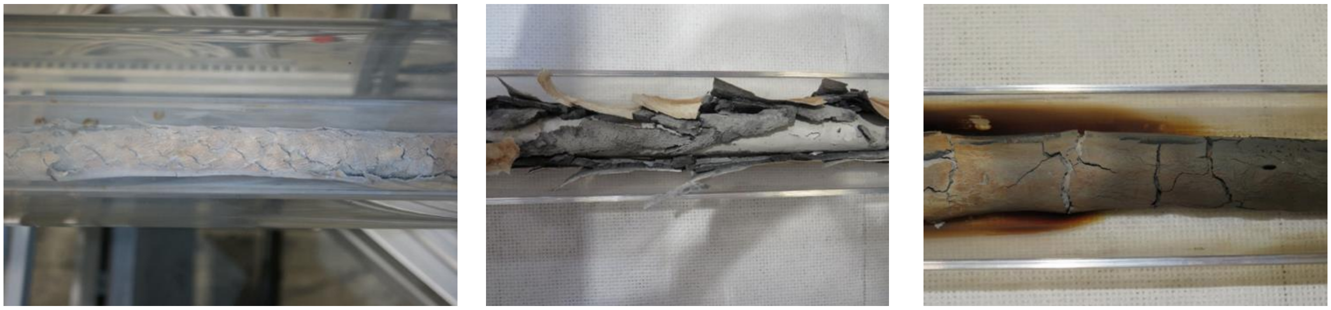


Figure 8: Cable deformation after well-ventilated (left), under-ventilated (middle) and oxidative pyrolysis (right) combustion conditions

The different gas concentration measurements (average values for repeated tests) during bypass operation are given in Fig. 9. For well-ventilated conditions, we observe a large fraction of oxygen and a high CO_2/CO ratio. In the under-ventilated case, the off-gas contains almost no oxygen and a high CO_2/CO ratio. In the pyrolysis case, almost no CO_2/CO is produced and we measure a large fraction of oxygen.

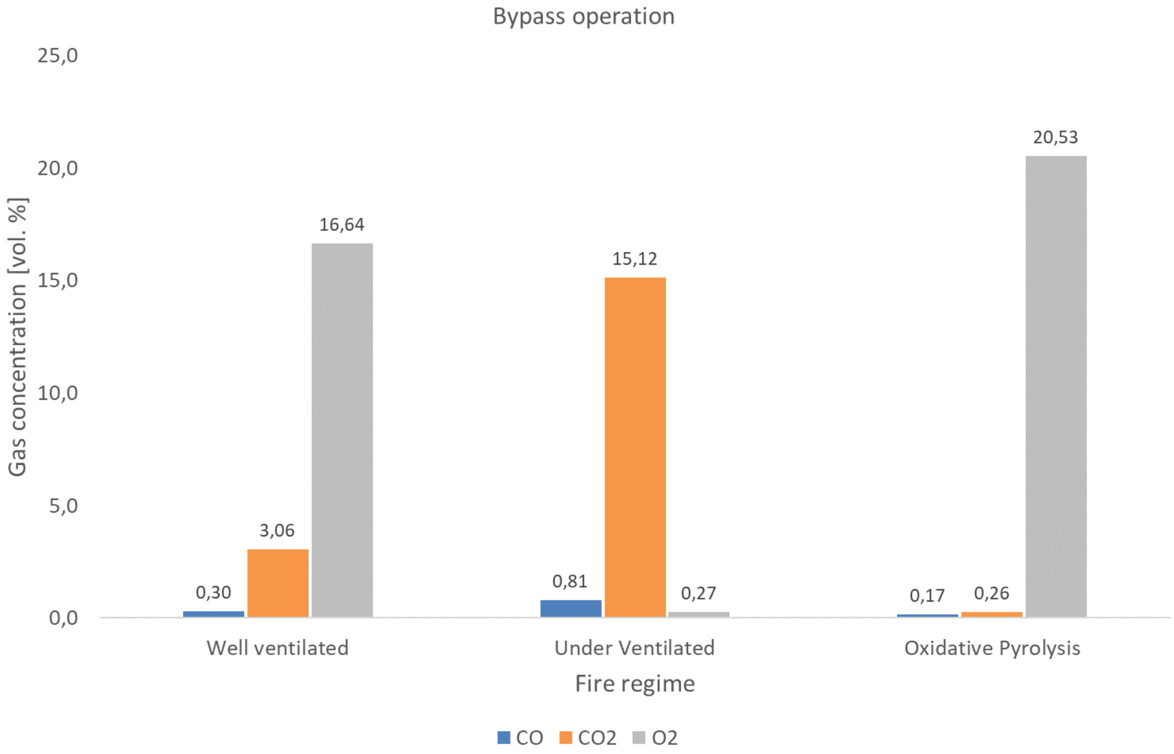


Figure 9: Outlet gas concentrations during bypass operation

5. Results

This subsection provides a comprehensive overview of the findings regarding the catalyst start-up behaviour for all three combustion regimes and for both catalyst materials used. The presentation of the results is structured according to the respective combustion regimes and compares the results of the different catalyst materials within each of them. At the end of each subsection, the main start-up characteristics of all the tests carried out in this particular regime are summarized in the form of a table.

5.1 Well-ventilated combustion

Experimental results of the tests with well-ventilated combustion with excess air for both catalysts are given in Figs. 10 and 11. The history plots show the gas temperature above the catalyst foil as an indicator of catalyst behavior (red curve, values of the primary ordinate axis), the hydrogen inlet concentration (blue line, secondary ordinate axis) and the CO_2 and CO outlet concentrations (purple and green lines, secondary ordinate axis) over time.

Figure 10 shows the experiment RF-A-07 performed with a Pt catalyst. After switching from bypass to reaction tube operation at about 14,400 s, the gas temperature inside the reaction tube increases from ~75 °C to ~90 °C due to the introduction of the hot combustion gases. Steady-state combustion conditions are established at approx. 15,000 s at ~2.0 vol.% CO_2 and very low CO concentration close to the detection limit.

At about 16,000 s, hydrogen injection starts at a level of ~1.0 vol.%. The sharp drop in CO_2 concentration during the H_2 injection phase is due to the change in the addition of the hydrogen/air mixture. The instantaneous increase in gas temperature above the catalyst of ~15 K indicates that the exothermic catalytic conversion of H_2 to H_2O starts without any delay. At about 17,600 s, H_2 is injected for a second time period, this time at a lower concentration (~0.65 vol.%). Again, an instantaneous start of the reaction can be observed from the instantaneous increase in gas temperature. At this point, however, the sharply decreasing CO_2 concentration indicates that the combustion process of the cable is almost complete and no more combustion gases are being produced. Shortly thereafter, the experiment is terminated and the gas temperature drops as a result of the now gradually decreasing furnace temperature.

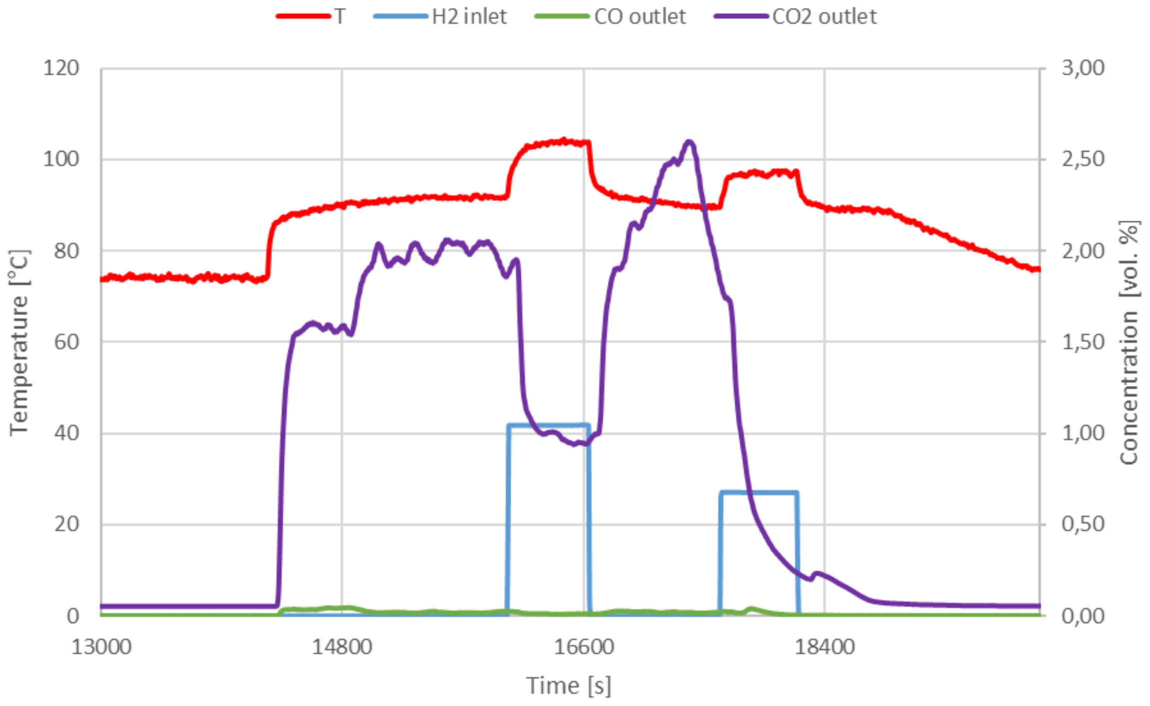


Figure 10: Pt catalyst behavior during well-ventilated combustion (RF-A-07)

Figure 11 shows experiment RF-B-01 performed with a palladium catalyst under the same combustion conditions and similar experimental procedure. Note, however, that during H_2 injection in the experiments with the Pd-based catalyst, the secondary air flow was reduced by the same amount in order not to further dilute the combustion gas (CO and CO_2 volumetric fractions in this diagram). After the catalyst foil is exposed to the combustion products, three hydrogen injection phases are performed from ~17,400 s, ~18,900 s and ~20,350 s. The hydrogen concentration is subsequently diminished with each new injection phase from 1.0 vol.% to 0.5 vol.% and 0.25 vol.%. In each of these cases, catalyst start-up occurs immediately after start of the injection as indicated by the temperature measurement (see auxiliary line for highlighting the temperature increase). Again, the end of the cable combustion process is indicated by the final drop of the CO_2 concentration starting at ~20,500 s during the third hydrogen injection.

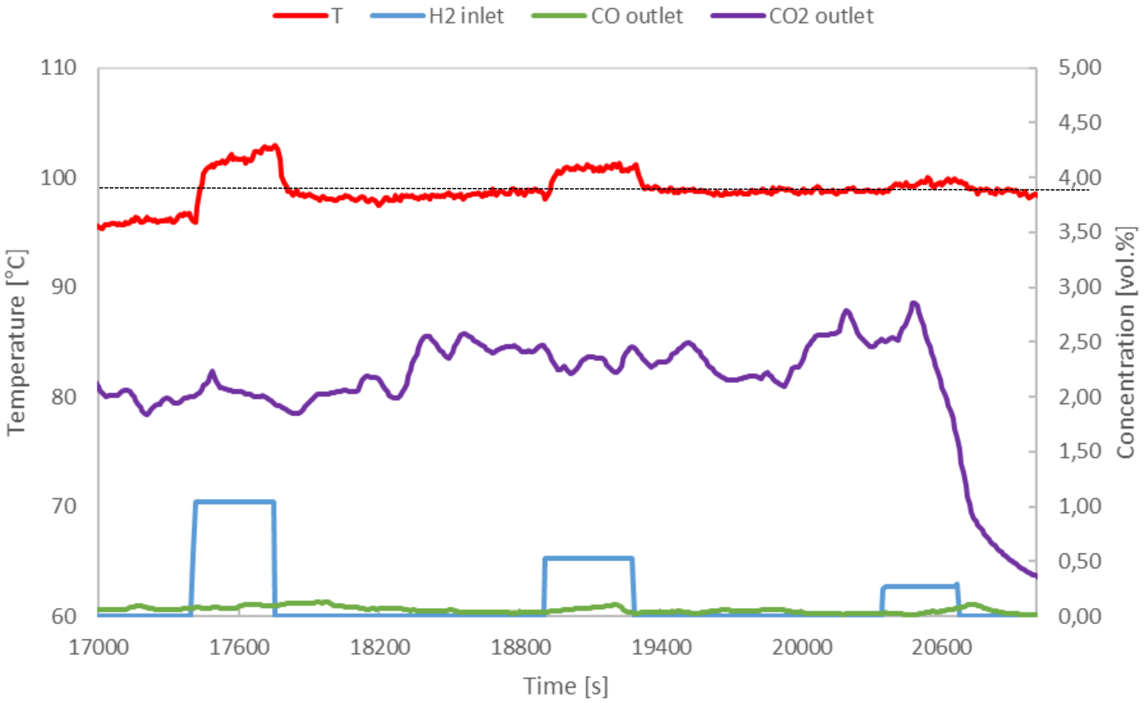


Figure 11: Pd catalyst behavior during well-ventilated combustion (RF-B-01)

Table 3 summarizes the findings of all tests performed under well-ventilated cable fire. The given concentration values for CO, CO_2 and O_2 are average values measured during the corresponding hydrogen injection phase. No impairment of the catalyst behavior has been observed in either case. Neither gaseous (CO_2 in relatively large amounts and very little CO) nor particulate (mainly soot) cable fire products obtained from well-ventilated cable combustion seem to affect the onset of the catalytic H_2 conversion of both Pt and Pd-based catalysts.

Table 3: Summary of catalyst start-up behavior in well-ventilated combustion
(green: immediate start-up, orange: delayed start-up, red: no start-up)

			CO / vol.%	CO2 / vol.%	O2 / vol.%	H2 / vol.%
well ventilated	**Pt**	**RF-A-02**	0.01	1.01	19.23	1.00
			0.02	1.21	18.94	0.67
		RF-A-07	0.01	1.15	19.32	1.00
			0.02	0.75	19.93	0.68
	Pd	**RF-B-01**	0.09	2.05	18.15	1.00
			0.07	2.31	17.83	0.50
			0.03	2.43	17.63	0.25
		RF-B-04	0.11	2.04	18.11	1.00
			0.09	2.07	18.10	0.50
			0.03	2.89	16.97	0.25

5.2 Under-ventilated combustion

Figures 12 and 13 illustrate the experimental results of the tests with under-ventilated cable fire for both Pt and Pd-based catalysts. Under-ventilated combustion conditions are obtained with a reduced primary air flow (see Tab. 2). Characteristic for these tests is the significant lower CO_2/CO ratio compared to well-ventilated combustion (see Tab. 1).

Figure 12 shows the experiment RF-A-08 performed with a Pt catalyst. Before exposing the catalyst to the cable fire products, a brief hydrogen injection is performed in order to confirm that the catalyst sample is active (~14,350 s). Switching from bypass to reaction tube operation at about 16,200 s leads to an increase of both CO_2 and CO concentrations, which both reach steady-state values at approx. 17,600 s (~1.0 vol.% CO_2 and ~0.2 vol.% CO).

When hydrogen injection starts at about 19,200 s at a level of ~1.0 vol.%, no increase of the gas temperature above the catalyst sample is observed. Again, the sharp drop in CO_2 concentration during the H_2 injection phase is due to the addition of the hydrogen/air mixture. Obviously, the present cable fire products inhibit the catalytic hydrogen recombination. In subsequent steps, the hydrogen volumetric fraction is increased to ~1.5 and ~2.0 vol.%, but the catalyst remains inactive.

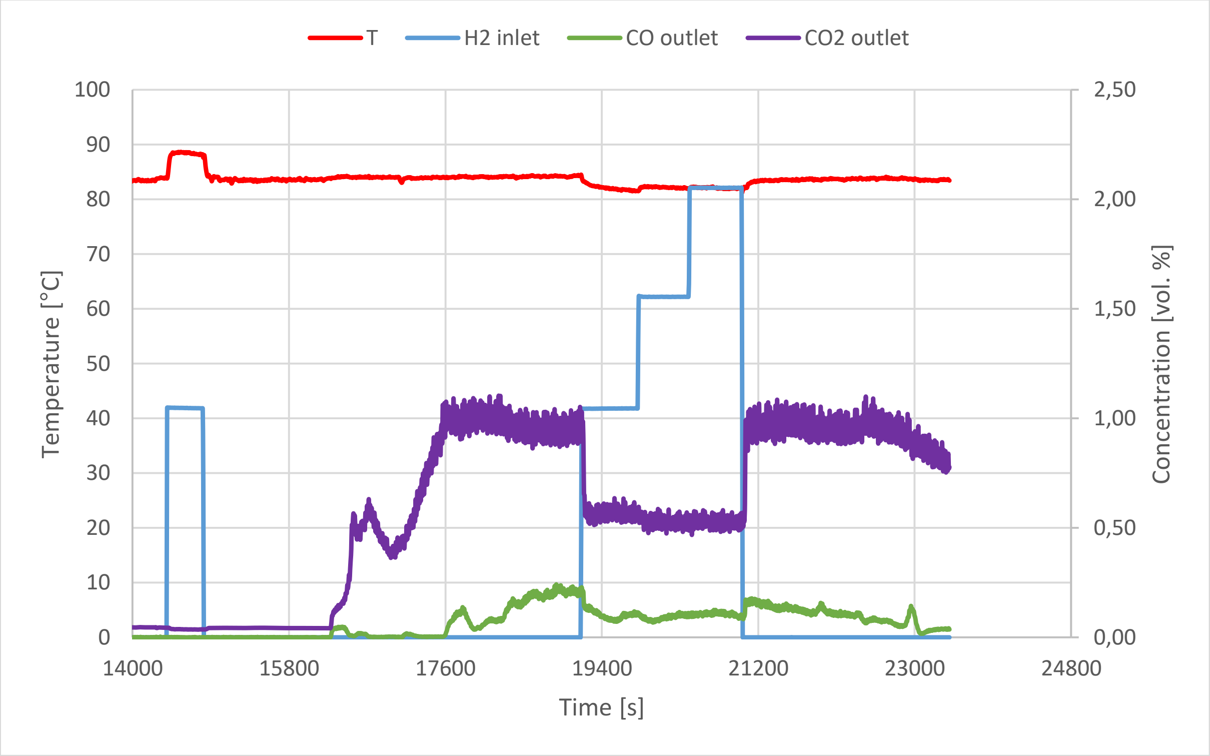


Figure 12: Pt catalyst behavior during under-ventilated combustion (RF-A-08)

Figure 13 shows experiment RF-B-05 performed with a palladium catalyst under the same combustion conditions and similar experimental procedure. As in all experiments with Pd-based catalysts, the secondary air flow is reduced during H_2 injection, in order to keep the combustion gas concentrations at constant level. After the catalyst foil is exposed to the combustion products, two hydrogen injection phases are performed from ~14,400 s and ~15,250 s at 1 vol.%. In both cases, catalyst start-up occurs immediately after start of the hydrogen injection as indicated by the temperature measurement. However, when a third hydrogen injection is performed at a reduced hydrogen concentration of 0.5 vol.% (~16,200s), the catalyst remains inactive.

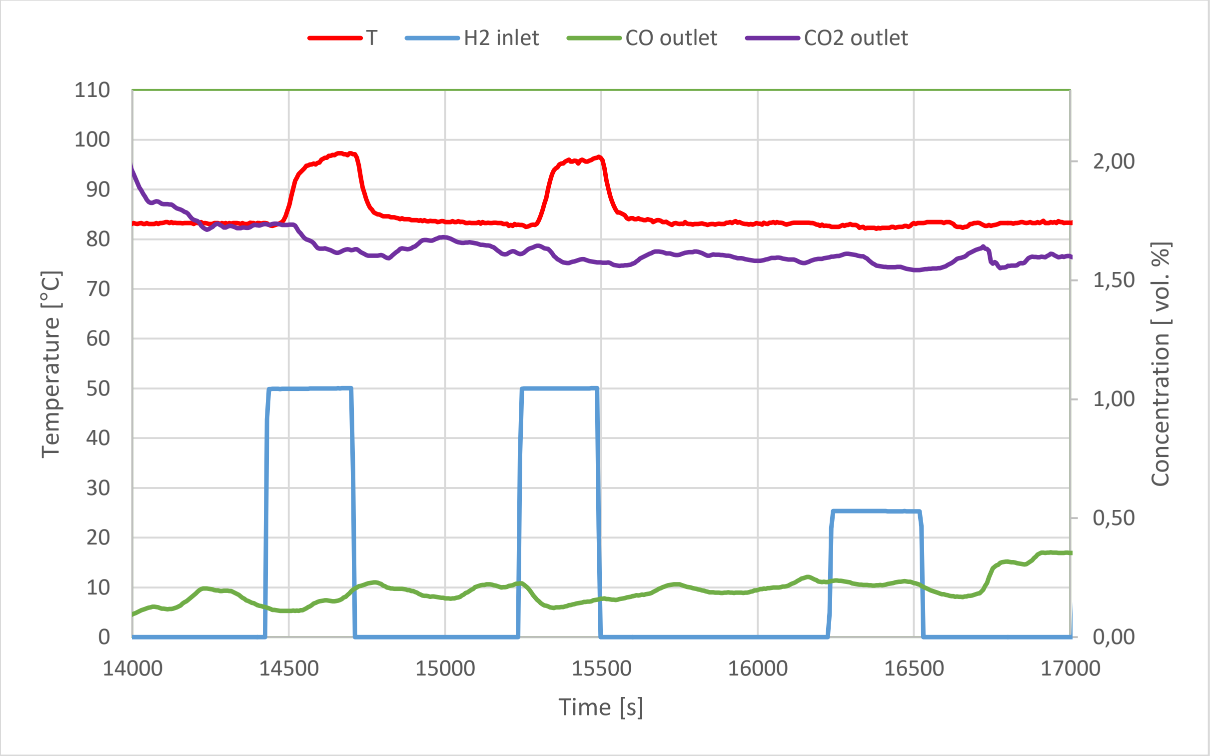


Figure 13: Pd catalyst behavior during under-ventilated combustion (RF-B-05)

The results of all tests performed with under-ventilated cable fire are summarized in Table 4. The given concentration values for CO, CO_2 and O_2 are average values measured during the corresponding hydrogen injection phase. While the Pt-based catalyst is significantly affected by the cable fire products, only minor impairment of the Pd-based catalyst is observed. As CO_2 can be ruled out as possible deactivating agent (see results under well-ventilated fire conditions), CO could be responsible for the deactivation of the Pt-based catalyst. Only in test RF-A-05, the catalyst managed to start with significant delay after increasing the hydrogen concentration to 2 vol.%. Although the conditions for Pd-based catalyst were similar, the only impairment could be observed when the hydrogen concentration had a very low value (0.5 vol.%). The insensitivity of the Pd catalyst to the conditions of an under-ventilated cable fire compared to the Pt-based catalyst is an interesting observation.

Table 4: Summary of catalyst start-up behavior in under-ventilated combustion
(green: immediate start-up, orange: delayed start-up, red: no start-up)

			CO / vol.%	CO2 / vol.%	O2 / vol.%	H2 / vol.%
under ventilated	**Pt**	**RF-A-05**	0.11	0.60	19.94	🟥 1.00
			0.08	0.45	20.19	🟥 1.28
			0.06	0.39	20.29	🟥 1.44
			0.05	0.45	20.22	🟥 1.69
			0.03	0.50	20.19	🟧 2.00
		RF-A-08	0.11	0.58	20.08	🟥 1.00
			0.09	0.53	20.16	🟥 1.56
			0.11	0.53	20.14	🟥 2.05
	Pd	**RF-B-02**	0.13	0.64	20.37	🟩 1.00
			0.09	0.63	20.40	🟩 1.00
		RF-B-05	0.14	1.68	18.45	🟩 1.00
			0.15	1.60	18.51	🟩 1.00
			0.23	1.58	18.46	🟥 0.50

5.3 Oxidative pyrolysis

Experimental results of tests with oxidative pyrolysis conditions are given in Figs. 14 and 15 for both Pt and Pd-based catalysts. The conditions inside the furnace yield low concentrations of CO and CO_2, but significant amounts of organic substances.

Figure 14 shows the experiment RF-A-06 performed with a Pt catalyst. Before exposing the catalyst to the cable fire products, a brief hydrogen injection is performed in order to confirm that the catalyst sample is active (~8,000 s). Switching from bypass to reaction tube operation at about 12,400 s leads to only minor increase of both CO_2 and CO concentrations.

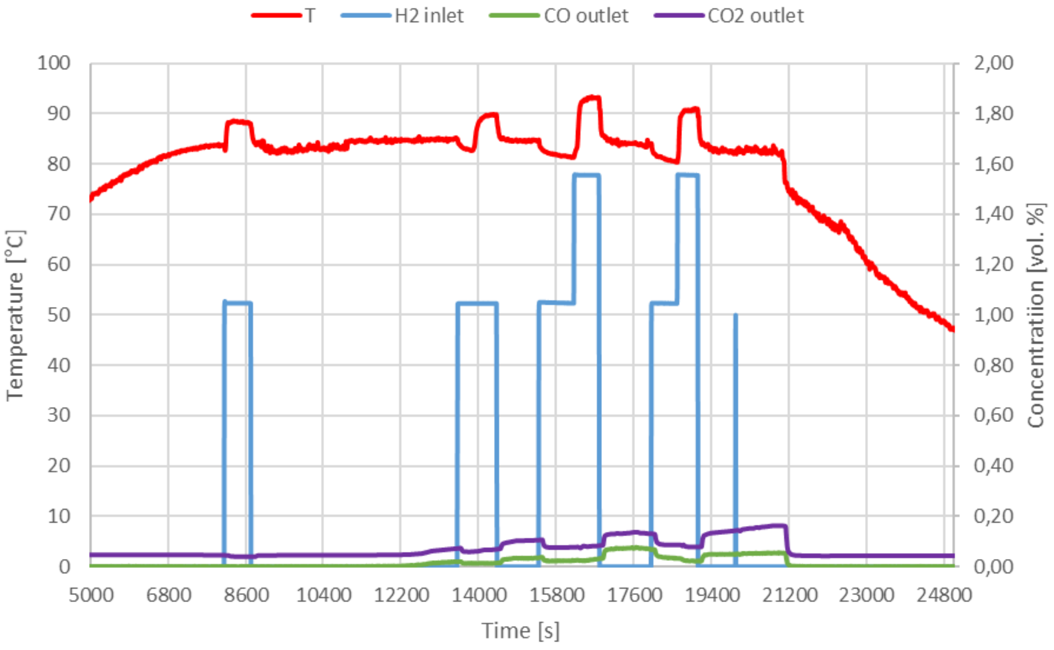


Figure 14: Pt catalyst behavior during oxidative pyrolysis (RF-A-06)

After the first hydrogen injection (1 vol.%, ~13,500 s), the catalyst starts with a delay of ~6 min. After the second injection (1 vol.%, ~15,400 s), no start-up is observed for 15 min. When the concentration is increased to 2 vol.%, the catalyst is immediately activated (~16,200 s). This procedure is repeated a second time with similar outcome (~18,000 – 19,100 s).

Similar observations are made in experiment RF-B-06 under oxidative pyrolysis conditions with a Pd-based catalyst (Figure 15). Several times, start-up delay is observed, e.g. in the first injection phase (~12,600 – 13,800 s) when the inlet hydrogen concentration needs to be increased to 2 vol.% to activate the catalyst. In a second injection series (~17,400 – 19,000 s), no start-up is observed at all. However, in-between injections of 1 vol.% hydrogen exhibit immediate or at least slightly delayed start-up of the catalyst.

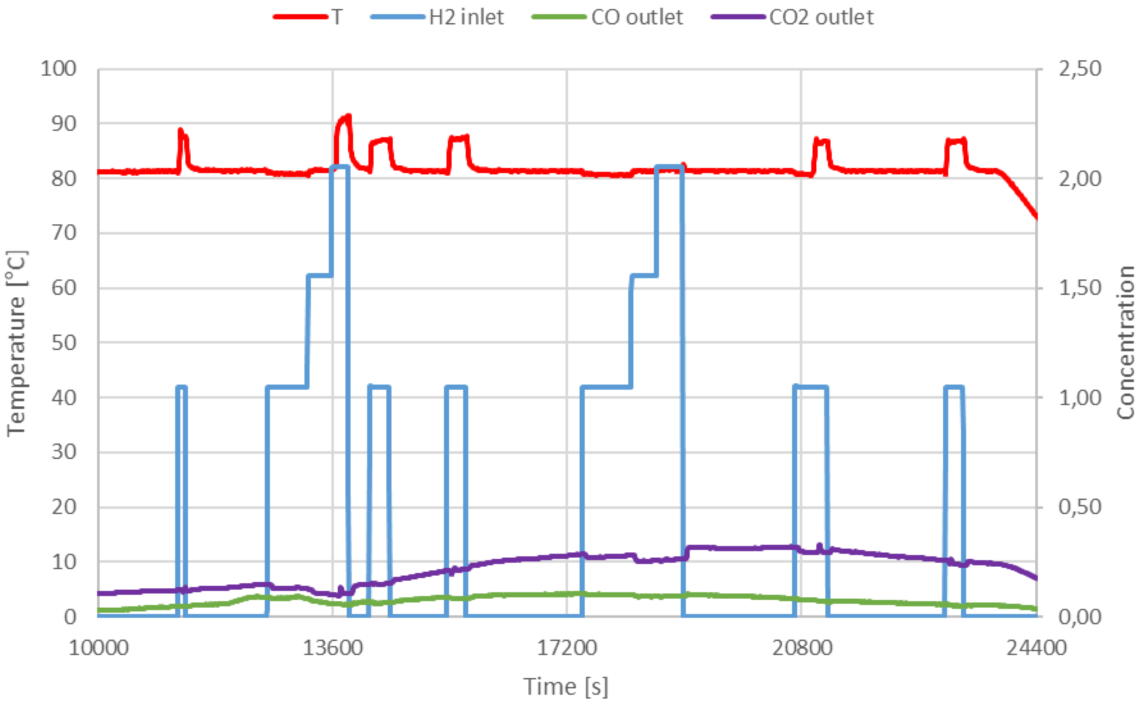
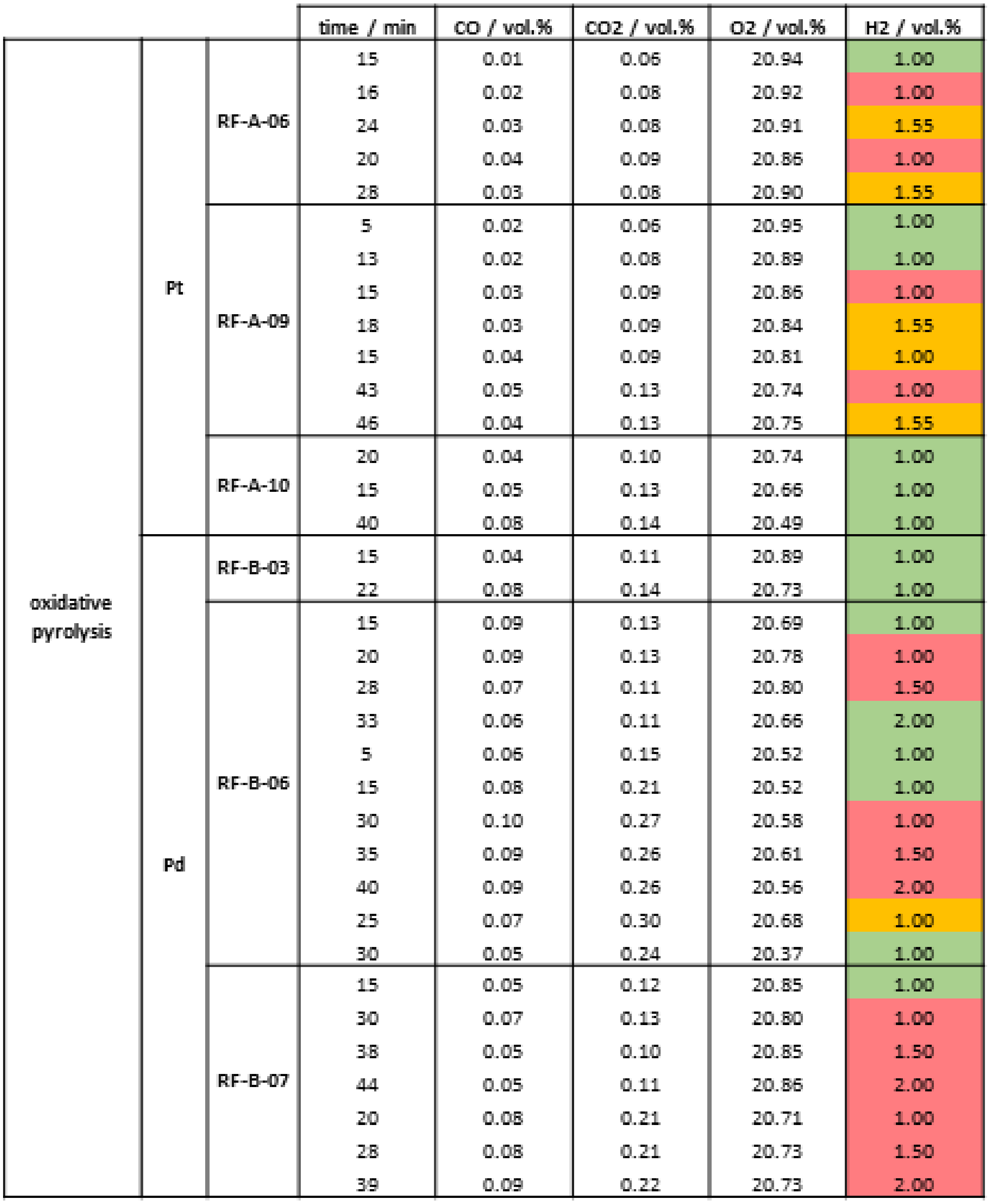


Figure 15: Pd catalyst behavior during oxidative pyrolysis (RF-B-06)

Table 5 gives an overview of the results obtained in all tests performed under oxidative pyrolysis. As we expect particulate deposition on the surface to be the origin for possible catalyst deactivation, the time of exposure before the corresponding hydrogen injection has started is given. However, the overall picture remains unclear. On the one side it is obvious that deactivation and start-up delay occur for both types of catalysts. There is also indication that the deactivation is more severe if the catalyst is exposed to the CFPs during a longer time. However, no distinct conclusion can be taken from the experimental data.

Table 5: Summary of catalyst start-up behavior under oxidative pyrolysis
(green: immediate start-up, orange: delayed start-up, red: no start-up)



			time / min	CO / vol.%	CO2 / vol.%	O2 / vol.%	H2 / vol.%
oxidative pyrolysis	Pt	RF-A-06	15	0.01	0.06	20.94	🟩 1.00
			16	0.02	0.08	20.92	🟥 1.00
			24	0.03	0.08	20.91	🟧 1.55
			20	0.04	0.09	20.86	🟥 1.00
			28	0.03	0.08	20.90	🟧 1.55
		RF-A-09	5	0.02	0.06	20.95	🟩 1.00
			13	0.02	0.08	20.89	🟩 1.00
			15	0.03	0.09	20.86	🟥 1.00
			18	0.03	0.09	20.84	🟧 1.55
			15	0.04	0.09	20.81	🟧 1.00
			43	0.05	0.13	20.74	🟥 1.00
			46	0.04	0.13	20.75	🟧 1.55
		RF-A-10	20	0.04	0.10	20.74	🟩 1.00
			15	0.05	0.13	20.66	🟩 1.00
			40	0.08	0.14	20.49	🟩 1.00
	Pd	RF-B-03	15	0.04	0.11	20.89	🟩 1.00
			22	0.08	0.14	20.73	🟩 1.00
		RF-B-06	15	0.09	0.13	20.69	🟩 1.00
			20	0.09	0.13	20.78	🟥 1.00
			28	0.07	0.11	20.80	🟥 1.50
			33	0.06	0.11	20.66	🟩 2.00
			5	0.06	0.15	20.52	🟩 1.00
			15	0.08	0.21	20.52	🟩 1.00
			30	0.10	0.27	20.58	🟥 1.00
			35	0.09	0.26	20.61	🟥 1.50
			40	0.09	0.26	20.56	🟥 2.00
			25	0.07	0.30	20.68	🟧 1.00
			30	0.05	0.24	20.37	🟩 1.00
		RF-B-07	15	0.05	0.12	20.85	🟩 1.00
			30	0.07	0.13	20.80	🟥 1.00
			38	0.05	0.10	20.85	🟥 1.50
			44	0.05	0.11	20.86	🟥 2.00
			20	0.08	0.21	20.71	🟥 1.00
			28	0.08	0.21	20.73	🟥 1.50
			39	0.09	0.22	20.73	🟥 2.00

6. Conclusions and outlook

Cable fires in a nuclear power plant can lead to the release of enormous amounts of aerosols alongside specific combustion gases (e.g. CO, CO_2). Both nature and amount of the CFPs depend on the combustion conditions. In the present investigation, the effect of CFPs obtained from FRNC cables on the start-up of two types of catalysts for hydrogen recombination has been studied.

Three different fire conditions have been considered. For well-vented cable fire, neither gaseous (CO_2 in relatively large amounts and very little CO) nor particulate (mainly soot) CFPs seem to affect the onset of the catalytic H_2 conversion for both Pt and Pd-based catalysts. In under-ventilated fire conditions, different effects on both types of catalysts can be observed. The Pt-based catalyst is significantly deactivated, while the only impairment for the Pd-based catalyst is observed at a hydrogen concentration as low as 0.5 vol.%. Higher CO levels when compared with well-ventilated cable fires are suspected to be the reason for the observed deactivations. For CFPs generated from oxidative pyrolysis, the overall picture is ambiguous. On the one side it is obvious that deactivation and start-up delay occur for both catalyst types. However, no clear conclusion can be taken from the experimental data that the deactivation is more severe if the catalyst is exposed to the CFPs during a longer time.

As a conclusion, the presence of carbon monoxide in the atmosphere as well as particulate depositions from cable pyrolysis, mostly long-chain n-alkanes, seem to be two potential mechanisms for catalyst deactivation. As cable fires could act as initiating event, the catalysts might be affected by corresponding CFPs before the actual severe accident occurs. As a consequence, hydrogen mitigation by PARs might be significantly delayed.

Future experiments are foreseen in order to further understand the effect of CFPs on catalyst deactivation. Based on the present study, focus will be on under-ventilated fires and oxidative pyrolysis. New tests will involve different plant-typical cable types, e.g. PVC cables.

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