

Passive Autocatalytic Recombiners Periodic Testing Issue

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ABSTRACT

During the refueling outage (RFO) 2013 at NPP Krško, the electric hydrogen recombiners, a system for the hydrogen control during severe accidents and design basis accidents, were replaced by passive autocatalytic recombiners (PARs).

During the next RFOs in 2015, 2016 and 2018, periodic tests of PAR cartridges were performed. The periodic testing of NIS-PARs shall prove that the catalytic reaction starts up as specified. According to the licenced testing procedure, each outage six cartridges were obtained and tested in the NIS PAR test device (TD). Randomly selected PAR cartridges did not pass the periodic test at room temperature (RT). Cartridges that do not pass the periodic testing have to be regenerated according to NEK procedure, followed again by a test in the TD to demonstrate the success of the regeneration. The effort of a full regeneration of all cartridges is not necessary and conservative. Due to significant unexpected workload during outages, the need for enhanced testing procedure with higher catalyst test temperature is priority. The concept for this is based on the conclusion that the PARs installed in NPP Krško were functional under accident conditions during the operational cycles (OL27, OL28 and OL29) even though PAR cartridges did not pass the periodic testing on RT (testing at higher but well below accident temperatures was successful). Revision of procedure and methodology in that direction requires development of the new TD. New TD will allow PAR cartridge measurements at defined elevated temperatures (range 40 - 70 deg C). It shall be vacuum oven type device or upgraded current NIS device. In both examples it shall provide testing of at least two cartridges at the same time, independently, however the whole cartridge shall be tested. Test gas remains 3 vol. % hydrogen in the air.

For a detailed plant specific investigation of this catalytic material behavior, increased testing of cartridges was developed. Additionally, testing of different batch behavior was performed.

Keywords: *passive autocatalytic recombiners, PAR, NIS PAR, periodic test, testing temperature*

1 INTRODUCTION

NPP Krško is a two loop Westinghouse PWR with a reactor thermal power of 1994 MWt. The reactor containment building is a cylindrical steel shell enclosed within an outer concrete shield building. Because of accident management review and as a response on the Fukushima accident in Japan, NPP Krško is enhancing its current plant safety even beyond postulated design basis (severe) accidents in sight of its predicted lifetime safe operation and safe shut down. As a part of this comprehensive project, for the hydrogen control during design basis and severe accidents, passive autocatalytic recombiners (PARs) replaced the existing electric hydrogen recombiners.

PARs are simple and passive devices independent of the need for electrical power or any other support system thanks to self-actuated catalytic exothermic reaction between hydrogen/carbon monoxide and oxygen and natural convection. Their purpose is to prevent and mitigate the consequences of generation of explosive gases inside containment even in case of reactor core melt. The following design bases apply for the PARs:

- The PARs are designed to sustain all normal loads as well as accident loads including

- The PARs are designed to survive and maintain required efficiency in the severe accident environment,
- The PARs are designed for a lifetime of 40 years, consistent with that of the plant,
- All materials used in the PARs are selected to be compatible with the environmental conditions inside the reactor containment during severe accident conditions.

The hydrogen accumulation in the containment atmosphere can be the result of production from several sources:

- Zirconium-steam reaction,
- Radiolysis of water,
- Post accident aluminum and zinc corrosion,
- Release of the hydrogen contained in the reactor coolant system,
- Molten core concrete interaction (MCCI) phenomenon

The following installation criteria apply for the PARs:

- The PARs are located in the containment such that they process a flow of containment air containing hydrogen at a concentration which is generally typical of the average concentration throughout the containment,
- The PARs are located away from high velocity air streams, such as could emanate from fan cooler exhaust posts, or they will be protected from direct impingement of high velocity air streams by suitable barriers such as walls or floors,
- The PARs are located in an area of the containment such that they will be protected from potential high energy missiles or jet impingement from broken pipes,
- The PARs are mounted on a substantial foundation with no ambient vibration,
- The PARs are located in such a manner that there is adequate area around the units for maintenance,
- The PARs arranged and other related equipment accounts for the fact that there may be very high local temperatures in the area of exhaust gas from the recombiners.

Data about PAR locations in NPP Krško are given in Table 1. An example of installed PAR is presented in Figure 1. The cartridge is shown in Figure 2.

The PAR technology uses hydrogen recombination to prevent the build-up of hydrogen gas, or other flammable gases like carbon monoxide that can collect and create an explosive atmosphere. The function is completely passive and self-starting at low temperatures and in steam environments. It is driven by natural convection generated by the heat from the hydrogen recombination. Chimney elongation of the PAR devices boosts the depletion rate. Each PAR has a hood to protect against containment spray.

Catalytic cartridges, which are inserted into the housing, could be removed and replaced without removal and replacement of the housing. The cartridge are fabricated from perforated stainless steel plates which hold the catalyst pellets. Catalytic element consists of a ceramic (aluminum oxide) sphere coated with a catalyst material (palladium) and hydrophobic polymer.

Table 1: PAR locations in NPP Krško

| PAR No. | Safety related | RB elevation | Mounting |
|----------|----------------|--------------|-----------------------|
| GHPARS01 | Yes | 115.55 | SG1 mall |
| GHPARS02 | Yes | 115.55 | RCP2 wall |
| GHPARS03 | No | 107.62 | Clamped on CV37 |
| GHPARS04 | No | 107.62 | HVAC chase wall |
| GHPARS05 | No | 107.62 | HVAC chase wall |
| GHPARS06 | No | 107.62 | Clamped on CV41 |
| GHPARS07 | No | 132.75 | Platform VA101AHU-02A |
| GHPARS08 | No | 132.75 | Platform VA101AHU-02A |
| GHPARS09 | No | 132.75 | Platform VA101AHU-01A |
| GHPARS10 | No | 132.75 | Platform VA101AHU-01A |
| GHPARS11 | No | 132.75 | Platform VA101AHU-02B |
| GHPARS12 | No | 132.75 | Platform VA101AHU-02B |
| GHPARS13 | No | 132.75 | Platform VA101AHU-02B |
| GHPARS14 | No | 132.75 | Platform VA101AHU-01B |
| GHPARS15 | No | 132.75 | Platform VA101AHU-01B |
| GHPARS16 | No | 132.75 | Platform VA101AHU-01B |
| GHPARS17 | No | 107.62 | Clamped on CV35 |
| GHPARS18 | No | 107.62 | Platform at SIATA02 |
| GHPARS19 | No | 100.30 | SG1 wall |
| GHPARS20 | No | 100.30 | SG2 wall |
| GHPARS21 | No | 123.00 | Platform VA111PLM-001 |
| GHPARS22 | No | 123.00 | Platform VA111PLM-001 |



Figure 1: An example of the installed PAR unit in NPP Krško

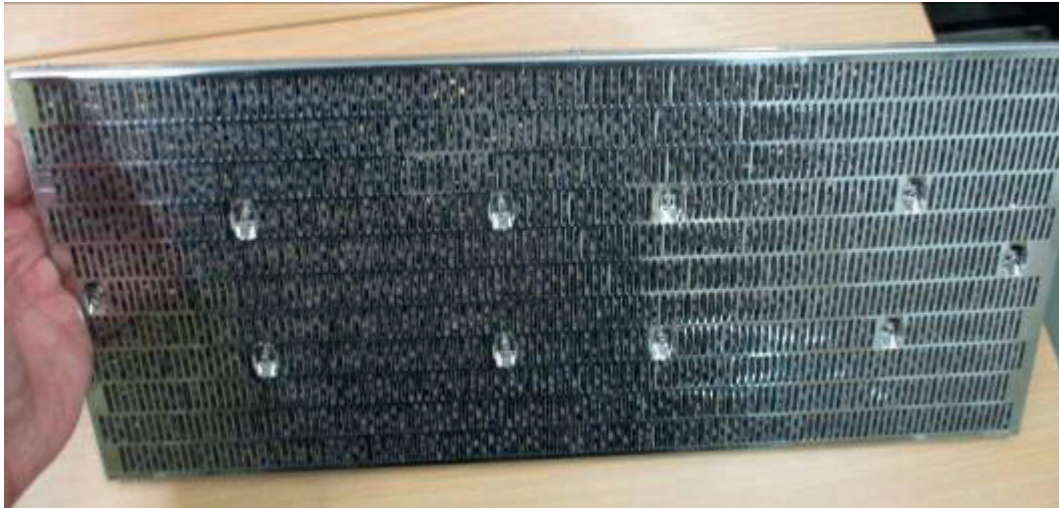


Figure 2: PAR cartridge with catalytic material

2 TESTING METHODOLOGY OF NIS PAR

Inspection and testing program for PARs provides 18 months inspection intervals (ones per each refueling) in compliance with the requirements of technical specification surveillance testing.

The reaction products of the catalytic recombination of hydrogen with the oxygen contained in the air are water and reaction heat. The heat of reaction results in a heat-up of the structure and the test gas. The respective temperature increase is determined by the amount of hydrogen converted. The converted amount of hydrogen depends essentially on the offered hydrogen and the efficiency of the conversion. At a constant gas flow rate and constant gas concentration the resulting heat is determined by the efficiency of the recombination. The relation of the heat entering into the structure and the heat entering into the gas flow is essentially constant for the same test conditions. Therefore, the temperature increase in the gas flow is proportional to the efficiency of the recombination.

The temperature increase in the test gas is determined by thermocouples and is used as an evaluation criterion for the efficiency of the hydrogen recombination.

2.1 Standard testing procedure

The operability of the PAR cartridges is determined with the functional test using NIS test device and demonstrated by a certain temperature increase of the cartridges within a certain time interval when exposed to a test gas with specified hydrogen concentration and gas flow.

The testing device consists of two test channels with a flap to insert a cartridge; two flow meters at front; four thermocouples mounted in each flow channel; a gas connection nozzle on the backside and a data logger with a PC-interface cable (Figure 3). The cartridge, which is to be tested (one PAR cartridge from each of the two safety-related PARs and from four non-safety related PARs), is inserted in the NIS PAR TD and creates a flow channel in it which is representative for a flow channel in PAR. Test gas with constant hydrogen concentration of about 3 ($\pm 0,25$ abs.) vol. % in air is used preferably from pressurized bottles with pre-mixed gas to obtain constant conditions. The temperature increase in the gas flow is measured by 4 thermocouples about 10 cm away from the gas entrance. The 4 temperatures are averaged and the rate of temperature increase is the criterion of the correct NIS-PAR function.

The standard NIS cartridge test is performed at a flow rate of 1500 l/h, room temperature and an input pressure of max. 1.5 bar differential pressure. In these conditions, it shall be demonstrated that the start-up behavior is acceptable. The acceptance criteria are to reach a temperature increase of 10 °C within 20 minutes or for delayed start-up 20 °C within 30 minutes.



Figure 3: NIS PAR testing device

2.2 Additional test

Randomly selected PAR cartridges at NEK site did not pass the periodic test at room temperature during RFOs in 2015, 2016 and 2018.

Regeneration is prescribed in case of failure of the test. Regeneration takes place in an oven at elevated temperature and under low pressure conditions to accelerate the desorption process. The temperature for regeneration is chosen based on practical reasons: a higher temperature speeds up the desorption of any components that are adsorbed at the catalytic surface and reduces the time,

which is necessary for regeneration. However, the temperature has to be below a level that could cause damage to the hydrophobic coating. A temperature chosen is 180 °C at a pressure level of a few mbar. The retesting of cartridges after the regeneration was performed to proof that the cartridge starts up again as specified.

The contractor coordinated investigation of the unexpected PAR testing results. Still a root cause for such a behavior of cartridges is not clearly identified. The purpose of the additional testing was to provide an apparent cause, analyse why the PAR cartridges did not pass the periodic testing and give recommendations for the future actions for testing the NIS-PARs at the NPP Krško.

Specific ageing testing program was developed [5]. Determination of the plant specific ageing characteristics of PAR is necessary to form a basis for a prediction of the behaviour of the cartridges. These tests were necessary in order to validate and define the new test procedure, and new temperature value for PARs testing. A test series were performed at different elevated starting temperatures to show whether the catalyst still works under accident conditions.

The goal of these additional tests was to reduce the effort in future outages. The concept for this is based on the conclusion that the PARs installed in NPP Krško were functional under accident conditions during the operational cycles even though PAR cartridges did not pass the periodic testing on RT (testing at higher but well below accident temperatures was successful) [2]. For a detailed plant specific investigation of this behavior, several cartridges have been tested at different starting temperatures. The elevated starting test temperature was obtained with two methods: preheating the cartridges in the oven and testing with the modified thermally isolated NIS TD, heated with the stream of preheated compressed air.

3 TEST RESULTS

During periodic testing, the cartridges taken from containment did not pass the test in the NIS testing device on room temperature according to SCP-6.630 [3] (Figure 4). As a consequence for 3 subsequent outages all cartridges had to be regenerated according to procedure COP-6.500 [4]. Regeneration was successful and all re-tested cartridges passed the test (Figure 5).

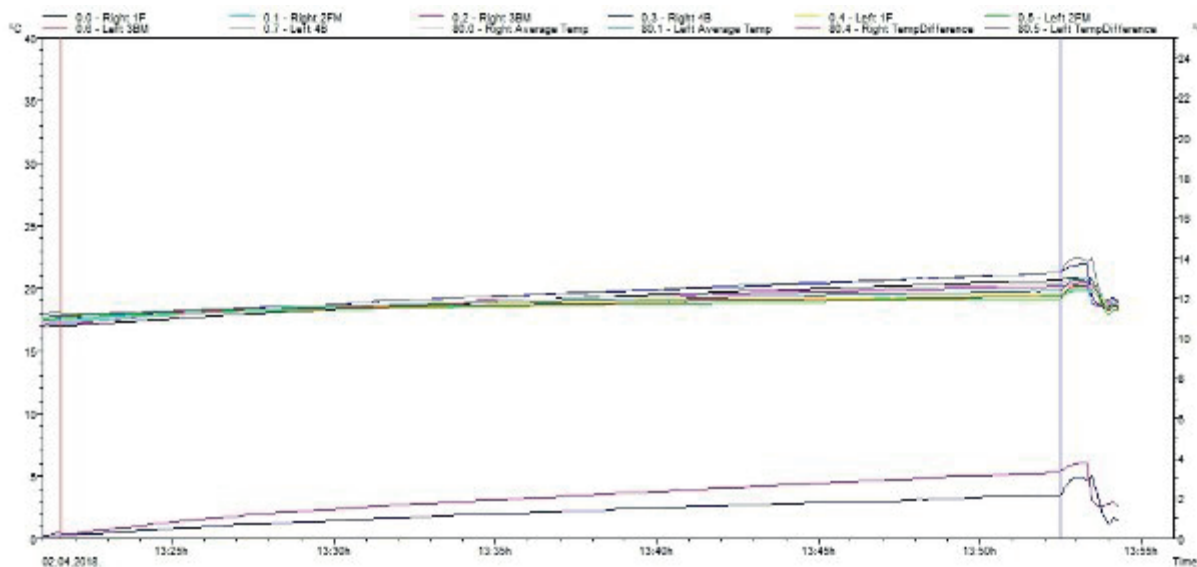


Figure 4: Standard periodic test of NIS PAR at NPP Krško

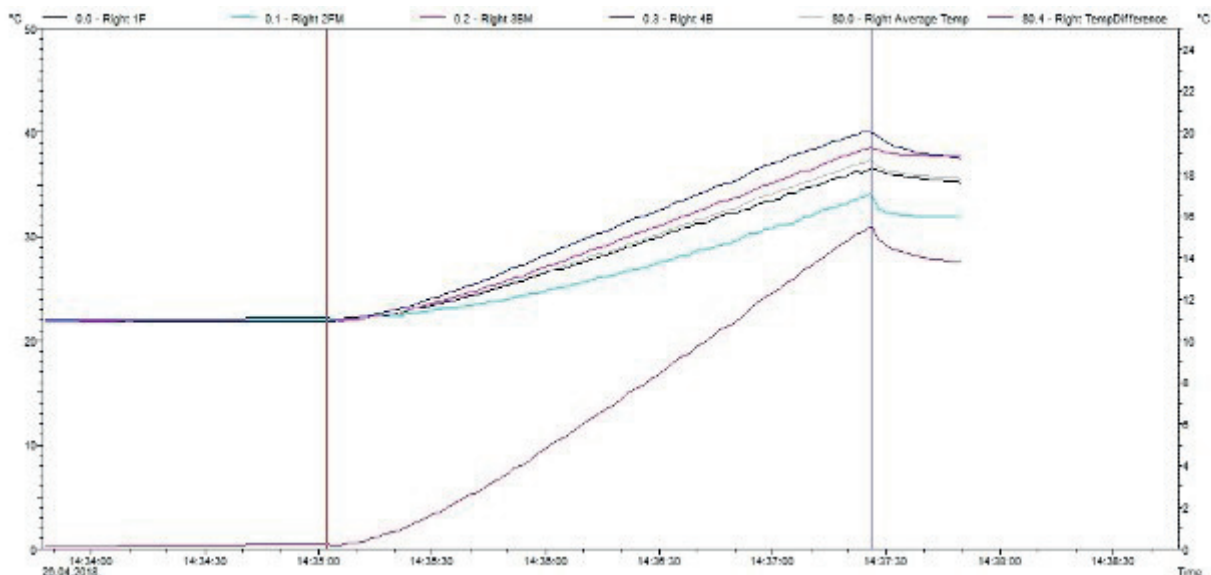


Figure 5: Test after regeneration of NIS PAR cartridge

The failure to pass the test was an unexpected behavior, given the operating experience of NIS-PARs: under normal containment conditions the start-up behavior of cartridges does not deteriorate to an extent that the test criteria are not met, even for many years of exposure to the containment atmosphere.

Specific testing program was suggested by contractor in technical document WEG-EEA-16-006 [5]. These tests were necessary in order to validate and define the new test procedure, and temperature value for PARs testing. The tests have been performed in 2016, just before and during the RFO, as well during outage in 2018.

The behavior of PAR during testing indicates that the one of the reasons for the failed tests could be a soiling. An investigation was coordinated by WEG. The catalyst material was tested in chemical laboratories to determine the exact source of soiling, based on the information which was available from NPP Krško. The exact source of soiling is still not identified and no root cause for such a behavior of cartridges could be clearly identified. To prevent exposure to any potential soiling agent, the cartridges had been inserted into the PARs and thus subjected to containment atmosphere only at the end of the outage, and were hence not exposed to the most of outage works nor have any such works been done in the current outage prior to the testing of the cartridges. It should be noted that a certain amount of reactor coolant pump (RCP) oil has been lost into the containment in the cycle before PARs had been installed in 2013 and during OL29. Confusing fact is that in the outage 2018, the only cartridge that passed the periodic test successfully according to SCP-6.630, was the one from GHPARS02 placed directly above reactor coolant pump RCP2.

Furthermore, the finding from the tests in NPP Krško is that the soiling is not localized but global effect, i.e. that PARs from all locations in the containment are affected.

In 2016 tests with cartridges preheated in an oven were conducted. Different starting temperatures were applied for testing (45, 50, 55, 60 deg C). Results showed the following: difficult manipulation of the heated cartridges; variable initial decrease of temperature caused by the transport of the heated cartridge from oven to TD, dependent on ambient temperature and on human performance. Conclusion was that the testing method and the system should be isolated and not influenced by human performance and ambient conditions [6].

In 2018 two parallel sets of test were performed: on room temperature with standard NIS TD and on elevated temperature using new experimental NIS TD (Table 2) [7].

The majority of cartridges failed the acceptance test at room temperature.

Unlike other batches (8989 and 7471), cartridges from batch 8770, from all 22 GHPARS units (meaning from different elevations and positions, see Table 1), have had successful test results on RT. The successful tests included as well three cartridges that were unregenerated and placed in the containment for two cycles. All the tests from batch 8770 showed delayed start up time (temperature increase) compared to a new cartridges (Figures 6 and 7). Furthermore, by selecting NIS-PARs at different elevations, it was shown that the cause for this PAR problem at NPP Krško is not just a soiling phenomenon. There has to be some influence of quality of catalytic material.

All tested cartridges on elevated temperature successfully passed the test. The new experimental PAR-TD device showed an initial heat-up time of about 8 hours and a heat up time to an steady state cartridge temperature on average about 20 min (Figure 8). The temperature measurements of the thermocouples in the device showed uncertainties in acceptable range. All these properties should be improved by the design of an industrial commercial test device.

Table 2: Summary of test results

| | BATCH | NO OF TESTS | SUCCESSIFUL | FAILED |
|------------------------------|-------|-------------|-------------|--------|
| Test on room temperature | 8989 | 66 | 3 | 63 |
| | 8770 | 36 | 35 | 1 |
| | 7471 | 8 | 0 | 8 |
| Test on elevated temperature | 8989 | 44 | 44 | 0 |
| | 8770 | 11 | 11 | 0 |
| | 7471 | 12 | 12 | 0 |

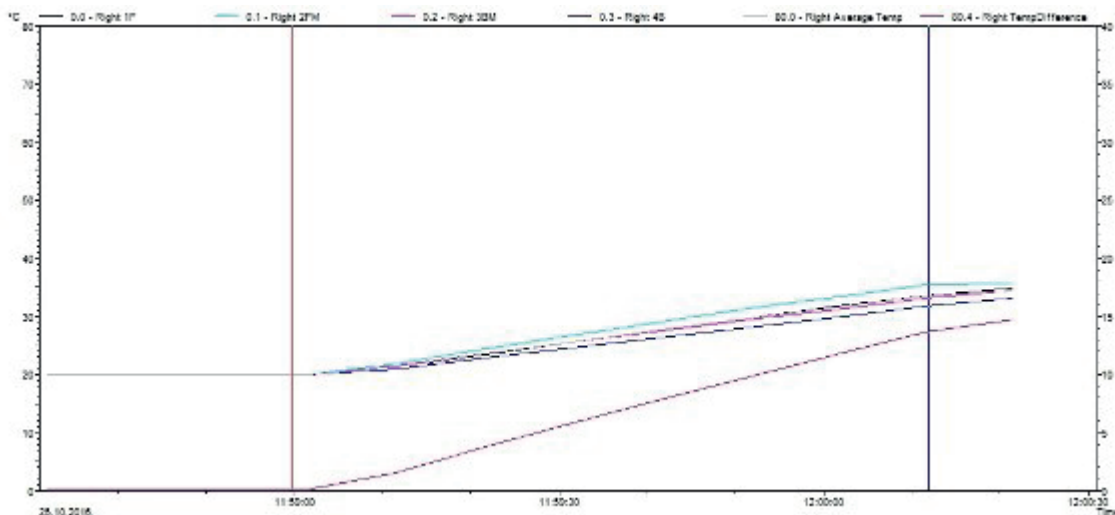


Figure 6: Standard test of the new cartridges

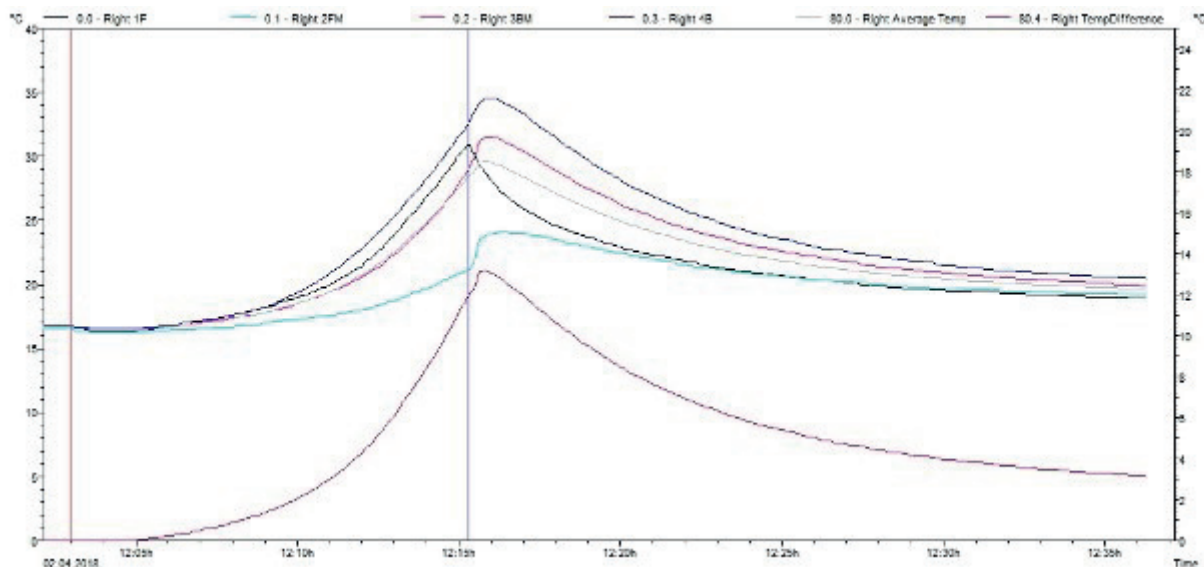


Figure 7: Standard test with the cartridge from batch 8770/C/xxxx

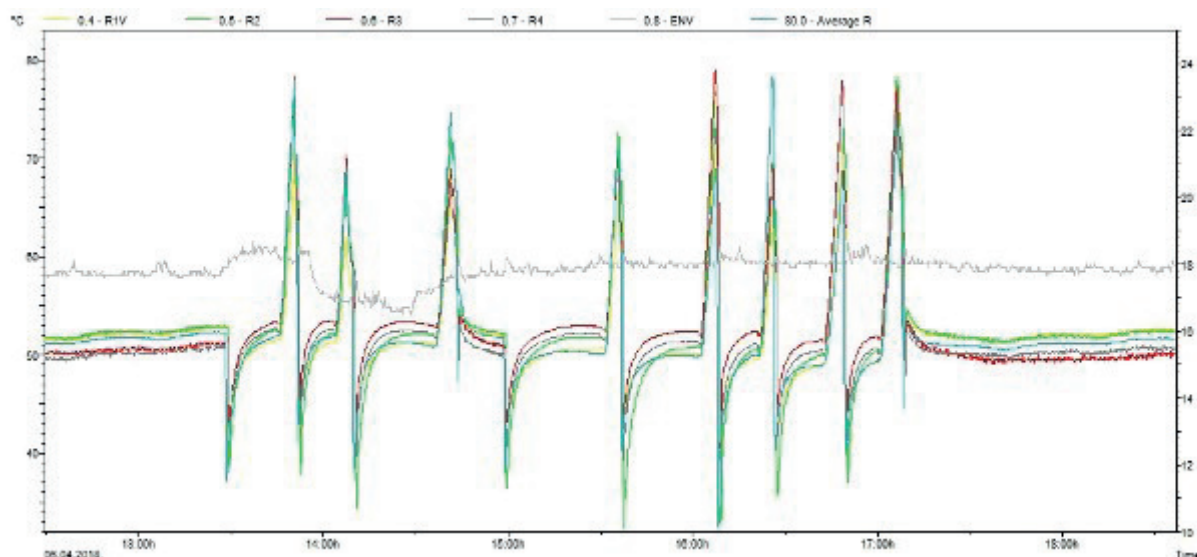


Figure 8: Test at elevated temperature with the modified TD

4 CONCLUSION

Based on the test results the following conclusions are derived:

- The PAR cartridge periodic tests showed a high failure rate for the tested cartridges on room temperature.
- Regarding possible soiling agent in NPP Krško containment, the evaluation of the performed tests did not show any spatial dependence nor identify a location of the soiling agent(s).
- Regeneration of the cartridges is successful and reduces the start-up time of reaction.
- Comparison of test data between different batches indicate that reasonable suspicion on the deficiencies in the series of autocatalytic material may exist. An investigation of the manufacturing process for all batches shall be done to investigate if there are significant differences.
- Successful PAR test at NPP Krško showed a delayed heat up rate compared to the tests of new cartridges.

- All cartridges tested on elevated temperatures passed the test. For testing of PAR cartridges on elevated temperatures (40-70 deg C) new testing device is required (a testing method and system should be isolated and not influenced by human performance and ambient conditions)
- A detailed analysis of the cartridge test data has to be performed for a definite root cause analysis of NPP Krško PAR testing issues.

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