Acta Polytechnica **61**(4):504–510, 2021
https://doi.org/10.14311/AP.2021.61.0504

Published by the Czech Technical University in Prague

CO_2 POWER CYCLE CHEMISTRY IN THE CV ŘEŽ EXPERIMENTAL LOOP

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Abstract. Power cycles using carbon dioxide in a supercritical state (sc-CO_2) can be used in both the nuclear and non-nuclear power industry. These systems are characterized by their advantages over steam power cycles, e. g., the sc-CO_2 turbine is more compact than the steam turbine with a similar performance. The parameters and lifespan of the system are influenced by the purity of the CO_2 in the circuit, especially the admixtures, such as O_2, H_2O, etc., cause the enhanced structural materials to degrade. Therefore, gas purification and purity control systems for the sc-CO_2 power cycles should be proposed and developed. The inspiration for the proposal of these systems could stem from the gas, especially the CO_2-cooled nuclear reactors operation. The first information concerning the CO_2 and sc-CO_2 power cycle chemistry was gathered in the first period of the project and it is summarized in the paper.

Keywords: Supercritical carbon dioxide, sc-CO_2, power cycle chemistry, materials, purification, purity control.

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1. Introduction

The increase of the electric power consumption and the CO_2 emissions reduction requirements demand new and effective energy sources. One way of increasing the conversion of mechanical power to electric power is by using carbon dioxide as a working medium in the power cycle. Currently, the power cycles that are based on supercritical CO_2 (sc-CO_2) have been investigated [1, 2]. Carbon dioxide becomes supercritical above a critical temperature of 30.98 °C (304.13 K) and above a pressure of 7.32 MPa [2].

Apart from the power industry, sc-CO_2 has been used in other technologies. As examples, the extraction [3, 4], dissolving [5, 6], nanoparticles preparation [7] and impregnation [8] could be mentioned.

The sc-CO_2 power cycle's efficiency of the conversion of mechanical power to electric power may exceed 50 % as compared to the conventional steam power cycle, which has a maximum efficiency of approximately 40 % [9, 10]. The efficiency of sc-CO_2 increases within the temperature range of 500–950 °C. Therefore, this technology is suitable for power conversions in both high temperature non-nuclear and nuclear technologies, including the generation IV nuclear reactors. The technologies with a possible use of sc-CO_2 cycles are listed in Table 1 [11]. Another advantage of the sc-CO_2 cycles is that they use more compact turbines as compared to the turbines for the steam power cycle [12].

2. R&D in sc-CO_2 technologies

For sc-CO_2 power cycles, several experimental devices as well as pilot plants can be investigated and verified. One of the larger devices is unit EPS100, which measures the exhaust heat usage in Echogen, USA. The power output of this unit reaches seven to eight MW. The optimum temperature of the source is 500-550 °C, and the minimum source temperature is 85 °C, which allows the low potential exhaust heat to be used [9].

Examples of smaller scale experimental units are as follows:

- Supercritical CO_2 Brayton Cycle Integral Experiment Loop (SCIEL), South Korea
- Experimental loop Knolls Atomic Power Laboratory (KAPL), USA
- Experimental loop Institute of Applied Energy (IAE), Japan
- sc-CO_2 loop SCARLETT (IKE) University of Stuttgart, Germany

See ref. [9] for details.

In Centrum výzkumu Řež s.r.o. (Czech Republic), the supercritical carbon dioxide experimental loop has recently been built (see the scheme of the loop in Figure 1). The purpose of the loop is to measure the thermohydraulic performance and physical parameters of the sc-CO_2 circuits. Because the loop is equipped with a test section, the loop can also be used for testing materials.

Application	Cycle type	Advantages	Output (MWe)	Temperature (°C)	Pressure (MPa)
Nuclear	Indirect heating	Efficiency, compactness, reduced water consumption	10-300	350-700	20-35
Fossil power stations	Indirect heating	Efficiency, reduced water consumption	300-600	550-900	15-35
Fossil fuels (synthesis and natural gas)	Direct combustion	Efficiency, reduced water consumption, carbon capture storage	300-600	1100-1500	35
Thermal solar power stations	Indirect heating	Efficiency, compactness, reduced water consumption	10-100	500-1000	35
Marine propulsion	Indirect heating	Efficiency, compactness,	< 10	200-300	15-25
Exhaust heat usage	Indirect heating	Efficiency, compactness, simplicity	1-10	< 230-650	15-35
Geothermal	Indirect heating	Efficiency	1-50	100-300	15

Table 1. Possible use of sc-CO$_2$ power cycles [5].

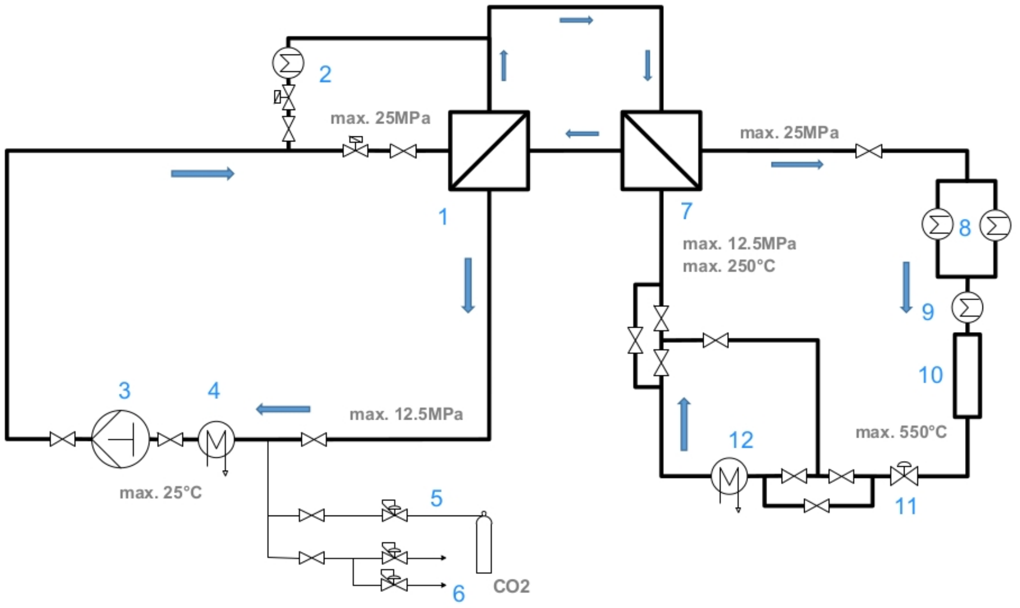

Figure 1. Scheme of the supercritical carbon dioxide experimental loop at CV Řež. 1: low temperature heat exchanger, 2: preheater, 3: main circulation pump, 4: cooler, 5: CO$_2$ dosing system, 6: sampling system, 7: high temperature heat exchanger, 8: cooler, 8, 9: heaters, 10: test section, 11: reduction valve, 12: cooler.

Maximum medium temperature	550 °C
Maximum pressure in the high-pressure section	25 MPa
Maximum pressure in the low-pressure section	12.5 MPa
Maximum flow rate	$0.4\,\mathrm{kg\cdot s^{-1}}$
The loop volume	$0.08\,\mathrm{m^3}$

Table 2. The main parameters of the supercritical carbon dioxide experimental loop at Centrum výzkumu Řež s.r.o.

Component	Natural gas (vol. %)	Synthesis gas (vol. %)
CO_2	91.80	95.61
H_2O	6.36	2.68
O_2	0.20	0.57
N_2	1.11	0.66
Ar	0.53	0.47

Table 3. Examples of the medium composition in the turbine inlet for the direct combustion cycle, according to the used fuel [13, 14].

For the main parameters of the loop, see Table 2. The function of the loop could be described as follows: after the passage through the heat exchanger in the high-pressure section (7), CO_2 flows to two parallel (8) and one serial (9) heater branches. After heating, the medium flows to the test section (10). A reduction valve (11) , which reduces the medium pressure to 12.5 MPa, is placed after the test section. Due to the accurate temperature reduction, a part of the flow is passed through the oil cooler (12), and the second part flows through the bypass. Following that, the medium reaches the low-pressure part of the high temperature heat exchanger (7), which has a maximum allowed temperature of 450 °°C. It then flows to the low temperature heat exchanger (1). Next, it flows through the cooler (4), which is situated before the entrance to the main circulator (3).

3. sc-CO_2 POWER CYCLES CHEMISTRY

In contrast to other power cycles, such as steam and helium, the data from the chemical composition of the sc-CO_2 medium, purification, and purity control is rather scarce. Some knowledge can be drawn from experience with nuclear reactors, which use carbon dioxide (not in a supercritical state) as the primary coolant. These reactors have been operated in Great Britain (MAGNOX and Advanced Gas Cooled Reactors) [15], and the first nuclear power plant in former Czechoslovakia, which is A1, also used carbon dioxide as a primary coolant [16].

3.1. Impurities in the CO_2 medium

Impurities in the unit's contents of volume percentage in the CO_2 medium influence the thermodynamic properties of the medium. For example, the power consumption of the compressor when working with a medium that is near the critical point increases by six percent, whereas the medium purity decreases by 4.4 %. With a medium of 90.9 % purity, the compressor power consumption increases by 34 % as compared to 100 % with pure CO_2. This increase in power consumption is caused by a decrease in the medium density, which is due to the impurities [17]. This phenomenon is mainly significant for the systems with a direct combustion. Examples of the medium composition in the direct combustion power cycles are listed in Table 3.

Furthermore, the impurities cause the materials and components to corrode and degrade, and they may be the source of undesirable physicochemical processes in the power cycle. The sources of the impurities are as follows:

- Impurities in the source gas
- Residual air or gases present in the system prior to the operation
- Corrosion and chemical reactions in the system
- Residual impurities on the component's surfaces
- Lubricant leakage
- Penetration from the outside environment due to the lack of tightness
- Desorption from the structural materials

Typical admixtures in the CO_2 medium are as follows: O_2, H_2O, H_2, CO, CH_4, N_2 [11, 18]. In the direct combustion cycles that use synthesis gas as a fuel, SO_2, SO_3, NO, NO_2, and halogen compounds may be present in the medium. Compounds of halogens and sulphur usually cause and accelerate the material's degradation by corrosion. If the medium

Compound	Average value in primary CO_2 coolant	Limit value for supply gas ($mg \cdot kg^{-1}$)	Average value in supply gas
H_2O	700-1200	20	15
oil	1–5	5	1
H_2	-	2	< 2
H_2S, NH_3 and others	-	1	< 1

Table 4. The impurities in the primary CO_2 coolant and supply gas in the A1 nuclear power plant [16].

does not contain these compounds, the corrosion is influenced by the water and oxygen content.

When using compressors and other devices, oils and other lubricants may be released into the circuit. These compounds are soluble in sc-CO_2. If the oil content in sc-CO_2 is higher than one percent by weight, the oil coats the internal surfaces and negatively affects the heat transfer properties [19].

As an example of CO_2 medium composition, the data for the CO_2 primary coolant purity in the nuclear power plant is listed in Table 4 [16].

3.2. Purification and purity control methods

In some devices, oil separators are used. For example, in the SCARLETT loop, the oil separator is located after the compressor. The separator separates 99 % of the oil that is contained in the medium in the loop [20]. To limit the damage to the turbines and other parts of the devices, the particle separators are inserted into the circuit. For lower flow rates, the "Y filters" (Figure 2) can be used, through which the medium passes.

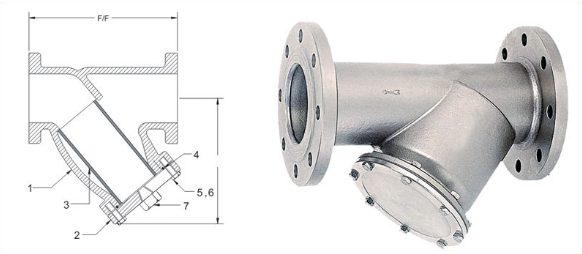

Figure 2. The Y-filter [21, 22].

For higher flow rates, other types of particle filters should be used, as shown in the experimental loop in SunShot in SwRI [11].

Other gaseous impurities can be separated by adsorption. The adsorption separation methods for medium purification in the supercritical carbon dioxide experimental loop in Centrum výzkumu Řež s.r.o. will be tested over the next few years. In ref. [23], the primary CO_2 purification method was based on condensation and a subsequent vaporization. Part of the gas flow was injected into the rectification column to separate the fission products (Xe, Kr, I).

3.3. Methods of analytical purity control

For the impurity content control, the analytical methods were based on gas chromatography (GC), gas chromatography with mass spectrometry (GC-MS), infrared spectroscopy, etc. The analytical system for the supercritical carbon dioxide experimental loop will also be developed over the next few years within the special project. Currently, the combination of the gas chromatography with the helium ionization detector (GC-HID) and the 1-channel moisture analyser is based on changes to the infrared light wavelength. The experience with these technologies was obtained in connection with another technology: the high temperature helium experimental loop. The details were published in ref. [24]. The GC-HID method is sensitive when determining the content of H_2, CO, CH_4, O_2, and N_2 (the contents of a 10^{-5} volume percentage can be detected). One disadvantage of this method is that the HID detector requires helium as a carrier gas. Helium must be added separately for the analysis, because the loop that the gas is based on, which is CO_2, will be sampled (in contrast to the helium loop), and the chromatographic method should be adjusted to these conditions. Additionally, the chromatographic analysis is relatively slow, as it lasts approximately 20 minutes.

The probe of the moisture analysis will be placed directly into the medium in the low-pressure part of the loop. The maximum gas pressure outside of the moisture analyser probe is 20 MPa. The data from the moisture content in the sc-CO_2 medium in the loop will be measured continually.

3.4. Organic impurities measured during the first long-term operation of the supercritical carbon dioxide experimental loop at CV Řež

During the first long-term (1,000 hours) operation of the loop, the sampling of the CO_2 medium in the loop was carried out on the seventh, 15th, and 34th day of operation. The purpose of the sampling was to determine the amount of undesired minor organic impurities in the medium in the loop. The loop was operated at a temperature of 550 °C in the test section and a pressure of 20 MPa in the high-pressure

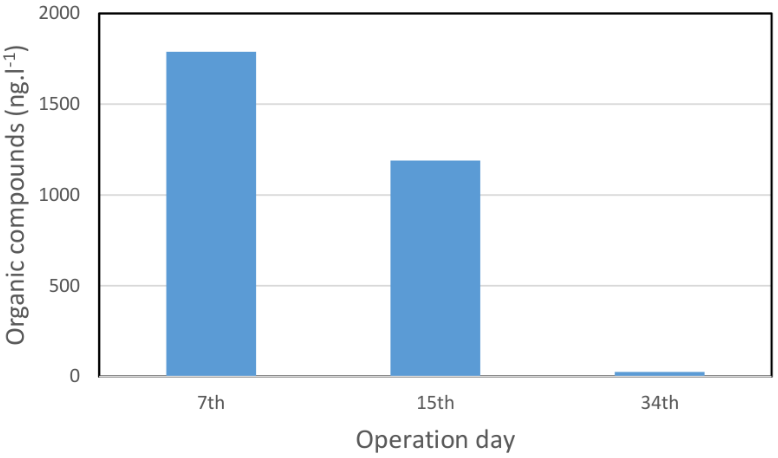

Figure 3. The sum of the organic compounds in the CO_2 medium samples.

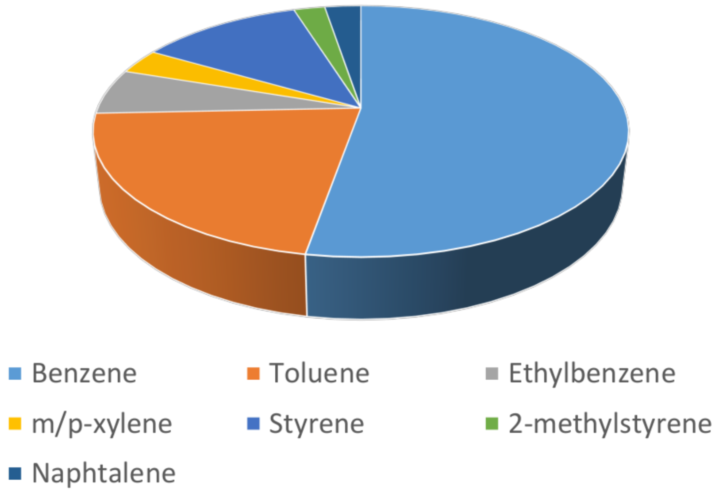

Figure 4. The relative distribution of organic compounds in the sample from the seventh loop operation day.

section. During the operation, an average of approximately 40 kg of CO_2 per day was drained from the loop and replaced to remove possible impurities from the medium in the loop.

The samples were taken by passing the gas through the sampling tubes with the active carbon. The volume of the samples was 10-170 l, with a pressure of 100 kPa and a temperature of 25 °C. In the next step, the compounds that were adsorbed by the active carbon were desorbed by carbon disulfide, which was subsequently determined by the GC-MS technique.

The amount of the organic compounds in the loop's medium that were determined in the samples has been recorded in the chart in Figure 3. The contents of the organic impurities in the medium decreased from ca. 1800 to 5 ng·l^{-1}. In the sample from the seventh day of operation, several organic compounds contained a large amount of benzene. The relative distribution of the organic compounds in the seventh operation day sample is shown in Figure 4. In the other samples, only benzene was detected. The source of the organic compounds in the loop medium could be the residual organics from the loop production, such as lubricants, degreasers, and dissolvents. The amount of organic impurities significantly decreased during the loop operation, which is likely due to the continuous replacement of CO_2 in the loop.

4. Conclusion

The sc-CO_2 power cycles are a perspective technology due to the high efficiency of the mechanical to electric power conversion, their compactness, etc. Centrum výzkumu Řež s.r.o. (Czech Republic), along with several other partners, has investigated this field. This research institution also operates a semi-industrial facility, which is the supercritical carbon dioxide experimental loop. The research aims to test materials for sc-CO_2 technologies, physical properties, and thermohydraulic properties of the sc-CO_2 medium as well as the coolant chemistry and the related purification & purity control methods.

As typical impurities in sc-CO_2 cycles with indirect heating, O_2, H_2O, H_2, CO, CH_4, N_2 and, in some cases, also organic compounds (oil, etc.) were identified. As analytical methods suitable for CO_2 purity control, Gas Chromatography with Helium Ionization Detector (GC-HID) connected directly with the sampling point of the circuit and optical hygrometer with probe placed directly next to the sc-CO_2 circuit were proposed. The methods will be tested. For the determination of trace concentrations of organic compounds, the Gas Chromatography with Mass Spectrometry detector (GC-MS) can be used. This method was verified by an analysis of real samples from a sc-CO_2 loop operation. For the separation of impurities from the CO_2, the processes based on adsorption will be tested within the continuation of the research program.

Acknowledgements

The presented work was financially supported by the Ministry of Education, Youth and Sport Czech Republic - project LQ1603 “Research for SUSEN”. This work has been performed within the SUSEN Project and co-financed within the framework of the European Regional Development Fund (ERDF) in project CZ.1.05/2.1.00/03.0108, and the European Structural and Investment Funds (ESIF) in the project CZ.02.1.01/0.0/0.0/15_008/0000293). Some results that have been presented in the article were achieved within the project No. TK02030023 supported by the Technology Agency of Czech Republic (TACR).

References

[1] Department of Energy. SCO2 power cycles for fossil fuels. [2020-04-03], `https://www.energy.gov/sco2-power-cycles/sco2-power-cycles-fossil-fuels`.

[2] E. G. Feher. The supercritical thermodynamic power cycle. *Energy Conversion* **8**(2):85–90, 1968. `https://doi.org/10.1016/0013-7480(68)90105-8`.

[3] G. Sodeifian, N. S. Ardestani, S. A. Sajadian, S. Ghorbandoost. Application of supercritical carbon dioxide to extract essential oil from Cleome coluteoides Boiss: Experimental, response surface and grey wolf optimization methodology. *The Journal of Supercritical Fluids* **114**:55–63, 2016. `https://doi.org/10.1016/j.supflu.2016.04.006`.

[4] G. Sodeifian, S. A. Sajadian, N. S. Ardestani. Optimization of essential oil extraction from Launaea acanthodes Boiss: Utilization of supercritical carbon dioxide and cosolvent. *The Journal of Supercritical Fluids* **116**:46–56, 2016. `https://doi.org/10.1016/j.supflu.2016.05.015`.

[5] G. Sodeifian, S. A. Sajadian, N. S. Ardestani. Determination of solubility of Aprepitant (an antiemetic drug for chemotherapy) in supercritical carbon dioxide: Empirical and thermodynamic models. *The Journal of Supercritical Fluids* **128**:102–111, 2017. `https://doi.org/10.1016/j.supflu.2017.05.019`.

[6] G. Sodeifian, F. Razmimanesh, S. A. Sajadian. Solubility measurement of a chemotherapeutic agent (Imatinib mesylate) in supercritical carbon dioxide: Assessment of new empirical model. *The Journal of Supercritical Fluids* **146**:89 –99, 2019. `https://doi.org/10.1016/j.supflu.2019.01.006`.

[7] G. Sodeifian, S. A. Sajadian, S. Daneshyan. Preparation of Aprepitant nanoparticles (efficient drug for coping with the effects of cancer treatment) by rapid expansion of supercritical solution with solid cosolvent (RESS-SC). *The Journal of Supercritical Fluids* **140**:72–84, 2018. `https://doi.org/10.1016/j.supflu.2018.06.009`.

[8] A. Ameri, G. Sodeifian, S. A. Sajadian. Lansoprazole loading of polymers by supercritical carbon dioxide impregnation: Impacts of process parameters. *The Journal of Supercritical Fluids* **164**:104892, 2020. `https://doi.org/10.1016/j.supflu.2020.104892`.

[9] V. Dostal, P. Hejzlar, M. J. Driscoll. The supercritical carbon dioxide power cycle: comparison to other advanced power cycles. *Nuclear Technology* **154**(3):283–301, 2006. `https://doi.org/10.13182/NT06-A3734`.

[10] K. Brun, P. Friedman, R. Dennis. *Fundamentals and Applications of Supercritical Carbon Dioxide (sCO2) Bases Power Cycles*, chap. 15 Research and development: Essentials, efforts, and future trends. Woodhead Publishing, Duxford, 2017.

[11] M. Li, et al. The development technology and applications of supercritical CO_2 power cycle in nuclear energy, solar energy and other energy industries. *Applied Thermal Engineering* **126**:255–275, 2017. `https://doi.org/10.1016/j.applthermaleng.2017.07.173`.

[12] K. Brun, P. Friedman, R. Dennis. *Fundamentals and Applications of Supercritical Carbon Dioxide (sCO2) Bases Power Cycles*, chap. 7 Turbomachinery. Woodhead Publishing, Duxford, 2017.

[13] R. Allam, et al. The oxy-fuel, supercritical CO_2 Allam cycle: new cycle developments to produce even lower-cost electricity from fossil fuels without atmospheric emissions. In *Proceedings of the ASME Turbo Expo 2014: Turbine Technical Conference and Exposition. Volume 3B: Oil and Gas Applications; Organic Rankine Cycle Power Systems; Supercritical CO2 Power Cycles; Wind Energy.* 2014. V03BT36A016, `https://doi.org/10.1115/GT2014-26952`.

[14] Environmental Protection Agency (EPA). Standards of performance for greenhouse gas emissions from new, modified, and reconstructed stationary sources: electric utility generating units, 2015.

[15] M. Perschilli, et al. Supercritical CO_2 power cycle developments and commercialization: Why sCO_2 can displace steam. power-gen india & central asia, 2012. [2020-04-03], `http://www.echogen.com/documents/why-sco2-can-displace-steam.pdf`.

[16] PRIS – power reactor information system. operational & long-term shutdown reactors. [2020-04-03], `https://pris.iaea.org/PRIS/WorldStatistics/OperationalReactorsByType.aspx`.

[17] K. Feik, J. Kmošena. *Jadrová elektráreň A1 v kocke.* Slovakia, Bratislava, 2010.

[18] Electric Power Research Institute (EPRI). Performance and economic evaluation of supercritical CO_2 power cycle coal gasification plant, 2014.

[19] T. Hudský. *Special purification and purity control methods for advanced nuclear reactors.* Diploma thesis, UCT Prague, 2015.

[20] C. Dang, K. Hoshika, E. Hihara. Effect of lubricating oil on the flow and heat-transfer characteristics of supercritical carbon dioxide. *International Journal of Refrigeration* **35**(5):1410–1417, 2012. `https://doi.org/10.1016/j.ijrefrig.2012.03.015`.

[21] W. Flaig., R. Mertz, J. Starflinger. Setup of the supercritical CO_2 test facility "SCARLETT" for basic experimental investigations of a compact heat exchanger for an innovative decay heat removal system. *Journal of Nuclear Engineering and Radiation Science* **4**(3):031004, 2018. `https://doi.org/10.1115/1.4039595`.

[22] Cast steel y type strainer. [2020-04-03], `http://www.pmtengineers.com/images/product/cast_steel_y_type_strainer.jpg`.

[23] B. Hatala. *Katalog JE A1 (chemia). Internal VUJE report.* Slovakia, Bratislava, 2019.

[24] J. Berka, et al. New experimental device for VHTR structural material testing and helium coolant chemistry investigation – High Temperature Helium Loop in NRI Řež. *Nuclear Engineering and Design* **251**:203–207, 2012. `https://doi.org/10.1016/j.nucengdes.2011.10.045`.