Investigation of material degradation and coolant chemistry for sCO_2 power cycles

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Power cycle chemistry

- The chemical composition of the coolant/heat transport media influence the lifetime and performance of power units
- Even trace content of some specific components could essentially affect coolant properties – particularly at high pressures and temperatures
- Conventional power stations (with water-steam power cycles):
  - The coolant composition is monitored especially the specific components concentrations
  - The standards were established

Chemistry of CO_2 heat transfer medium

- Only limited data in technical and scientific literature, databases etc.
- Limited information of CO2 primary coolant composition in nuclear power plants (MAGNOX, AGR, A1 – Jaslovské Bohunice)

The impurities in the primary CO2 coolant and supply gas in the A1 nuclear power plant

Compound	Average value in primary CO_2 coolant	Limit value for supply gas (mg.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

Chemistry of sCO_2 power cycles

- Limited information
- Max. sCO_2 temperature 500 – 950 °C → the composition of medium may influence of corrosion intensity, etc.
- Higher content of impurities (in units of % by volume or higher) may influence the thermodynamic properties of medium and the power cycle efficiency
- The power consumption increase is caused by the decrease of medium density

sCO_2 medium purity (% by volume)	Compressor power consumption (%)
100	100
95.6	106
90.9	134

Sources of impurities in sCO_2 medium

- Source gas supposed for power units: CO2 of purity 3.0, 4.0, 4.5 or 4.8
- CO_2 available on the market

CO_2 type	Purity	Impurities (vppm)					
	% vol.	H_2O	O_2	CO	C_nH_m	N_2	Oil
SFC/SFE	99.9993	1	2	0,5	1	3	-
CO_2 for food industry (E290)	99.5	52	-	10	-	-	5
4.8	**99.998**	**5**	**2**	**1**	**2**	**10**	**-**
4.5	**99.995**	**5**	**15**	**1**	**2**	**30**	**-**
R-744	99.9	10	15	1	2	30	-
3.0	**99.9**	**120**	**500**	**-**	**50**	**500**	**-**
5.3	99.9993	1	2	0,5	1	3	-

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Sources of impurities in sCO_2 medium

- Leakage of air, moisture, lubricants
- Desorption from internal surfaces
- Products of chemical reactions in the circuit
- Expected admixtures in cycles with indirect heating: O_2, H_2O, H_2, CO, CH_4, N_2
- In cycles with direct combustion also the combustion products are expected: SO_2, SO_3, NO, NO_2

Example of sCO_2 composition in direct combustion cycle

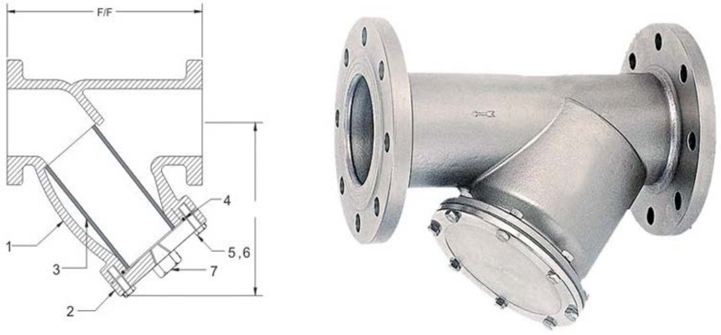
Component/fuel	Natural gas (vol. %)	Synthesis gas (vol. %)
CO_2	91.80	95.61
H_2O	6.36	2.68
O_2	0.20	0.57
N_2	1.11	0.66
Ar	0.53	0.47

Expected effect of impurities

- Affection of corrosion and material properties (even in concentration bellow 1 % by volume): H_2O, O_2, SO_x, CO, H_2, CH_4
- Affection of heat transfer: Oil (in higher concentration higher than 1 % by weigh)
- Affection of power cycle efficiency: Impurities in higher concentrations. Especially in case of the cycle with direct combustion

sCO2 purification methods

- Very poor information concerning existing units and devices
- In some devices oil separators used
  - SCARLETT loop oil separator localized behind the compressor. Efficiency higher than 99 %
- Particle separators to prevent turbine damage due to particles

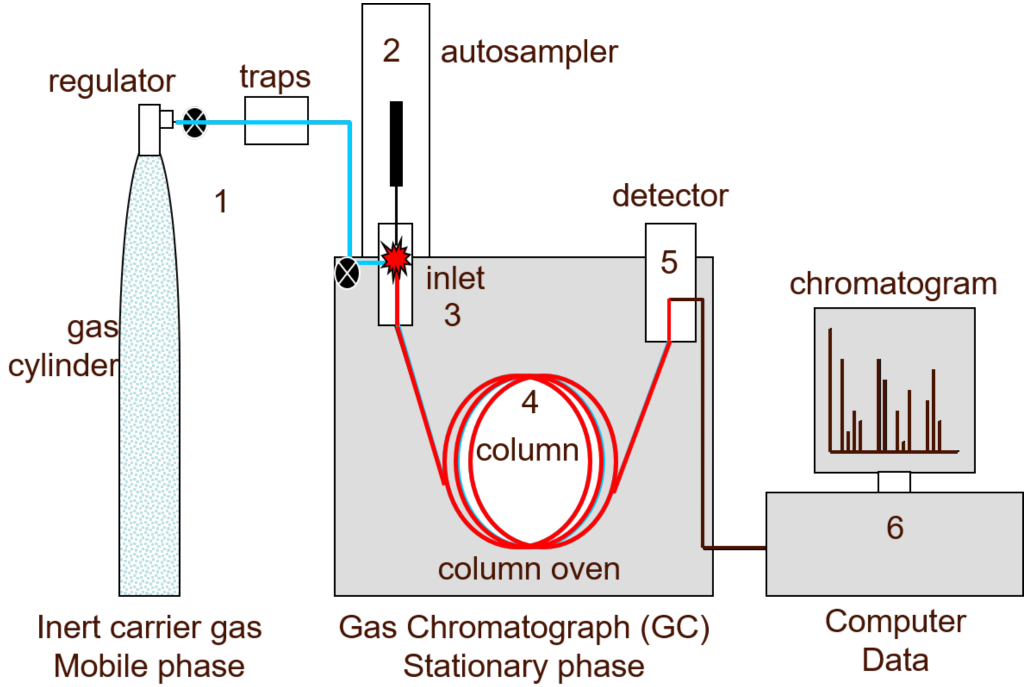


The particle separator „Y-filter“

[http://www.pmtengineers.com/images/product/cast_steel_y_type_strainer.jpg]

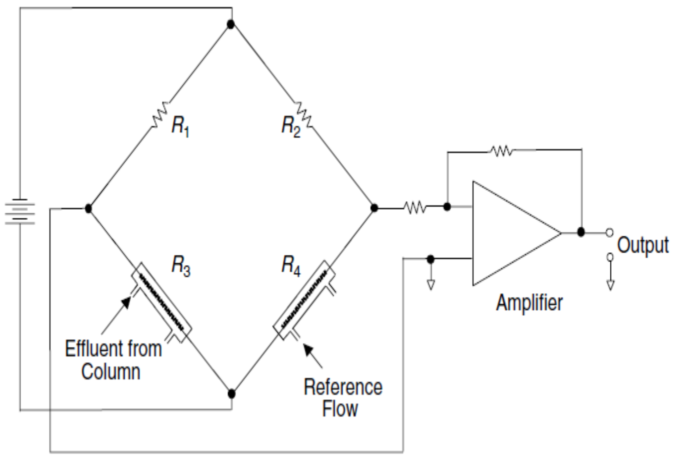
Proposed sCO_2 analytical purity control

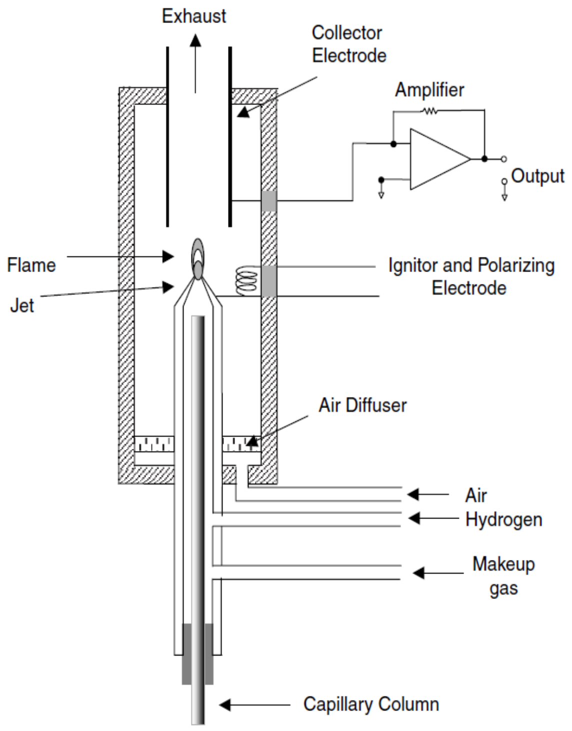
- Analytical methods based on gas chromatography
- The sensitivity and applicability depends on:
  - The system configuration
  - Chromatographic column
  - Detector
  - Chromatographic method
  - Sampling method
- Other methods



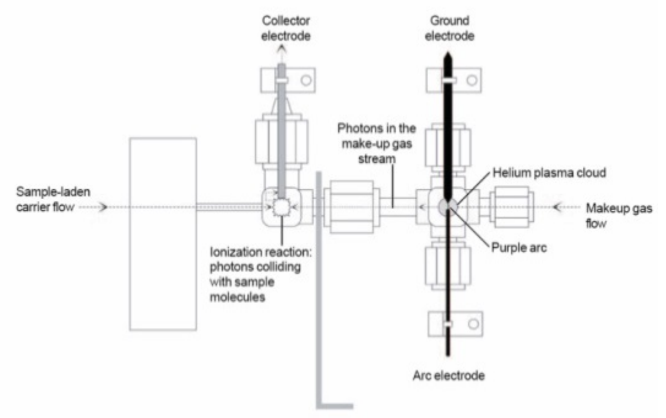
Selected gas chromatographic methods

- **Gas chromatography with Thermal conductivity detector** (GC-TCD)
  - Universal for wide spectrum compounds detection
  - Detection limit about 10 vppm
  - Not suitable for mixtures containing H_2 and carrier gas He
- **Gas chromatography with Flame ionization detector** (GC-FID)
  - Sensitive for flammable compounds, especially C_xH_y
  - For permanent gases not sensitive





Selected gas chromatographic methods



- **Gas chromatography with Helium ionization detector (GC-HID)**
  - Universal
  - Very sensitive (detection limit for some compounds bellow 0.1 vppm)
- **Gas chromatography with Mass spectrometry (GC-MS)**
  - Very sensitive
  - Convenient especially for detection of trace concentration of organics
  - Expensive (purchase, operation, maintenance)
  - Demanding on operating staff qualification

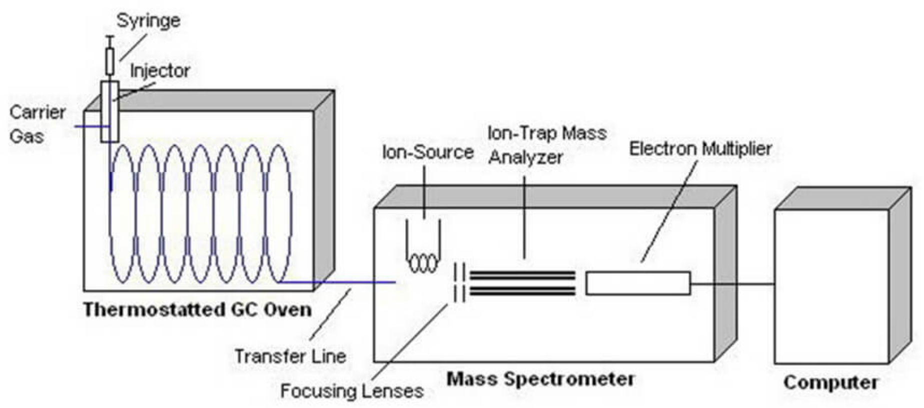


Figure 1 – Diagram of Gas Chromatograph with Mass Spectrometer attached

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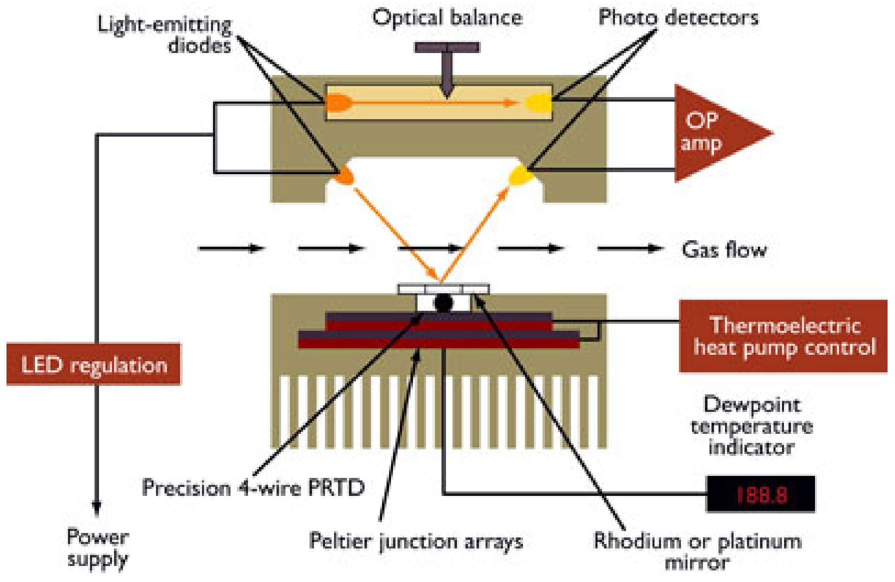
Analytical methods for H_2O monitoring

- Gas chromatography is not suitable for quantitative H_2O monitoring (especially in low concentration)
- Methods for H_2O monitoring
  - Karl Fischer titration: $SO_2 + I_2 + H_2O \rightarrow H_2SO_4 + 2HI$
  - Cooled mirror
  - **Capacity hygrometers**
  - **Optical hygrometers**
  - Absorption spectroscopy (TDLAS)
  - Other methods



Cooled mirror principle

Parameters of analytical methods for H_2O monitoring

Method	Maximal pressure (MPa)	Range of measurement – dew points (°C)	Uncertainty (°C)	Note
Cooled mirror	1,1 (2)	- 35 až + 25 (- 65 až + 25)[a]	± 0,2	[a]Depends on the connected probe
Cooled mirror (mobile)	10	- 35 až + 25 (-50 až + 25)[b]	± 1	[b]depends on ambient temperature
Optical	**25**	- 80 až + 20	± 1	
Capacity	**34,5**	- 80 až +10	± 2 (± 3)	Frequent calibration needed
QCM	0,4	- 80 až - 13	± 3 až ± 1	
TDLAS	0,17	- 71 až - 2,6*	± 4 až ± 0,1	

Project „Purification and purity control of CO_2 gas in power cycles“

- Supported by TA CR
- Involved organizations: Centrum vyzkumu Rez s.r.o. and University of chemistry and technology Prague
- Duration: 09/2019 – 06/2025
- Objectives
  - Extend and improve knowledge and experience of methods usable for sCO_2 medium purification and purity control
  - Verification selected methods in laboratory and sCO_2 loop operation
  - Propose the purification and purity control system for sCO_2 power cycle

Activities within the project

- Summary of information concerning:
  - sCO_2 medium composition
  - Analytical methods available for sCO_2 purity control
  - Applicable purification methods – especially based on adsorption processes – knowledge transfer from other technologies
- Experimental program aimed to verification of analytical methods and purification processes
- Experiments are planned to be performed within next period
  - Tests of moisture separation from CO_2 on selected materials are planned soon

Planned during 2021 - 2022

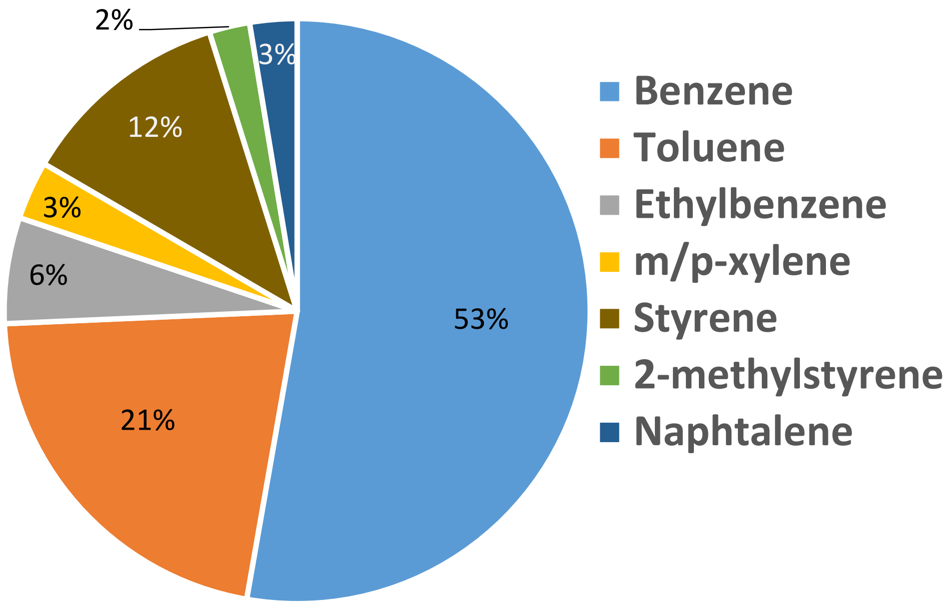
Organic impurities monitoring during sCO_2 loop operational campaign

- Source of organic impurities in circulating medium
  - Lubricants, degreasers and dissolvent from production
  - Penetration (e.g. from compressor, vacuum pumps, etc.)
  - Subsequent chemical reaction on the circuit during operation
- Loop operating parameters
  - 550 °C in the test section
  - 25 MPa in high-pressure section
  - Campaign duration: 1000 hours
  - Loop filled with high-purity CO_2 (4.8)
  - Dosing of 40 kg of „fresh“ CO_2 per operation day

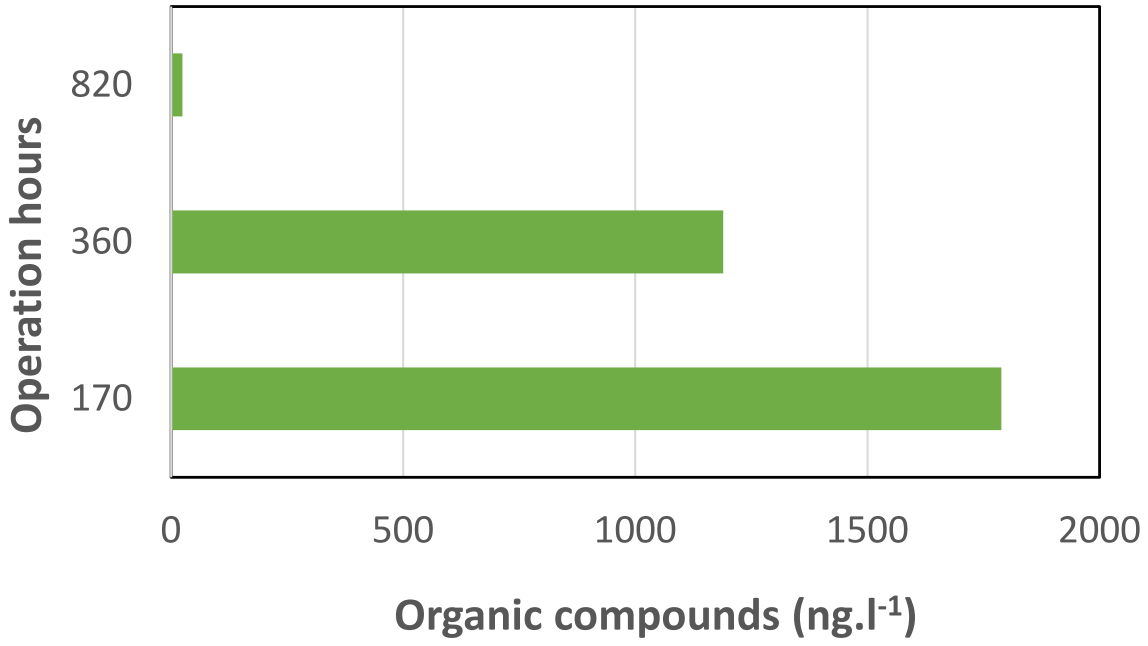
Organic impurities monitoring during sCO_2 loop operational campaign

- Sampling by using the sampling tubes with active carbon
- Determination of organic compounds by GC-MS after desorption by carbon disulfide
- The concentration of organics decreased during operation (from ca. 1800 to 5 ng/l at 25 °C and 1 bar)
- In the 1st sample after 170 operational hours various organic compounds was detected
- In the next samples only benzene was detected

Organic impurities monitoring during sCO_2 loop operational campaign



The sample after 170 operational hours

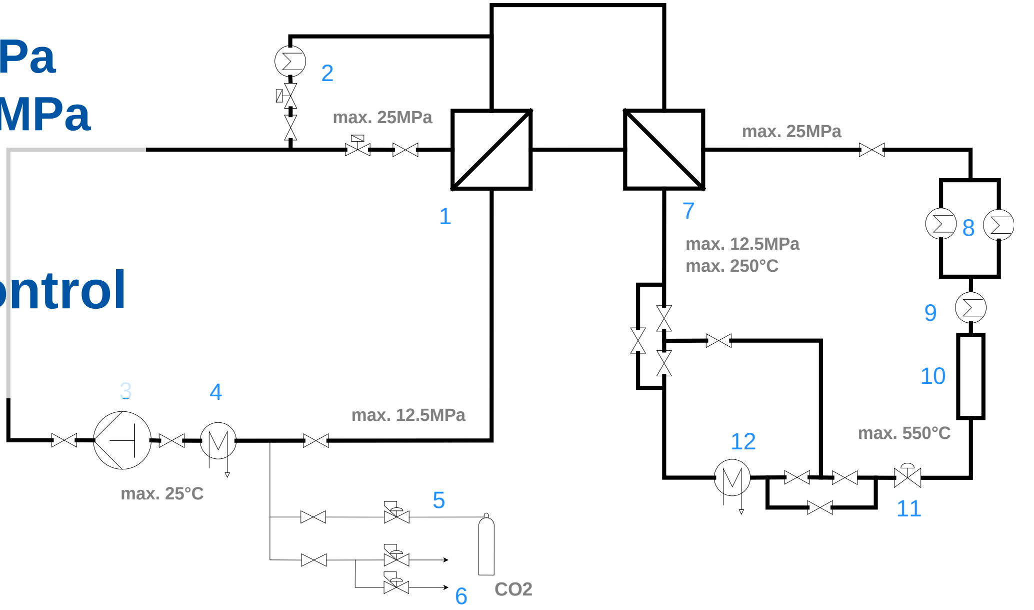


Analytical purity control system for sCO_2 loop

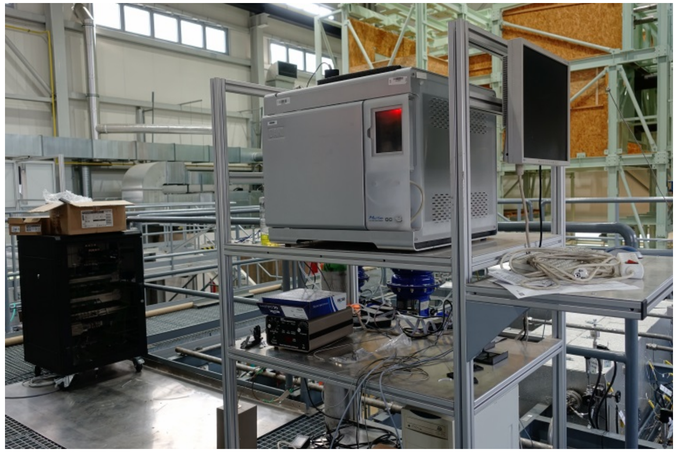
- GC-HID for H_2, CO, CH_4 and other simple compounds monitoring
- Optical hygrometer

Planned during 2021 - 2022

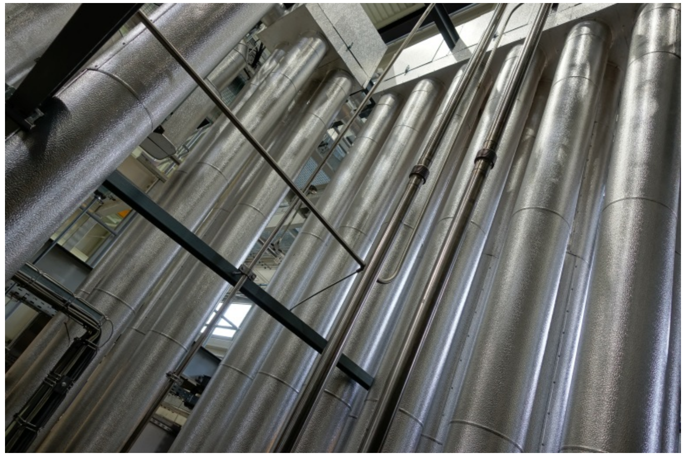
Max. temperature: 550 °C
Max. pressure in HP section: 25 MPa
Max. pressure in LP section: 12.5 MPa
Max. flow rate: 0.4 kg/s
Total volume: 80 l
No purification and purity control implemented yet

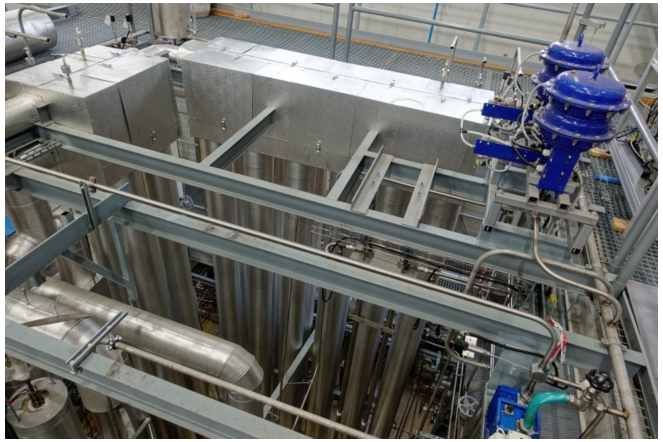


The sCO2 experimental loop. 1: low temperature heat exchanger, 2: preheater, 3: main circulation pump, 4: cooler, 5: CO2 dosing system, 6: sampling system, 7: high temperature heat exchanger, 8: parallel heaters, 9: heater, 10: test section, 11: reduction valve, 12: cooler



GC-HID prepared to assemble to sampling line

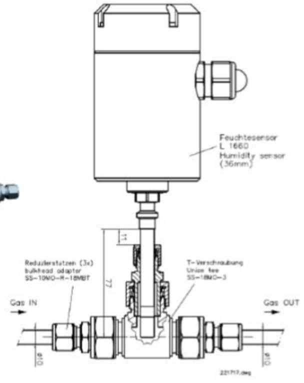




Optical hygrometer for on-line moisture monitoring

Planned during 2021 - 2022

- Optical hygrometer Bartec Hygrophil®
- Measurement based on of change of infrared light wavelength in dependence on moisture content
- Used in natural gas transportation
- In CV Rez used for H_2O monitoring in High Temperature Helium Loop – very good experience
- Detection limit 1 vppm
- Max. temperature 70 °C and pressure 20 MPa in the probe site



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Adaptation of Bartec Hygrophil® for sCO_2

- Special calibration needed
- Recommendation for reaching the accurate values of moisture content :
  - Temperature of CO_2 in the probe site: 10 – 40 °C
  - Pressure in the probe site: 1 – 50 bar (0.1 – 5 MPa)

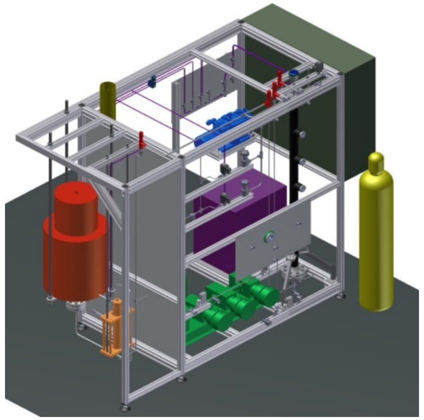
→

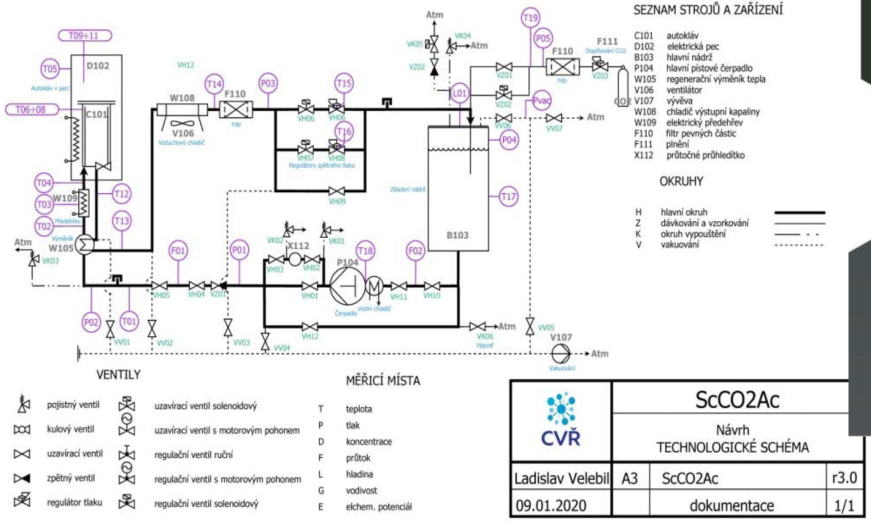
- The probe should be in the separate section parallel to the main circuit heated to 40 °C
- The pressure in the probe section should be reduced to 50 bar

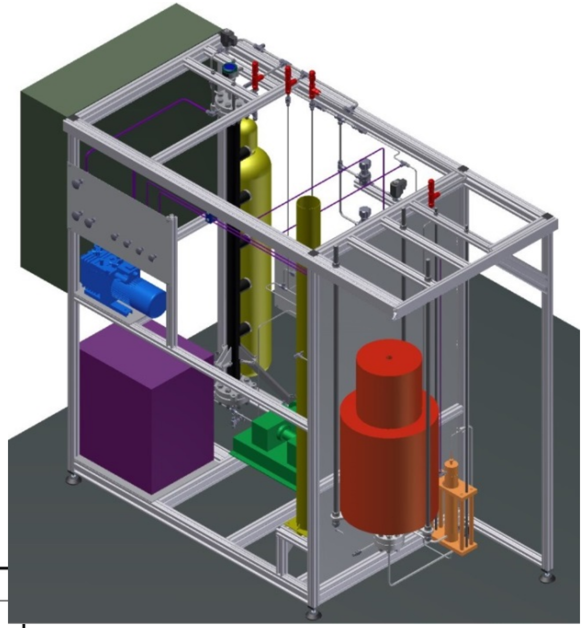
sCO_2 autoclave for material testing

Planned during 2021 - 2022

- Purpose: materials of purification units testing in sCO_2 environment
- Usable also for another purposes
- Parameters
  - Max. temperature: 700 °C
  - Max. pressure: 30 MPa







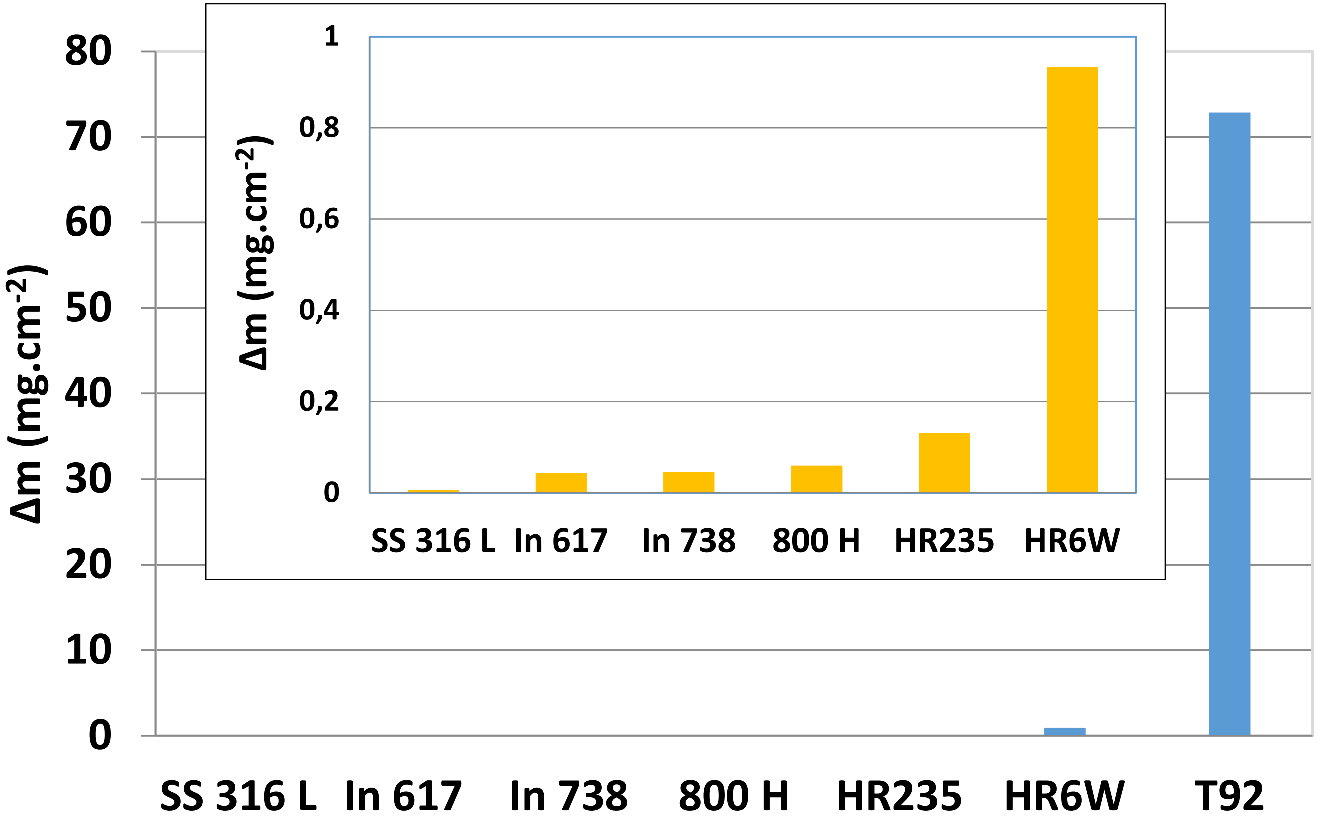
Test of material degradation

- Samples exposed during 1000 hours sCO_2 loop campaign
  - t = 550 °C
  - p = 25 MPa
- About 20 types of alloys assumed to be used in sCO_2 power cycles
- Examples:
  - Ferritic steel T92
  - Austenitic steel: 316L
  - Alloy 800 H
  - Nickel based alloys: HR6W, HR235, Inconel 738, Inconel 617

Selected results of material test

- The analyses of exposed samples (SEM-EDS, GD-OES, LOM…) are still in progress

Mass gains after exposure



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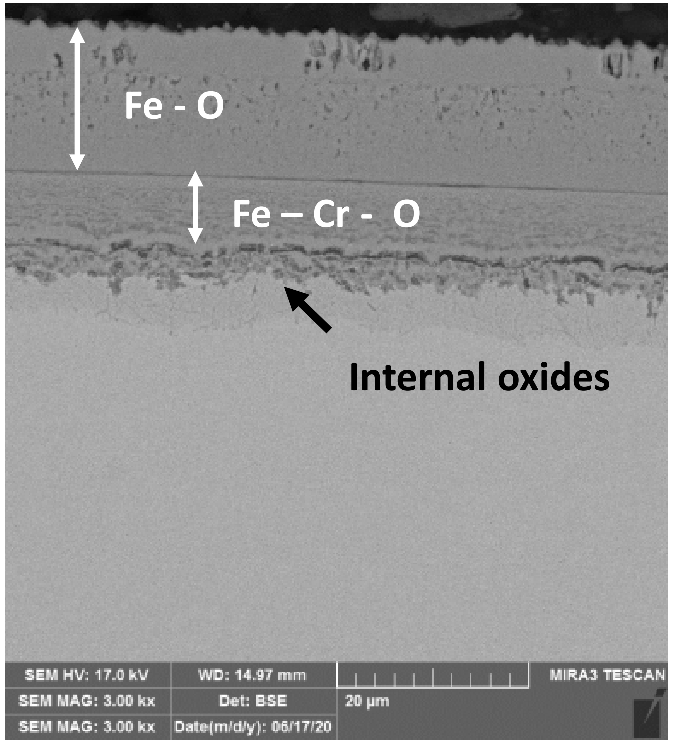
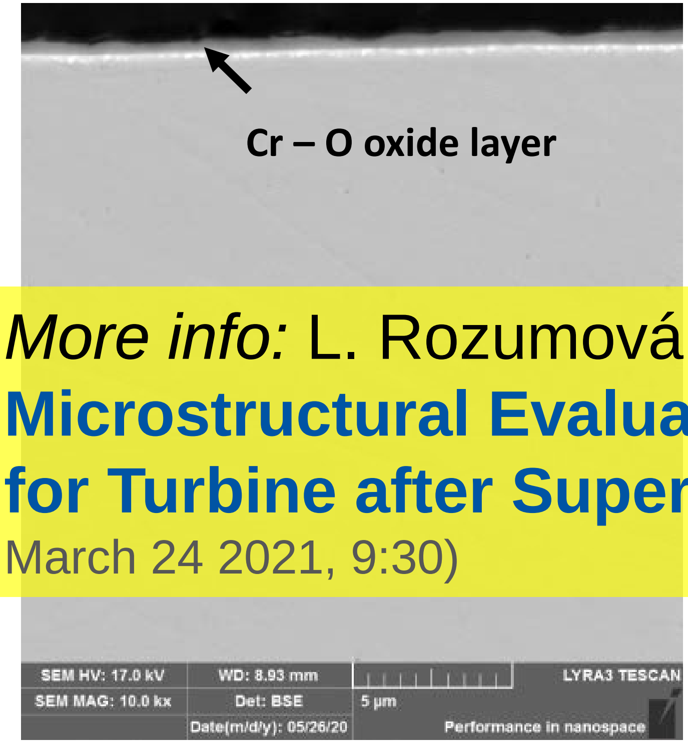
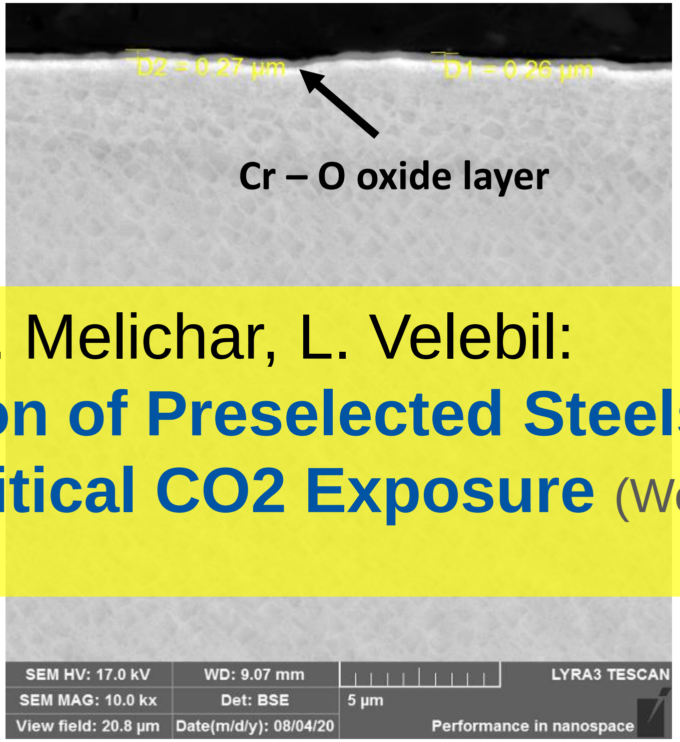
SEM cross section of exposed samples



T92



HR6W



Inconel 738

More info: L. Rozumová, T. Melichar, L. Velebil: **Microstructural Evaluation of Preselected Steels for Turbine after Supercritical CO2 Exposure** (We, March 24 2021, 9:30)

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Conclusion

- Research activities of Czech organizations are also focused on:
  - sCO_2 power cycle chemistry
  - Degradation of materials in sCO_2
- Objectives
  - Improve knowledge of sCO_2 purification and purity control
  - Purification and purity methods verification
  - Propose the purification and purity control system for sCO_2 power cycles
  - Gain experience on material degradation in sCO_2
- Activities started during last 2 years:
  - Impurities expected in sCO_2 medium
  - Available purification and purity control methods
  - 1000 h. material test in sCO_2 loop performed

Conclusion

- Activities planned in the next period
  - Verification of GC-HID and optical hygrometer for sCO2 purity control in experimental loop
  - Laboratory tests of selected impurities separation
  - Autoclave for material testing construction and operation

Contacts for questions

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