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I S T C
М Н Т Ц

# Progress Report on the ISTC project #3592 “Investigation of Corium Melt Interaction with NPP Reactor Vessel Steel” (METCOR-P)

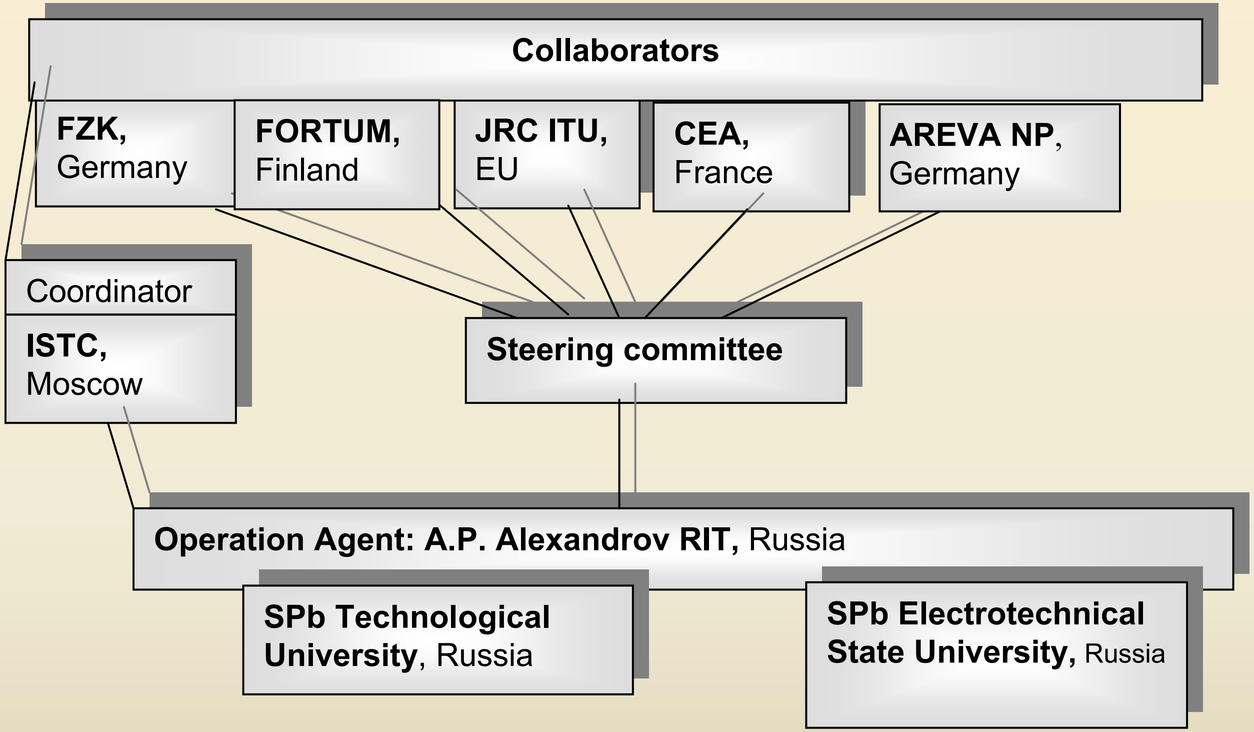
Presented by S. Bechta
17th CEG-SAM meeting
Madrid, Spain
March 29-31, 2010

# Contents

# METCOR-P project general information

## Investigation of Corium Melt Interaction with NPP Reactor Vessel Steel (#3592 METCOR-P)

## Project participants and coordination



**Collaborators**

**FZK,** Germany

**FORTUM,** Finland

**JRC ITU,** EU

**CEA,** France

**AREVA NP,** Germany

Coordinator

**ISTC,** Moscow

**Steering committee**

**Operation Agent: A.P. Alexandrov RIT,** Russia

**SPb Technological University**, Russia

**SPb Electrotechnical State University,** Russia

| Project duration | 36 months |
|---|---|
| Financial party | Europe |
| Project status | Started in April 2007 |

# Objectives of METCOR-P project

**Qualification and quantification of physicochemical phenomena of corium melt interaction with reactor vessel steel with particular interest to:**

- Interaction characteristics at the vertically positioned interface
- Peculiarities of interaction with European vessel steel
- Corium melt oxidation transients

# Experimental matrix for METCOR-P project

| # | Item | Experimental conditions | | | Notes |
|---|---|---|---|---|---|
| | | Composition | Surface temperature, °C | Atmo-sphere | |
| 1 | Interaction at vertically positioned interface | $UO_2$-$ZrO_2$ C100 | 1400 (Steel) | Ar | Reference-test * |
| | | $UO_2$-$ZrO_2$-Zr C30 | | | MCP1: MC6 conditions |
| | | Fe-U-Zr-Cr-Ni-O | | | Metallic phase of the melt enriched with U and Zr |
| 2 | Interaction at molten corium oxidation transients | $UO_2$ - $ZrO_2$-Zr C30 with vessel steel specimen | | Ar steam | 10-hour exposure in Ar until the interaction stabilizes. Replacement of Ar with steam after it |
| | | $UO_2$-$ZrO_2$-Zr C30 without vessel steel specimen | 2500 (Melt) | | The oxidic melt is in contact with a calorimeter |
| | | Fe-U-Zr-Cr-Ni-O without vessel steel specimen | | | Molten metal enriched with U and Zr is in contact with a calorimeter |
| 3 | Interaction of molten corium with european vessel steel | $UO_2$-$ZrO_2$-Zr C30 | 1400 (Steel) | Ar | 20 MnMoNi5-5 steel – was provided by collaborators |
| | | $UO_{2+x}$-$ZrO_2$<br>$UO_{2+x}$-$ZrO_2$-$FeO_y$** | 1300 (Steel) | Air** | |

***) In accordance with the 1st project meeting decision it is replaced by MCP-2 test with $UO_{2+x}$– $ZrO_2$ corium in air and horizontal position of interface**

****) In accordance with a decision taken at the 3rd project meeting, the test was performed in air (instead of steam) and regimes with $UO_{2+x}$ - $ZrO_2$ - $FeO_y$ melt were added**

# Interaction of molten corium with European vessel steel in oxidizing atmosphere (air)

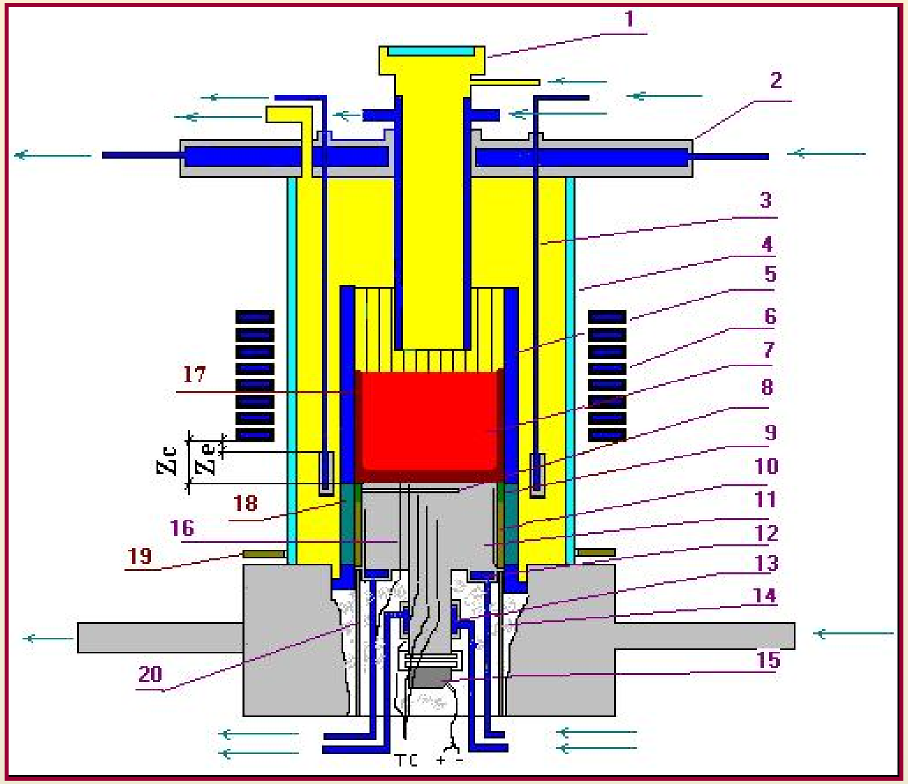
## TEST MCP-4

### Objectives

- Comparison of corrosion rates for the European and Russian vessel steels in the oxidizing atmosphere

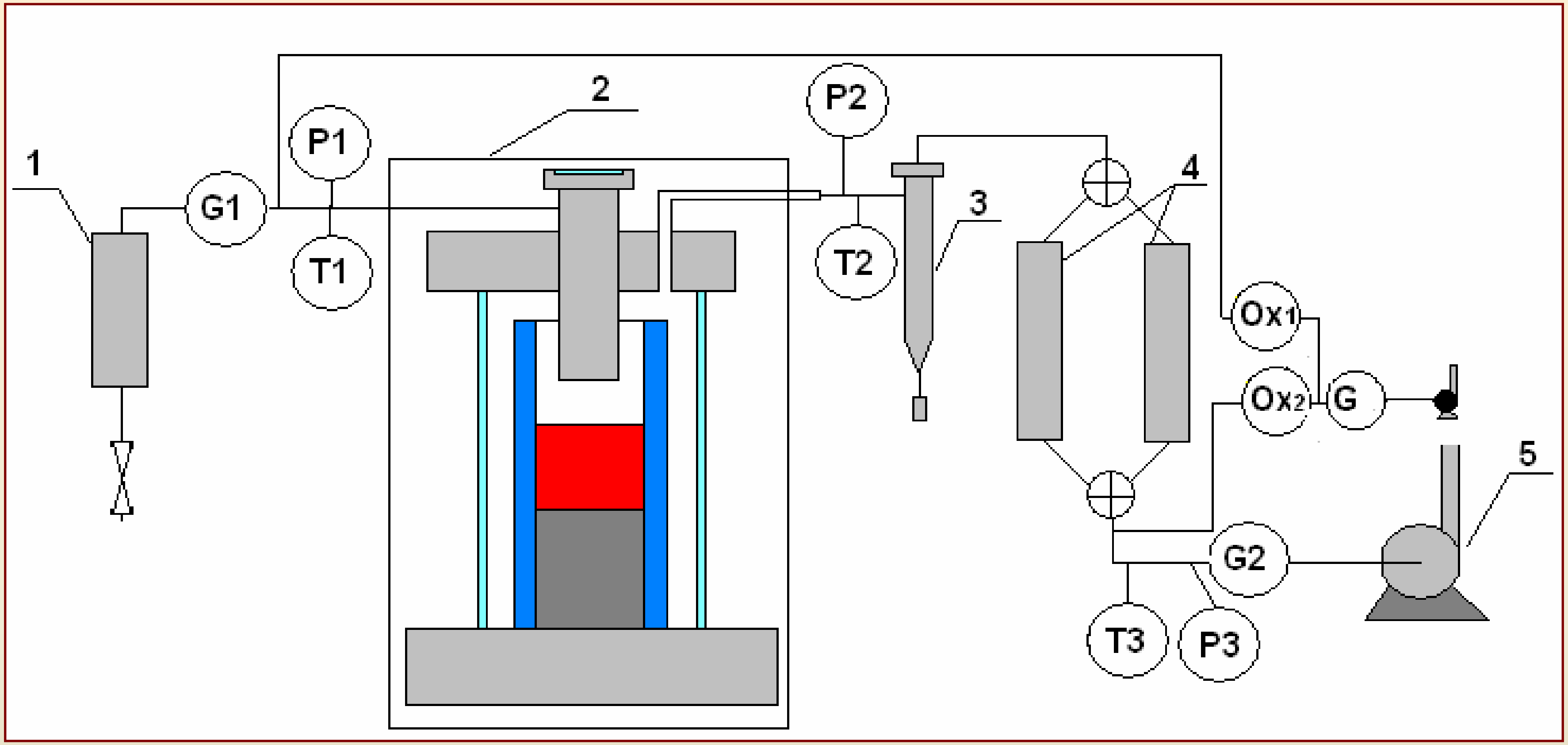
# RASPLAV-3 Installation

## Furnace schematics



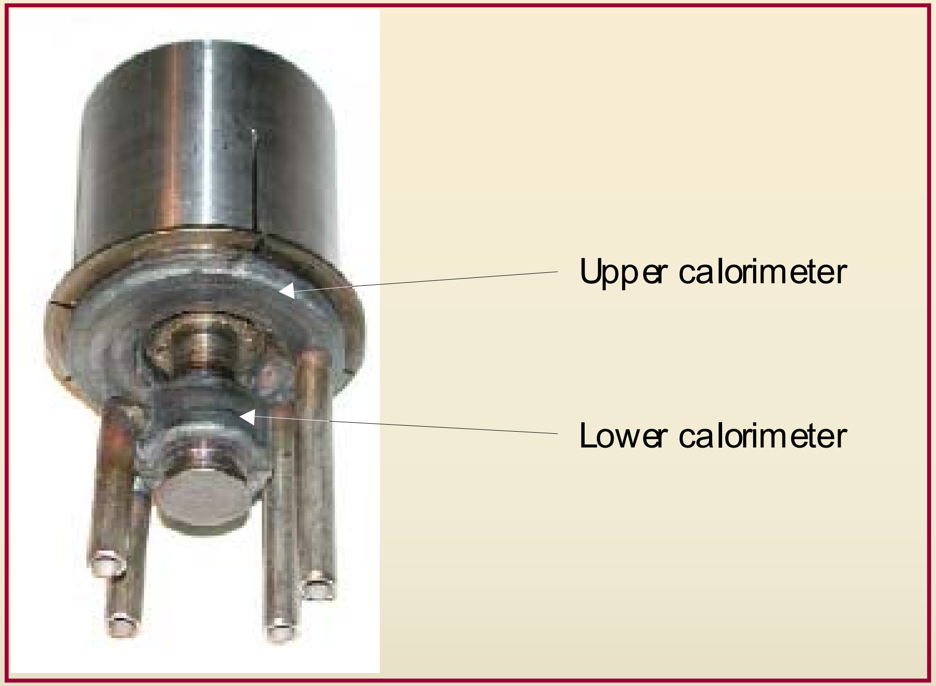
1 –pyrometer shaft; 2 –cover; 3 –electromagnetic screen; 4 – quartz tube; 5 – crucible section;
6 – inductor; 7 –melt; 8 – acoustic defect; 9 – molten $ZrO_2$; 10 –$ZrO_2$ powder thermal insulation;
11 – vessel steel specimen; 12 –upper calorimeter of the specimen;
13 – lower calorimeter of the specimen; 14 – kaolin wool insulation; 15 –ultrasonic sensor;
16 –thermocouples; 17 – crust, 18 – electromagnetic screen; 19 – uncooled electromagnetic screen;
20 – cylindrical support of the specimen

# Air supply and evacuation diagram



1 - silica gel dehumidifier; 2 - furnace; 3 – cyclone; 4 – large area filters (LAF); 5 - vacuum pump; P1-P3 – pressure transducers; G1,2 – flow transducers; T1-T3 – thermocouples; Ox- electrochemical oxygen sensor

# Vessel Steel Specimen



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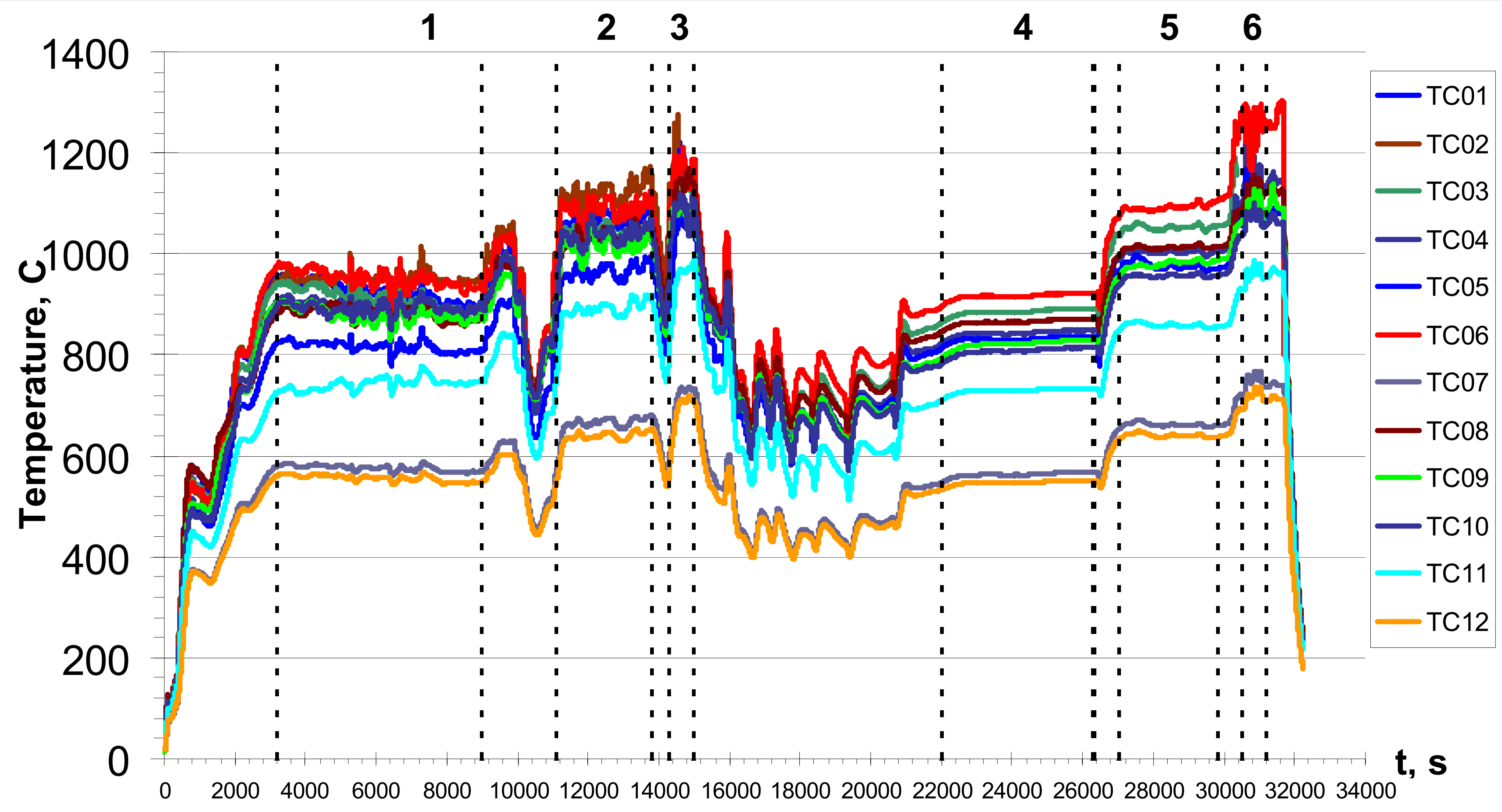
# Location of K-type thermocouples in the specimen

| Thermocouple № | TC 01 | TC 02 | TC 03 | TC 04 | TC 05 | TC 06 | TC 07 | TC 08 | TC 09 | TC 10 | TC 11 | TC 12 | TC 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Angle, α, degrees | 180 | 315 | 135 | 45 | 270 | 90 | 225 | 180 | 90 | 45 | 315 | 225 | 45 |
| Distance between the specimen axis and TC hot junction, mm | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 29.0 | 29.0 | 29.0 | 29.0 | 29.0 | 7.5 |
| Distance between the specimen top and TC hot junction, mm | 1 | 1 | 3 | 4 | 6 | 2 | 20 | 1 | 2 | 4 | 8 | 20 | 104 |

# Experimental procedure

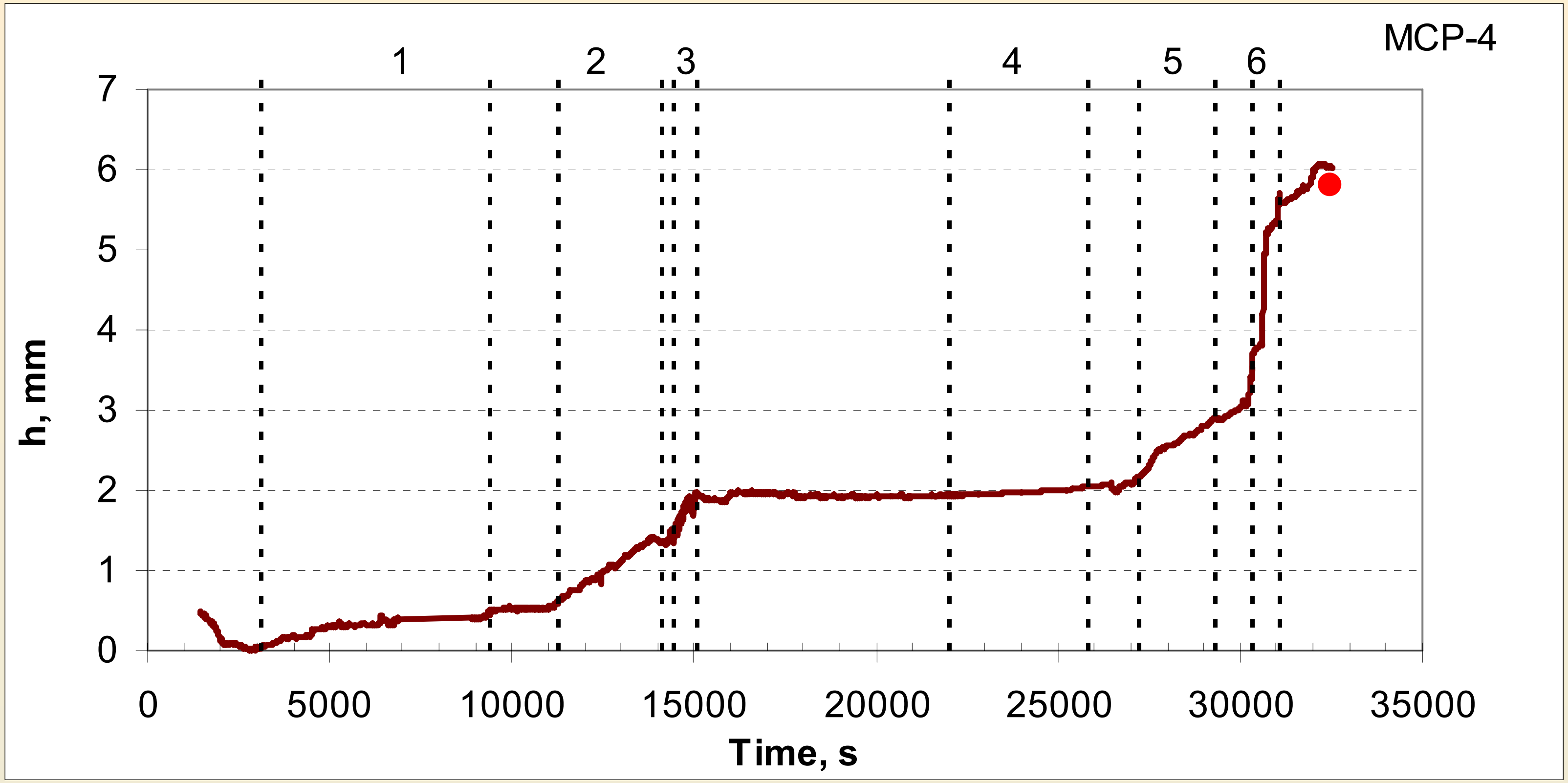
| Time, s | Description |
|---|---|
| 0 - 280 | Startup heatihg |
| 280 - 3470 | Molten pool $UO_{2+x}$-$ZrO_2$ is formed. Sample No.1 taken |
| 3470 - 9000 | The first temperature plateau. $T_{surf}$≈1000°C |
| 9000 - 11200 | Transition to the 2nd temperature plateau |
| 11200 - 13800 | The 2nd temperature plateau. $T_{surf}$≈1100°C |
| 13800 - 14400 | Transition to the 3rd temperature plateau. Sample No.2 taken |
| 14400 - 15000 | The 3rd temperature plateau. $T_{surf}$≈1200°C |
| 15000 - 23000 | Specimen temperature reduced. Fe added into the melt. Molten pool is exposed for added Fe oxidation and $UO_{2+x}$-$ZrO_2$-$FeO_y$ melt formation. Sample No.3 taken. Transition to the 4th temperature plateau |
| 23000 - 26400 | The 4th temperature plateau. $T_{surf}$≈900°C |
| 26400 - 27100 | Correcting amounts of $UO_2$ and $ZrO_2$ introduced. Sample No.4 taken. Transition to the 5th temperature plateau |
| 27100 - 30000 | The 5th temperature plateau. $T_{surf}$≈1100°C |
| 30000 - 30400 | Transition to the 6th temperature plateau |
| 30400 - 30900 | The 6th temperature plateau. $T_{surf}$≈1200°C |
| 30900 | Sample No.6 taken |
| 31690 | Inductor switched off |

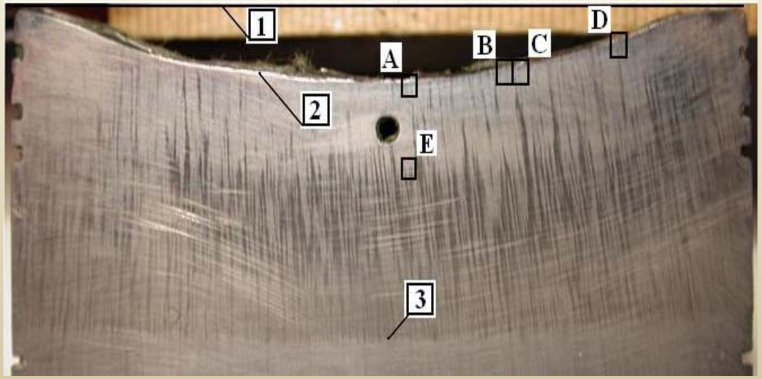
# Specimen temperature versus time



- **1, 2, 3 – $UO_{2+x}$- $ZrO_2$    4, 5, 6 - $UO_{2+x}$- $ZrO_2$- $FeO_y$**

# Corrosion depth measurements

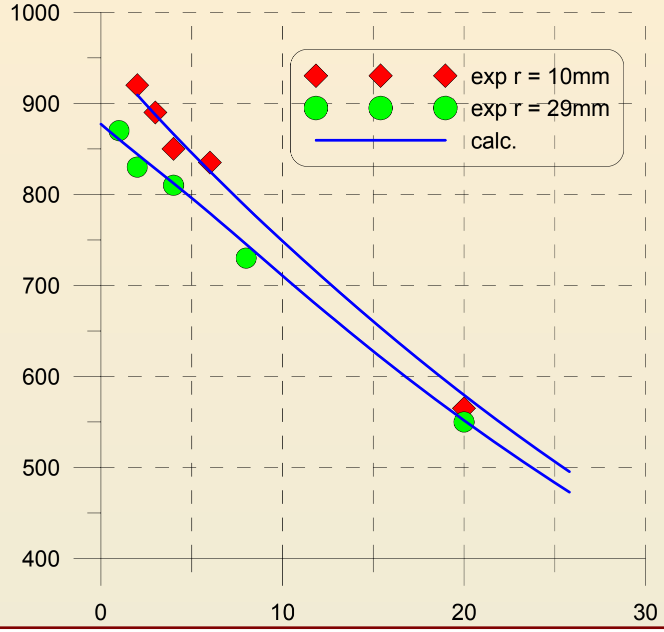


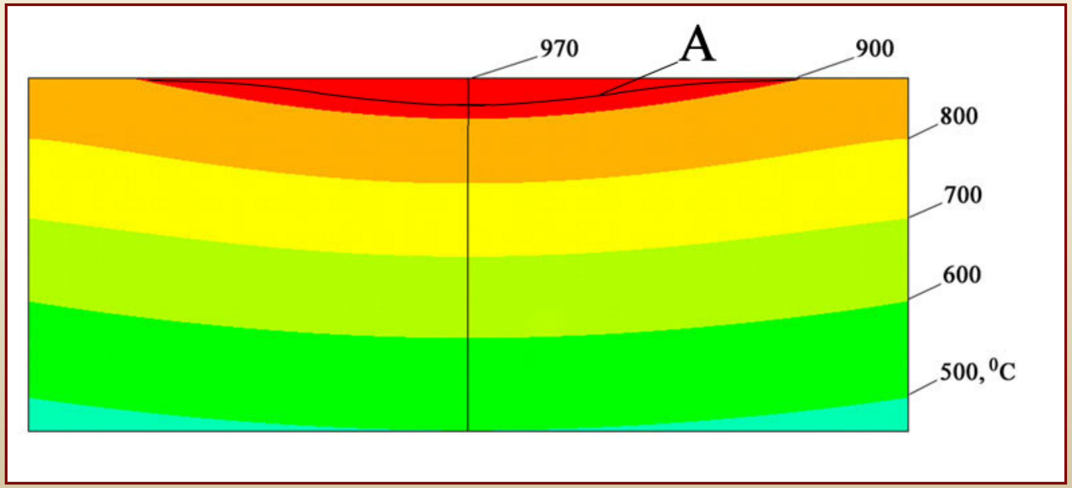


- — **US measurement**
- ● **– Post test measurement of specimen section**
- **The maximum corrosion depth was ~ 6 mm**
- **1, 2, 3 – $UO_{2+x}$ - $ZrO_2$**
- **4, 5, 6 – $UO_{2+x}$ - $ZrO_2$ - $FeO_y$**

# Processed experimental data

## Temperature profile and field in the specimen upper part (Reg. 4)

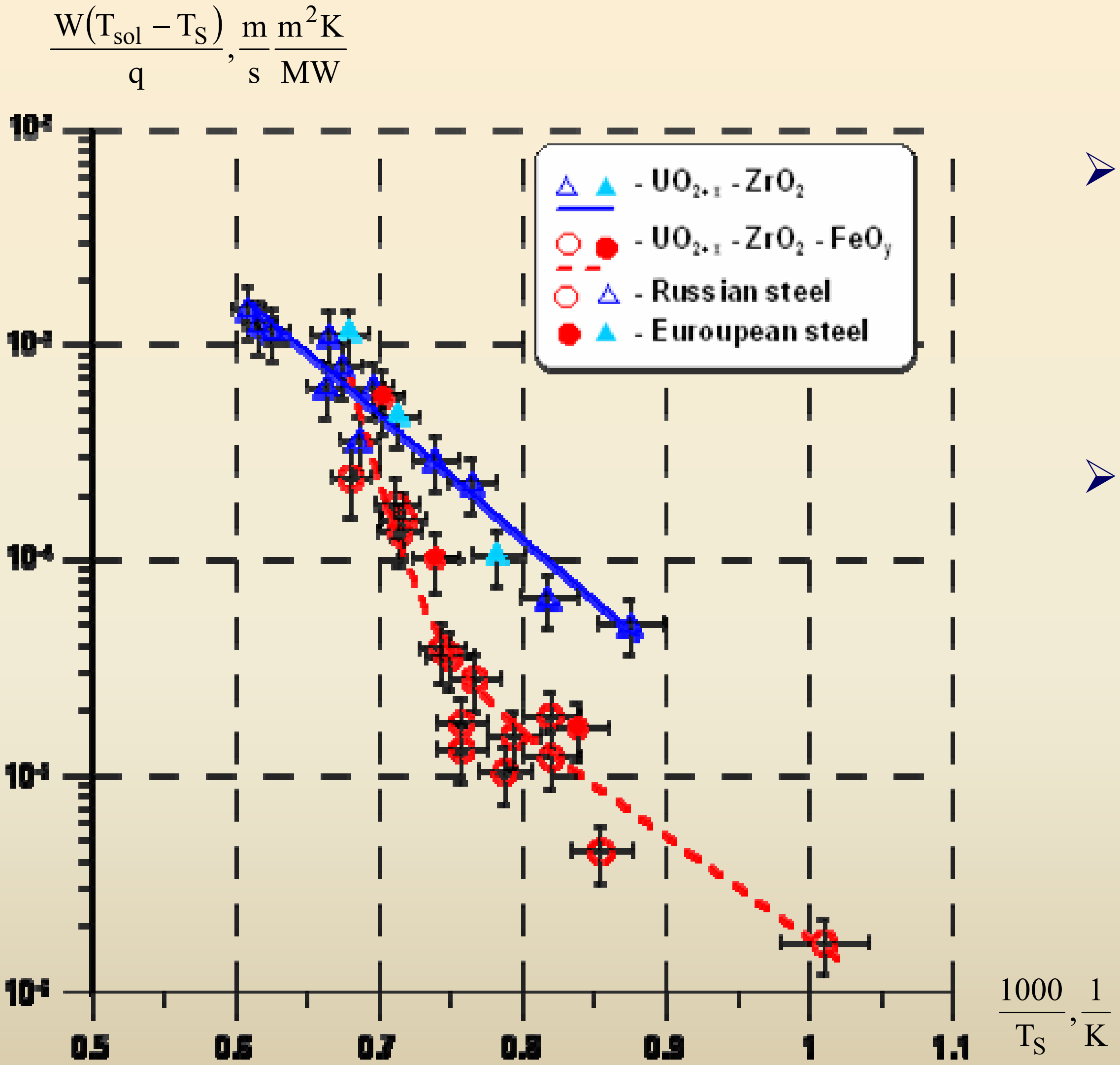




## Resulting data used in comparison

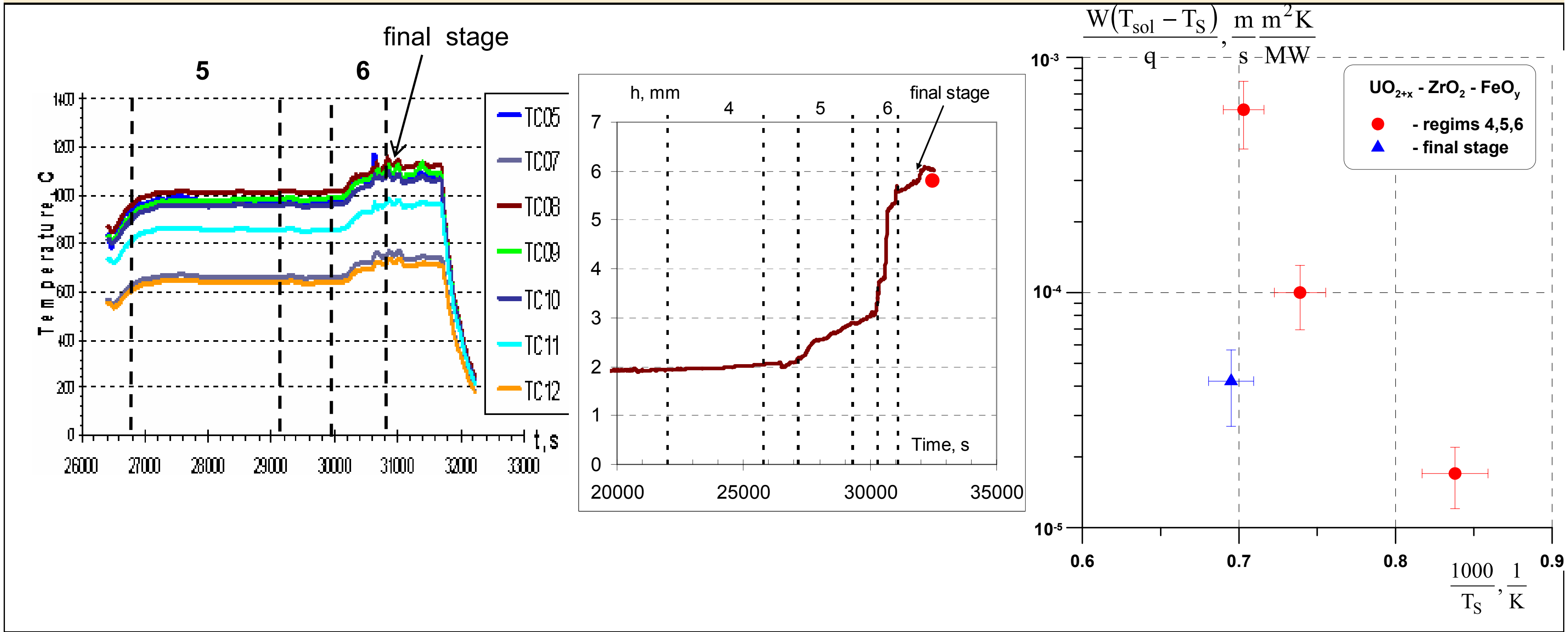
| Reg. # | Temperature of steel surface, $T_s$, °C | Heat flux, q, $MW/m^2$ | Corrosion rate, $W\times10^6$, m/s |
|---|---|---|---|
| 1 | 1005 | 0.77 | 0.056 |
| 2 | 1130 | 0.86 | 0.3 |
| 3 | 1200 | 0.91 | 0.81 |
| 4 | 920 | 0.71 | 0.028 |
| 5 | 1080 | 0.82 | 0.32 |
| 6 | 1150 | 1.0 | 3.0 |

# Comparison of corrosion rates for the European and Russian vessel steels



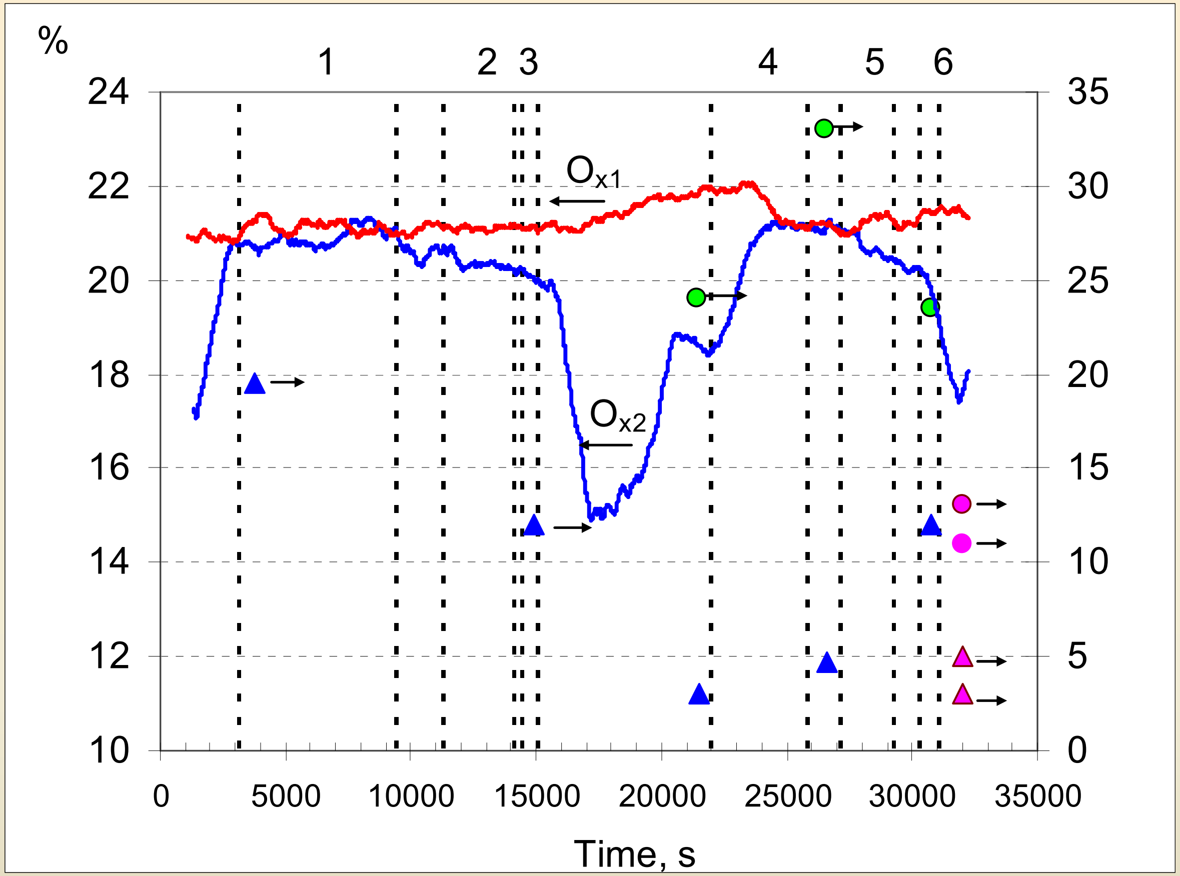
- ➢ **Difference in values for European and Russian steels is insignificant (in logarithmic coordinates)**
- ➢ **The data inventory for European steel is too limited to construct generalizing correlations**

# Specific features of corrosion at the final stage of experiment



- **Temperature on the interaction interface is the highest, it is close to the temperature of regime 6**
- **Corrosion rate is much smaller than in regime 6, it is close to regime 5**
- **Why?**

# Dynamics of oxygen concentration in the gas out and changes of melt oxygen potential versus time



- ➢ “Gas data” are measured with a delay due to the gas line transport and inertia of the gas bulk in the furnace volume
- ➢ Drop in the oxygen potential of the melt when heated steel has a high oxidation rate
- ➢ Lower corrosion rate at the final stage of experiment is explained by the insufficient air supply to the melt and by its decreased oxygen potential

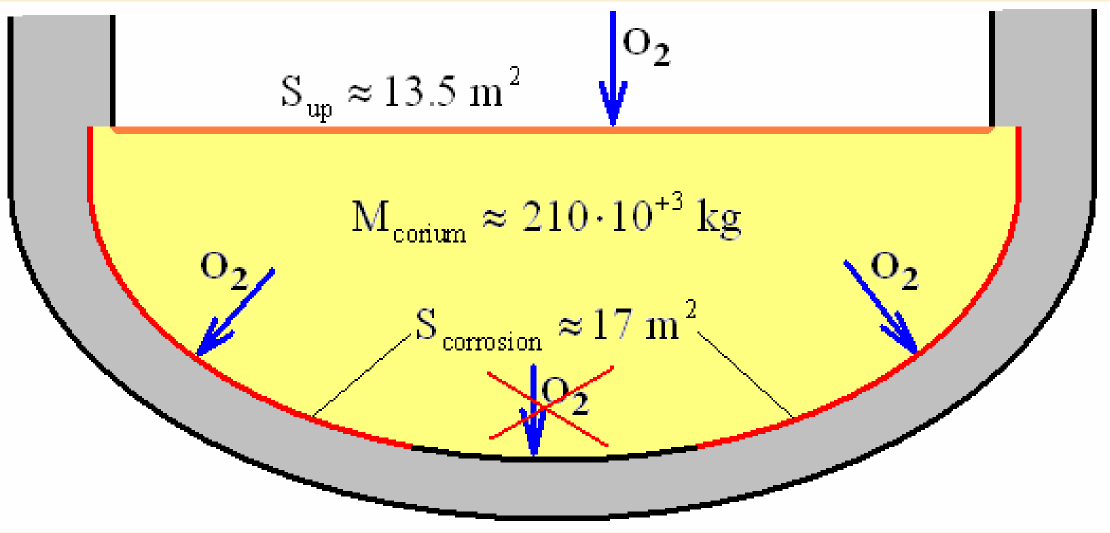
**$Ox_1$ – concentration of oxygen in**
**$Ox_2$ – concentration of oxygen out**

● ● – $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ▲▲– $U^{6+}/(U^{4+}+U^{6+})$

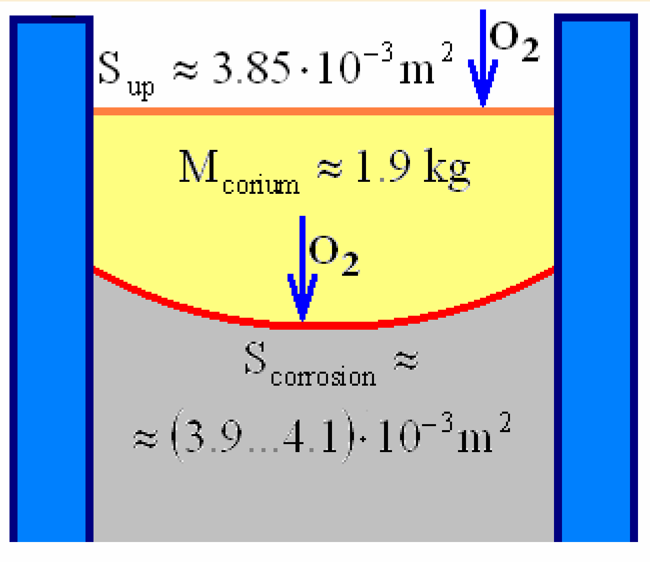
●▲– samples ●▲ – ingot

# Comparison of parameters influencing the oxygen balance in the VVER molten pool, METCOR tests

**VVER-1000**



**METCOR-P tests**



| Parameter | | VVER-1000 | METCOR-P tests |
|---|---|---|---|
| $M_{corium}/S_{corrosion}$ | kg/m² | 12 400 | 460…490 |
| $M_{corium}/S_{up}$ | | 15 600 | 494 |
| $S_{corrosion}/S_{up}$ | 1 | 1.26 | 1.01…1.06 |

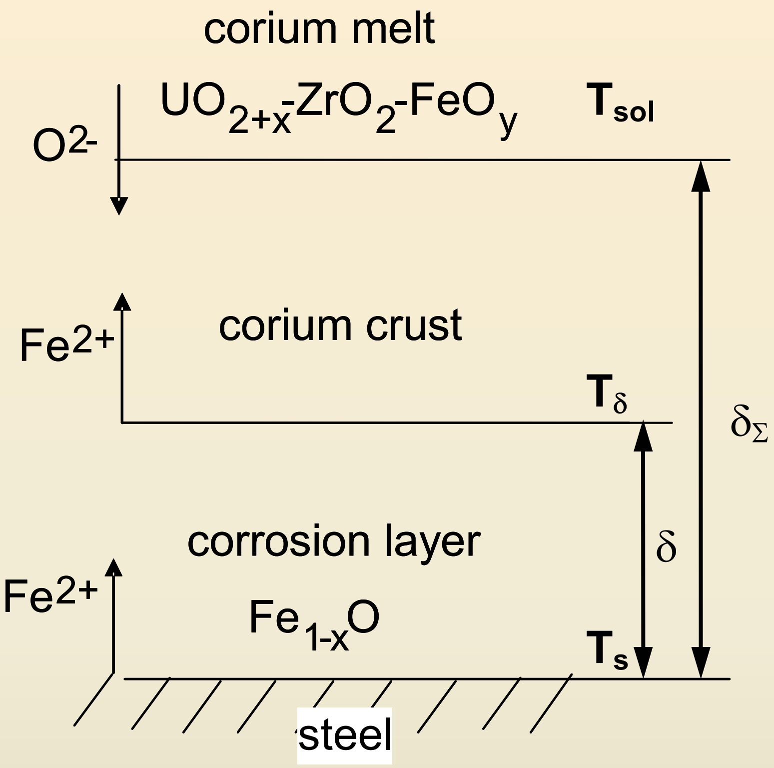
- ✓ The melt mass vs. corrosion area and the area of molten pool surface, through which the melt is oxidized, do not comply with the requirements for prototypic experimental conditions
- ✓ Oxygen potential of the melt on the vessel bottom is less sensitive to the vessel wall corrosion than in the tests

# Conclusions

- The data on European steel are too limited both for a decision about the applicability of correlations developed for VVER steel for describing EU steel corrosion, and for developing correlations specific for this steel
- In the final regime of MCP-3 the vessel steel corrosion rate was so high that the oxygen supply into the pool from air was insufficient for maintaining the steady oxygen potential in the melt. A decrease in the melt oxygen potential caused a slowdown of corrosion rate. It is necessary to check the influence of this effect at other regimes
- In order to determine the corrosion rate at a fixed oxygen potential of the melt we can recommend a higher flow rate of oxidant through the furnace, an increase in the melt mass and a smaller diameter of the steel specimen (crucible diameter being the same)

# Response to M. Veshchunov comments on the METCOR model of corium melt – steel interaction in the oxidizing atmosphere (16-th CEG-SAM Meeting)

# METCOR Model



corium melt

$UO_{2+x}$-$ZrO_2$-$FeO_y$ $T_{sol}$

$O^{2-}$

$Fe^{2+}$ corium crust

$T_\delta$

$\delta_\Sigma$

$\delta$

$Fe^{2+}$ corrosion layer

$Fe_{1-x}O$

$T_s$

steel

$\delta_\Sigma >> \delta$

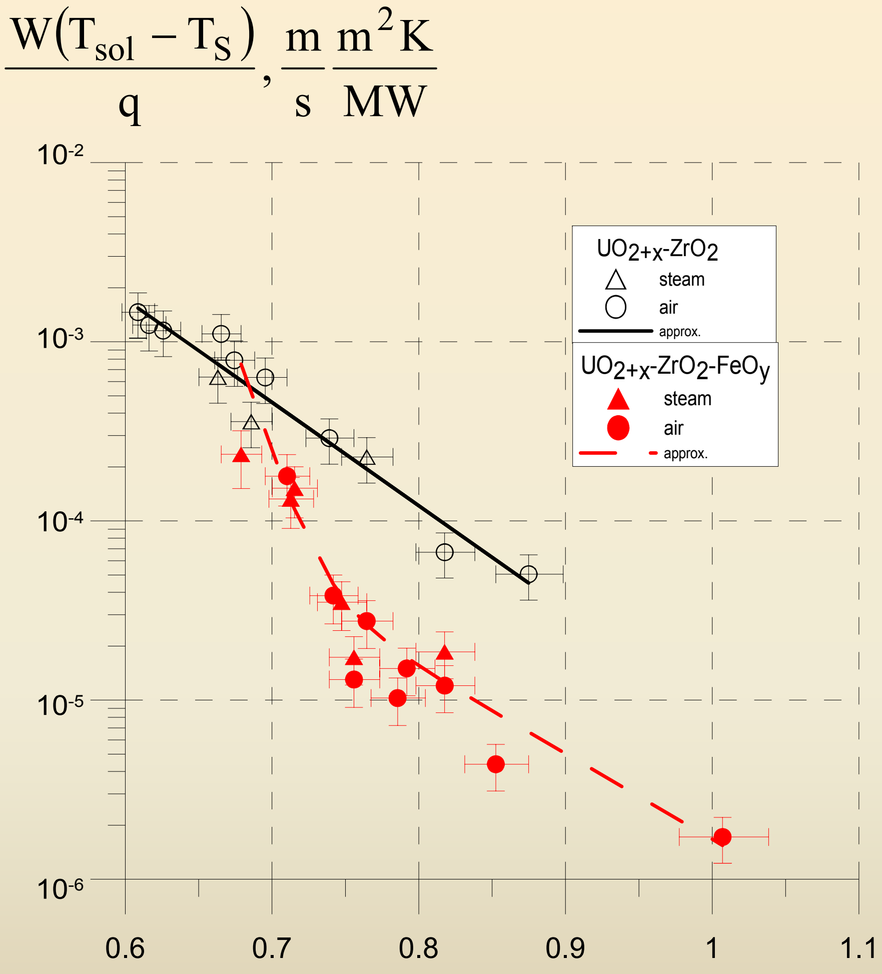
- Main diffusion resistance for $Fe^{2+}$ ions – corium crust on steel surface
- Crust thickness $\delta_\Sigma$ is determined by the heat conductivity equation; it does not change in time (at steady temperature on the corrosion front)

$$\delta_\Sigma = \frac{\lambda\left(T_S - T_{sol}\right)}{q}$$

- Corrosion rate is evaluated by Tamman equation:

$$W = A\exp\left(-\frac{E_a}{RT}\right)\frac{1}{\delta_\Sigma}$$

# METCOR Results



Diffusion coefficient D at T=800°C

$$D = \left(10^{0} \ldots 10^{-2}\right) \cdot \lambda \frac{W\left(T_s - T_{sol}\right)}{q},\ m^2/s$$

↓

Depends on $FeO_y$ concentration in molten corium

$UO_{2+x}$-$ZrO_2$-$FeO_y$: $D=(10^{-11} \ldots 10^{-9})$ $m^2/s$

$UO_{2+x}$-$ZrO_2$: $D \approx 10^{-10}$ $m^2/s$

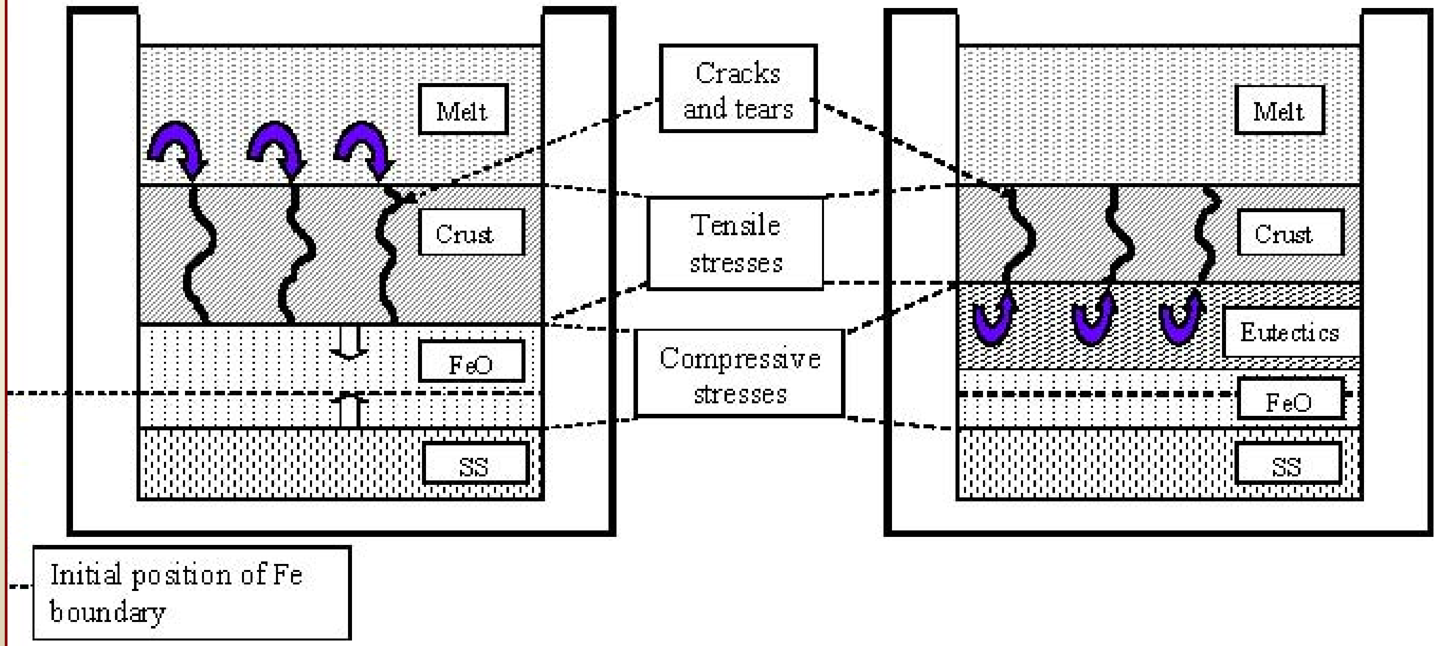
# Comments of M. Veshchunov

- **Coefficient of Fe diffusion in $ZrO_2$ at T=800°C**

  $D \approx 10^{-23}$ $m^2/s << D_{METCOR}$

- **Proposed alternative model**

- "Flowering" mechanism (2)



Low temperatures

High temperatures

# Response

- **Corium crust composition**

**For $UO_{2+x}$-$ZrO_2$-$FeO_y$ melt**

**$UO_{2+x}$~46, $ZrO_2$~40, $FeO_y$~14, mass.%**

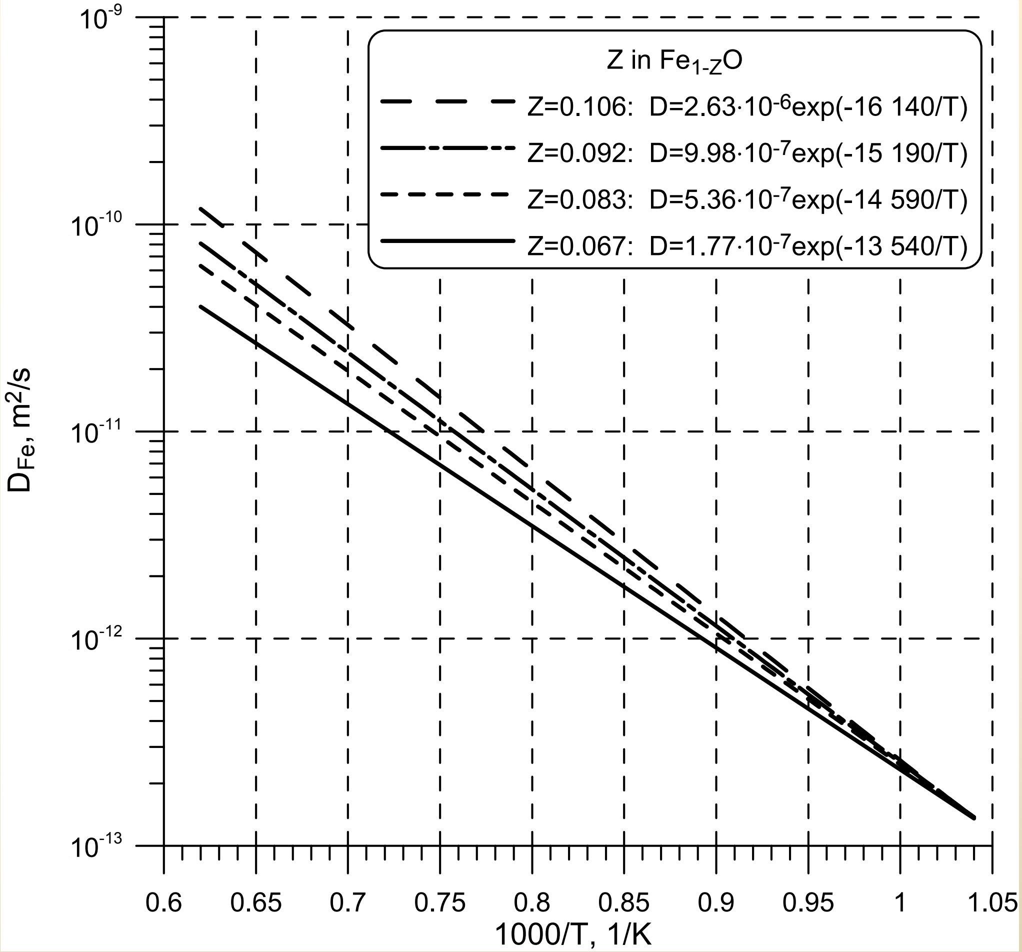
**For $UO_{2+x}$-$ZrO_2$ melt**

**$UO_{2+x}$~72, $ZrO_2$~ 28, mass.%**

- **$ZrO_2$ is not the main component in the corium composition. Consequently it does not determine the diffusion coefficient in the METCOR crust**

# Response (2)

## Coefficient of $Fe^{2+}$ diffusion in FeO



**Kofstad P., 1972. Nonstoichiometry. In: Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley-Interscience, New York.**

**At T=800°C $D \approx 10^{-12}\ m^2/s >> 10^{-23}$**

**But no data available on $Fe^{2+}$ diffusion in $UO_{2\pm x}$!**

# Response (3)

- The flat steel surface in METCOR does not produce a compressing impact on the FeO layer (differently from a cylindrical fuel rod)
- There are no reasons for stochastic (in time and space) generation of cracks in the crust (flowering)
- Even if the generation of cracks takes place, they are healed during the corium melt ingress by low local temperatures [see the dissertation of Yu. Petrov]
- In accordance with the Veschunov model a transition from “low” to “high” temperatures should always result in the qualitative changes of corrosion process. But this is not observed in case of $UO_{2+x}$-$ZrO_2$ corium

**Conclusion: No reasons for rejecting the METCOR model**

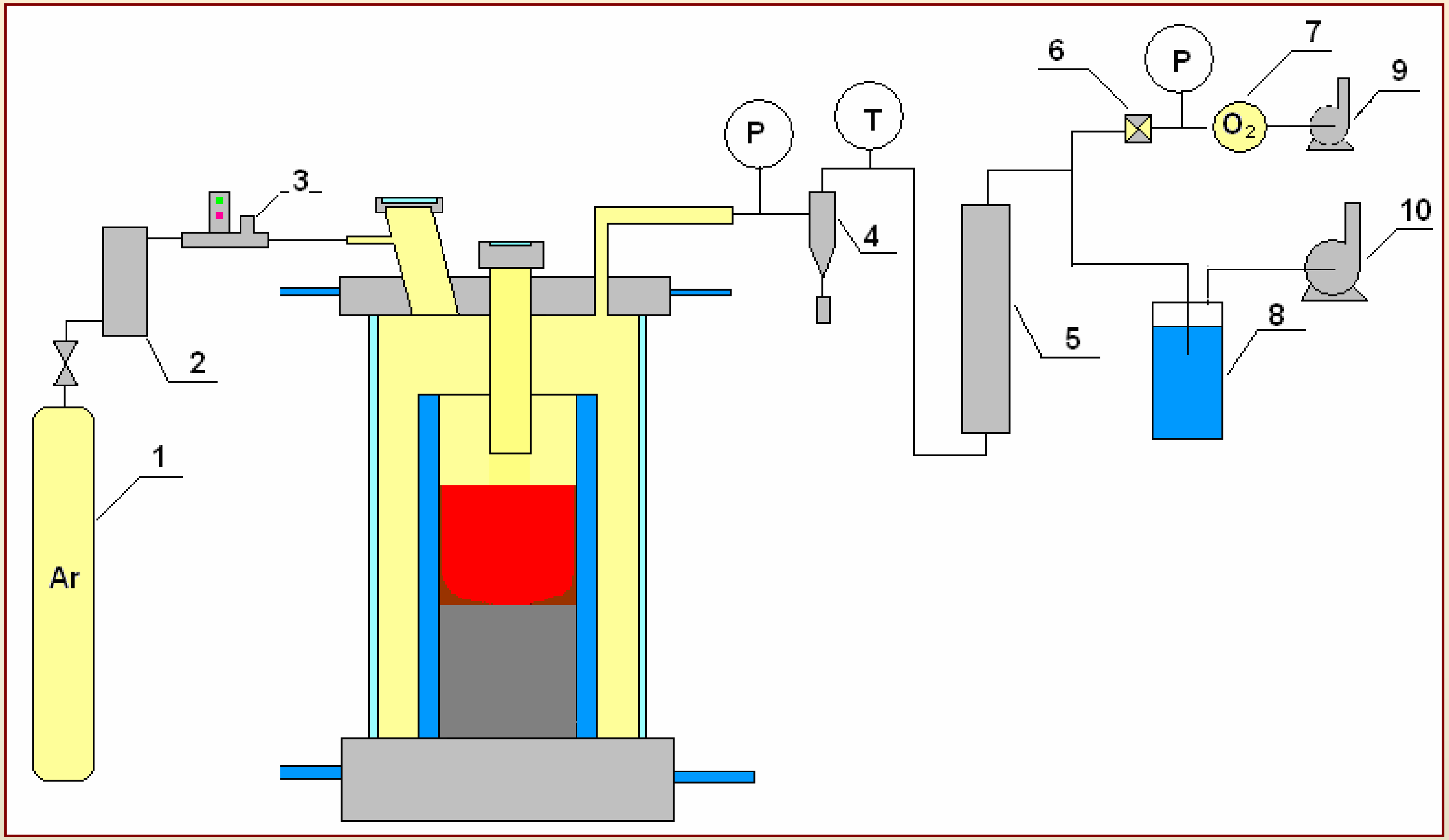
# Interaction of suboxidized molten corium with European vessel steel

## TEST MCP-5

### Objectives

- **Comparison of the corrosion rate and depth for European and Russian vessel steel at its interaction with suboxidized molten corium**

# Argon supply and gas-aerosol system

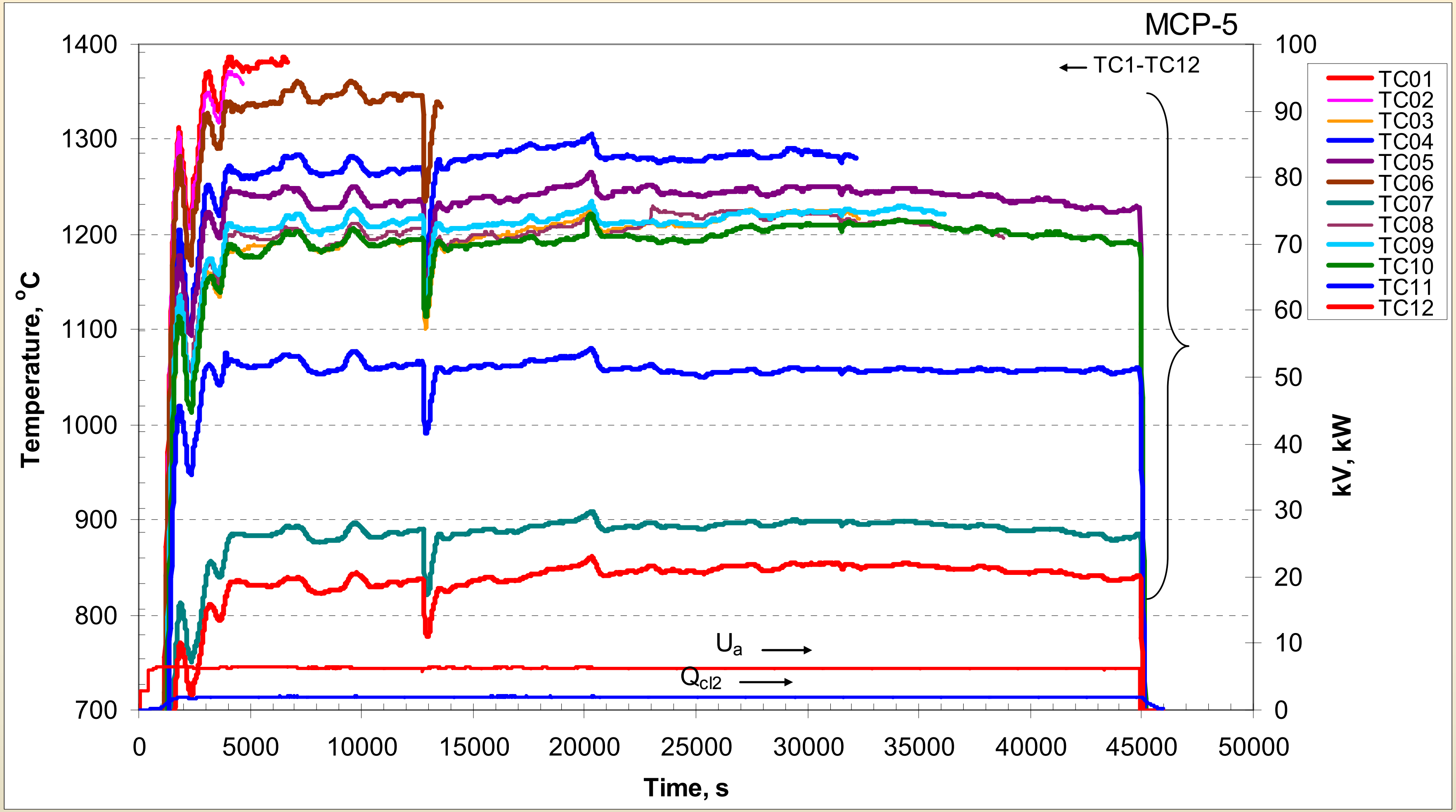


**1 – Ar tank; 2 – silica gel dehumidifier; 3 – flow-rate transducer; 4 – cyclone; 5 – LAF filter; 6 – AFA filter; 7 – electrochemical oxygen detector; 8 – hydro lock; 9,10 – vacuum pump**

# Experimental procedure

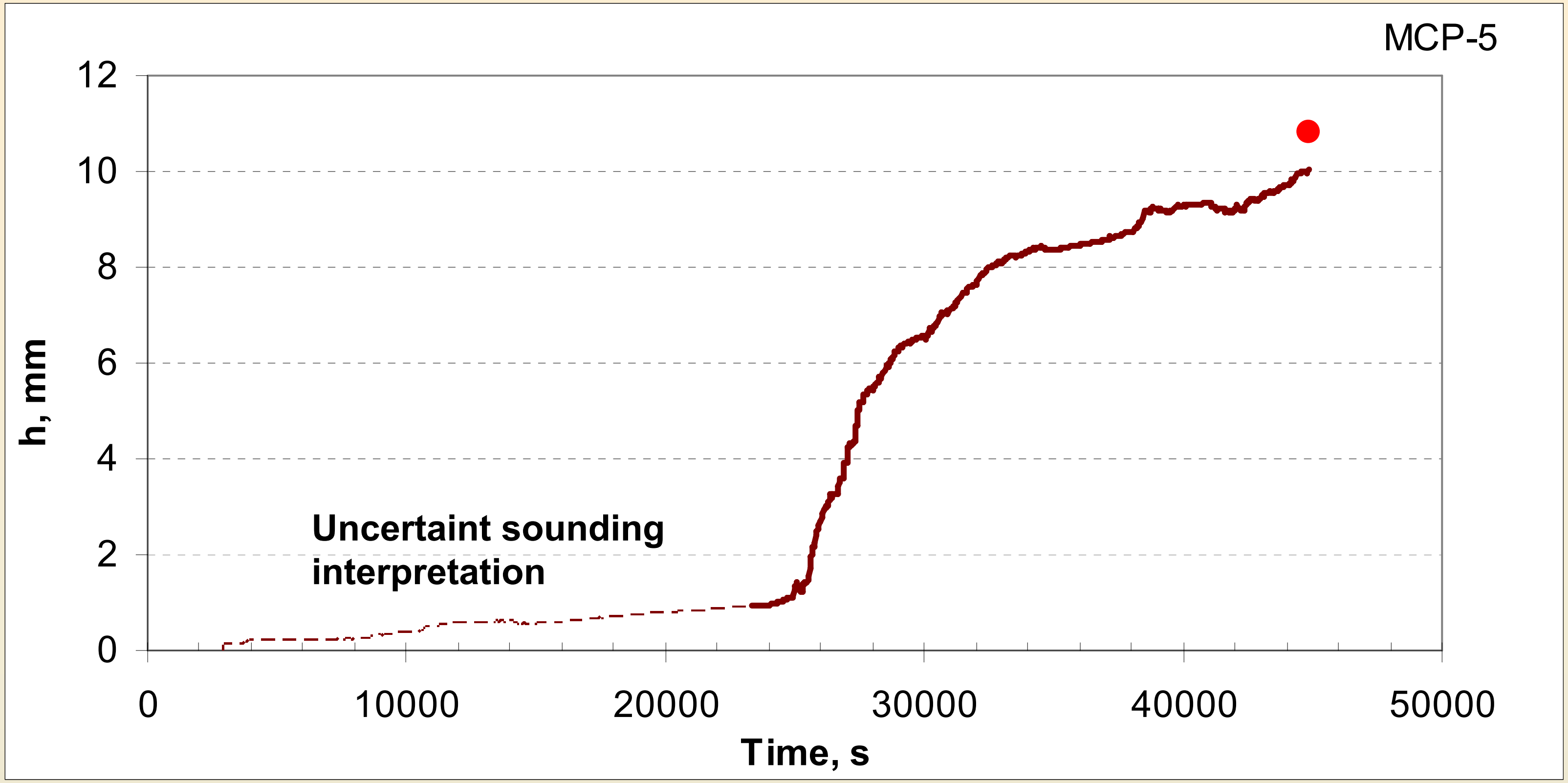
| Time, s | Description |
|---|---|
| 0 - 1870 | Startup heating in the argon atmosphere. Molten pool formation. First melt sample is taken. $T_{melt}$≈2400°C; $T_s$≈ 1300°C |
| 1870 - 2610 | $U_{ind}$ adjustment; the screen is shifted to get $T_s$≈1400°C. $T_{melt}$≈2400°C |
| 2610-44920 | Specimen temperature stabilization regime. Investigation of vessel steel corrosion kinetics at its interaction with corium through the crust in argon atmosphere. Large-area filter LAF-1 is replaced |
| 13000 | Automatic disconnection of HF heating, which was immediately reestablished |
| 13050 – 44920 | The temperature stabilization regime is in progress, it is monitored by the indications of operating thermocouples. Large-area filters LAF-2,3 are replaced. The second melt specimen is taken. |
| 44920 - 45200 | The generator is disconnected, the melt is cooled and frozen in the argon atmosphere |

# Specimen temperature versus time



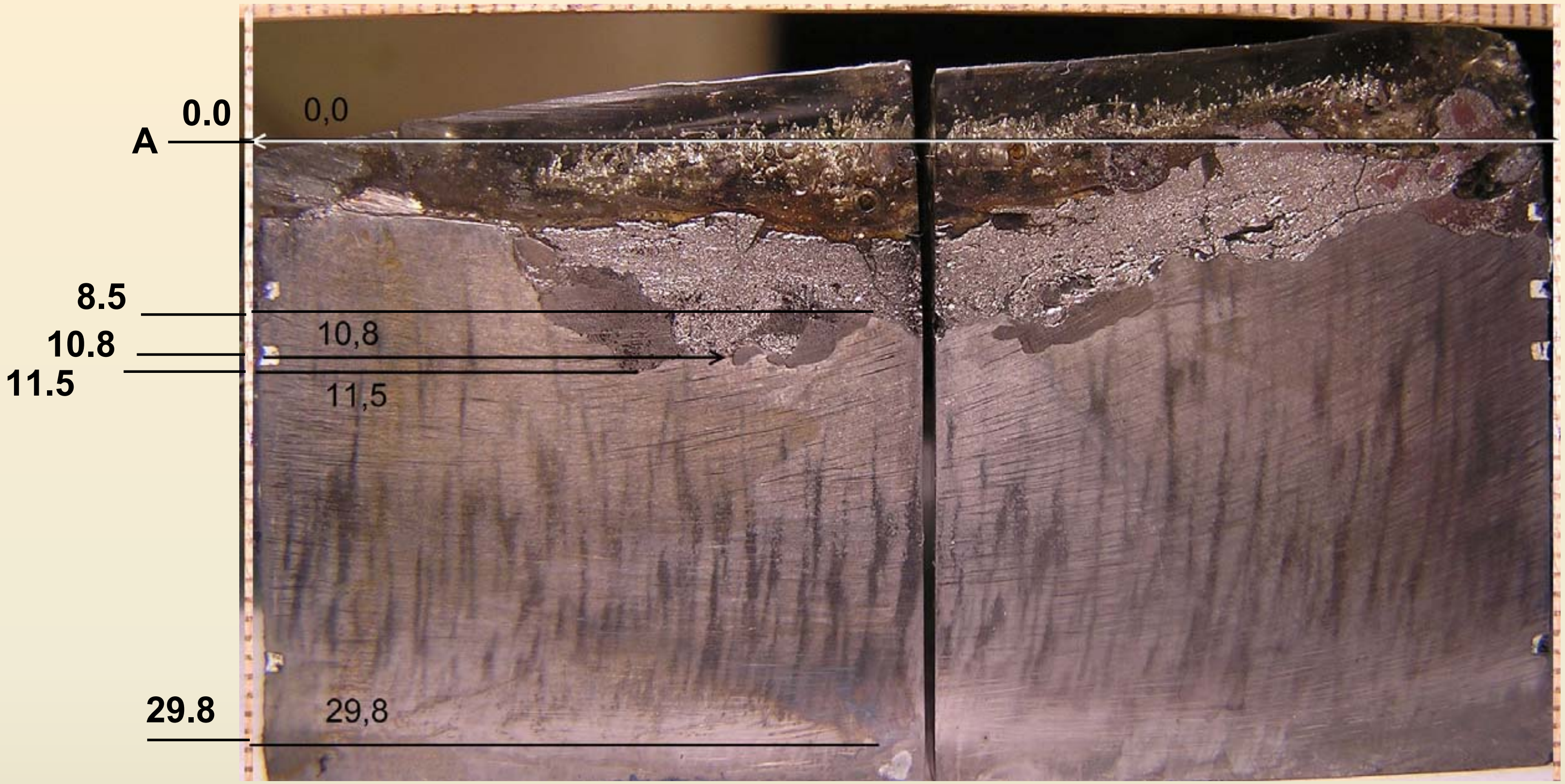
- ✓ Thermocouple readings in the plot are cut at times of TC breaks down due its corrosion caused by the impact of U-Zr-Fe melt
- ✓ As the heated top-level TCs break down, the stationary regime is controlled using the indications from of lower and cooler thermocouples

# Corrosion depth dynamics



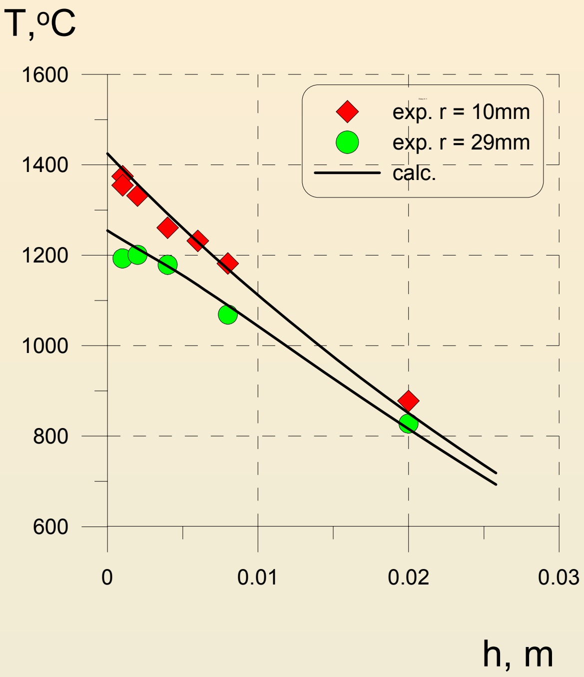
- ✓ Long incubation period - approximately 20 000 s
- ✓ Corrosion decreases as its front progresses into the specimen bulk – a lower-temperature region
- ✓ Difference in final depths determined by the US monitoring and by direct measurement in the axial section of the specimen

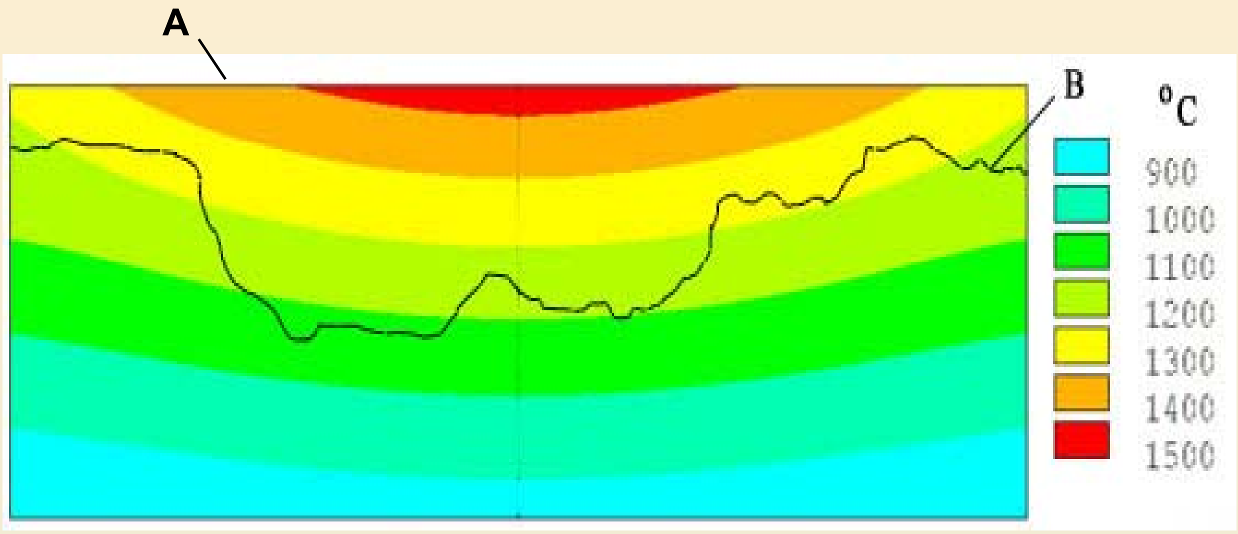
# Photograph of the specimen axial section



- ✓ The section plane and the ultrasonic defect axis are perpendicular
- ✓ A – initial position of the specimen surface
- ✓ Non-even boundary of the interaction zone
- ✓ 2 different structural components of the IZ, distinguished at the macrolevel

# Specimen temperature conditions





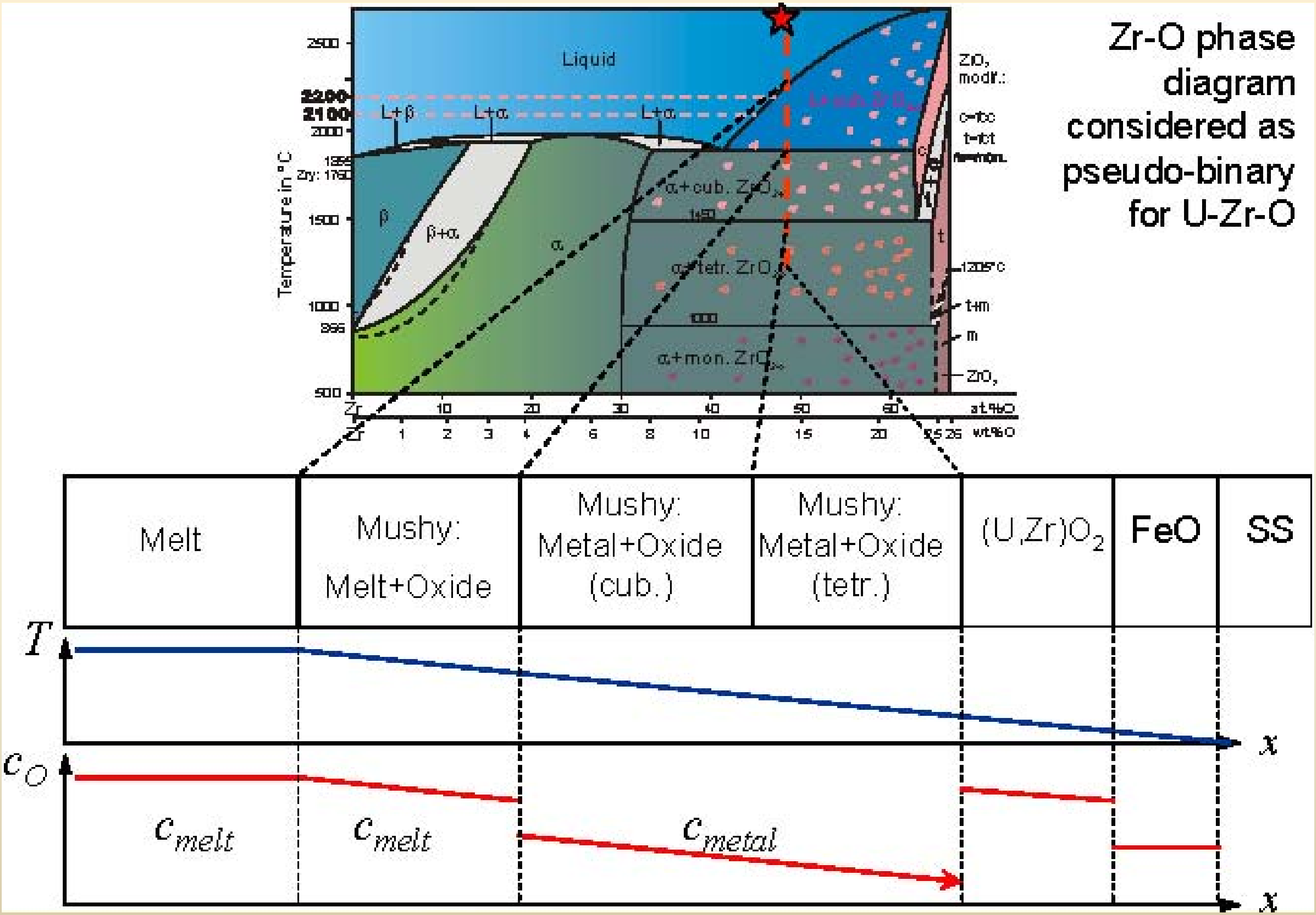
- ✓ Calculated by the ANSYS code using the measured boundary conditions and temperatures in certain points
- ✓ A – initial position of the specimen surface, B – final boundary of the interaction zone
- ✓ It follows from the figure that the final interaction zone boundary is in the 1150- 1250 °C temperature region

# First conclusions

- Corrosion kinetics in MCP-5 and MC6 tests are qualitatively similar and have incubation phase, transient to fast corrosion and saturation phase
- In comparison with MC6 the MCP-5 incubation period increased from 16000 s to 20000 s
- Differently from MC6 the final boundary of interaction zone is irregular (not smooth)
- The final position of the interaction zone boundary was found in the temperature range of 1150-1250 °C ( For comparison: MC6 – 1120…1200°C, MCP-5 – 1060…1250 °C)
- Posttest analysis is in progress

# Comments to M. Veshchunov model of suboxidized corium melt – steel Interaction (16-th CEG-SAM Meeting)

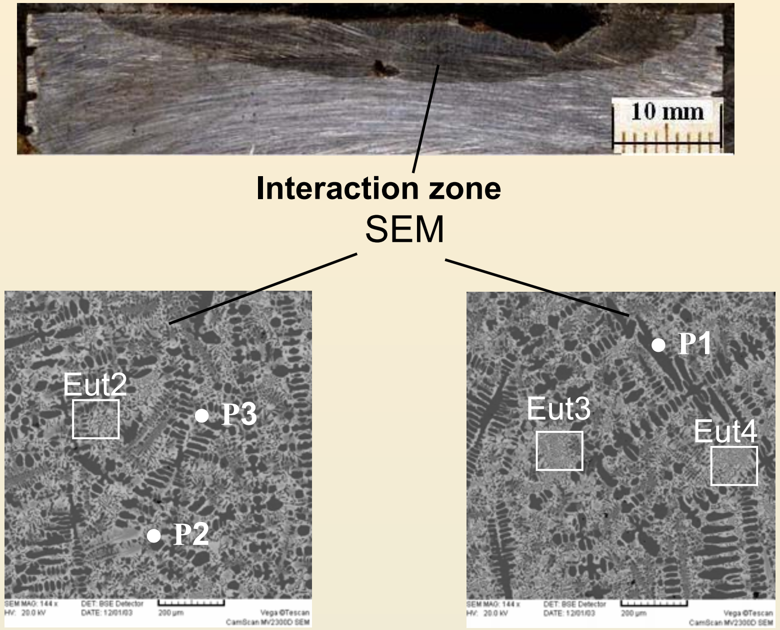
# Oxygen diffusion through mushy crust ($UO_2$+$ZrO_2$+Zr melt)



Zr-O phase diagram considered as pseudo-binary for U-Zr-O

# Comments

## Test MC6, corium C-30, (U, Zr)aт≈1.2



SQ3 SQ4

### EDX data

| # | | U | Zr | Fe | Cr | Ni | O |
|---|---|---|---|---|---|---|---|
| SQ3 (1×1 mm) | mass.% | 24.02 | 5.15 | 66.71 | 2.02 | 0.83 | 1.27 |
| SQ4 (1×1 mm) | mass.% | 23.56 | 4.79 | 67.08 | 2.21 | 0.8 | 1.56 |
| P1 | mass.% | - | - | 95.94 | 3.7 | - | 0.36 |
| P2 | mass.% | 22.57 | 22.09 | 51.79 | 0.64 | 1.06 | 1.85 |
| P3 | mass.% | 59.89 | 2.31 | 34.07 | - | 0.94 | 2.79 |
| Eut2 | mass.% | 35.63 | 2.55 | 57.54 | 1.41 | 1.1 | 1.77 |
| Eut3 | mass.% | 38.53 | 1.04 | 56.5 | 1.24 | 1.21 | 1.48 |
| Eut4 | mass.% | 37.94 | 1.29 | 56.77 | 1.24 | 1.11 | 1.65 |

- **In the Veschunov model the distribution of components does not reflect the real picture**
- **Corrosion of steel at its interaction with suboxidized corium melt is caused not by its oxidation, but by eutectic melting (dissolution) of steel**
- **Redistribution (repartitioning) of components, including oxygen, between the melt and interaction zone is similar to the components' repartitioning between oxidic and metallic melts (MASCA) with certain peculiarities explained by thermal gradient conditions**

Proc. of ICAPP′04, Paper 6054
Proc. of ICAPP′06, Paper 4114

# Planning

- According to the Experimental Matrix of the Project, 3 more tests are to be performed
- Participants' proposals concerning the remaining tests concretization and possible corrections to the Experimental Matrix have been discussed at the last, 3rd Meeting and by e-mails. Next test procedure will be distributed before the mid of April
- Due to a delay in Project implementation a 6-month project time extension without additional funding has been approved by the ISTC

# METCOR-P project reporting

| Report code | Title | Status |
|---|---|---|
| RMP- 01 | Interaction of molten corium with vertically positioned vessel steel specimen in the neutral atmosphere. Test MCP-1 | Done |
| RMP- 02 | Interaction of molten corium $UO_{2+x}$-$ZrO_2$ with horizontally positioned vessel steel specimen in the steam atmosphere. Test MCP-2 | |
| RMP- 03 | Interaction of suboxidized corium melt with steel at the replacement of neutral atmosphere by oxidizing atmosphere. Test MCP-3 | |
| F1-3592/2008 | Annual report on METCOR-P. First year | |
| F2-3592/2009 | Annual report on METCOR-P. Second year | |
| RMP- 04r | Interaction of molten corium with European vessel steel in oxidizing atmosphere. Test MCP-4 | Ready in Russian version |
| - | Interaction of suboxidized molten corium with European vessel steel. Test MCP-5 | In progress |

✓**First three reports have been sent to ITU under export control conditions**

# Publications during METCOR-P

1. Bechta S.V., Granovsky V.S., Khabensky V.B., Krushinov E.V., Vitol S.A., Sulatsky A.A., Gusarov V.V., Almjashev V.I., Lopukh D.B., Bottomley D., Fischer M., Piluso P., Miassoedov A., Tromm W., Altstadt E., Fichot F., Kymalainen O. Interaction between Molten Corium $UO_{2+x}$-$ZrO_2$-$FeO_y$ and VVER Vessel Steel // Proceeding of ICAPP'08, Anaheim, CA USA, June 8-12, 2008, Paper 8052.
2. Bechta S.V., Granovsky V.S., Khabensky V.B., Krushinov E.V., Vitol S.A., Sulatsky A.A., Gusarov V.V., Almjashev V.I., Mezentseva L.P., Krushinov E.V., Kotova S.Yu., Kosarevsky R.A., Barrachin M., Bottomley D., Fischer M., Fichot F. Corium Phase Equilibria from MASCA, METCOR and CORPHAD Results // Nucl. Eng. and Design, 238, p. 2761-2771 (2008).
3. Bechta S.V., Granovsky V.S., Khabensky V.B., Krushinov E.V., Vitol S.A., Sulatsky A.A., Gusarov V.V., Almjashev V.I., Lopukh D.B., Bottomley D., Fischer M., Piluso P., Miassoedov A., Tromm W., Altstadt E., Fichot F., Kymalainen O. VVER Vessel Steel Corrosion at Interaction with Molten Corium in Oxidizing Atmosphere // Nucl. Eng. and Design, 239 (2009), p. 1103-1112.

# Publications during METCOR-P (2)

4. Bechta S.V., Granovsky V.S., Khabensky V.B. et.al. VVER Steel Corrosion during In-Vessel Retention of Corium Melt // Proceeding of the 3rd European Review Meeting on Severe Accident Research (ERMSAR 2008), Paper 2.7, Nesseber, Bulgaria, September 23-25 (2008).
5. Bechta S.V., Granovsky V.S., Khabensky V.B. et.al. Interaction between Molten Corium $UO_{2+x}$-$ZrO_2$-$FeO_y$ and VVER Vessel Steel // J. Nucl. Technology, Vol. 170, №1 (2010), p. 210-218