Technical Meeting Compatibility Between Coolants and Materials for Fusion Facilities and Advanced Fission Reactors

Some Coolant Chemistry Issues for Corrosion Mitigation Strategy in Advanced Fission Reactors

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MEPhI NATIONAL RESEARCH NUCLEAR UNIVERSITY

Vienna 30 Oct. - 3 Nov. 2023

CONTENT

- ✓ Basic safety requirements and regulations to coolant chemistry at reactor units
- ✓ Materials/coolant interactions (chemistry's aspects)
- ✓ Principles for conduct of coolant chemistry
- ✓ Protective oxide films
  - Chemistry control strategy for HLMC
  - Chemistry control strategy for SCWR
- ✓ Conclusions

OBJECTIVE - SAFETY

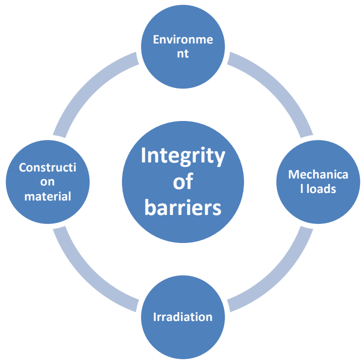
Safety philosophy [1)2)]**:** The chemical regime of advanced fission reactors should be developed and maintained in such a way as to ensure :

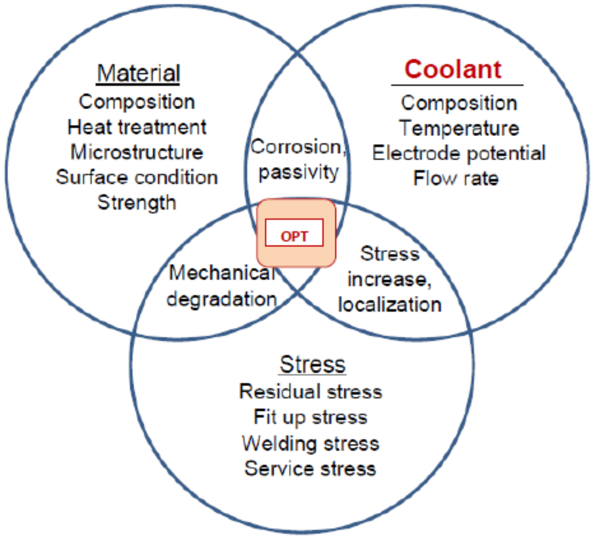
- ✓ **integrity of physical barriers** (fuel elements and the boundaries of the coolant circuit of the reactor) - the integrity of various barriers with respect to the potential for corrosion of components;
- ✓ **optimizing occupational radiation exposures** in the plant
- ✓ **limiting releases** of radioactive material and chemicals to the environment

1) Safety of Nuclear Power Plants: Design Specific Safety Requirements, IAEA Safety Standards Series No. SSR-2/1(Rev. 1), IAEA, Vienna (2016)
2) Safety of Nuclear Power Plants: Commissioning and Operation, IAEA Safety Standards Series No. SSR-2/2 (Rev. 1), IAEA, Vienna (2016)

Basic Regulatory Documents

General Requirements for Chemical Regimes of Advanced Fission Reactors





- ✓ Russian Federal **Rules and Regulations** in the field of nuclear energy establish a number of **requirements to chemistry** at NPP **for chemistry control**. :
- ✓ **NP-001-15 -** Basic Safety Rules for Nuclear Power Plants;
- ✓ **NP-082-07 -** Nuclear Safety Rules for Nuclear Plant Reactor Units;
- ✓ **NP-018-05 -** Requirements to the Content of Safety Analysis Report for Nuclear Power Plants with Reactors on Fast Neutrons;
- ✓ **NP-089-15 -** Rules for the Arrangement and Safe Operation of Equipment and Pipelines of Nuclear Power Plants.

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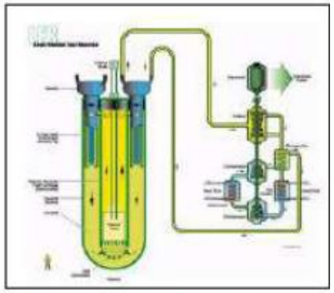
Basic Regulatory Documents

General Requirements for Chemical Regimes of Advanced Fission Reactors

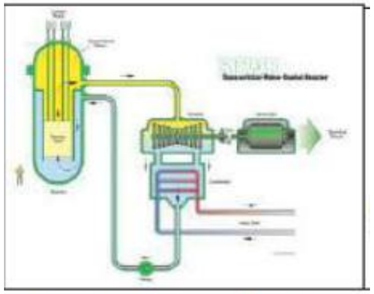
NP-001-15 - Basic Safety Rules of Nuclear Power Plants - the requirements of normative documents for Coolant chemistry **are of a general nature** and are limited to indications that:

(1) in design of NPP should be established (in Safety Analysis Report should be reflected) the **requirements to the chemical regimes** in the systems and elements of NPP, which should be observed during operation of NPP in order to maintain the integrity of physical barriers to the spread of ionizing radiation and radioactive substances into the environment (p. 3.1.19 of NP-001-15).

(2) in Technical Specifications of the NPP unit must be established **operational limits and conditions** for safe operation relating to **control of the chemical regime (**p. 4.1.3 of NP-001-15**)**



Lead-cooled Fast Reactor (LFR)



Supercritical Water cooled Reactor (SCWR)

New Regulatory Documents for Lead Cooled Reactor (BREST Reactor Design)

NP-107-21 was enacted on 08.06.2021
(Order of Rostechnadzor No.112 of 24.03.2021).
10 standards of the SC Rosatom within the series of standards for "***Ensuring integrity of the RPV, equipment, pipelines and reactor internals of the lead-cooled nuclear power installation***" were developed and put into effect in support of NP-107-21 and included into the summarized list of documents on standardization in the field of atomic energy use.

STO 95 12040…46, 50, 51, 54-2019

NP-108-21was enacted on 16.10.2021
(Order of Rostechnadzor No. 258 of 21.07.2021).
5 standards of the SC Rosatom within the series of standards for "***Ensuring integrity of the RPV, equipment, pipelines and reactor internals of the lead-cooled nuclear power installation***" were developed and put into effect in support of NP-108-21 and included into the summarized list of documents on standardization in the field of atomic energy use.

STO 95 12047…49, 52, 53-2019

New Regulatory Documents for Lead Cooled Reactor (BREST Reactor Design)

New federal rules and regulations in the field of the use of atomic energy and documents on standardization for fast neutron lead-cooled nuclear installations are to be developed in line with the plan approved by the State Corporation Rosatom and agreed with Rostechnadzor.

BREST-OD-300

Draft NP-119-XX is under development

4 standards of the SC Rosatom (within the series of standards "***Core elements of the lead-cooled reactor installation***") were developed and put into effect in support of NP-119-XX.

ФЕДЕРАЛЬНЫЕ НОРМЫ И ПРАВИЛА
в области использования атомной энергии

Требования
к обоснованию целостности активной зоны реакторной установки со свинцовым теплоносителем

НП-119-XX

STO 95 12076…79-2022

Basic Safety Requirements

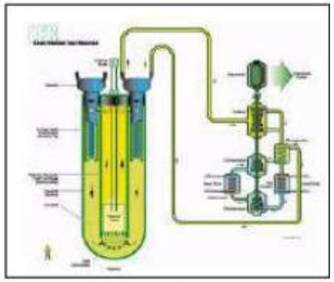
Chemistry requirements are set to minimize:

- corrosion (general, localized, erosion corrosion),
- fouling
- activity transport,
- optimize thermal performance,
- maximize component lifetime.

✓ Chemistry regime is achieved by system design, the use of chemical additives, and operational methods (e.g., purification).

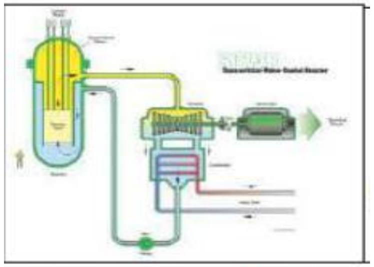
✓ The coolant is never absolutely pure liquid, but always contained chemical additives or contaminated by corrosion products, gases, salts etc.

✓ A key requirement of any chemistry control regime is that chemistry “control parameters” must be monitored and adjusted within a specified timeframe.



Lead-cooled Fast Reactor (LFR)

Pilot Demonstration Energy Complex with BREST-OD-300 Reactor

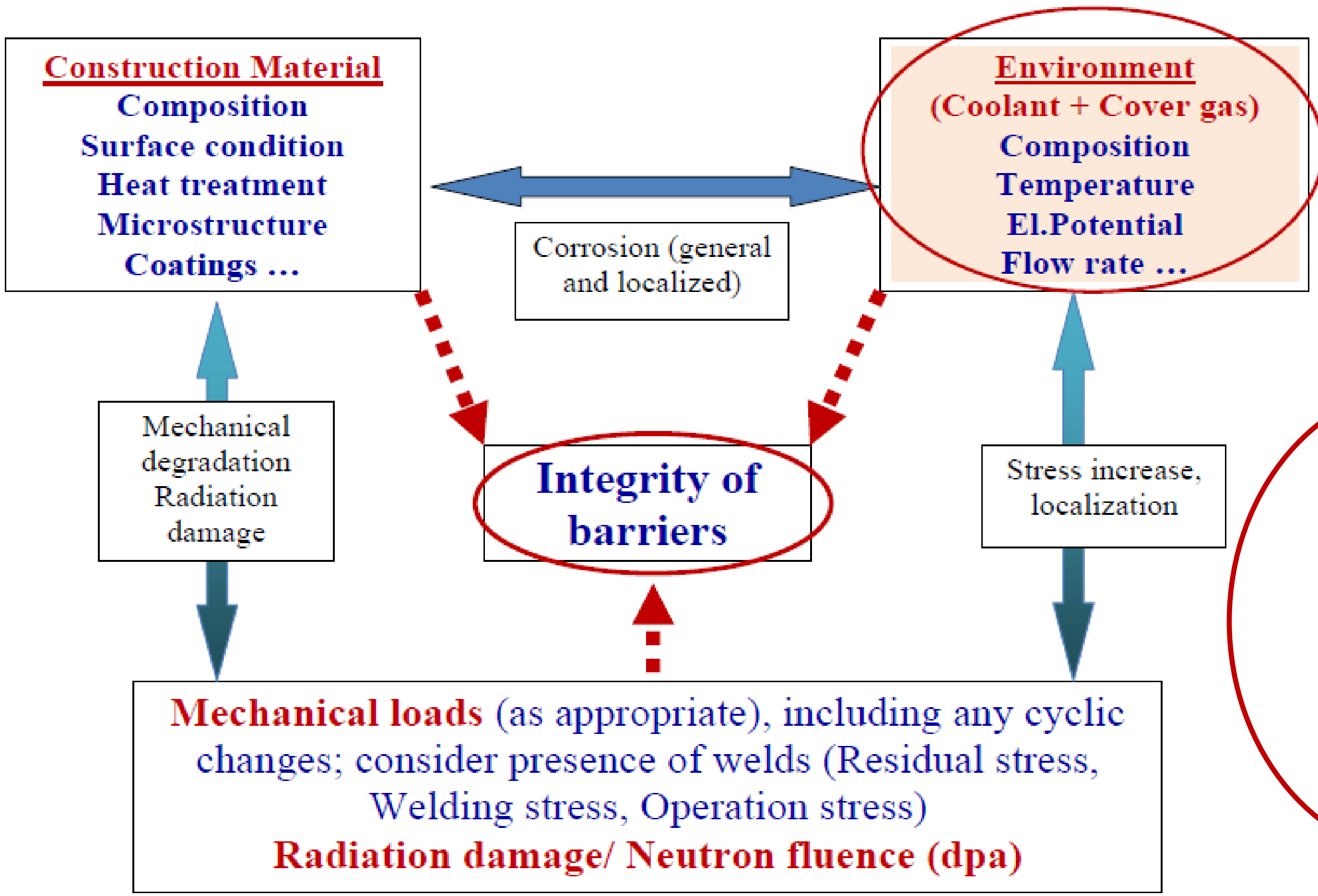


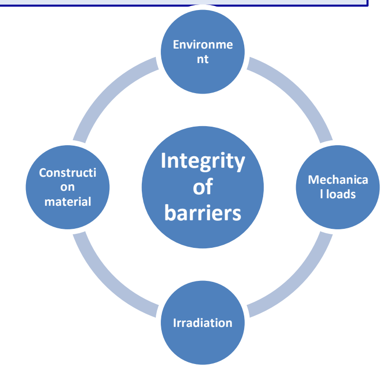
Supercritical Water cooled Reactor (SCWR)

true for HLMC and SCW

Materials/Coolant Interactions

Thermo-chemistry and thermo-physics of coolant(s) at mechanical and radiation loads are strongly interconnected

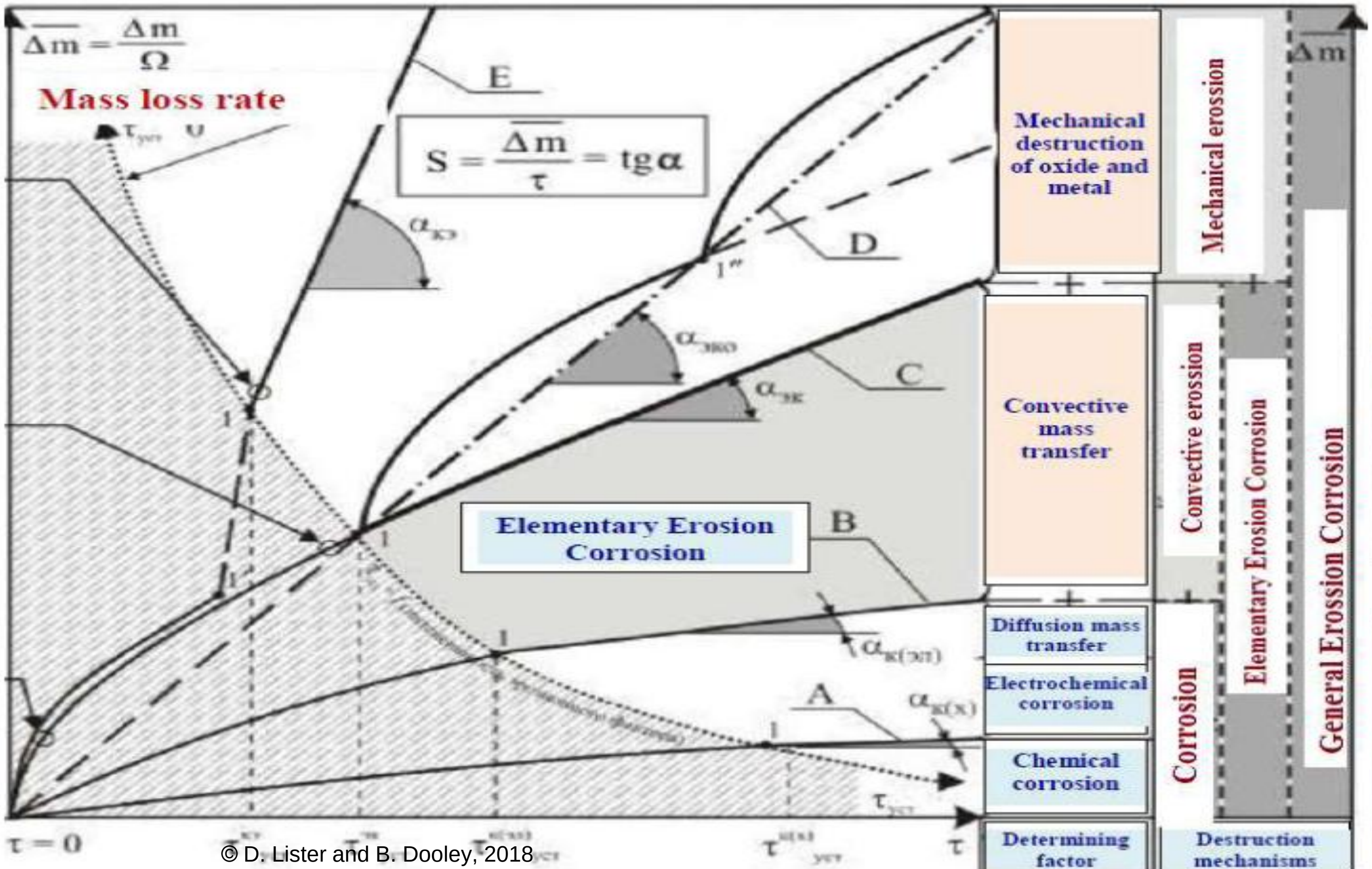




Corrosion, stress-corrosion cracking, embrittlement **enforced and/or assisted by irradiation**

Materials/Coolant Interactions

Determining factors and kinetics of mechanisms of destruction of metals of power equipment



The primary requirement of chemistry control strategy is to reduce material degradation rates

PROTECTIVE OXIDE FILMS
Steady-state conditions

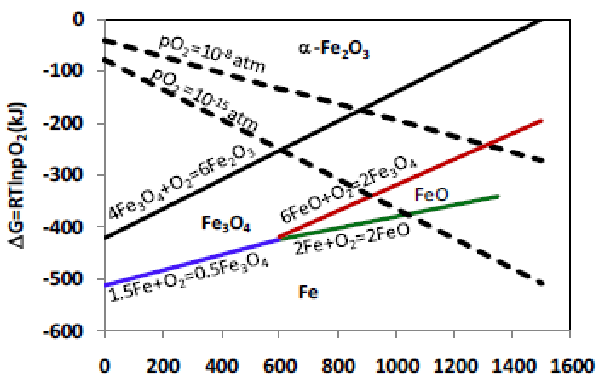
✓At high temperatures and irradiation most structural materials, including iron-based ferritic-martensitic and austenitic steels, are unstable in coolant of advanced fission reactors without special measures (e.g. supercritical high purity water and HLMC).

✓Properties of protective (oxide) films under various conditions, especially at high temperatures and irradiation, often determine the possibility of using certain metals as structural materials for innovative advanced fission reactors

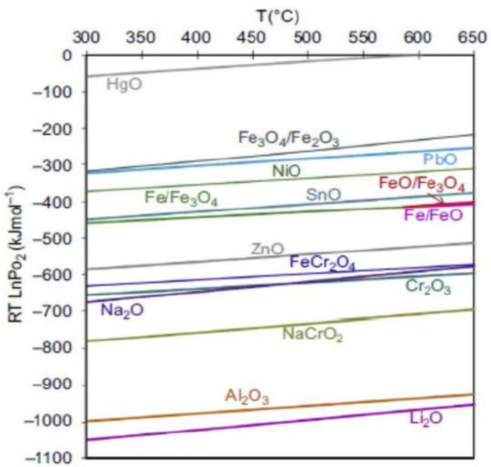
✓Physical and chemical stability of oxide films under various coolant conditions also determine an important process – *contamination of the coolant with corrosion products*

Ellingham diagram as function of oxygen concentration and temperature **(Fe-system and M**etal oxide stability)

Pourbaix diagram for Fe in SCW



$$\frac{2n}{m} M + O_2 = \frac{2}{m} M_n O_m \qquad \Delta G^o = RTln(p(O_2$$



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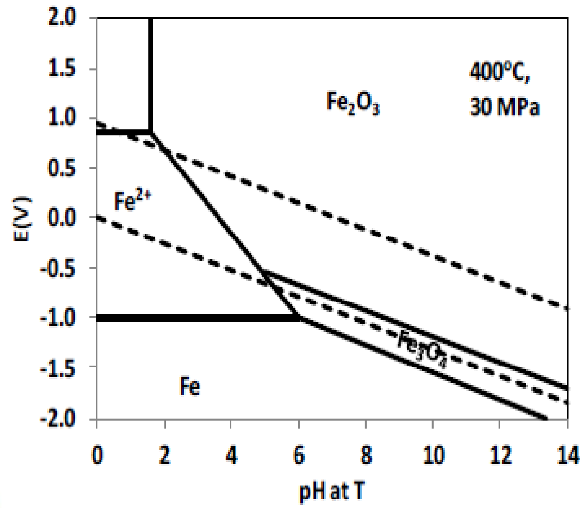
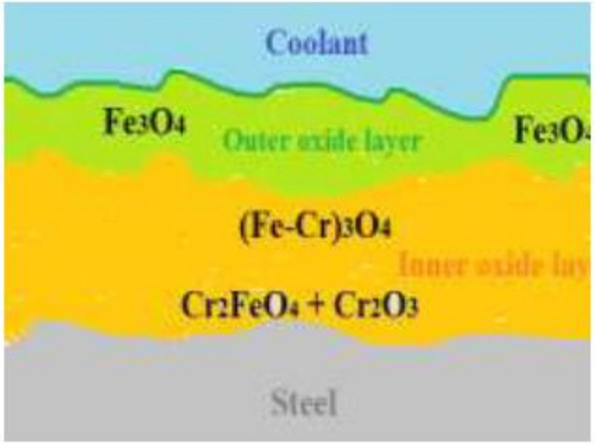
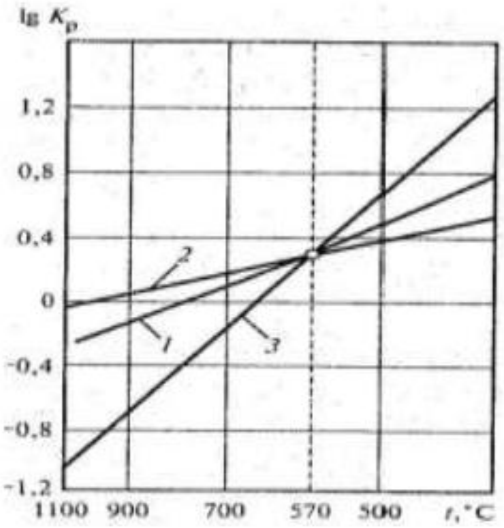


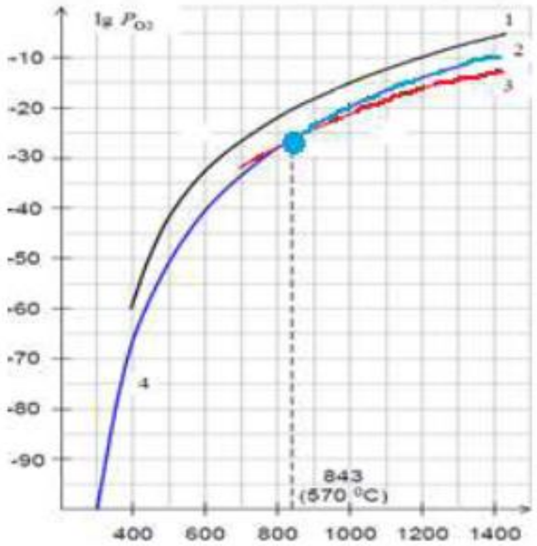
© D.A. Guzonas and W.G. Cook, “Corrosion in a Supercritical Water-cooled Reactor – Developing a Mechanistic Framework”, The 3rd China-Canada Joint Workshop on Supercritical-Water-Cooled Reactors, CCSC-2012, Xi’an, China, April 18-20, 2012

Structure of the oxide layer and stable oxide phases of α-Fe depending on temperature and oxygen concentration





Shodron diagram [*]:
1 – Fe—Fe_3O_4;
2 – Fe—FeO;
3 – FeO—Fe_3O_4



1 – Fe_2O_3;
2 – $6FeO + O_2 \rightarrow 2Fe_3O_4$;
3 - FeO;
4 – $3Fe + 2O_2 \rightarrow Fe_3O_4$ [**]

✓Coolant temperatures of advanced fission reactors may be higher than 570 ºC. Consequently, in this temperature area, an outer protective film of magnetite may be unstable.

✓To select the optimum chemistry is necessary to have information on the conditions of formation the protective film on the construction materials surfaces

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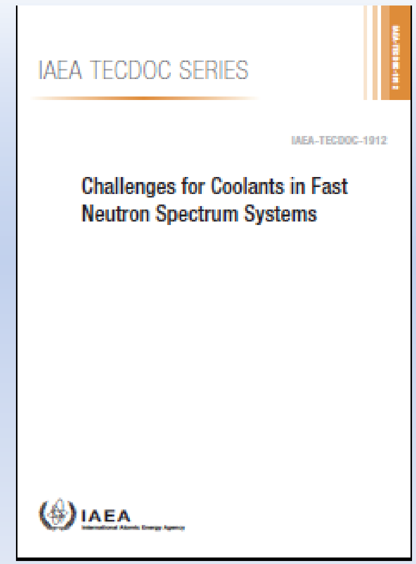
Chemistry control in a HLMC

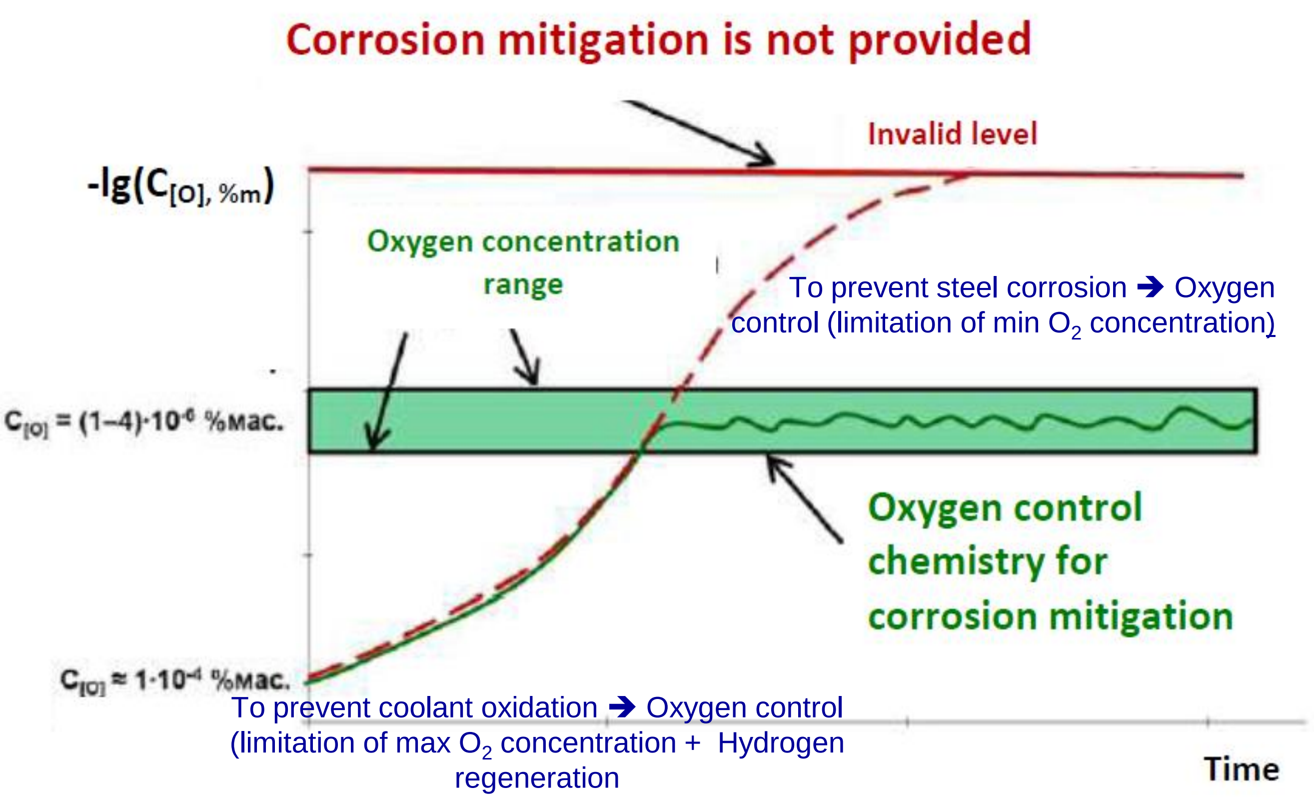
Heavy liquid metal coolants make ***significant corrosion and erosion impact*** on construction steel elements*).

- Oxygen-control technology of steel surface passivation
- Oxygen-control implies formation of protective oxide films on the steel surface and assurance of their integrity during plant operation by maintaining specified oxygen potential of coolant.
- Operation without supply of dissolved oxygen to the coolant spontaneous deoxidization of coolant takes place down to the level, at which corrosion protection of structural steels can not be provided.



*) CHALLENGES FOR COOLANTS IN FAST NEUTRON SPECTRUM SYSTEMS, IAEA-TECDOC-1912, (2020)

Chemistry control in a HLMC



©Askhadullin R.Sh., Legkikh A.Yu., Uliyanov V.V., Voronin I.A. Current state and issues of the heavy liquid metal coolant technology development (PB, PB-BI). Proc. of the International Conference on Fast Reactors and Related Fuel Cycles FR22: Sustainable Clean Energy for the Future. CN291-57

- ✓This technology may be successful only through a strict control and accurate measurements of the oxygen and/ or hydrogen content in the whole facility.

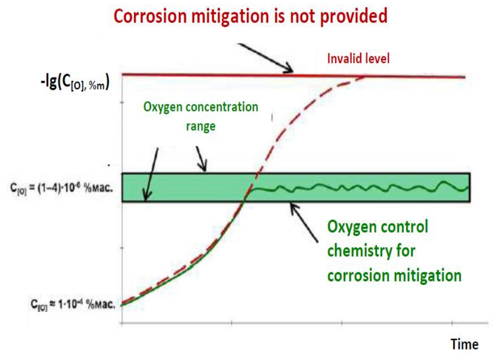
- ✓Ensuring the good resistance of these oxide layers first requires understanding their formation mechanism, then modeling the oxidation kinetics in order to predict long term steel behavior under given conditions.

Chemistry control in a HLMC

Maintaining specified oxygen potential of coolant

✓ *Issue* to provide the quality of the coolant to maintain the design limits and conditions specified in the project in a narrow range of oxygen concentrations to create a protective layer on the steel surface (Fe_3O_4);

✓ *Issue* to ensure *accurate oxygen concentration in a large volume of reactor* due to thermal stratification



The main processes and factors influencing oxygen distribution:

- concentration of oxygen dissolved in the coolant ;
- rate of change of coolant temperature ;
- coolant temperature Tmax, Tmin ;
- difference ΔT=Tmax-Tmin;
- condition and size of the surfaces of the coolant mirror and structural materials in contact with the coolant;
- coolant flow rate and flow mode;
- composition and amount of the protective gas above the surface of the coolant and directly in the coolant ;
- intensity of exchange between different volumes of the circuit ;
- processes of coolant technology, the design of devices for implementing these processes and the entire circuit as a whole

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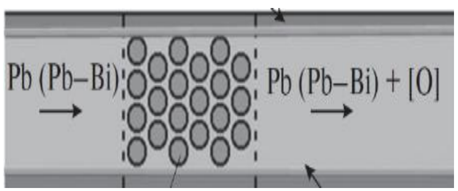
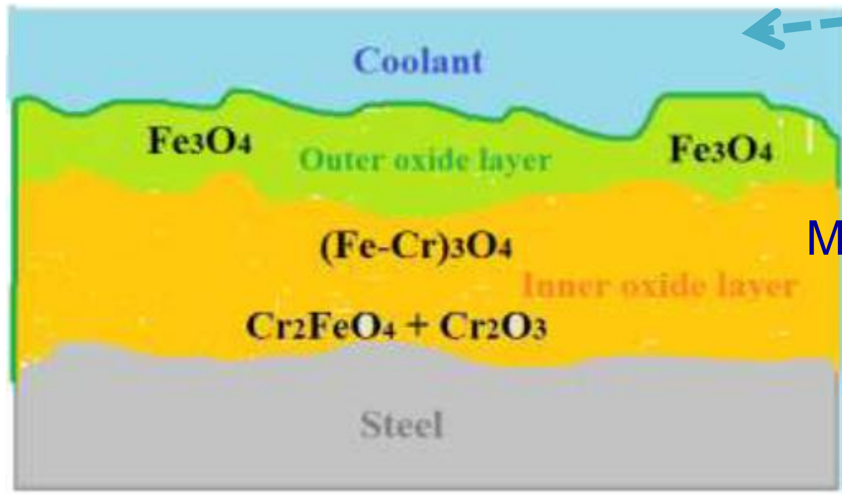
Chemistry control in a HLMC

Oxygen

Hydrogen





$Me_xO_y + y\ H_2 = x\ Me + y\ H_2O$

$[O] + H_2 = H_2O$

$Me_xO_y = x\ [Me] + y\ [O]$

- ✓ Special methods are required to ensure the conditions for oxide (Fe_3O_4) formation and keeping on steel.
- ✓ The solid-phase control method is recognized as optimal, which involves the use of soluble PbO granules as an oxygen source.
- ✓ Hydrogen regeneration of coolant and circulation circuit surfaces from lead oxide-based slags

©**Sorokin A.P.** LEYPUNSKY: THERMOPHYSICS OF LIQUID-METAL COOLANTS FOR NUCLEAR POWER ENGINEERING Voprosy atomnoy nauki I tekhniki. Seriya: Fizika yadernykh reaktorov — Problems of Atomic Science and Technology. Series: Physics of Nuclear Reactors, 2023, issue 3, pp. 150—190

Chemistry control in a HLMC

Providing objective data on the physical-chemical state of the coolant → <u>Reliable instrumentation devices to control oxygen in HLMC</u>

Issue: Signal of oxygen activity sensors in HLMC may change at constant oxygen concentration (oxide layer on reference electrode!)

Possible solution:

Improve the metrological characteristic of solid electrolyte oxygen sensor **potential of coolant**

The thermodynamic activity of oxygen is determined by the formula

$$a = C / C_S$$

where C, C_S —*current concentration and saturation concentration* of dissolved oxygen in the volume of coolant with a fixed temperature

For HLMC corrosion mitigation fundamentally important for the safety of reactor:

✓ ensuring the ***required purity*** of the coolant to maintain design limits and conditions specified in order to maintain the integrity of physical barriers in the path of ionizing radiation;

✓ ***excluding the slagging*** with lead oxides and corrosion products of structural materials of heat transfer surfaces of safety-important systems, as well as safety systems;

✓ providing the ***minimum corrosion*** of structural steels of equipment and pipelines in contact with lead coolant;

✓ providing the ***minimum deposits*** *on the heat transfer* surfaces of fuel rods, equipment and in pipelines of safety-important systems (including in gas systems);

✓ providing the ***instrumentation devices to control*** the process correctness, equipment and pipelines integrity

✓excluding the generation of ***hydrogen explosive*** concentrations in systems and equipment where the hydrogen accumulation is possible

The normative documents on the chemical regimes of HLMC **should formulate the requirements** for the *technological procedures* such:

- ✓ preparation of coolant (Pb-Bi or Pb) and ***filling of NPP circuits***;
- ✓ ***preliminary passivation*** of reactor plant elements before their installation;
- ✓ ***passivation of the inner surface*** of the primary circuit of the reactor plant;
- ✓ coolant technology concerning ***repair and refueling procedures***;
- ✓ coolant ***purification and removal of impurities*** from the circuit surfaces during normal operation;

The normative documents on the **chemical regimes of HLMC** should formulate the **requirements** to :

- ✓ control of coolant ***oxidizing potential*** during operation of NPP with HLMC;
- ✓ purification of cover gas in the liquid metal circuit providing the ***instrumentation devices to control*** the process correctness, equipment and pipelines integrity;
- ✓ excluding the generation of ***hydrogen explosive*** concentrations in systems and equipment where the hydrogen accumulation is possible during operation.

Chemistry control strategy for SCWR

The choice of SCWR chemistry can be based on fossil-plant experience → significant industry experience with the use of SCW in fossil-fired power generation (*but chemistry strategy that work well for a fossil-fired SCW plant may not be adequate for an SCWR*!)

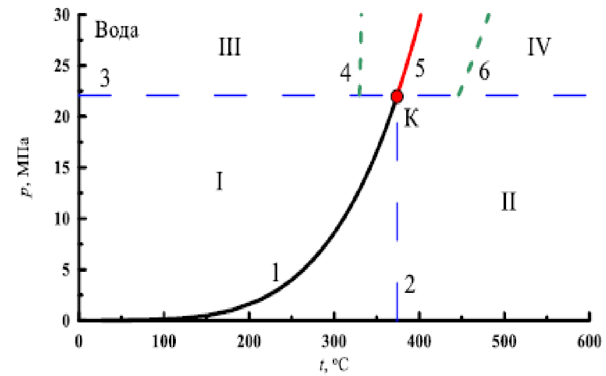
Radiation effects.

Radyolytic production of oxidizing species (e.g. OH, H_2O_2, O_2, …):

- Increase corrosion of reactor components;
- affect on corrosion product transport and deposition
- how to monitor and control relevant chemistry parameters, such as conductivity, pH, concentrations of dissolved ions and redox species (e.g., H_2, O_2), and particulate content

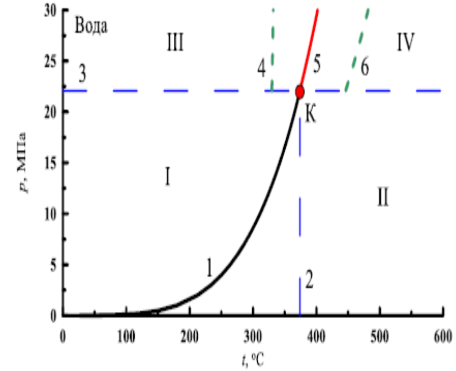
Temperature effects

- Corrosion mechanism changes with temperature (oxide solubility, oxide stable state);
- Alkalinity control - may be possible to effect chemistry (pHt) only below pseudocritical temperature



CHEMISTRY CONTROL STRATEGY FOR SCWR (major challenges):

- ✓ The experimental data are very limited to estimate the construction materials behavior under the such conditions, to validate materials integrity and asses water radiolysis, and to validate computational codes;
- ✓ The establishment of a chemistry-control strategy to minimize water-radiolysis effect and activation-product transport.
- ✓ One of a major challenge will be to find an effective means of suppressing the net radiolytic production of oxidizing species in the reactor core.
- ✓ The development of cladding materials to withstand the high pressure and high temperature environment



CONCLUSIONS

- The limitations of the current understanding of the physical-chemical processes in the coolant, along with the lack of data on the properties of candidate structural materials, are among the main problems that need to be solved to ensure the safety and reliability of advanced fission reactors.
- Interaction of coolant with surface (oxide) film is of key importance.
- Direct measurement of chemical and physicochemical parameters under extreme conditions (temperature, pressure and radiation fields) is difficult.
- **The most promising approach seems to include a combination of theoretical calculations, chemical models and experimental work**.

Thank you for your attention!

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