Numerical and analytical modelling of concurrent physico-chemical processes passing at the boundary of steel in a liquid-metal coolant leading to film formation

A V Avdeenkov¹, O I Achakovsky¹ and A I Orlov²

¹JSC "SSC RF-IPPE", Obninsk
²Proryv JSC, Moscow

oai@proryv2020.ru

Abstract. We analyse an engineering model for a self-consistent calculation of the growth of an oxide film in circulation circuits with a heavy liquid metal coolant and concentrations of impurities (oxygen, iron, magnetite) from the point of view of possible uncertainty in determining the activity of oxygen. The modelling of thermohydraulic and physicochemical processes is based on solving the associated three-dimensional equations of hydrodynamics, convective-diffusive transport, and the formation of chemically interacting impurity components in the coolant volume and on the surface of steels. Model calculations of the influence of the uncertainty of oxygen activity on the rate and integral yield of iron, which under the given conditions of the oxygen regime after interaction with oxygen determines the appearance of magnetite. It is numerically demonstrated that in the saturation mode there is a model-independent characteristic, which is determined by the parabolic constant and thickness of the oxide film characteristic of steel. Understanding these processes is highly important for justification of loops with HLMC and steadiness of structural materials that are in contacts with HLMC.

1. Introduction
The experience of operating circulation loops with HLMC has shown that impurities enter the coolant that interact with each other, with the coolant and structural materials, the products of these interactions spread around the loop and could localize in specific areas [1]. As a result of these interactions and mass transfer processes, disruptions to the performance of the circuits are possible, which are expressed in the following [2, 3]:

- deterioration of thermohydraulic characteristics due to the deposition on surfaces of the circuit of phases containing oxides of coolant components and circuit materials;
- violation of the tightness of the circuit or the appearance of various defects and destruction of its materials due to the aggressive action of the coolant.

The composition, physical state and amount of impurities largely depend on the stage and operating conditions of circuits. The presence of particles of structural materials (SM) in slags is associated with the release of materials from them due to the occurrence of diffusion and corrosion-erosion processes during the contact of HLMC with SM. As shown by the results of numerous studies of the composition
and chemical properties of slags in the overwhelming majority of cases the bulk share consists of the components of the phases PbO, Pb (and Bi for Pb-Bi HLMC). Slag also contains oxide phases from Bi$_2$O$_3$, Fe$_3$O$_4$, Fe$_2$O$_3$ and oxides of other elements. Therefore understanding these processes and having reliable physical and mathematical models for physico-chemical processes occurring in the circuit with heavy liquid metal coolant is highly important [4].

The purpose of this work is to study only one, but an important component of the formation of impurities, namely, the yield of iron and the formation of magnetite, since this process is precisely due to the specificity of self-consistent physicochemical processes in the oxide film and at the interface between the media, while the other processes are due to the specifics of the design and operation of the circuits.

The paper presents model calculations of the influence of the uncertainty of oxygen activity on the rate and integral yield of iron, which, under the given conditions of the oxygen regime, after interaction with oxygen, causes the formation of magnetite.

Since at the moment there is no sufficient amount of data on the behavior of magnetite in the circuit (the degree of deposition, coagulation, solubility), modeling allows us to make only calculated estimates of the rate of its generation and its integral amount in the circuit by the emission of iron into a circuit.

2. Calculated estimates of emission of iron into the coolant

The article presents the results of corrosion processes kinetics and changes in the oxide layer modeling using MASKA-LM software complex. The complex is intended for numerical simulation of three-dimensional non-stationary processes of mass transfer and interaction of impurity components in a heavy liquid metal coolant (HLMC: lead, lead-bismuth). The software complex is based on numerical solution of coupled three-dimensional equations of hydrodynamics, heat transfer, formation and convective-diffusive transport of chemically interacting components of impurities.

A system of three-dimensional equations of an incompressible multicomponent medium in a Cartesian coordinate system was used to describe the processes of formation, transformation, and transfer of impurities in the primary circuit of a reactor with HLMC. The system includes hydrodynamic equations in the Boussinesq approximation, equations of conservation and transfer of thermal energy, equations of physicochemical kinetics of impurities [5], equations of conservation and transfer of components of a multicomponent medium. The system of equations is solved by finite-difference methods.

For simplicity, a system is considered only with the formation of magnetite and the release of iron. This approach is fully justified, since the mobility of iron is an order of magnitude higher than that of, for example, chromium, and its release into the coolant is at least an order of magnitude more intense. In the developed model, at the first stage, the iron flux "remaining" in the near-wall layer is determined as the difference between the fluxes through the oxide film and the flux that has gone into the coolant. The "counter" flow of oxygen from the coolant is determined according to the stoichiometry of the magnetite formed. In this approximation, it is unambiguously assumed that the growth of the film (magnetite) occurs due to the reaction on the surface of the oxide layer:

$$3\text{Fe} + 4\text{PbO} \rightleftharpoons \text{Fe}_3\text{O}_4 + 4\text{Pb},$$

(1)

and at the same time all four components of the reaction are in chemical equilibrium. Since the rate of chemical reactions is much higher than the characteristic rates of all other physical processes, then in the volume of the coolant at each moment of time, chemical equilibrium can be considered steady and the distribution of components depends significantly on thermohydraulic processes.

Basic equations of the model for the growth of a conventionally single-layer film $\delta$, fluxes and concentrations of impurities at the steel - coolant interface:

$$\frac{4M_O}{3M_{Fe}} \left( J^\delta_{Fe} - J^\delta_{Fe} \right) = J^\delta_{O} - J^\delta_{O},$$

(2a)
or

\[
\frac{4M_0C^\delta_{Fe}}{3M^\beta_{Fe}} \left( \frac{K_p}{2\delta} - \chi_{Fe}(C^\gamma_{Fe} - C^\beta_{Fe}) \right) \approx \chi_0 \left( C^\beta_0 - C^\delta_0 \right),
\]  

(2b)

\[
\frac{d\delta}{dt} = \frac{K_p}{2\delta} - \chi_{Fe}(C^\gamma_{Fe} - C^\beta_{Fe})
\]

(3)

where \( J^\beta_{O,Fe} \) – oxygen and iron flows in the coolant flow and the film, respectively,

\( C^\delta_{Fe} \) – concentration of iron in the oxide film (designation \( \delta \)),

\( C^\beta_{Fe} \) – iron concentration in the coolant flow,

\( C^\gamma_{Fe} \) – concentration of iron on the surface of the oxide layer due to the reaction (designation \( \gamma \)),

\( C^\beta_O \) – oxygen concentration in the coolant flow,

\( C^\delta_O \) – oxygen concentration in the oxide film,

\( \chi_{Fe}, \chi_0 \) – mass transfer coefficients for iron and oxygen,

\( M_O, M_{Fe} \) – molar masses of oxygen and iron,

\( K_p \) – parabolic constant.

Parametrizations of parabolic constants for EP-823, T91, 316L and others are given in [6-16].

From expression (3) it follows that the film thickness at reaches its limit value (saturation thickness):

\[
\delta_e = \frac{K_p}{2 \chi_{Fe}(C^\gamma_{Fe} - C^\beta_{Fe})} C^\delta_{Fe}
\]

(4)

The joint solution of the equations of thermal hydraulics, the equations of chemical equilibrium processes describing the formation of oxide, and the equations of film change (2, 3) of the MASKA-LM code makes it possible to determine the thickness of the oxide film and the fluxes of impurities at the interfaces at any time.

3. Model calculations for different steels

For numerical analysis, a simple model of the flow of lead coolant of a given temperature in a pipe was chosen: the length of the computational domain is 1 m; diameter 50 mm, Reynolds number \( 10^5 \), which corresponds to the coolant flow velocity \( v=1.736 \) m/s. Pipe surface area \( S=0.157 \) m\(^2\).

When using the MASKA-LM code, a rectangular computational grid with constant spatial steps in a Cartesian coordinate system was placed, consisting of 250,000 cells (50x50x100) - along the directions of the coordinate axes.

To estimate the iron yield, it is sufficient to know its flux at the boundary of the oxide film \( J^\beta_{Fe} \), which can be obtained from the solution of the above-described model equations. Knowing the flow, it is possible to determine the total yield of iron from the surface per unit of time and its integral yield as a function of time.

In further calculations, the scatter of oxygen concentration values is assumed: ±20% and ±50% [17].

In further analysis, most of the model calculations were carried out for the basic mode and coolant temperature of 640°С to assess the scale of iron release into the coolant.

As is well known, the oxygen regime for the coolant is selected on the basis of currently available experimental material for bench tests of structural steels and can be further adjusted [18]. The upper
limit of the range is selected based on prevention of conditions for formation of a solid phase of lead oxide in the "cold" part of the circuit. The lower limit is determined based on the oxygen content corresponding to the level of potential destruction of the outer layer of protective oxide coatings on the surfaces of structural steels. When the concentration of dissolved oxygen in the coolant drops below the critical value, i.e., less than the lower limit of the concentration range, reliable anti-corrosion protection of structural steels is not provided. Exceeding the upper limit of the concentration range, i.e. the presence of a significant amount of oxygen in the loop, can lead to the accumulation of an unacceptable amount of slag deposits on the heat exchange surfaces of the loop and equipment.

Figure 1 and 2 show the rate of iron yield, its integral yield and the spread of values with an uncertainty of oxygen concentration up to ± 50%. Just as for the thickness of the oxide film, the numerical range of the studied values is from ~ 30% to ~ 100% for the lower and upper values. Figure 3 shows the results of comparative calculations of the amount of iron in the film and the amount of iron released into the coolant. The released iron, due to the constancy of the maintained oxygen concentration, quickly reacts with oxygen, forming magnetite, which in the form of deposits can stay in the circuit. The results show that most of the iron is released into the coolant, which obviously needs constant filtration.

Figure 1. The spread of values of iron yield rate in the tube made of EP-823 steel with the spread of oxygen concentration values ± 20% and ± 50% of the base value $10^{-6}$ mass%. $T=650^\circ$C.
Figure 2. The spread of values of integral yield in the tube made of EP-823 steel with the spread of oxygen concentration values ± 20% and ± 50% of the base value $10^{-6}$ mass%. $T=650°C$.

Figure 3. Comparison of integral yield of iron in the film with the amount of iron released into the coolant. Steel EP-823.

Figure 4 shows the results of calculations of the release of iron into the coolant at different temperatures. At a temperature of 500°C, the integral yield of iron is approximately three orders of magnitude less than at 640°C, which is obviously explained by the higher mobility of iron cations in steel and film at high temperatures.
Figure 5 shows the results of calculations of release of iron into the coolant at various coolant flows. At a higher speed, the mass transfer is obviously more intense, which leads to an increase in the rate of iron release up to several times.

Figure 6 and 7 show the same as figure 1 and 2, but for increased oxygen concentration. The proportions in uncertainty of 30% and 100% are also the same as for the basic oxygen regime. A significant difference from the basic oxygen regime is the result that a comparable part of iron goes into the oxide film, and the actual release of iron into the coolant is several orders of magnitude smaller, then at the basic oxygen regime for the same times. It should be noted here that at an increased oxygen concentration, the film grows for a long time (up to tens of thousands of hours) according to a parabolic law and reaches values of up to several millimeters, which, based on the available experimental data and general concepts, is hardly possible, since erosion processes should "rip off" such thick film. But at the moment, the model does not take into account the erosive processes of film stripping due to the lack of experimental information.

Figure 4. Integral iron yield at different temperatures for EP-823 steel.

Figure 5. Comparison of the accumulation of the amount of iron in the film with the amount of iron released into the coolant for different average velocities of the coolant. EP-823 steel. T=640°C.
Figure 6. The spread of the values of iron yield rate in a tube made of EP-823 steel with the spread of the oxygen concentration values ± 20% and ± 50% from $4 \times 10^{-5}$ mass%. $T=650^\circ$C.

Figure 7. The spread of the values of the integral yield in a tube made of EP-823 steel with the spread of the oxygen concentration values ± 20% and ± 50% from $4 \times 10^{-5}$ mass%. $T=650^\circ$C.
Figure 8. Scatter of values of iron formation rate in a tube made of T91 steel with a scatter of oxygen concentration values ± 20% of the base value of $10^{-6}$ mass%. Comparison for $T=640^\circ$C and $T=500^\circ$C.

Figure 9. Scatter of values of integral release of iron in a tube made of T91 steel with scatter of values of oxygen concentration ± 20% of the base value $10^{-6}$ mass%. Comparison for $T=640^\circ$C and $T=500^\circ$C.

Figure 8 and 9 show a comparison of the investigated values at $T=640^\circ$C and $T=500^\circ$C with confirmed uncertainties and a demonstration that the iron yield at a higher temperature is approximately three orders of magnitude higher.

Figure 10-17 show the results of comparative calculations of the yield of iron for different steels at different temperatures and different rates of coolants. All the carried out calculations confirm the above observations and conclusions for other steels as well. But here it is necessary to make an essential remark. As can be seen from these figures, starting from a certain moment in time, the rate of release of iron no longer depends on the type of steel and is the same for all. This moment in time is the moment when the thickness of the oxide film reaches the saturation value. For different steels, this moment occurs at different times.

It is quite obvious that the result obtained is a consequence of the assumption that the film is the same for all steels, that is, magnetite. And since upon reaching saturation, the film thickness no longer
changes, the differences in the properties of the steels behind the film no longer affect the iron yield, and it is determined by magnetite itself. It is also quite obvious that if we take into account that for each steel its film will have a different composition, then such an exact coincidence will not happen. It should be noted that since the density of spinel and the density of magnetite differ quite slightly (less than 10%), the expected differences will also be insignificant.

Calculations confirm the statement about the consistency of the value

$$\frac{J_{Fe}^\beta}{S \cdot C_{Fe}^J} = \frac{K_p}{S \cdot 2\delta_c}$$

and reaching a certain constant rate of iron release, which is determined by the ratio of the parabolic constant and the thickness of the oxide film in saturation mode, $K_p/\delta_c$.

Figure 10. Comparison of values of iron yield rate for different steels. T=650°C.
Figure 11. Comparison of values of the integral yield for different steels. T=650°C.

Figure 12. Comparison of values of the output rate of iron for different steels. T=500°C.
Figure 13. Comparison of values of the integral output of iron for various steels. T=500°C.

Figure 14. Comparison of values of the output rate of iron for different steels. T=640°C at increased oxygen concentration.
Figure 15. Comparison of values of the integral output of iron for different steels. T=640°C at increased oxygen concentration.

Figure 16. Comparison of values of the rate of output of iron for different steels. T=640°C at an average speed of the coolant v=0.1 m/s.
Figure 17. Comparison of values of the integral yield of iron for various steels. $T=640^\circ C$ at an average speed of the coolant $v=0.1\, m/s$.

For the considered example of the growth of an oxide film in a tube, the ratio of the volume of the coolant in the tube to the steel surface area is rather large and amounts to $\sim 12.5\, mm$. Let’s consider another example, where this ratio is much smaller ($\sim 2.7\, mm$), namely, a bundle of rods in a triangular package with a diameter of $10\, mm$, a length of $0.97\, m$, with a pitch of $14\, mm$.

For numerical implementation, only the sector of such a triangular packing is considered. figure 18 and 19 show the results of calculations for this geometry. The results obtained with an accuracy of the ratio of the surface areas of steels of these two geometries repeat the results for the tube (figure 8 and 9).

Thus, as for the thickness of the oxide film, the geometry itself has no significant effect on the magnitude and rate of iron release, and small differences are determined by a small difference in the coolant flow rate. However, this is obviously the expected result that the properties of the coolant (velocity and temperature fields) determine the features of physicochemical processes at the steel-coolant interface and are necessary preliminary data obtained directly from 3D thermohydraulic calculations.

Figure 18. A bundle of rods. Comparison of iron yield rates for different steels. $T=640^\circ C$. 
Figure 19. A bundle of rods. Comparison of values of integral iron yield for various steels. T=640°C.

4. Estimation of relative loss of iron in steel

The calculated values of the rate of iron yield and the integral yield of iron obtained above can be used in assessing the conditionally removed steel material. The iron left from the sample can be converted to the volume of the removed steel. For a tube, this volume can be equivalently converted to the "eaten" steel thickness by diameter. For a tube with a diameter of 50 mm, the "expansion" of the tube due to the loss of steel lies in the region of 5 mm for different steels at T = 640°C (table 1). In this case, the contribution of iron transferred into the film is insignificant in comparison with the contribution of iron released into the coolant. Thus, the yield of iron with such parameters is very noticeable.

At low speed of coolant (Table 2), the "eatable" tube thickness is much smaller, while the thickness of the oxide film is much larger. This is quite understandable, since the main amount of iron comes out already after the oxide film reaches the saturation value and according to the ratio (6)

$$J^p_{Fe} \frac{1}{\delta_e}$$

At a temperature of 500 °C (Table 3) the iron yield is almost three orders of magnitude lower than at 650 °C and the thinning of steel is only 8-10 microns after 10,000 hours.

Table 1. Iron loss from the tube surface.

| Steel | Total flow of iron into the coolant at a moment in time 10000 hours, kg/s | Iron, kg | «Eatable» thickness, mm |
|-------|-------------------------------------------------------------|----------|------------------------|
| EP-823 | 1.72E-7                                                   | 6.2      | 5.05                   |
| T91   | 1.72E-7                                                   | 6.45     | 5.25                   |
| 316L  | 1.72E-7                                                   | 6.15     | 5.0                    |
Table 2. Iron loss from the tube surface at low coolant velocity.

| Steel     | Total flow of iron into the coolant, kg/s | Iron, kg | «Eatable» thickness, mm |
|-----------|------------------------------------------|----------|-------------------------|
| EP-823    | 1.55E-8                                  | 9.1E-01  | 7.45E-01                |
| T91       | 3.5E-08                                  | 2.2      | 1.8                     |
| 316L      | 1.45E-08                                  | 6.2E-01  | 5.05E-01                |

Table 3. Iron loss from the tube surface at T=500°C.

| Steel     | Total flow of iron into the coolant, kg/s | Iron, kg | «Eatable» thickness, mm |
|-----------|------------------------------------------|----------|-------------------------|
| EP-823    | 2.6E-10                                  | 1.00E-2  | 8.2E-3                  |
| T91       | 2.75E-10                                 | 3.70E-02 | 3.0E-02                 |
| 316L      | 2.60E-10                                 | 1.20E-2  | 9.8E-3                  |

It should be noted that the numbers are approximate since they do not take into account, for example, the yield of chromium and the change in material properties in time. It is possible that structural changes in steel occurring over time due to the release of iron also affect the rate of formation and structure of the film, which in turn affects the rate of release of iron. But for the implementation of these processes at the moment there is not enough experimental data.

5. Conclusion
The release of iron and the formation of magnetite is managed by the specificity of self-consistent physicochemical processes in the oxide film and at the interface.

Model calculations of the influence of the uncertainty of oxygen activity on the rate and integral yield of iron have been carried out, which, under given conditions of the oxygen regime, after interaction with oxygen, causes the formation of magnetite.

The scatter of the calculated values of iron yield is essentially determined by the accuracy of measurements of oxygen activity and varies from several tens of percent to values close to one hundred percent in case of unsatisfactory calibration of the oxygen sensor. The calculated values of the release of iron from the coolant have the same errors as the thickness of the oxide at a given oxygen regime and temperature.

It is numerically demonstrated that temperature significantly affects the yield of iron and can make significant influence on the changes in the structure of steel due to the high intensity of the process.

It is numerically demonstrated that in the saturation mode there is a model-independent characteristic, which is determined by the parabolic constant and the thickness of the oxide film typical to this steel.

A simple model relationship is proposed for assessing the power of the mass transfer apparatus.

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