

On the control of coolant parameters in long-life facilities*

Yury G. Cherednichenko¹, Oleg E. Levin¹

¹ IPPE JSC, 1 Bondarenko Sq., Obninsk Kaluga reg., 249033, Russia

Corresponding author: Yury G. Cherednichenko ((cheryug@ippe.ru)

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Abstract

When nuclear power plants with heavy coolants are brought to operating mode as well as during their operation, it is necessary to control and maintain the oxygen content in the coolant within the specified limits. As a rule, the oxygen content in metal melts is controlled by sensors based on solid oxygen-ionic electrolytes. The article presents an analysis of the methodological aspects of dissolved oxygen control in non-isothermal circulating loops with metal coolants, using such sensors. It is shown that in the presence of dissolved loop wall materials and suspensions of their various oxides in the coolant, control over the values of the oxygen activity and concentration calculated for a pure coolant is in general unjustified. The authors present the experimental results of the distribution of oxidation potentials along the loop depending on the coolant temperature, obtained during long-term tests of cladding samples in a lead melt in two circulation facilities – SM2-M and TsU1-M – which differ in principal methods for maintaining specified oxygen conditions. In the low temperature region, the experimental values of the oxidation potential in both facilities are lower than those calculated for pure lead, which leads to a difference by two or more times of the calculated oxygen concentrations for the regions of the loop with T_{\min} and T_{\max} , i.e., the so-called oxygen ‘non-isoconcentration’ is observed along the loop. In deoxidation mode during hydrogen ejection into the coolant, the oxidation potential in the loop changes in a complex way, and it makes no sense to talk about the oxygen concentration. It is concluded that in long-life facilities, the coolant parameters for oxygen must be controlled not by the calculated oxygen activity or concentration but by the oxidation potential in the maximum temperature region. To obtain the correct values of the oxidation potential, measurements should be carried out in temperature-stable modes of throughout the facility.

Keywords

Control, oxygen, heavy coolant, circulation loop, oxygen-ionic electrolyte, oxidation potential

In nuclear power plants with heavy coolants, it is necessary to continuously maintain optimal conditions for the formation of oxide protective films on all surfaces exposed to the melt (i.e., to create conditions for the continuous passivation of loop materials with dissolved oxygen from the coolant). For this, it is required to control the

coolant deoxidation and makeup with oxygen during the start-up passivation of materials and operation of the nuclear power plant.

The dissolved oxygen concentration in the melt is controlled by the EMF method using electrochemical cells based on solid electrolytes (Talanchuk et al. 1992). Using

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this method, it is possible to experimentally measure with high accuracy the oxidation potential of the melt, ΔG , based on the law of conversion of chemical energy into electrochemical energy.

The EMF of the electrochemical cell, E , is determined by the difference between the oxidation potentials (Gibbs energies) in the reference electrode, ΔG_{ref} , and in the melt (coolant), ΔG_{cool} :

$$E = (\Delta G_{\text{ref}} - \Delta G_{\text{cool}}) / (2 \times F), \quad (1)$$

where $F = 9.648456 \times 10^4$ C/mol is the Faraday constant; ΔG is the oxidation potential, J/g-at.O.

The oxidation potential of the melt, ΔG_{cool} , with any content of impurities is written as

$$\Delta G_{\text{cool}} = \Delta G_{\text{cool}}^0 + RT \times \ln a_o, \quad (2)$$

where $R = 8.31441$ J/(mol \times K) is the universal gas constant; T is the temperature, K; ΔG_{cool}^0 is the melt oxidation potential in the oxygen saturation state, (J/g-at.O); $a_o = C_o/C_o^s$ is the oxygen activity in the melt; C_o is the dissolved oxygen concentration in the melt; C_o^s is the dissolved oxygen concentration in saturation mode.

In the reference electrode $a_o = 1$ (the melt is in the oxygen saturation state) and $\Delta G_{\text{ref}} = \Delta G_{\text{ref}}^0$ is a known function. Then the oxidation potential of any coolant, ΔG_{cool} , with any impurity content at any point in the loop is written as

$$\Delta G_{\text{cool}} \equiv \Delta G_{\text{ref}}^0 - 2F \times E(V). \quad (3)$$

When analyzing the state of the coolant in physical chemistry, it is customary to deal with the Gibbs free energy (ΔG) or, in other words, with the oxidation potential of the melt.

In practice, reactor physicists operate with the parameter of the impurity concentration in the coolant. To visualize the real deviations of activity from ideal conditions, the well-known a - C - T - E diagram is used (Shmatko and Rusanov 2000a), which is calculated according to equation (2) for an ideal case, namely, the coolant is pure, without any impurities (including gases), except oxygen.

In circulation facilities, as in reactor plants, there is a constant supply of metallic impurities (iron, chromium, etc.) from the walls of the loop, which causes the coolant deoxidation. To compensate for deoxidation, additional sources of dissolved oxygen to liquid metal are used (Shmatko and Rusanov 2000a, Shimkevich and Shmatko 1999).

Over time, a finely dispersed solid phase based on iron oxides (Fe_3O_4 , $\text{PbO} \times 5\text{Fe}_2\text{O}_3$ etc.) is formed in the coolant of the loop. It controls the coolant oxidation potential in the entire nonisothermal circulation loop (Blokhin et al. 1995, Blokhin and Ivanovsky 2000).

Since the formation and decomposition of these oxides due to temperature changes occurs slowly (with a long delay time), a composition with a constant content of oxides and dissolved oxygen and iron throughout the loop is formed in the circulating coolant. This is indicated by the

absence of any noticeable hysteresis of the EMF sensors when the coolant moves from the cooler to the maximum temperature (T_{max}) region and vice versa in the circulation facilities during their life tests.

Impurities can significantly affect both the composition of the oxides in the coolant (i.e., the ΔG^0 value of the coolant (Shmatko and Rusanov 2000)) and its C_o^s (Arnoldov et al. 2015, Shmatko and Rusanov 2002, Gromov and Shmatko 1996, Shmatko 2007). Consequently, the values of the oxygen activity and concentration calculated in the model of a pure coolant will differ from their true values in the loop. In practice, on the generally accepted a - C - T - E diagram, this is manifested in the form of "non-isoconcentration" oxygen distribution ($C_o \neq \text{const}$) along the loop. For example, as it was shown in (Shmatko and Rusanov 2000a), in the coolant loops with BREST-OD-300 parameters, the diagram practically does not have a region of isoconcentration oxygen distribution. "Non-concentration" should especially occur during the coolant deoxidation when hydrogen is injected into the loop.

According to the form, the temperature dependences for ΔG^0 and C_o^s for a real coolant with impurities will look the same as these dependences do for a pure coolant, but the coefficients included in them will be different. Therefore, in the case of a linear temperature dependence $\Delta G_{\text{cool}}(T)$ and, consequently, the EMF $E(T)$ in the circuit, $C_o = \text{const}$ is always observed. However, for calculating the true values of the oxygen activity and concentration (especially in reactor plants), it is necessary to have the ΔG^0 and C_o^s dependences for a real coolant with impurities, which is hardly feasible or at least difficult in practice.

Therefore, in general terms of the physics of the process, to control the deoxidation and passivation of materials and the coolant makeup with oxygen both at the start-up stage and during operation of the plants, it is necessary to control not the oxygen activity and concentration (due to the uncertainty of ΔG^0 и C_o^s in the coolant), but the difference between the oxidation potentials of the coolant, ΔG_{cool} , and oxide, $\Delta G^0(\text{Fe}_3\text{O}_4)$:

$$\delta \Delta G = \Delta G_{\text{cool}} - \Delta G^0(\text{Fe}_3\text{O}_4) > 0, \quad (4)$$

where $\Delta G^0(\text{Fe}_3\text{O}_4)$ is the oxidation potential of Fe_3O_4 , which forms a protective film on the inner surfaces of the loop.

This condition must be met for any impurities in the coolant.

In fact, it is necessary to control, at the maximum temperature, T_{max} , in the loop, the EMF E value of the oxygen activity sensor (OAS) in the coolant relative to the calculated EMF $E(\text{Fe}_3\text{O}_4)$, at which the depassivation of the films begins (Figs 1, 2), i.e., the following condition must be met

$$E = E(\text{Fe}_3\text{O}_4)(T_{\text{max}}) - \delta E(T_{\text{max}}). \quad (5)$$

Permissible (minimum and maximum) values of $\delta \Delta G_p(T_{\text{max}})$, $\delta E(T_{\text{max}})$ should be obtained on the basis of preliminary resource tests of materials in the circulation

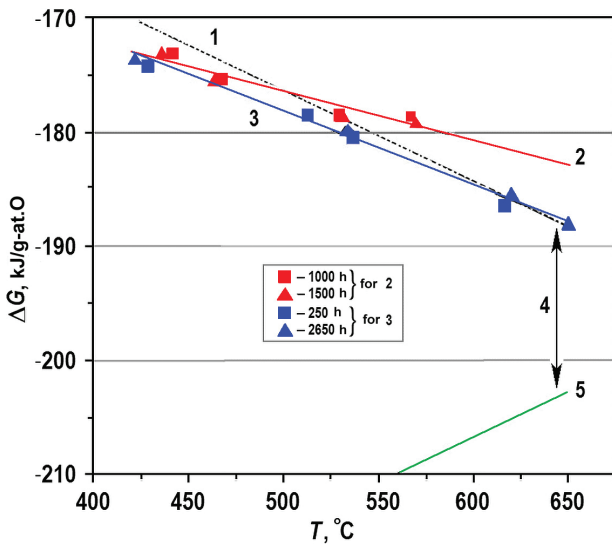


Figure 1. Changes in the lead coolant oxidation potential in the SM-2 and TsU-1M loops during their life tests: 1 – ΔG_{pb} ($C_O = 2 \cdot 10^{-6}$ % wt); 2 – ΔG_{cool} (TsU-1M); 3 – ΔG_{cool} (SM-2); 4 – $\Delta \Delta G(T_{max})$; 5 – $\Delta G^0(Fe_3O_4)$.

facilities. In the case of small deviations of the true oxidation potential values of the real coolant, ΔG_{cool} , from ΔG of the coolant without impurities, the mode on the resource can be controlled by the oxygen activity or concentration from the known a - C - T - E diagram, after preliminary evaluations of the permissible oxygen “non-isoconcentration” along the loop.

To illustrate the foregoing, Fig. 1 shows the experimental data and their linear approximations on the changes in the oxidation potential depending on the temperature, $\Delta G_{cool}(T)$, in the SM-2 and TsU-1M loops with the lead coolant in stationary conditions during the life tests of fuel element cladding samples. Figure 2 shows the $E_{cool}(T)$ dependences of the EMF sensors (OAS) corresponding to those in Figure 1. For all the sensors, the Bi-Bi₂O₃ system (oxygen-saturated bismuth) was used as a reference electrode. The modes on the resource were controlled by the oxygen concentration calculated from the a - C - T - E diagram for a pure lead coolant by the values of the EMF sensors located in the maximum temperature region where the test samples were placed or close to it. The EMF values of the sensors at $T \approx T_{marc}$ corresponded to the calculated oxygen concentration $C_O \approx 2 \cdot 10^{-6}$ %wt. Figures 1 and 2 also show the calculated $\Delta G_{pb}(T)$ and $E_{pb}(T)$ dependences for a coolant without impurities at $C_O = 2 \cdot 10^{-6}$ %wt, as well as $\Delta G^0(Fe_3O_4)$ and $E(Fe_3O_4)$.

For the SM-2 and TsU-1M facilities, there was a fundamental difference in the methods for maintaining test conditions. In the SM-2 facility, a slow constant increase in the EMF of all the OASs was observed on the resource, which is equivalent to a decrease in the coolant oxidation potential, a decrease in the concentration of oxygen dissolved in the coolant, most likely due to its binding by iron diffusing through the protective films. To maintain the oxygen concentration in the range of the set values, gaseous oxygen was periodically metered into the gas cavity of

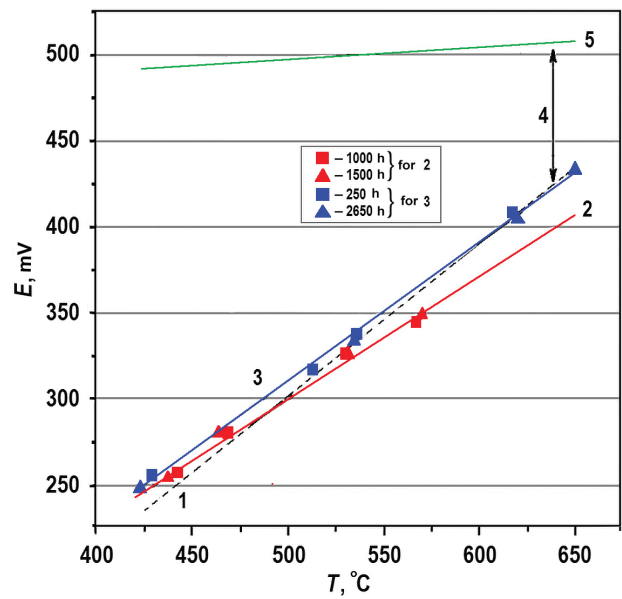


Figure 2. Changes in the OAS EMF in the SM-2 and TsU-1M loops during their life tests: 1 – E_{pb} ($C_O = 2 \cdot 10^{-6}$ % wt); 2 – E (TsU-1M); 3 – E (SM-2); 4 – $\Delta E(T_{max})$; 5 – $E(Fe_3O_4)$.

the centrifugal pump to the melt surface. On the contrary, in the TsU-1M facility, the resource showed a constant decrease in the EMF of all the OASs, which is equivalent to an increase in the coolant oxidation potential and an increase in the concentration of oxygen dissolved in the coolant, most likely due to the decomposition of various solid oxide impurities when they are in a significant amount in the facility. To maintain the oxygen concentration in the range of permissible values, an argon-hydrogen mixture was periodically metered into the gas cavity of the centrifugal pump to the melt surface. In other words, the SM-2M facility was conditionally “clean” and the TsU-1M facility was conditionally “dirty”, which is confirmed by the fact that there is a significantly larger amount of slag in the melt when the coolant is drained in TsU-1M than in SM-2.

In Figures 1 and 2, the linear $E_{cool}(T)$ and $\Delta G_{cool}(T)$ dependences can be seen, which, as mentioned above, indicates the isoconcentration oxygen distribution along the loop. However, the slope of the experimental dependences differs from the slope of the calculated $E_{pb}(T)$ and $\Delta G_{pb}(T)$ for a pure coolant. Put it another way, the a - C - T - E diagrams of both facilities showed the “non-isoconcentration” dissolved oxygen distribution along the loop. The C_O values calculated for a clean coolant at low temperatures, $T \approx 420$ °C, are less than C_O for $T \approx 570$ – 650 °C by about two or more times. The maximum difference of $\Delta G_{cool}(T)$ and $E_{cool}(T)$ from $\Delta G_{pb}(T)$ and $E_{pb}(T)$ is observed for the “conditionally dirty” TsU-1M facility. This confirms the fact that in real long-life facilities, control of the coolant conditions under the assumption of the isoconcentration oxygen distribution along the a - C - T - E diagram for a pure coolant is unjustified. For example, when the mode is maintained according to the C_O value calculated for the low temperature region, the real oxidation potential in the

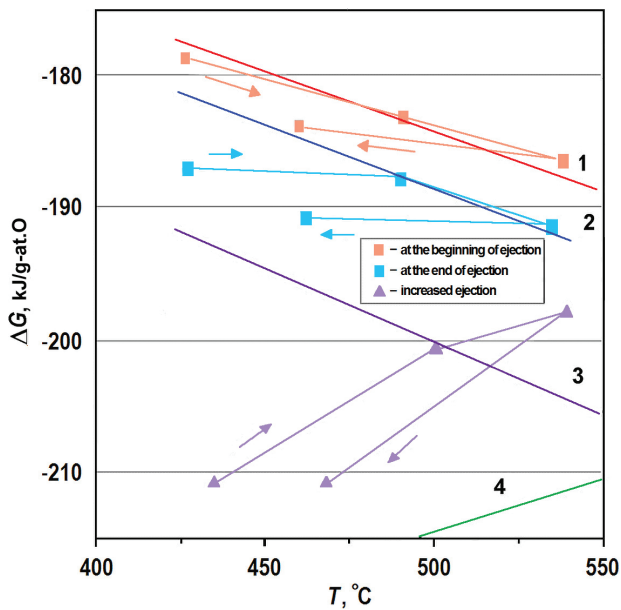


Figure 3. Changes in the coolant oxidation potential in the loop of the TsU-1M facility during the ejection of hydrogen into the loop: 1 – ΔG_{pb} ($C_O = 6 \times 10^{-7}$ % wt); 2 – ΔG_{pb} ($C_O = 3 \times 10^{-7}$ % wt); 3 – ΔG_{pb} ($C_O = 5 \times 10^{-8}$ % wt); 4 – ΔG^0 (Fe_3O_4).

T_{max} area will be higher than the calculated one and (in the case of significant contents of oxides in the coolant) may exceed the permissible limits.

Even more unjustified is the control of the coolant by the oxygen activity or concentration during its hydrogen regeneration (deoxidation), especially when hydrogen is ejected directly into the loop. Figure 3 shows the changes in the coolant oxidation potential in the TsU-1M facility during periodic hydrogen ejection into the loop to maintain the preset mode as well as during increased ejection in the course of deoxidation. The arrows indicate the coolant movement direction from the pump to the T_{max} area and exit from the cooler. The calculated ΔG_{pb} dependences for a pure coolant at oxygen concentrations, according to which deoxidation was controlled, are also presented. As can be seen in the figure, there is no sense in talking about the oxygen concentration in this case. The oxidation potential is constantly changing as the coolant moves along the loop and does not correspond at all to the change in $\Delta G_{pb}(T)$.

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Conclusion

1. In real long-life facilities, the amount and chemical composition of impurities in the coolant (i.e., ΔG_{cool}^0 and C_O^s) are generally unknown. Therefore, the modes should be controlled not by the calculated values of the oxygen activity or concentration, but by the changes in the coolant oxidation potential $\Delta G_{cool}^0(T)$ or EMF of the sensors.
2. In the maximum temperature (T_{max}) region (i.e., the reactor core), the placement of oxygen activity sensors is hardly possible, otherwise these sensors will have a short service life. Therefore, to assess the oxidation potential in the T_{max} region, the sensors must be installed in the loop at several points (at least three) with different temperatures, namely:
 - immediately before and after the T_{max} region;
 - before and after the cooler (heat exchanger, steam generator); and
 - before and after the pump (hydrogen ejector).

This will make it possible

- to control with some degree of certainty the coolant oxidation potential in maximum temperature region on the resource by extrapolating the experimental data, $\Delta G_{cool}^0(T)$, obtained in the low-temperature region; and
 - to control the oxidation potential distribution along the loop during the coolant deoxidation, including the volume) where the ejection takes place.
3. To obtain the $\Delta G_{cool}(T)$ and $E_{cool}(T)$ dependences and their correct extrapolations to the T_{max} region, the EMF should be measured in the facility under temperature-stable conditions. Obtaining these dependences by changing the temperatures with respect to the circulation loop is not quite justified, since the physicochemical processes in the coolant and on the loop walls change, which, due to circulation, leads to a change in the chemical composition of the oxides and their ratio in the entire volume.

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