

Investigation of Steel Corrosion Products Mass Transfer in Sodium

V.Alekseev, F.Kozlov, A.Sorokin, E.Orlova

JSC “State Scientific Center of Russian Federation - Institute for Physics and Power Engineering” (“SSC RF-IPPE”), Obninsk, Russian Federation

Abstract. The report observes the behavior of the system sodium - oxygen - stainless steel with regard to the sodium cooled circulation loop. Computational and theoretical analysis of mass transport of corrosion products in the channels of non-isothermal circuit in view of chemical interaction of the steel components with oxygen in sodium, including the reaction of sodium oxide with chromium in sodium is prepared. In the proposed model, we consider the reaction of sodium oxide with chromium in sodium in chromium-nickel steel circuit, taking into account the transfer of the reaction products in sodium and dynamics of sodium flow. The processes of impurities interaction with channel walls, formation and transport of suspended particles in the flow of coolant is considered. Closing relations include the equations describing the mass transfer of impurities between the coolant flow and the channel walls, the deposition of particles on the channel surface, the heat exchange between the coolant flow and channel walls. Experimental study of mass transfer components of steel in sodium at low and high oxygen content in sodium is carried out. The comparison of the calculation results with the experimental data on distribution of the chromium deposits in the cooling channels is completed, on which basis are defined updated values of the constants that characterize the mass transfer of chromium by dissolving stainless steel in sodium.

Key Words: Corrosion products, chromium-nickel steel circuit, deposition, sodium.

Introduction

The problem of corrosion products mass transfer is paid much attention because it may affect:

- formation rate of impurity deposition on surfaces of the equipment of liquid metal circuits;
- radiating conditions at the installation;
- necessary productivity and capacity of coolant purification systems, the requirement to some devices for impurity control, application of additional devices for coolant purification.

In the presented work on the basis of the calculation and the theoretical analysis is refined information about physical and chemical constants, characterizing the mass transfer of corrosion products in sodium at presence of increased content of oxygen. Experimental study of mass transfer components of steel in sodium at low and high oxygen content in sodium is carried out. For the case of high oxygen concentration are performed two experiments: the oxygen content in sodium of 80 ppm and 140 ppm.

1. Model description

Basic positions of model of mass transfer in the cooling channel as the individual element of the circulation circuit are as follows:

- in coolant containing dissolved impurities a supersaturated solution is formed, in the certain channel section spontaneously germs of solid phase are formed;
- enlargement of the particles formed is not only due to crystallization on the surface of the solute, and also due to the aggregation of the colliding particles;
- on the channel walls can be formed depositions by the crystallization of the solute and the deposition of particles.

In case of increased oxygen content in sodium it is need to take into account its chemical interaction with steel components. This primarily relates to the iron and chromium.

X-ray analysis shows that the reaction product of sodium oxide and iron is a ternary oxide $(\text{Na}_2\text{O})_2\text{FeO}$ [1]. It is also known that increasing the oxygen content in sodium leads to an increase of nickel solubility [2].

In the chrome-nickel stainless steel circuits are formed under certain conditions along sodium oxide Na_2O , oxygen and sodium compounds with components of structural materials Na_4FeO_3 NaCrO_2 . Moreover, at temperatures above $500\text{ }^\circ\text{C}$ thermodynamically more stable NaCrO_2 , while the least stable sodium oxide [3].

The interaction of chromium oxide with sodium takes the following reaction



We consider that the oxygen in sodium is in the form of Na_2O . Other reactions of sodium oxide is neglected. The choice of chromium is justified for the following reasons: first, the thermodynamically most probable reaction of chromium with oxygen, compared with other major elements that make up the structural material and, secondly, chromium is present in the sodium-oxygen-structural material in large numbers (up to tens of percent in structural materials).

The equilibrium constant of reaction (1) is expressed through the activity of the components:

$$k = \frac{a(\text{NaCrO}_2) \cdot a(\text{Na})^3}{a(\text{Cr}) \cdot a(\text{Na}_2\text{O})^2}. \quad (2)$$

The kinetic equation for this reaction, if we consider the change in concentration NaCrO_2 , expressed by dependence:

$$\left(\frac{dc(\text{NaCrO}_2)}{d\tau} \right)_p = K^{\rightarrow} c(\text{Cr})c(\text{Na}_2\text{O})^2 - K^{\leftarrow} c(\text{NaCrO}_2)c(\text{Na})^3. \quad (3)$$

The index "p" here indicates a change in the concentration of complex oxide by reaction (1). Given that the chemical equilibrium constant of the initial reaction to $K = K^{\rightarrow} / K^{\leftarrow}$, as well as the convective transport of the dissolved complex oxide in sodium, we find a change in its concentration in the coolant in the mole fractions:

$$\frac{dc(\text{NaCrO}_2)}{d\tau} = K^{\rightarrow} \left(c(\text{Cr})c(\text{Na}_2\text{O})^2 - \frac{c(\text{NaCrO}_2)}{K} \right) + 4\chi_{\text{ox}} \left(\frac{c(\text{NaCrO}_2)_w - c(\text{NaCrO}_2)}{D_k} \right), \quad (4)$$

where D_k – channel diameter, m; χ_{ox} – the mass transfer coefficient of a complex oxide from the channel wall, m/s; the index "w" characterizes the near-wall concentrations.

Changes in sodium concentration of chromium in the differential form in view of its convective transport in the channel we obtained also in the mole fractions

$$\frac{dc(\text{Cr})}{d\tau} = - \left(\frac{dc(\text{NaCrO}_2)}{d\tau} \right)_p + 4\chi_x \left(\frac{c(\text{Cr})_w - c(\text{Cr})}{D_k} \right). \quad (5)$$

Similarly, for changes of oxygen concentration (in oxide form) in sodium obtained an expression

$$\frac{dc(\text{Na}_2\text{O})}{d\tau} = -2 \left(\frac{dc(\text{NaCrO}_2)}{d\tau} \right)_p + 4\chi_0 \frac{c(\text{Na}_2\text{O})_w - c(\text{Na}_2\text{O})}{D_k}. \quad (6)$$

To close the resulting system of equations determined by near-wall concentration of the components for the following reasons. Since the concentration of sodium oxide much higher than the other components in the solution (several orders of magnitude) can be taken

$$c(\text{Na}_2\text{O})_w = c(\text{Na}_2\text{O}). \quad (7)$$

Chromium concentration near wall $c(\text{Cr})_w$ calculated on the basis of the balance of chromium fluxes:

- 1) deposited on the surface of the channel

$$J_{\text{ox}} = K_r \beta_k (c(\text{Cr})_w - c(\text{Cr})_s^w); \quad (8)$$

- 2) transferred to the sodium stream due to convection

$$J_{\text{ox}} = \chi_x (c(\text{Cr})_w - c(\text{Cr})). \quad (9)$$

Jointly solving (8) and (9) we obtain

$$c(\text{Cr})_w = \frac{(\chi_x \cdot c(\text{Cr}) + K_r \beta_k \cdot c(\text{Cr})_s^w)}{(\chi_x + K_r \beta_k)}, \quad (10)$$

where $c(\text{Cr})_s^w$ – the saturation concentration of chromium in sodium near channel wall, mole fractions; K_r – coefficient taking into account the surface roughness; β_k – constant crystallization rate, m/s; χ_x – mass transfer coefficient of chromium on the channel wall of the, m/s.

The concentration of double chromium oxide near wall is determined based on equation (2), recorded for the corresponding conditions:

$$c(\text{NaCrO}_2)_w = k \cdot c(\text{NaCrO}_2)_s \frac{c(\text{Cr})_w}{c(\text{Cr})_s} \left(\frac{c(\text{Na}_2\text{O})}{c(\text{Na}_2\text{O})_s} \right)^2, \quad (11)$$

where $c(\text{Na}_2\text{O})_s$ – the saturation concentration of sodium oxide in sodium, mole fractions.

χ ratio is determined from the known dependence of heat and mass transfer criteria dependence [4]:

$$\text{Nu}_d = 5 + 0,025 \cdot \text{Pe}_d^{0,8}, \quad (12)$$

where $\text{Pe}_d = \frac{U \cdot D_k}{D_i}$.

$$\chi_i = \frac{\text{Nu}_d \cdot D_i}{D_k}, \quad (13)$$

where D_i – the diffusion coefficient of impurities in the coolant (where the index i characterizes the type of impurity), m^2/s .

The equilibrium constant (2)

$$k = \exp\left(-\frac{\Delta G^0}{RT}\right). \quad (14)$$

where ΔG^0 - the Gibbs energy, J/mol.

The equation to describe the evolution of a disperse system in the form of a differential (change of density of particles distribution by mass in time)

$$\frac{df(m)}{d\tau} = \frac{1}{2} \int_0^m \beta(m-m')f(m-m')f(m')dm' - \int_0^{\infty} \beta(m,m')f(m)f(m')dm' + \frac{I_1(m)}{m \cdot dm} - k_o(m)f(m) \frac{S}{V} \quad (15)$$

where $f(m) = dn(m)/dm$ – density of particles distribution by mass; m, m' – the mass of the colliding particles; S and V – the surface area washed by the coolant, and the volume of the considered section of the channel; $k_o(m)$ – the deposition coefficient of particle of mass m on the channel surface; β – the core of the equation; $I_1(m)$ – the intensity of the volume source of particles of mass m , $kg/(m^3)$.

Closing relations include the equations describing the mass transfer between the coolant flow and the channel wall, the deposition of particles on the surface of the channel, the heat transfer between the coolant and the wall of the channel. In addition, taking into account the excess of components incomes in sodium over limit of their solubility, is estimated the source capacity of the dispersed phase in coolant flow.

The solution of the above system of equations allows calculate the distribution of dissolved components and dispersed phase in sodium along the coolant flow as well chromium flux on the wall in the cooled channel.

A software module for the numerical solution of the above system of equations is developed [5].

2. Description of the experimental unit and the conditions of the experiment

Studies were carried out on the high temperature section (WTU) of experimental sodium loop "Protva-1". The scheme of the experimental section in FIG. 1 is shown.

The section operates as follows. Sodium at ~ 400 °C out of the loop is pumped in the shell side of the heat exchanger with a heat and mass transfer tube (1), where it is heated to about 650 °C, and then enters the heater (2), after which at the temperature ~ 750 °C is entered the source of contaminants (3). From the source (3) sodium is transported in heat and mass transfer tube for which a cooled surface is carried impurities, and then enters the filter for suspensions (4) and then returned to the loop.

After the experiment the inner tube is pulled out of the heat exchanger and cut into 20 pieces, FIG. 2.

Details of the impurities source and experimental conditions in Table I are shown.

Oxygen supply to the circuit was carried out by feeding in gas cavity of pump tank a mixture of argon and oxygen. According to the plugging meter (blockage temperature) were determined the value of the mass concentration of oxygen in sodium. Experiments were carried out at oxygen concentration in sodium 80 ppm and 140ppm and temperature in the impurity source of 770 °C.

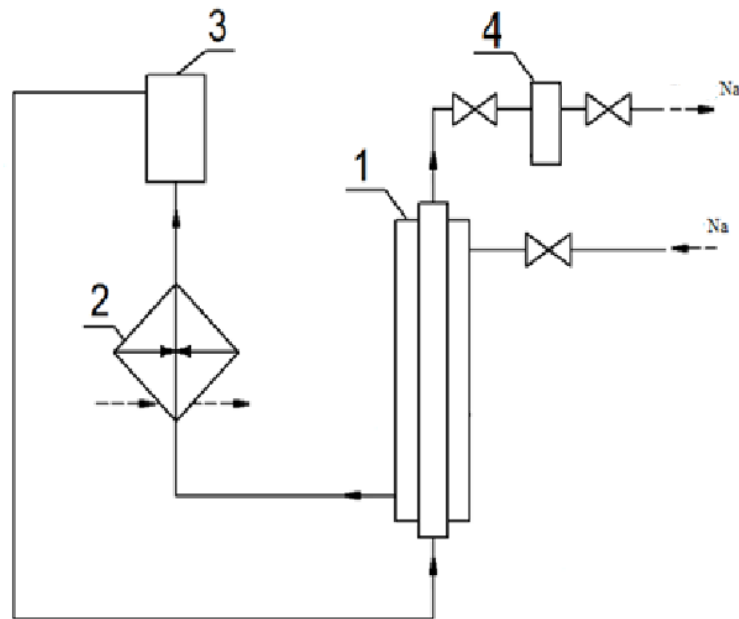


FIG. 1. Diagram of high temperature section of loop "Protva-1": 1 – recuperator with heat and mass transfer tube, 2 – heater, 3 – source of impurities (with samples of materials) 4 – filter.



FIG. 2. The tube pieces with deposits after cutting.

3. Results of experiment

On the inside surface of the heat and mass transfer tube pieces using a lathe was cut chips thickness of about 0.5 mm. Then for each portions of chips in experiment number 1 was

determined the content of chromium and iron, and in experiment number 2 nickel and chromium by chemical means.

As a result of chips sample analysis on chromium content is obtained the data of chromium fluxes to the channel walls, FIG. 3. Green and red curves in this figure represent experimental values.

TABLE I: CHARACTERISTICS OF THE IMPURITIES SOURCE AND THE EXPERIMENTAL CONDITIONS.

Number of experiment	number 2	number 1
Material of heat and mass transfer tube	Iron	Nickel
Source impurities	Chips of X18H10T	Chips of X18H10T
The surface area of chips; S , m^2	1.09	1.03
Weight of chips; m , kg	0.99	0.58
The temperature of sodium; t , $^{\circ}C$: in impurity source at entrance of the heat and mass transfer tube at exit of heat and mass transfer tube	780 745 505	770 745 460
The oxygen concentration in the sodium entering the high temperature section, ppm	140	80
The sodium velocity in the heat and mass transfer tube; m/s	1.0	0.55
The accumulation time of the impurity; h	161	116

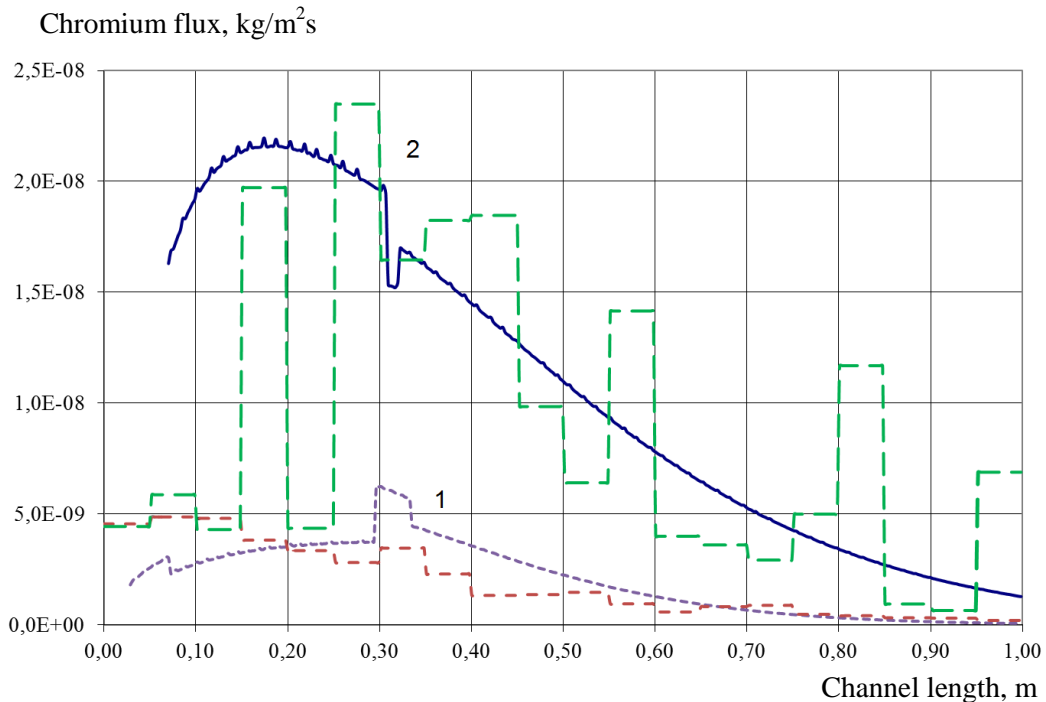


FIG. 3. Chromium flux along the wall of the channel distribution (the oxygen concentration in sodium experiment 1 ≈ 80 ppm, experiment 2 ≈ 140 ppm).

X-ray analysis revealed the presence of compounds NaCrO_2 , CrO , on the surface of a sample of chromium (disposed after the impurity source), tested at 770°C in experiment number 1. The possibility of the presence of compounds Na_4FeO_3 , NaCrO_2 in chips, taken from the inner surface of the nickel tube, tested at 450°C and 750°C in sodium.

Parametric calculations for a model and comparing the results with the experimental data to determine the distribution of chromium deposits on length of tube at an oxygen concentration in sodium 80 ppm and 140 ppm were conducted, see FIG. 3. The precised values of constants characterizing the mass transfer of chromium in the cooling channel are determined, Table II.

The results of research of mass transfer steel components in sodium with a low oxygen concentration are presented in [6].

For the versions with and without chemical reaction takes place the same values of the following constants:

- Factor of increased surface due roughness – 2;
- Crystallization rate constant of chromium in sodium – 3×10^{-4} m / s.

TABLE II: PARAMETERS CHARACTERIZING THE MASS TRANSFER OF STEEL COMPONENTS IN THE COOLING CHANNEL.

Constants	Chemical reactions are taken into account		Without the chemical reactions	
	iron	chromium	nickel	chromium
The impurity concentration at the inlet of the channel, kg/m^3	3×10^{-3}	4.5×10^{-4} ¹ 0.0027 ²	7.5×10^{-6}	4.28×10^{-5}
The diffusion coefficient of the impurities in sodium, m^2/s	1×10^{-9}	5×10^{-9}	2×10^{-9} at $T < 800$ K; $9 \times 10^{-11}T - 7 \times 10^{-8}$ at $T > 800$ K	3×10^{-9}
The impurities solubility in sodium, ppm	$10^{4.72 - 4116/T}$	$10^{9.35 - 9010/T}$	$\exp(1.077 - 3615/T)$	$10^{6.96 - 8920/T}$ at $T < 750^\circ\text{C}$
The saturation concentration of the ternary oxide in sodium, mole fractions	10^{-8}	10^{-8}	-	-
The constant of reaction rate of ternary oxide formation	$5 \times 10^3 \times \exp(0.0477/(T - 1023))$, $1/(\text{m.f.}^3 \cdot \text{s})$	$10^8 \times \exp(0.0477/(T - 1023))$, $1/(\text{m.f.}^2 \cdot \text{s})$	-	-

FIG. 4 shows the data determined of the chromium concentration in sodium on inlet of cooled channel (points 3-5). For comparison, the curves are shown of chromium solubility in the sodium saturated by corrosion products of steel [6] (curve 2) and proposed in [7] (curve 1). We assume that at the inlet of cooled channel a chromium concentration in sodium corresponds to the saturation. It follows that with increasing level of dissolved oxygen in sodium the chromium solubility also increases.

¹ experiment 1

² experiment 2

Conclusion

With regard to the system of sodium-oxygen-steel has been developed the mathematical description of physical and chemical processes of mass transport of corrosion products based on the chemical interaction and the corresponding calculation program to simulate the one-dimensional approximation of the mass transfer of steel components in the cooled channel.

Experimental study of mass transfer was completed at low and elevated oxygen content in sodium. At low oxygen content in the composition of the sediment bulk similar to that of steel dissolved. For the case of increased oxygen concentration performed two experiments: the oxygen content of 80 ppm in sodium and 140 ppm. A comparison of the calculation results with experimental data on the distribution of chromium deposits in the cooling channels was held, on which are defined the updated values of the constants characterizing the chromium mass transfer by dissolution of stainless steel in sodium.

It is found that at increasing level of dissolved oxygen in sodium also increases the chromium solubility.

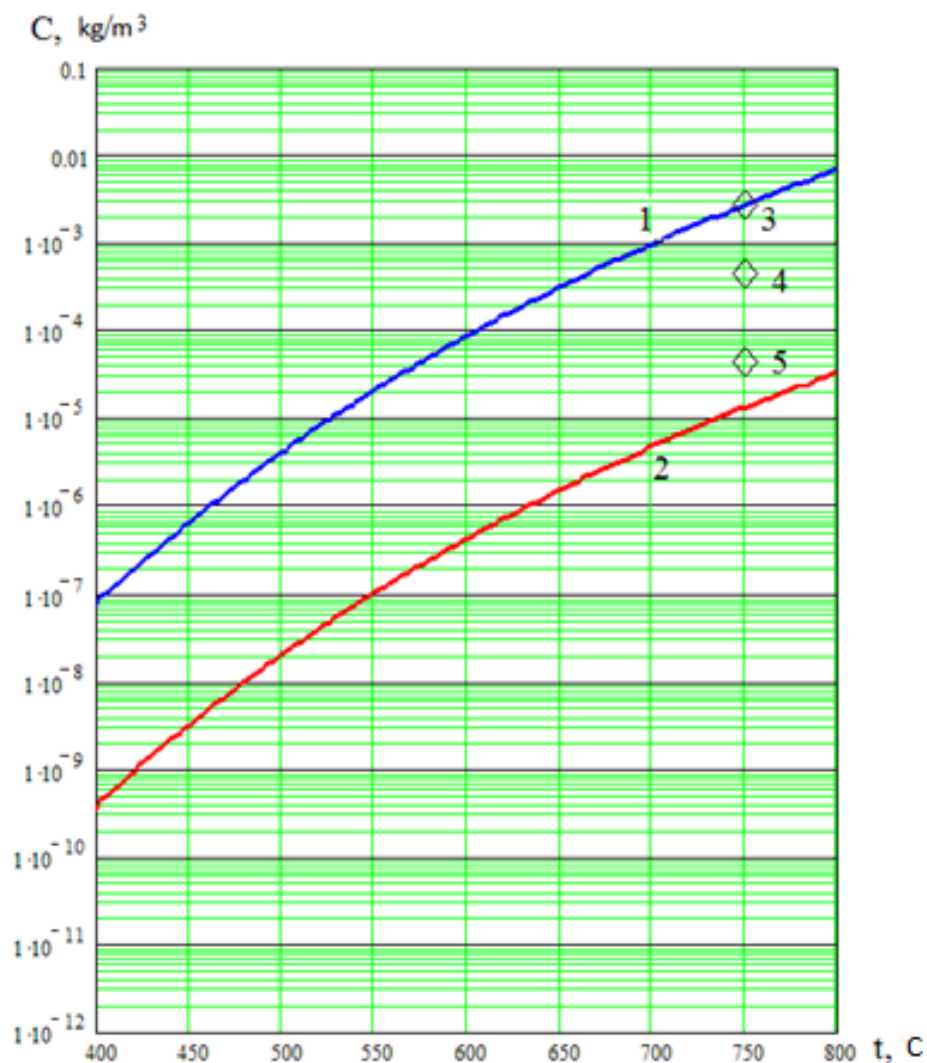


FIG. 4. Chromium concentration in sodium: 1 – $10^{9.35 - 9010/T}$ [7]; 2 – $10^{6.97 - 8920/T}$ [6]; 3 – ~140 ppm oxygen in sodium; 4 – ~80 ppm oxygen in sodium; 5 – 2-3 ppm oxygen in sodium.

References

- [1] HORSLEY, G.W. J., Iron and steel inst **182**, (1956) 43.
- [2] KOVACINA, T.A., MILLER, R.R., Nucl. sci. and engng **10** (1961) 163.
- [3] AZAD, A.M., SREEDHARAN, O.M., GNANAMOOTHY, J.B., J. Nucl. Mat. **151** (1988) 293.
- [4] KIRILLOV, P.L., YURYEV, YU.S., BOBKOV, V.P., Handbook of thermal-hydraulic calculations, 2nd ed., Energoatomizdat, Moscow (1990) (in Russian).
- [5] KONDRATEV, A.S., “Simulation of corrosion products mass transfer, taking into account the chemical interaction in the system Na - structural material – impurities” Thesis for the degree of Candidate of Technical Sciences. - SSC RF-IPPE, Obninsk (2011) (in Russian).
- [6] ALEKSEEV, V.V., “Mass transfer of structural materials corrosion products and tritium in circuits with sodium coolant” Thesis for the degree of Doctor of Technical Sciences. - SSC RF-IPPE, Obninsk (2002) (in Russian).
- [7] SINGER, R.M., et. al., Corrosion by Liquid Metals. (Eds. DRALEY, J.E., WEEKS, J.R.), Plenum Press, New York (1970).