Specifics of high-temperature sodium coolant purification technology in fast reactors for hydrogen production and other innovative applications

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Available online 25 March 2017

Abstract

In creating a large-scale atomic-hydrogen power industry, the resolution of technological issues associated with high temperatures in reactor plants (900 °C) and large hydrogen concentrations intended as long-term resources takes on particular importance. The paper considers technological aspects of removing impurities from high-temperature sodium used as a coolant in the high-temperature fast reactor (BN-HT) 600 MW (th.) intended for the production of hydrogen as well as other innovative applications. The authors examine the behavior of impurities in the BN-HT circuits associated with the mass transfer intensification at high temperatures (Arrhenius law) in different operating modes. Special attention is given to sodium purification from hydrogen, tritium and corrosion products in the BN-HT. Sodium purification from hydrogen and tritium by their evacuation through vanadium or niobium membranes will make it possible to develop compact highly-efficient sodium purification systems. It has been shown that sodium purification from tritium to concentrations providing the maximum permissible concentration of the produced hydrogen (3.6 Bq/l according to NRB-99/2009) specifies more stringent requirements to the hydrogen removal system, i.e., the permeability index of the secondary tritium removal system should exceed 140 kg/s. Provided that a BN-HN-type reactor meets these conditions, the bulk of tritium (98%) will be accumulated in the compact sodium purification system of the secondary circuit, 0.6% ($\sim 4 \cdot 10^4$ Bq/s), will be released into the environment and 1.3% will enter the product (hydrogen). The intensity of corrosion products (CPs) coming into sodium is determined by the corrosion rate of structural materials: at a high temperature level, a significant amount of corrosion products flows into sodium. The performed calculations showed that, for the primary BN-HT circuit, the amount of corrosion products formed at the oxygen concentration in sodium of 1 mln^{-1} exceeds 900 kg/yr with fuel element claddings made of EP-912-VD steel and 464 kg/yr with molybdenum alloy claddings. For the secondary circuit, the amount of corrosion products totals 263 kg/yr for each loop. Taking into account the high-temperature experiments which demonstrated high efficiency of retaining corrosion product suspensions by the strainers located in the low-temperature area, it is proposed to cool sodium to the required temperature alongside the corrosion products retention on the mass transfer surfaces, including strainers. It is shown that, by using 30% of the power required to produce hydrogen with 50% efficiency, the BN-HT is capable of producing about $0.6 \cdot 10^6 \text{m}^3$ of hydrogen per 24 hours which is sufficient for modern large-scale enterprises processing medium-grade crude oil or the implementation of other technologies.

Introduction

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Conceptual studies on the appearance of a high-temperature sodium-cooled fast power reactor (BN-HT) to create a large-scale atomic-hydrogen power industry have shown that developing of such a reactor is a real technical challenge [1]. In this context, a particularly important task is resolving technological issues associated with high tempera-

tures in reactor plants and large hydrogen concentrations intended as long-term resources, including: developing a sodium coolant technology to be used at high temperatures and large hydrogen concentrations intended as long-term resources and ensuring corrosion stability of heat- and radiation-resistant high-temperature structural materials at the oxygen concentration in the sodium coolant of $1\,\text{mln}^{-1}$. Specific assessments were carried out for the BN-HT 600 MW (th.). The problems of removing impurities from high-temperature sodium were considered; special attention was given to the problem of sodium purification from hydrogen, tritium and corrosion products (CPs), the source intensity of which in the primary circuit of a high-temperature reactor plant intended for the hydrogen production increases by orders of magnitude.

Behavior of impurities in the BN-HT circuits in different operating modes

The heat removal by means of the coolant used in the reactor plant is accompanied by its interaction with impurities available in the liquid-metal system and their negative impact on the structural materials. The direction of these processes is determined by the difference of chemical potentials [2].

In a real nonisothermal system ($dT/dx \neq 0$), for its chemical potential, this relation is valid

$$\frac{\partial \mu}{\partial x} = \frac{dT}{dx}\left[\left(\frac{d\mu_0(T)}{dT} + \text{R}\ln\left(\frac{C}{C_{\text{sat}}}\right)\right)\cdot\frac{1}{dC/dx}\right.$$
$$\left. + \text{R}T\frac{C_1}{C_{\text{sat}}}\left(C_{\text{sat}} - C\frac{dC_{\text{sat}}/dx}{dC/dx}\right)\right]\frac{dC}{dx} = B\frac{dC}{dx} \qquad (1)$$

if, for the real system,

$$j = -\alpha \cdot d\mu/dx = -aB\mu \cdot dC/dx = -D \cdot dC/dx. \qquad (2)$$

From (1) and (2), it is clear that the transfer of components in the nonisothermal fixed system, in addition to the coefficient α characterizing the diffusion properties of the medium, depends on a number of factors, including the impurity solubility, chemical potential temperature dependence (physical–chemical characteristics of the system) and temperature gradient which have a dominant role. When the fluid is moving, the hydrodynamic characteristics will also contribute to the mass transfer processes.

Using the temperature dependence of the constants characterizing the heat and mass transfer (Arrhenius formula),

$$k = k_0 \exp\{-E/(RT)\}, \qquad (3)$$

(k is the constant characterizing the process; k_0 is the constant factor; E is the activation energy; R is the universal gas constant ($R = 8.31\,\text{J/(mole K)}$); T is the absolute temperature, K), it becomes clear that, when specific liquid metal system processes are considered, e.g., diffusion, permeability, solubility, absorption rate, gas pressure equilibrium, etc., their values will increase in the transition to high temperatures.

An increase in the constant for the above-mentioned processes is determined by their activation energy and temperature rise. But $T_2/T_1 \leq 2$, and the activation energy varies from

hundreds to tens of thousands of J/(mole K) and it is virtually temperature-independent for such a characteristic as the hydrogen pressure equilibrium over sodium. The highest values are characteristic of diffusion, permeability in solids and gas absorption rate kinetics. For the solubility of impurities, the activation energy is at least orders of magnitude lower than that of the diffusion processes. It should be noted that, for the same process, the activation energy of different materials may vary by several times and, in some cases, by an order of magnitude.

The qualitative analysis of the behavior of impurities in the liquid metal BN-HT systems in different operating modes shows that the coolant purification during the sodium receipt from transport containers, commissioning works and in standby modes can be done in cold traps (CTs). In modes of the sodium receipt from transport containers and commissioning works, conventional CT connection schemes can be used. In standby modes, if they are implemented after the stabilization of nominal conditions and operation under normal conditions, the inevitable appearance of radioactivity in the coolant should be considered.

In high-temperature systems with carbon concentrations of tens of mln^{-1}, the carbon thermodynamic activity due to the high sodium solubility as compared to NPPs of the BN-600 type increases by orders of magnitude. Therefore, in order to avoid carburization of structural materials, it may become necessary to remove carbon from hydrogen by the hot trap before switching to the nominal operating parameters.

Purification in nominal and standby modes required a special analysis since the intensity of the sources of hydrogen, tritium and corrosion products increases by orders of magnitude.

Sodium purification from hydrogen and tritium in high-temperature nuclear power plants

The specific behavior of hydrogen, tritium and cesium and their removal are considered in [3,4]; therefore, we shall focus only on the main results obtained for the BN-HT 600 MW.

With increasing hydrogen flows from the tertiary circuit into the secondary one by two–three orders of magnitude as compared to the hydrogen source in NPPs with the BN-600 reactor, it is possible to create compact purification systems with the required performance at hydrogen concentrations of tens of mln^{-1}, as the purification system (PS) performance in a first approximation is proportional to the hydrogen concentration in sodium. In this connection, sodium purification from hydrogen and tritium should be performed not by a cold trap (CT) but by their evacuation through the vanadium or niobium membranes. The combination of these two factors will create a highly compact system for removing hydrogen from sodium.

Sodium purification from tritium to concentrations providing its maximum permissible concentration (MPC) of 3.6 Bq/l in the produced hydrogen specifies more stringent requirements to the hydrogen removal system, i.e., its performance (permeability, and hence the size) should be increased.

Table 1

The intensity of CPs coming into sodium in the BN-HT primary and secondary circuits during the operation at nominal parameters, kg/yr.

Primary circuit				Secondary circuit[a]	
Homogeneous system	Heterogeneous system			Homogeneous system	
All equipment – EP-912-VD 900	Fuel element – Molybdenum (alloys) Negligible	IHE – EP-912-VD 464		IHE – EP-912-VD 662	Pipeline – EP-912-VD 914

[a] For the six secondary loops, 263 kg/yr of CPs flows into sodium of each loop.

Provided that a NPP with the BN-HN reactor meets these conditions, the bulk of tritium (98%) will be accumulated in the compact sodium purification system of the secondary circuit, 0.6% ($\sim 4 \cdot 10^4$ Bq/s), will be released into the environment and 1.3% will enter the product (hydrogen). In the event of a release in compact purification systems $\sim 4 \cdot 10^4$ Bq/s, the requirements for normal environmental conditions set forth in [5] can be easily satisfied by the methods that are widely used today in the nuclear industry.

As a large mass of tritium is accumulated in compact purification systems, the problem related to the subsequent hydrogen handling, if these NPPs are used on a wide scale, requires special consideration.

Behavior of corrosion products in sodium-cooled facilities

During the NPP operation, corrosion products are constantly coming into sodium. Numerous studies on corrosion of structural materials are presented in the monographs [6,7]. Research studies in this area have been ongoing for the past 20 years (e.g., [8–11]).

It is evident that the intensity of corrosion products (CPs) coming into sodium is determined by the corrosion rate of structural materials: the intensity of the CPs for the BN-HT primary and secondary circuits was calculated by equation [12]

$$J_{cp} = J_0 \cdot C_O{}^m \cdot f \cdot \exp(-B/T), \qquad (4)$$

where J_0 is the pre-exponential factor, kg/m² s; $C_O{}^m$ is the oxygen concentration in the coolant, mln⁻¹; $f = (w/w_k)^{0.33}$ if the flow rate $w \leq w_k$ and $f = 1$ if $w > w_k$, w_k is the coolant limit speed, м/c; T is the temperature, K; $m = 1.2$, $B = 12,900$ K are the parameters.

In calculations for EP-912-VD steel, it was assumed that $J_0 = 7,5 \cdot 10^{-4}$ kg/m² s, $C_0 = 1$ mln⁻¹, the fuel element peak temperature $= 1025$ °C and the temperature distribution was considered along the length of the intermediate heat exchanger core. The intensity estimations of CP sources in the BN-HT are presented in Table 1.

It should be noted that, in a nonisothermal system, the corrosion rate in the high-temperature area should depend on the temperature difference between the circuit hot and cold areas: if this difference decreases in the high-temperature zone, the corrosion rate should decrease. In Eq. (4), this effect is not taken into account; therefore, we may state that the results shown in the table give an inflated estimation. As a result of

Fig. 1. Strainer after experiment: total deposits – 6.2 g, including those on the bottom – 5.2 g and on the strainer screen – 1 g.

our estimations, it is assumed that the amount of CPs coming into sodium decreases by six times.

Justification for the system of sodium purification from corrosion products

Possible design concepts for the corrosion product removal system

It is well known that the effectiveness of CTs for sodium purification from CPs at modern NPPs is rather low. However, special experiments have shown that CPs were efficiently retained by the strainer located behind the heat exchanger, in which the sodium temperature decreased from 750 °C (at this temperature, sodium flowed about the source of CPs) to 420 °C, (Fig. 1).

In addition, the CP retention ratio was estimated to be close to unity and the fraction of impurities deposited on the heat exchange tube surface $\sim 3\%$ of the CP amount found in the filter. Considering these results, the CT operation principle was chosen to develop the CP removal system: sodium is cooled to the desired temperature followed by the retention of CP suspensions on the strainers.

We shall assume that the CP removal system included in the combined BN-HT purification system is structurally made of a recuperative heat exchanger (RHE) combined with a strainer. To eliminate the CP crystallization in the low-temperature zone, the purification system should provide the CP concentration in the flow as follows: $C_{\text{flow}} < C_{\text{CP}}{}^{\text{sat}}$
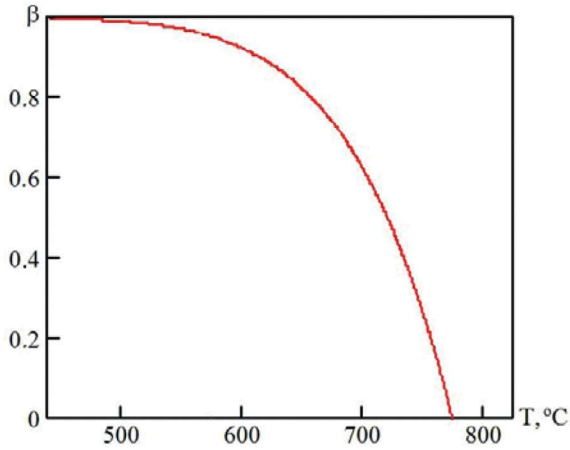
Fig. 2. Temperature-dependent chromium crystallization efficiency at the BN-HT primary circuit CP removal system outlet.

$(T_{min} - \Delta T)$. For further calculations without optimization, it was assumed that $\Delta T = 30\,°C$.

CP removal system temperature conditions

In this device, sodium can be cooled to 110°C. In this case, the transition of CPs into the crystalline phase is maximal but the removed power is also maximal. If the heat removal in the CP removal system decreases, the outlet temperature will rise and the amount of PCs being crystallized in the CP removal system is reduced: this will result in the system performance degradation. This effect can be calculated according to the equation

$$\beta = (C_{flow} - C_{sat}))/(C_{flow} - C_{sat}23\,K)). \tag{5}$$

In the calculations, it was assumed that the chromium temperature-dependent solubility is expressed by equations:

$$C_{Cr}^{sat} = 10^{5.8 - 5800/T}, \tag{6}$$

$$C_{Cr}^{sat} = 10^{9.35 - 9010/T}, \tag{7}$$

$$C_{Cr}^{sat} = \exp(16.2 - 20746/T) = 10^{7.04 - 9014/T}. \tag{8}$$

The calculation results are shown in Fig. 2. It can be seen that, for C_{flow} at 775 °C (primary circuit) more than 95% of CPs should change into the crystalline phase at the system outlet temperature of 575 °C. Therefore, when the temperature is lowered to 100–150 °C, the inappropriately removed capacity will increase by more than three times and the purification efficiency will improve to a maximum of 5%.

Taking into account the need to include the CP removal system in the combined purification system, this temperature was increased to 650°C.

Sodium flowrate through the CP removal system (Q_{PS}): If it is assumed that, in the CP removal system, sodium is cooled to T_K^{min}, then, the CP flow into it (its performance) complies with the relation

$$J_{CP} < Q_{PS}\left[C_{flow}(T_K^{min} - 30) - C'_{PS}(T_{PS}^{min})\right]\beta. \tag{9}$$

Table 2
Required flowrate through the PS removal system of the primary (C_{flow}^{sat} (1043 K)) and secondary (C_{flow}^{nac} (1018 K)) circuits.

Chromium solubility	Primary circuit	Secondary circuit
$C_{Cr}^{sat} = 10^{5.8 - 5800/T}$ (6)[a]	2.5	1.1
$C_{Cr}^{sat} = 10^{9.35 - 9010/T}$ (7)	0.7	0.36
$C_{Cr}^{sat} = 10^{7.04 - 9014/T}$ (8)	150	77

[a] Formula (6) was derived by Ye.V. Varseyev based on data in literature sources.

Hence, the sodium flowrate through the CP removal system should be no less than

$$Q_{PS} \geq J_{CP}/\{[C_{flow}(T_K^{min} - 30) - C'_{PS}(T_{PS}^{min})]\beta\}. \tag{10}$$

In the calculations, it is assumed that the intensity of the sources in the primary and secondary circuits is: for the primary circuit: 151 and 77 kg/yr for homogeneous and heterogeneous systems, respectively, and 44 kg/yr for each loop of the secondary circuit. Given that the calculation was made based on chromium, it was assumed that $J_{CP} = 5J_{Cr}$. The calculation was made for the CP removal system least temperature of 650 °C and three chromium-sodium solubility-temperature dependences (6)–(8). The CP retention rate is assumed to be equal to unity. The results are listed in Table 2.

There is a discrepancy between the results obtained using the solubility data [13,14] by two orders of magnitude. Note that, when using data on the so-called "solubility of steels" [15], the flowrate through the primary circuit should be approximately equal to 104 t/h. Our detailed analysis of the data obtained in the high-temperature experiments, in particular, on the CP retention rate on the strainer indicates that the results obtained using Eq. (6) should be taken as the basic ones. The calculations show that the dimensions of the main CP removal system components (i.e., BN-HT recuperative heat exchanger, strainer) will be acceptable.

Conclusion

Based on the results obtained by the proposed method for calculating the mass transfer of hydrogen and tritium with due account for sodium circuits, it has been shown that the efficiency of such a system is about 40% and the amount of hydrogen produced is 28 m³/s (under normal conditions). The real danger of tritium in the finished product occurs in the case of hydrogen combustion in the atmosphere. In this case, the bulk of tritium will be present in the form of HTO compounds (hydrogen-tritium-oxygen). Therefore, in the calculations of parameters for the purification system and operable concentrations of hydrogen and tritium in sodium of the secondary circuit in accordance with the NRB-99/2009, it was assumed that the maximum permissible concentration of tritium in the produced hydrogen should not exceed 3.26 Bq/l. The values of the maximum permissible concentration of tritium in the air by almost three orders of magnitude higher, i.e., 2.44·10³ Bq/l. Sodium purification from tritium specifies additional requirements to the hydrogen removal system, i.e., the permeability index of the secondary purification system for tritium should exceed 140 kg/s.

For the BN-HT primary circuit, the amount of corrosion products formed at the oxygen concentration in sodium of $1\,mln^{-1}$ exceeds $900\,kg/yr$ with fuel element claddings made of EP-912-VD steel and $464\,kg/yr$ with claddings made of molybdenum alloy, respectively; for the secondary circuit, it totals $263\,kg/yr$ for each loop. Taking into account the high-temperature experiments (900 and $750°C$), which demonstrated high efficiency of retaining corrosion product suspensions by the strainers (the retention rate is close to unity) located in the low-temperature area, it is proposed to cool sodium to the required temperature alongside the retention of corrosion products on the mass transfer surfaces, including strainers.

A BN-HT-type reactor with a thermal capacity of $600\,MV$, using 30% of the power required to produce hydrogen with 50% efficiency, could produce about $0.6{\cdot}10^{6}\,m^{3}$ of hydrogen per day, which is sufficient for modern large-scale enterprises processing medium-grade crude oil and the implementation of other technologies.

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