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5. SODIUM AND LEAD TECHNOLOGIES

5.1. INTRODUCTION

The term "coolant technology" means a complex of methods and means assuring operation of facility under rated conditions and possible abnormal conditions. The main tasks related to coolant technology are as follows:

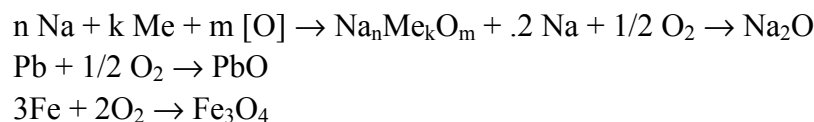
1. Development of coolant quality standards;
2. Analysis of impurities condition, their sources and accumulation rate in the circuit;
3. Analysis of corrosion and mass transfer;
4. Development of methods and equipment for keeping impurity content in the coolant within acceptable limits;
5. Analysis of different operating procedures and evaluation of related impurities input;
6. Control of coolant quality during operation.

Coolants produced by the industry (Na, Pb, etc.) do not always meet technological requirements. Therefore additional procedures are performed prior to filling circuit with the coolant in order to bring the coolant to required condition. Mounting and repair works are always required during facility life although resulting in pollution of the coolant. Another cause of changes in the coolant composition is corrosion, resulting in deterioration of mechanical properties of structural materials. Corrosion products are transported along the circuit, and depositions are formed that can affect hydrodynamics and heat transfer, and hence reliability of facility. All circumstances mentioned above lead to the necessity of permanent control over the impurities content and corrosion processes in the circuit.

The main elementary corrosion processes in the liquid metal are as follows:

1. Interaction of coolant with passive or oxide films-passivation or activation of materials.
2. Dissolving of steel components and their chemical interaction with non-metal impurities (oxygen, hydrogen, etc.).
3. Penetration of liquid metal into solid materials causing frontal and inter-granular corrosion.
4. Transport of structural material components along the circuit.

Interaction of Na, Pb and Fe with oxygen occurs by the following reaction:



Direction of corrosion process is determined by thermodynamic properties of the system. The reactivity is determined by the change in isobaric-isothermal potential or Gibbs energy (ΔG):

$$\Delta G = RT \ln a, \quad (5.1)$$

where: R -thermodynamic constant, J/kg K; $a = \gamma N_i$ -thermodynamic activity of i -th component, N_i -mole fraction of the component, γ — its activity factor. Component dissolving takes place, if $\Delta G < 0$, while crystallization occurs with $\Delta G > 0$.

In order to predict the direction of corrosion and mass transfer, it is essential to have data on thermodynamic properties of chemical compositions and steel components as a function of temperature. If the liquid metal is flowing at high velocity, the material is subject to erosion. Formation of the film (consisting of both steel and liquid metal coolant components) on the structural metal surface is another type of corrosion, since this is not protective film. Due to the difference in chemical activity between sodium and lead, technologies of these coolants are quite different, although some methods share a number of common features.

5.2. SODIUM TECHNOLOGY

5.2.1. Impurities sources

Typical composition of commercial-grade sodium determined by standard methods of analysis is given in Table 5.1, where 1 ppm= $10^{-4}\%$.

Among permanent contributors of impurities under normal operating conditions are corrosion related hydrogen from steam generators, tritium from the reactor core, oxygen and hydrogen from cover gas and corrosion products. Sources of impurities in liquid sodium determined in the BN-350 and BN-600 reactors under operating conditions are shown in Table 5.2 [5.1]. They have the following characteristics:

1. Initial impurity content due to oxygen absorption on the circuit surface is 3.4 g/m^2 (I circuit) and 2.2 g/m^2 (II circuit), that is in a good agreement with the experimental data ($1.4\text{--}2.4 \text{ g/m}^2$). Total amount of oxygen absorbed is about 30 kg.
2. Impurities introduced during repair operation are Na_2O , NaOH and Na_2CO_3 . Assessments have shown that during operation (20 years) about 200 kg of substances aforementioned is introduced [5.2.].
3. Impurities added during subassembly loading. Assuming 2 g/m^2 specific content, total amount is equal to about 200 kg.
4. Impurities caused by diffusion from other sources. Diffusion rate is evaluated to be about $50 \text{ g O}_2/\text{day}$. Total amount of impurities is about 720 kg.

TABLE 5.1. TYPICAL COMPOSITION OF COMMERCIAL-GRADE SODIUM

Components	Content (mass)
Total (Na)	99.9%
Metal (Na)	99.8%
Potassium (K)	200 ppm
Calcium (Ca)	250 ppm
Barium (Ba)	< 5 ppm
Iron (Fe)	< 20 ppm
Chlorine (Cl)	< 10 ppm

TABLE 5.2. SOURCES OF IMPURITIES IN LIQUID SODIUM

Sources	Oxygen	Water, kg/year	Hydrogen	Corrosion products from reactor, kg/year	Tritium from the core, g/hour
Cover gas	1 kg/year*	0.1–0.5	$(3\div 6) \cdot 10^{-2}$ g/h**	20**	$6.3 \cdot 10^{-5}$ *
Repair works	6 kg/year*	0.6	0.5–1 g/h**	60*	
Steel (Cr18Ni10Ti)	0.01 g/m ²	-	$4.4 \cdot 10^{-3}$ g/kg		
Steel (11/4 Cr2Mo)	0.01 g/m ²	-	$6.4 \cdot 10^{-3}$ g/kg		

Note: * — BN-600 reactor, ** — BN-350 reactor.

5.2.2. Purification of sodium and cover gas

At the present time, sodium purification technique with the use of cold traps based on decreasing solubility of the major part of impurities in sodium with temperature decrease has found the most wide practical application [5.3, 5.4]. In the cold trap sodium is cooled within the settling tank and the section upstream the filter. This results in reduction of oxygen and hydrogen concentrations respectively to 1 and 0.05 ppm. Cold trap is capable of retaining impurities in amount up to ~30% of its volume [5.5].

Carbon is confined in the cold trap as suspension, the purification process being 10 times longer than that for oxygen. In order to catch caesium, graphite based purification technique was developed [5.6, 5.7]. Upon 10 years of the BN-350 reactor operation capacity of the secondary traps was exhausted and their hydrogenation was carried out. The basic amount of sodium transformed to caustic phase was removed at 420°C. Thus, normal operation of traps was restored [5.3].

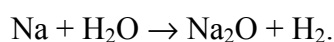
As regards the cover gas, it is necessary to purify source argon eliminating impermissible release to the environment of ^{133, 135}Xe and ^{85, 87, 88}Kr, short-term total activity of which in the BN-600 reactor reached $6.7 \cdot 10^9$ Bq/L value. This problem was solved using special filters and activated coal as absorbent [5.1, 5.3].

5.2.3. Control of impurities content in the coolant and cover gas

Control of the content of non-metal impurities in the coolant (O₂, H₂ and C) and cover gas (H₂O, CH₄ and N₂), as well as ⁹⁰Sr, ¹³¹I, ¹³⁷Cs, ⁵⁴Mn and ^{58, 60}Co in the primary circuit is most important.

Oxygen control. In order to make measurements of oxygen activity in sodium the electrochemical control technique based on galvanic cell has been mastered with sodium flowing over electrolytic pellet of thorium and yttrium sealed into the metal tube. Reference electrode is located inside the tube. E.m. F. generated depends on the temperature and oxygen concentration: e.m. F. = f(T, C_{O₂}). Service life of such device is over 10⁴ hours.

Hydrogen control. The necessity in hydrogen control was caused by the need for detection of water leak into sodium resulting in the following reaction:



Diffusion technique that has found the widest application is the method using metal membrane permeable to hydrogen in combination with different secondary devices (mass-spectrometer, magnetic discharge pump, etc.). So, the flow rate of hydrogen passing through the nickel membrane into vacuum cavity is measured by the system equipped with magnetic discharge pump, where gas ionization takes place. Automatic hydrogen detector is capable of detecting 10–30 g water leak to 100 t of secondary sodium. Description of other techniques can be found in [5.3].

Carbon control. Carbon needs to be controlled for evaluating carburization of structural materials because of possible impact on their mechanical properties. Diffusion and electro-chemical cells similar to those mentioned above are used for carbon control, with the salt mixtures (Na₂CO₃-Li₂CO₃ and CaC₂-LiCl) used as electrolytes.

Control of initial temperature of impurity crystallization (plugging indicator). Operation of plugging indicator is based on impurity deposition from supersaturated solution in the narrow gaps. Super-saturation is achieved by decreasing temperature of the coolant flowing through the indicator. As the temperature becomes lower than the saturation point, the flow rate through the indicator decreases, this being registered by the indicator. Actually, indicator measures the temperature at which rate of impurity deposition or solubility is sufficient to detect change in the flow rate. Presence of different impurities in the coolant makes it possible to detect several "plugging temperature" values. It should be noted that saturation temperature is determined within the accuracy of 3°C.

Radioactive impurity control. Prompt control of radioactive impurities in the primary sodium is made using three methods:

- measurement of γ -radiation from piping 10–12 days after reactor shutdown;
- measurement of activity of fission and corrosion products on special-purpose bypass section 10 days after its disconnection from the primary circuit;
- measurement of concentration of selected products (Cs, I) in graphite compound.

5.2.4. Corrosion processes in sodium

By now, comprehensive studies have been performed and reliable industrial experience has been gained on material corrosion in sodium. Corrosion intensity in sodium is significantly lower than that in water or lead-based coolants [5.9]. In sodium, as well as in the other liquid metals, corrosion rate depends on many factors (temperature level, coolant velocity, impurity content, temperature difference, time, etc.). When evaluating corrosion rate, the major part of researchers took into account only the most contributing factors. Empirical equations for corrosion rate were most commonly derived for 316 steel at the coolant velocity of > 4 m/s and oxygen content of ≤ 10 ppm. The most reliable results were obtained in [5.10, 5.11] for corrosion rate K , $\text{mg}/\text{cm}^2\text{h}$, that can be expressed as follows:

$$K = 0.61(C_o)^{1.5} \exp\left(-\frac{18000}{RT}\right) \quad (5.2)$$

It was found that chromium alloyed and austenitic steels have high corrosion resistance. The equivalent corrosion rate of two steels such as HT-9 and Fe9Cr1Mo was measured after their exposure during 4000 hours at 600–650°C temperature, 6 m/s flow velocity and 1 ppm oxygen content. The results of measurements are given in Table 5.3 [5.12, 5.13, 5.14].

TABLE 5.3. EQUIVALENT CORROSION RATE OF AUSTENITIC AND CHROMIUM STEELS

Materials	Equivalent corrosion rate, $\mu\text{m}/\text{year}$	
	600°C	650°C
HT-9	1.15	3.1
Fe9Cr1Mo	0.7	2.3

The operational experience of a number of LMFRs during long time (20–30 years) has shown, that sodium is practically non-corrosive with respect to stainless steel, the content of impurities, mainly oxygen and carbon, being held at acceptable low level by the cold traps.

5.3. LEAD TECHNOLOGY

5.3.1. Basic issues of technology

Basic technological challenge of using lead as reactor coolant is assurance of such quality of the coolant (as well as that of the surfaces contacting coolant), that the following conditions are realized:

- sufficient corrosion resistance of structural materials;
- stable hydrodynamics and heat transfer during life time.

Presence of impurities in lead coolant is injurious for at least two reasons, namely:

- 1) possible partial or full plugging of the coolant flow cross section area, that disturbs hydrodynamics and hence heat transfer;
- 2) deposits formed on heat transfer surfaces (especially on the fuel elements of the reactor core causing rise of cladding temperature).

5.3.2. Impurities contributors

The following impurities are present at the initial stage of circuit filling:

- residual oxygen, remaining after evacuation, and water vapours;
- gas adsorbed on the inner surfaces;
- steel corrosion products;
- casual impurities (chip, welding hail, etc.).

Under operating conditions, the basic factors causing increase of impurities content in the lead circuit are:

- structural material corrosion;
- erosion and abrasion of materials;
- penetration of grease from pump seals and bearings;
- cover gas entrainment by the coolant;
- admixtures to the coolant aimed at forming protective films.

Impurities can be located in such parts of circuit as cover gas plenum and stagnant sections, as well as on the free surface of molten lead (since density of practically all impurities is lower than that of lead) and structures (as deposits). During facility operation the impurities are transported along the circuit. The methods of impurity control in lead and cover gas are shown in Table 5.4.

TABLE 5.4. METHODS OF IMPURITY CONTROL IN LEAD AND COVER GAS

Impurities	Sources	Methods of control
Water vapour in cover gas	Steam generator leak	1. Condensation of vapour from cover gas 2. Permanent chromatography control of cover gas
Hydrogen in cover gas	Cleaning of coolant and circuit from impurities	Measurement of hydrogen content in cover gas: <ul style="list-style-type: none"> • thermal conductivity method • chromatography
Oxygen in lead	Maintaining required oxygen content	Galvanic cell (measurement of e.m. F. induced in solid electrolyte with ion conductivity)

5.3.3. Cleaning from slag

Oxide-based slag (PbO) can be removed from the coolant by settling and reducing with hydrogen. Slag originating dispersed impurities caused by lead interaction with structural materials (Fe, Cr and Ni) are removed by mechanical filter or by settling. Oil and pyrolysis products can be removed using organic solvents or water vapour injected into the circuit.

5.3.4. Corrosion processes in lead [5.15–5.20].

The development of corrosion resistant structural materials is apparently the main problem in lead cooled reactor technology. Lead exhibits strong erosion-corrosion effect on structural materials, such as material dissolving, embrittlement, thermal transport of mass and inter-granular penetration of lead.

The most resistant to lead are refractory metals followed by chromium steels and austenitic steels being less resistant because of high solubility of incorporated nickel. Stabilization of austenitic steels by Ti, Nb and Mo enhances their resistance to lead.

The main type of corrosion damages in liquid Pb, Bi and Pb-Bi is the dissolution of structural materials (steels) and their components in these coolants. The kinetics of dissolution processes can be of different nature. For example, in some cases the dissolution is localized on boundaries of grain, causing interstructure infiltration of liquid metal (Pb, Pb-Bi) into steel.

The basic kind of corrosion damage, which is the most dangerous for structural materials both in Pb-Bi and in Pb coolants, is local corrosion of materials appearing as the separate corrosion-erosion centres (“pittings”). Local through corrosion damages of structural elements may appear at temperatures over 550°C after holding for some hundred hours under the following conditions: unbalance of alloying elements and impurities in steel, poor quality of metal, absence of coolant quality control and non-optimal coolant flow regimes. The typical corrosion rate in such cases is estimated as 2.55 mm/year.

The principle solutions ensuring high corrosion resistance of structural materials in heavy liquid metal coolant were found using oxygen dissolved in the coolant. It has been shown as a result of long-term studies that this corrosion resistance essentially depends on concentration of dissolved oxygen.

Upon reaching certain level of concentration of dissolved oxygen corrosion processes is stopped due to protective oxide film formed on the steel surface. At high temperatures an indispensable condition of corrosion inhibition is presence of silicon in steel as additional alloying element. The silicon content in steels is varied within 1–3.5% range depending on steel type.

Oxide films formed on the steel surface prevent it from interaction with liquid lead. Since breakdown of oxide films is possible during operation, precautions must be taken for resuming and maintaining their thickness and density.

Thus, steel corrosion in molten lead can be significantly slowed down by the oxide film formed on the steel surface. The main technological problem is maintaining such oxygen content in the coolant which, on the one hand, would provide stability of oxide film (Fe_2O_4) on the steel surfaces, but, on the other hand, would preclude generation of lead oxide (PbO) in the coolant, that could result in the circuit slagging.

There are some ranges of content of oxygen dissolved in lead meeting these two conditions, for instance ($\sim 5 \cdot 10^{-6} - 10^{-3}$ wt%) range. Oxygen content in lead can be controlled by injecting gaseous oxygen or dissolving solid PbO .

Required oxygen content in lead can be maintained in two ways: (a) bubbling of argon, hydrogen and water vapour mixture or gaseous oxygen through molten lead; (b) lead oxide filling through which molten lead is pumped.

In order to change oxygen content and remove surplus PbO, reactions with water vapour or hydrogen can be used. To determine oxygen content in molten lead (similarly to Pb-Bi technology development) galvanic cell can be used.

The problem of hyperthermal corrosion resistance of structural materials was got over by development of preliminary protective coatings for the working steel surfaces. In particular, the most important structural units of circuit, e.g. fuel rod claddings and steam generator tubes, are covered by these coatings at the final stage of their manufacture. Additional barriers are also formed directly on the inner surfaces of liquid metal circuit under effect of the coolant in the early stage of the reactor operation.

The best results of using technology of preliminary oxidation of circuit components were achieved by application of media with low partial pressure of oxygen, namely: Pb-Bi-O, H₂O+H₂ and CO₂. These methods, first of all, make it possible to avoid critical kinetic stage of preliminary passivation of uncoated surfaces of steel structures of the circuit. Moreover, they prove to extend the range of permissible decrease of oxygen concentration in the coolant.

Therefore, the basic factors ensuring high corrosion-erosion resistance of structural materials in heavy liquid metal coolant (Pb, Pb-Bi) are as follows:

- application of silicon alloyed steels;
- passivation by oxygen using special regime of coolant;
- using additional corrosion barriers such as oxide films formed on working surfaces of circuit components under reactor start-up conditions.

In reaction of PbO reduction, water vapours are efficiently removed from the circuit. Small amount of moisture acts as diluted oxidizer preventing from achieving reduction conditions for oxide films on the steel surface.

Parameters of all these processes have to be developed with necessary control of hydrogen content in cover gas and oxygen activity in liquid lead.

Preliminary studies have shown that principal possibility exists to develop the technology mentioned, but it should be noted that conditions of experiments did not correspond to those of real operation.

It was found in the tests performed on the experimental and industrial facilities, that corrosion rate for chromium steels in PbBi alloy is 6–60 mg/m²h at 450–500°C. It can vary with temperature, coolant velocity, oxygen content and other parameters. In lead, this value is about 0.026 mg/m²h at 600°C with no mass transfer [5.20].

5.3.5. Comparison of PbBi technology for submarine and Pb technology for NPP

There are problems of applicability of data gained on lead-bismuth cooled submarine facilities to lead cooled nuclear power plants (NPP), which are caused by the following factors:

1. The inner surface area of the primary circuit contacting liquid metal in fast reactor NPP exceeds by a factor of 10 that of submarine facility (see Table 5.5).

TABLE 5.5. INNER SURFACE AREA OF THE PRIMARY CIRCUIT IN CONTACT WITH LIQUID METAL

Coolant	Type of plant	Electric power, MW	Surface area, m ²
PbBi	Submarine facilities	~30	~2000
Na	BN-600	600	21600
Na	Super Phenix	1240	24600
Na	EFR	1580	22800

2. NPP operating period is about 6000–7000 h/year that is at least one order greater than that of submarines.
3. The average temperature of lead circuit is 150–200°C higher as compared with that of PbBi circuit.
4. Some other effects causing corrosion take place in the NPP, such as iron diffusion through passivated protective oxide film, high steam generator pressure, etc.

Therefore, it can be concluded that direct transfer of already developed PbBi technology to the stationary NPP operating conditions is impossible, and additional expensive studies are required for many years.

Evaluations have shown that the increase of corrosion products amount in the circuit could be as high as hundreds of kg per year. Thus, it is obviously needed to develop special-purpose mass transfer equipment designed for catching corrosion products with permanent passivation of steel surface in contact with liquid metal.

CONCLUSIONS

1. Sodium technology developed up to the industrial scale for fast reactors has demonstrated that existing methods and control means are capable of solving the majority of the problems concerning future nuclear power. The possibility of continuous improvement of the technology already brought into commercial use ensures that such work will not require significant additional expenses.
2. Scientific and engineering approaches to be used in heavy metal coolant technology are essentially clear, but their implementation calls for time and financial resources yet difficult to estimate.
3. Direct application of data gained on lead-bismuth alloy to lead coolant is doubtful, and it should be noted, that further long-term studies are required.

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6. THERMOHYDRAULICS OF REACTOR CORE AND SOME ASPECTS OF FAST REACTOR ENGINEERING

6.1. INTRODUCTION

High power rating and temperature impose special requirements to fast reactor thermohydraulics. Analysis of thermohydraulic issues assumes reliable hydraulic and heat transfer relationships to be worked out. As a result, distributions of the coolant flow rate, its velocity, and finally, fuel and core structure temperatures would be obtained. All mentioned parameters are required for evaluation of core integrity and mechanical behaviour.