РОСАТОМ

ГОСУДАРСТВЕННАЯ КОРПОРАЦИЯ ПО АТОМНОЙ ЭНЕРГИИ «РОСАТОМ»

Liquid metal coolants technology for fast reactors

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Selection of NPP coolant

Investigation of liquid metals as coolant in nuclear engineering started at the end of 40th – beginning of 50th in last century

In the Soviet Union Academician Alexander Il'ich Leypunsky was organizer and ideologist of the works devoted to liquid metal coolants

The similar works were performed in other countries – France, Great Britain, USA, Germany, Japan

The following liquid metals were chosen as a coolant for NPP:

- **fast breeder reactors – sodium**
- **nuclear submarine – lead-bismuth eutectic alloy**
- **spacecraft – sodium-potassium eutectic alloy, in future – lithium**

The characteristics of liquid metals as coolant candidates for NPP

Liquid metal	Occurance, % of weight	Cost, rbl. / kg	Chemical activity	Corrosivity	Toxicity
Lithium (Li)	0.005	60-100	Is less active, than Na or K	is more active, than Na or K	is more toxic, than Na or K
Sodium (Na)	~2.4	1-3	High	Low	Low
Potassium (K)	~2.4	~4	High	Low	Low
Mercury (Hg)	$\sim 5 \cdot 10^{-4}$		Low	High	High
Lead (Pb)	0.016	~1	Low	High	High
Bismuth (Bi)	$\sim 10^{-5}$	40-50	Low	High	High
Na-K		3-5	High	Low	Low
Pb-Bi		25-30	Low	High	High
Cs	$6.5 \cdot 10^{-4}$	30-3000	Significant	Low	Low

Physical chemistry and technology of LMC

Approach was developed where liquid metals are considered
as multicomponent heterogenous system, the state of which is determined
by mutual interaction in the system "coolant – admixtures – structural materials – protective gas" (taking into account admixture sources and sinks)

Behavior of the system is characterized by:

- solubility of different impurities in metals
- their mutual influence on solubility
- reaction kinetics in the coolant
- diffusion contacts
- melt structure and form of impurities' existence

The sources of impurity, their intensity, possible negative consequences in NPP during campaign have been defined

Allowable level of impurities in the coolant and protective gas was found

Impurities in alkaline metal coolants

Liquid metal system of NPP includes theoretically the whole Mendeleev's table, but it is necessary to pay primary attention to oxygen, hydrogen, nitrogen, iron, chromium, nickel, fuel, and its products (first of all, gas fission products, cesium, tritium)

Impurity / Coolant	H	C	N	O	Corrosion products: Ti, Cr, Fe, Ni	Division product			
						T	Kr, Xe	I	Cs
Lithium (Li)	+	+	+ +	+ +	+	⊕	⊕ ⊕	⊕ ⊕	⊕ ⊕
Sodium (Na)	+	+	⊗	+ +	+	⊕	⊕ ⊕	⊕ ⊕	⊕ ⊕
Potassium (K)	+	+	⊗	+ +	+	⊕	⊕ ⊕	⊕ ⊕	⊕ ⊕
Na-K	+	+	⊗	+ +	+	⊕	⊕ ⊕	⊕ ⊕	⊕ ⊕
Cs	+	+	?	+ +	+	⊕	⊕ ⊕	⊕ ⊕	⊕ ⊕

\+ - is present

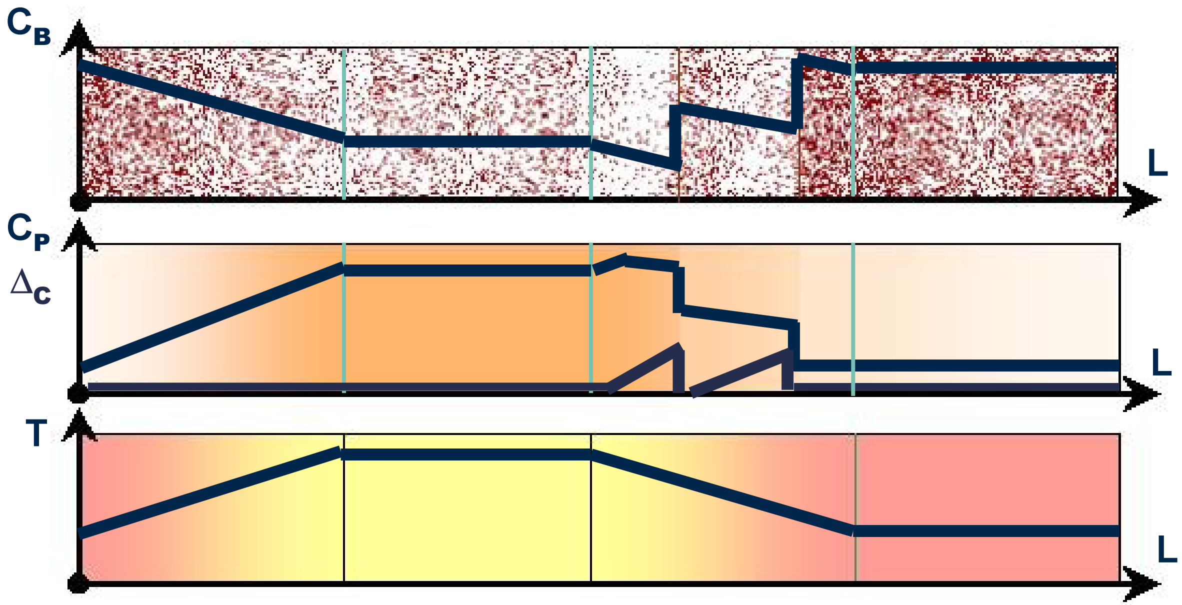
\+ + - is present considerably

⊕ - enters coolant due to diffusion through fuel rod cladding, in lithium coolant is formed due to neutron - lithium interaction

⊕ ⊕ - enters coolant in case of fuel rod depressurization

⊗ - concentration in the coolant is some orders as less, than concentration of oxygen, in protective gas - not less 0.3 % vol.

Physical-chemistry and mass transfer in non-isothermal LMC contours



Reactor core (RC)	Volume between RC and IHE	Intermediate heat exchanger (IHE)	Volume between IHE and RC

Intensity of impurity sources is determined by specific technologies, selected options and design

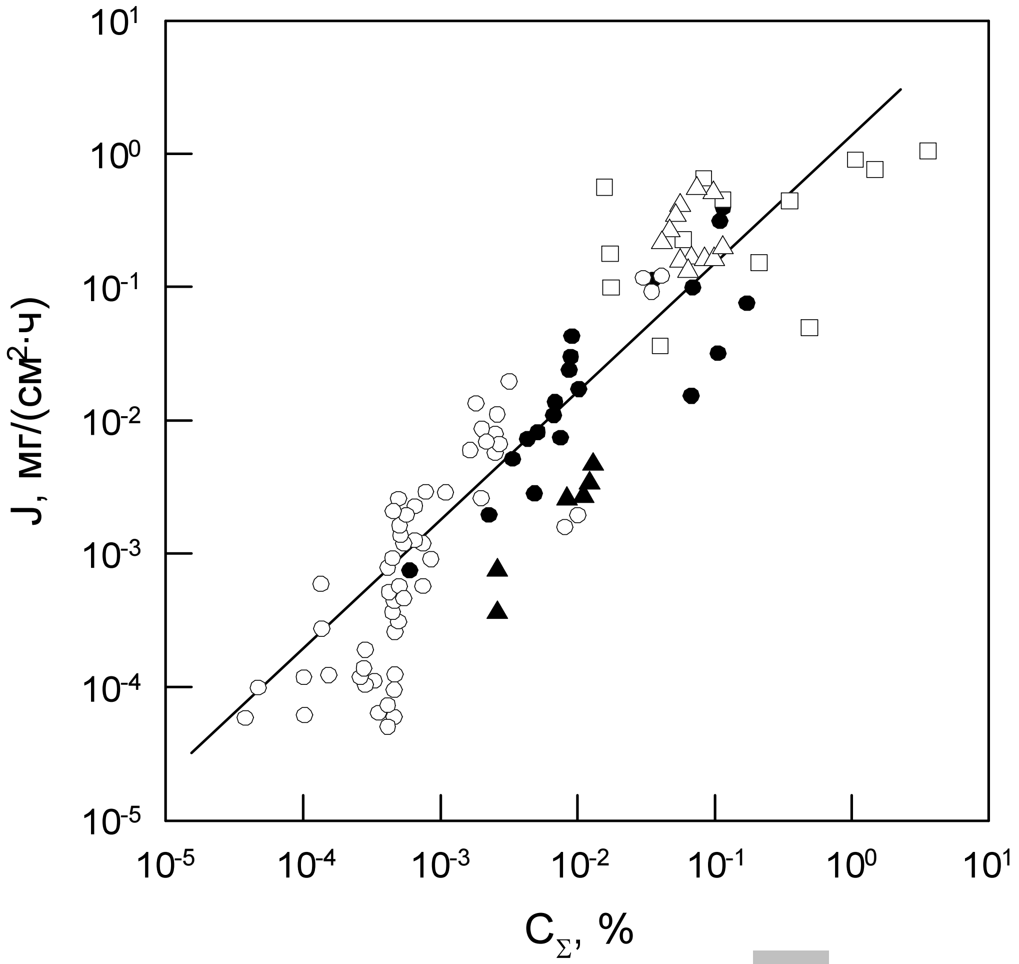
Examples: corrosion products: BN-600 – 11 kg/year, BREST-300 – 50 kg/year

SG leak: BN-600 (operation is impossible)

BREST-300 (it is supposed that reactor can operate in case of SG leakage)

Total dissolubility of 316SS

One of the main factors determining a rate of steel corrosion is total dissolubility of steel components in liquid metals



Dependence of 316SS steel corrosion rate at 500°C on total dissolubility of components in liquid metals

- ○ – sodium
- ▲ – sodium-potassium
- ● – lithium
- △ – lead
- □ – lead-bithmus

Concentration of impurity components is shown in atomic fractions

Total dissolubility of SS316

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The observed dispersion of the data on SS316 components dissolubility in liquid metals is connected with an availability of oxide inclusions of colloidal type. Being in the melts they intensify corrosivity in liquid metals. In order to decrease corrosion it is necessary to clean the melts from impurities. Such technology is rather effective for sodium and is employed in operating reactor facilities

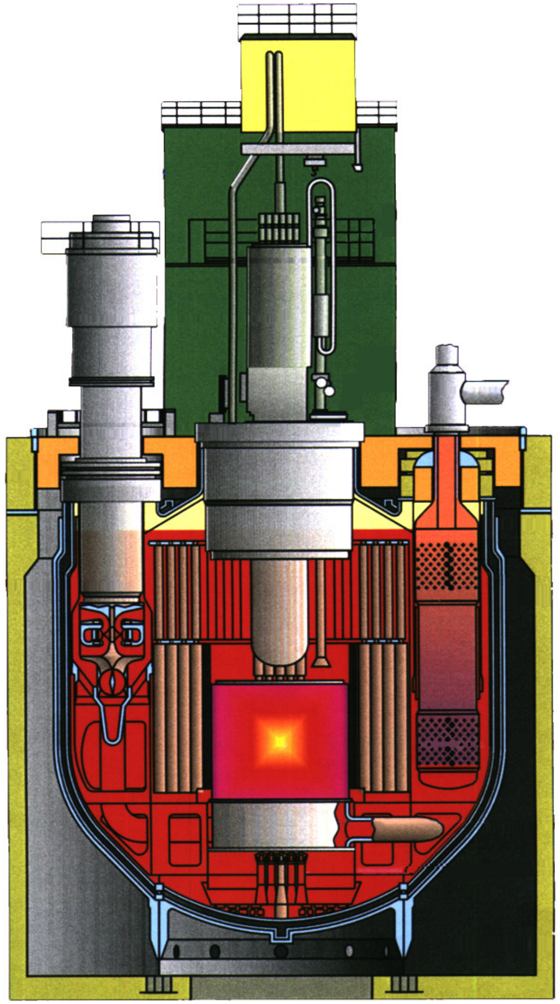
Analysis of carbon and hydrogen behavior in sodium, nitrogen in protective gas has allowed to develop systems and devices monitoring impurity level in the coolant and guaranteeing minimum corrosion of structural materials in sodium

Steel SS 316 in heavy LMC is as 3-4 orders more corrosive, than in alkaline LMC. Decision is the following: to develop diffusion barrier in the form of the film covering steel, which provides the main resistance to mass transfer from steel into the coolant

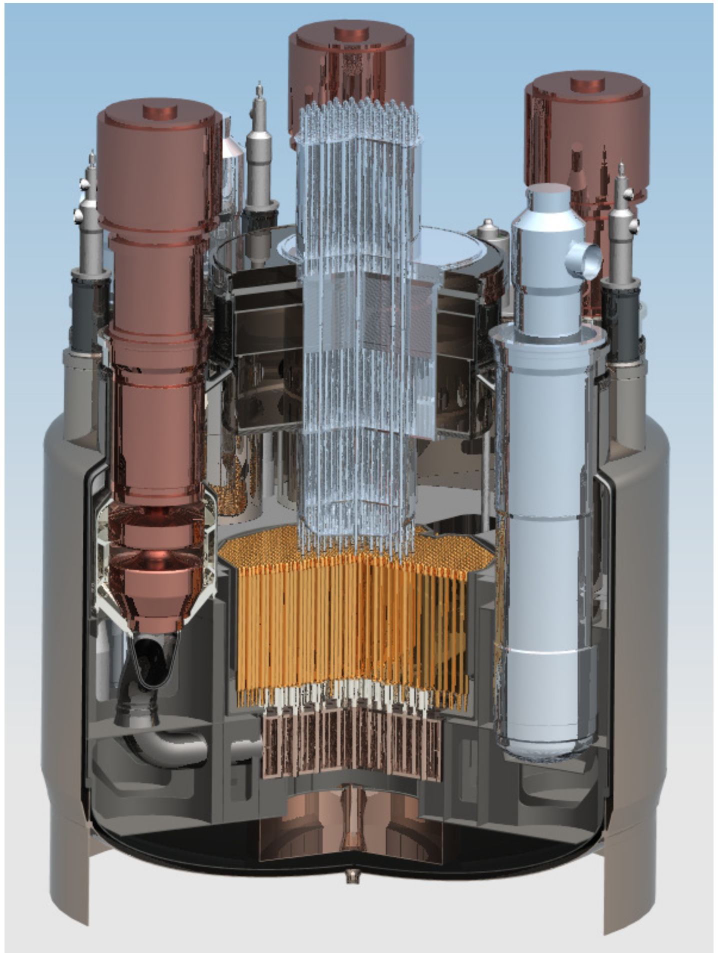
In order to provide conditions securing capacity for work of HLMC technology, the methods and devices for clearing, control and keeping of given quality of alloy have been developed

Sodium technology for fast reactors

An extensive knowledge and great experience of sodium coolant of fast reactors was gained in NPP: BOR-60, BN-350, BN-600 (USSR), Rapsodie, Phenix and Superphenix (France), EBR-II and FFTF (USA), DFR and PRF (UK)



BN-800



BN-1200

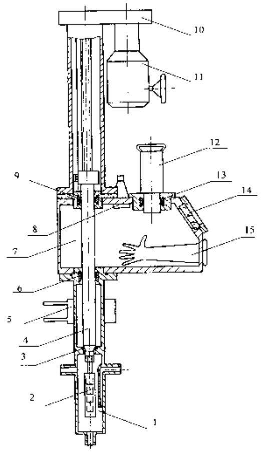
Purity test of liquid metal coolants

To control impurities the different methods are used: a sampling of coolant and subsequent analysis, also different devices for definition of impurity level in the coolant located in a contour

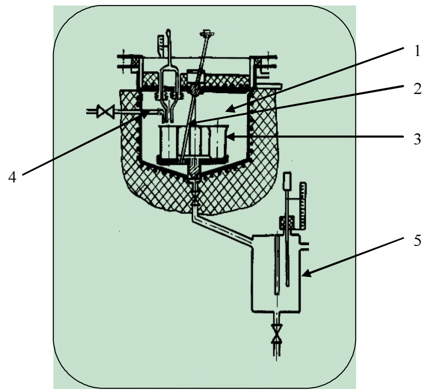
Among them:

- Sampling in metallical pipes and special samplers (sleeves, ampula)
  and their subsequent chemical analysis (AMC and HM)
- Sampling in a sampler-distiller and subsequent chemical analysis both rest after distillation, and gases discharged from assay during distillation (AMC)
- Definition of purity of coolant with the help suberic indicator of impurities) (AMC)
- Devices working on a principle
  of a electrochemical cell (HM, AMC)
- Sensors with diffusive membranes (AMC)

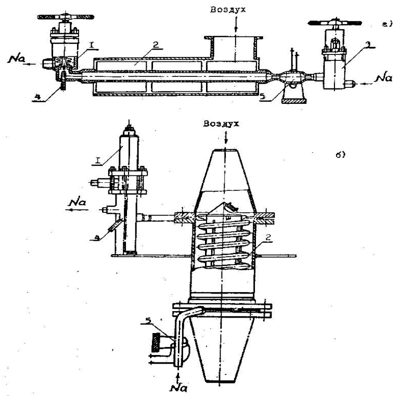
Sampler
of radioactive sodium



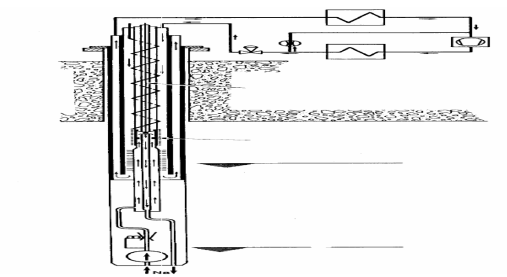
Sampler-distiller



Designs of suberic indicators



Primary integrated plugging meter

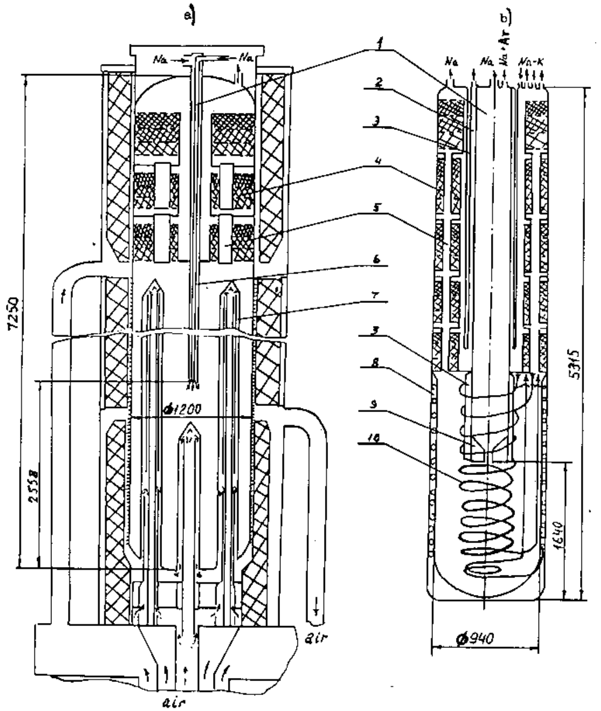


Alkaline liquid metal purification

It is recommended: cold and hot traps for oxygen, hydrogen, nitrogen (lithium), and carbonic traps for cesium

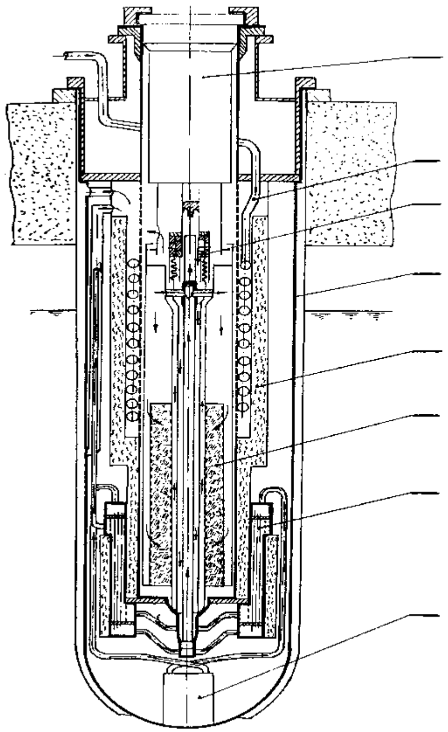
- Cold trap is the MAIN DEVICE for clearing AMC. The cold trap represents a heat and mass transfer device, where supersaturated solution of impurity is generated as a result of coolant cooling. So, crystallization of impurity occurs both on the immovable surfaces, and on the suspensions in the coolant flow
- In the advanced NPP the concentration of oxygen and hydrogen in sodium, in NaK, and in lithium resulting from cold trap clearing provides working thermohydraulic parameters and low corrosion rate of the used structural materials (steel, high-nickel alloys)

Devices of cold purification AMC (cold traps)



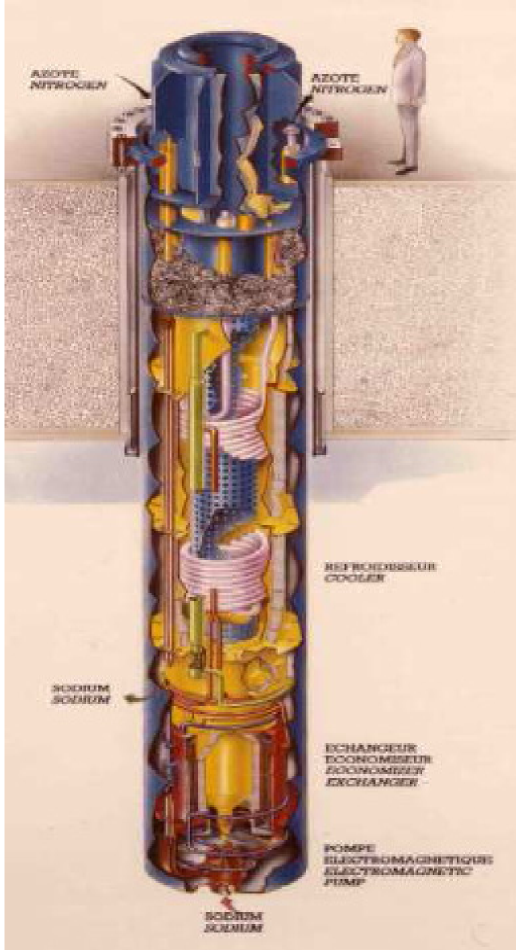
1 – central tube; 2 – external channel of the recuperator; 3 – air thermal insulation; 4 – filter; 5 – bypass pipes; 6 – ring channel (second input of sodium); 7 – tube of air cooling; 8 – jacket of cooling; 9 – cone for increase of input velocity; 10 – coil pipes of cooling

Schemes CT of sodium impurities for BN-600 and BN-350



1 – removed part; 2 – cooling system; 3 – valve; 4 – housing; 5 – heat insulation; 6 – filter; 7 – recuperator; 8 – pump

Primary integrated purification system



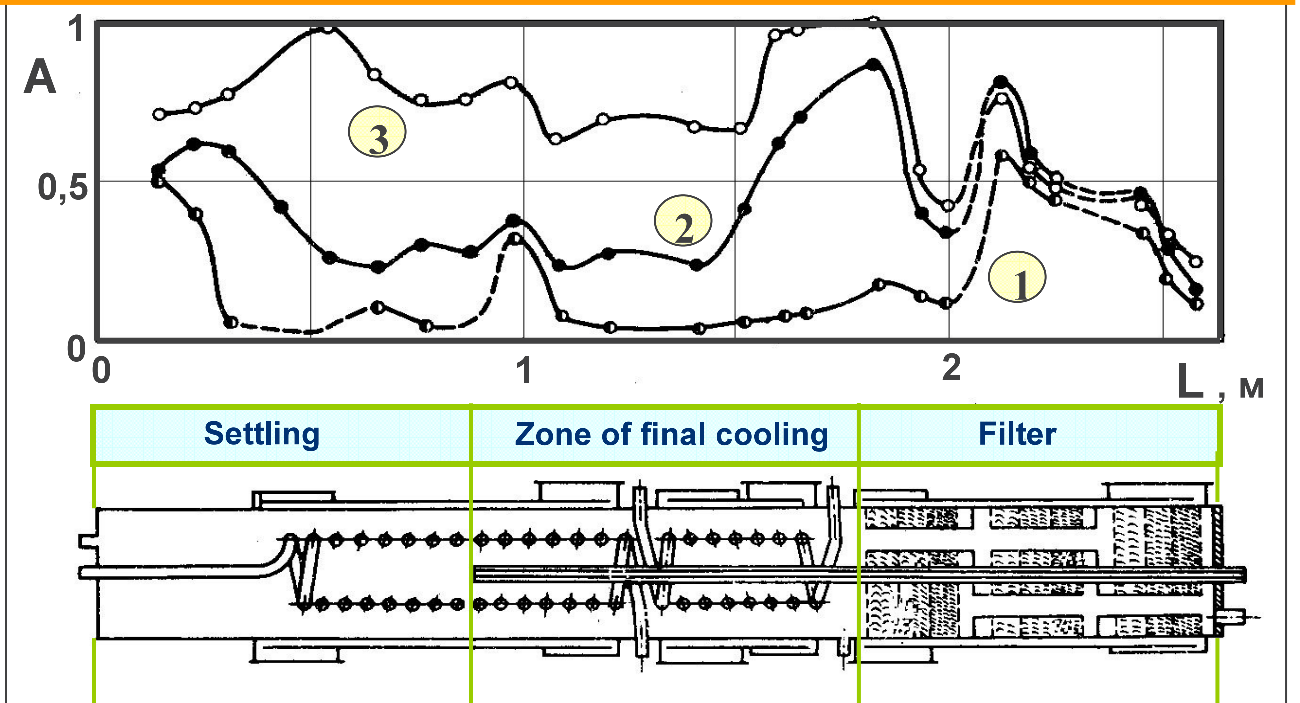
Primary integrated purification system

Purification of sodium from impurities

The cold trap should have three sequentially arranged zones: cooled settling, zone of final cooling and isothermal filter

Relative distribution of sodium oxide lengthwise of prototype of the cold trap BN-600, measured by a γ-method

№ experience	General weight of stored sodium oxide, kg
1	14
2	63
3	111



	Settling	Zone of final cooling	Filter	
Part of keeping Na_2O	45	39	16	%
Volume concentration	27	28	15	

Sodium clearing of cesium

The method was developed of sorbate clearing of sodium by the use of nonrecoverable compact graphitic stuffs, which arranged in reactor core instead of subassembly or into side screen assembly

Установка	БОР-60	БН-350	БН-600
Продолжительность, ч	382	199	346
Отношение масс графита и натрия, 10^{-5}	8,2	2,0	1,2
Температура, °С	235±10	250;175	220±10
Удельная активность Cs после очистки, МБк/кг	42	70	110
Отношение мощности дозы до и после очистки	3,4	1,8	1,5

Among 12 tested materials the graphites of the marks ГМЗ, РБМ and ГМЗ-6 are recommended for application in radionuclide traps

Clearing regimes:
- temperature 160-320°C
- flow rate is determined by the type of installation and trap design

Tritium in NPP contours

Tritium and hydrogen are twins. Tritium enters of fuel elements on coolant and protective gas

The main mass of tritium falls into the primary and secondary cold traps

The primary cold trap accumulates by 1,5 times more

In third contour the mass of tritium carried out through steam generator by 2-3 order less then disposal in cold trap

In BN-600 operation a tritium outlet is estimated as 33 Ku/year

Total outlet with feed water is 86 Ku/year

Cold traps regeneration

a) Removal of maximal quantity of sodium from CT at temperature ~130-150°C (for example by means of inert gas pressure)

b) Pumping out the CT

c) Warming of the CT up to temperature ~450-500°C

d) Cooling of the CT up to 130-150°C

e) Pumping out the CT

f) Filling sodium in the CT and put in nominal purification regime

Mass transfer:

- long operation life
- enhanced parameters
- off-optimum situation

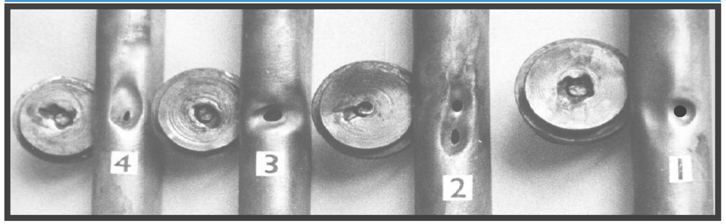
Mass transfer stages:

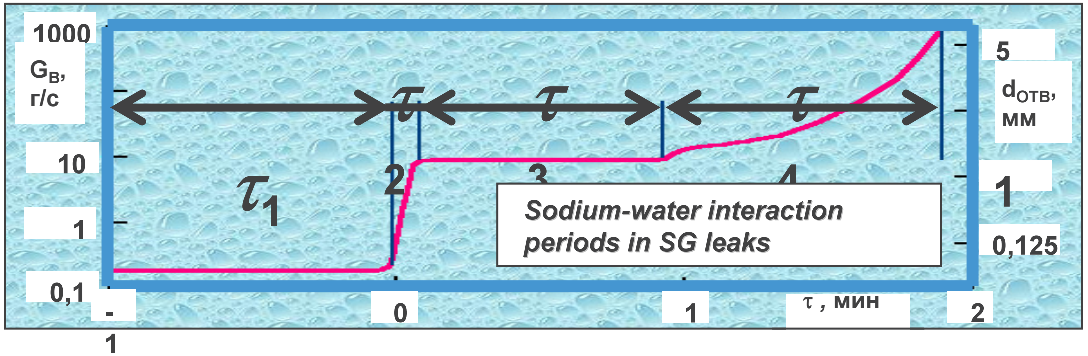
- Structure components outlet (Fe, Cr, Ni) into the coolant
- Transportation of structure components by coolant flow
- Generation of solid phase germs when the coolant is supersaturated by metallic impurities (in cooled sections)
- Particle coagulation in the formed fine-dyspersated system
- Particle precipitation at the setting surface
- Particle precipitation at the dead space
- Deposit of permeate admixtures at the particles surface or particles' dilution
- Deposit of permeate admixtures at the surface of setting

Sodium-water SG leaks

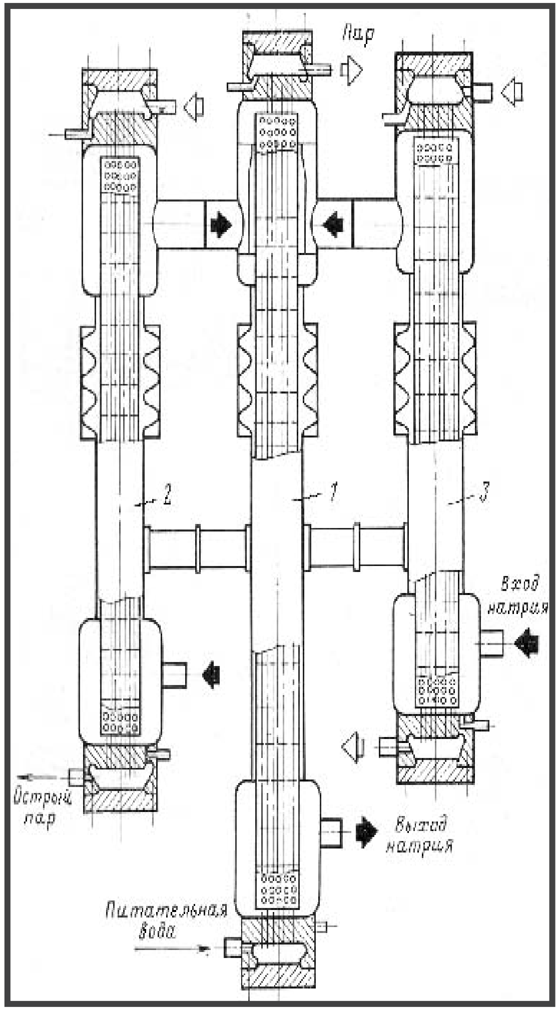
- Under conditions of water leakage into sodium a wall corrosion rate increased by some orders
- Small leaks is self developing and it is transformed into great one
- High-temperature jet is generated, which actively affects adjacent tubes and destroys them

Fracture patterns of SG steel 10X2M in leakage area



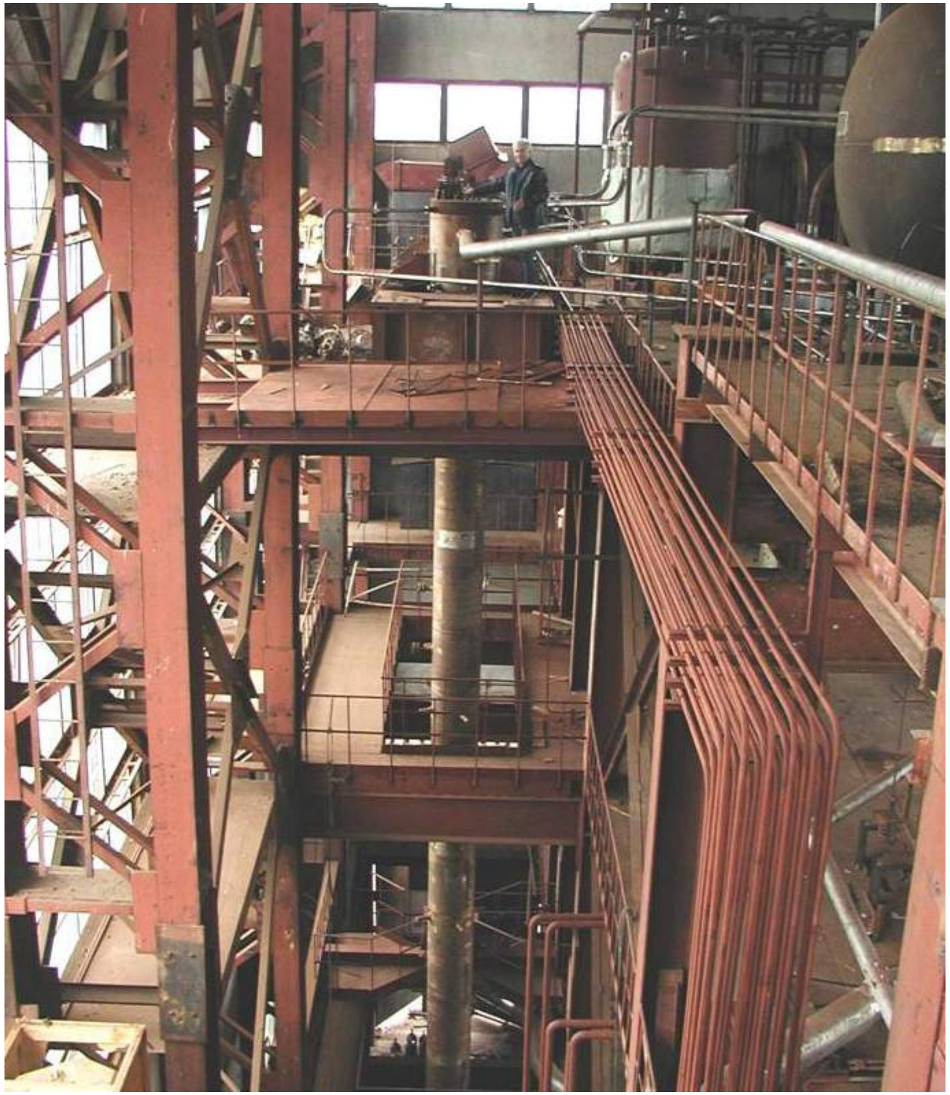


BN-600 SG



Sodium – water SG safety

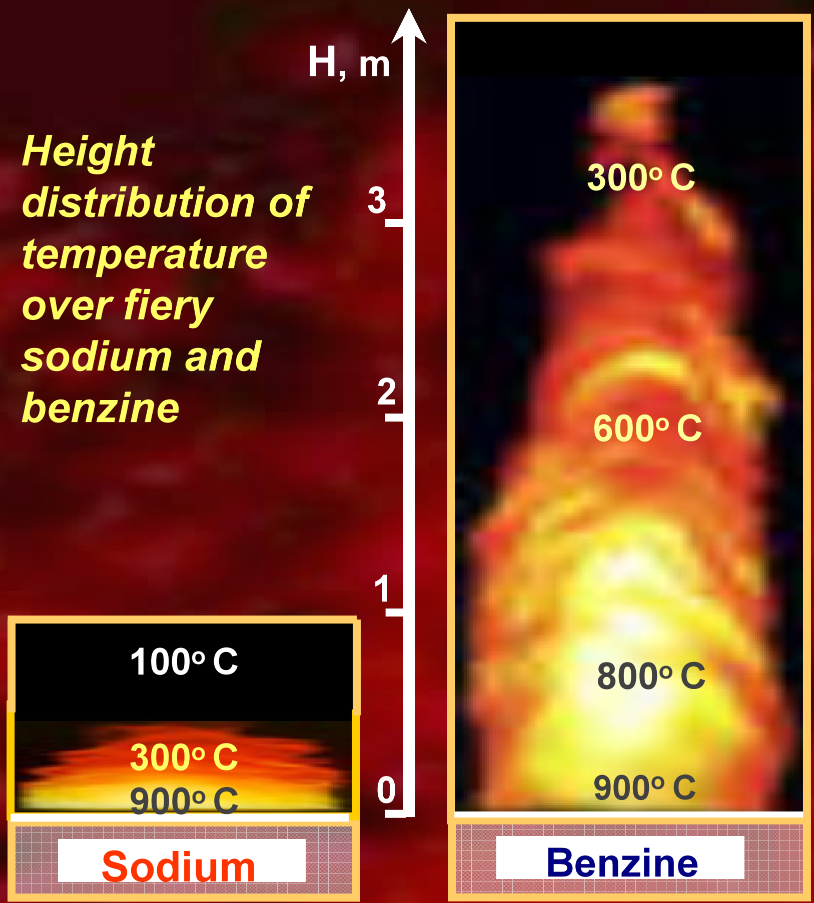
- The requirements to leakage detection system have been written
- Automatic protection of SG systems have been developed
- Experimental facility CAZ in IPPE in Russia is under construction for testing automatic protection of improved large-scale SGs



Facility SAZ is under construction

Sodium leakage into atmosphere

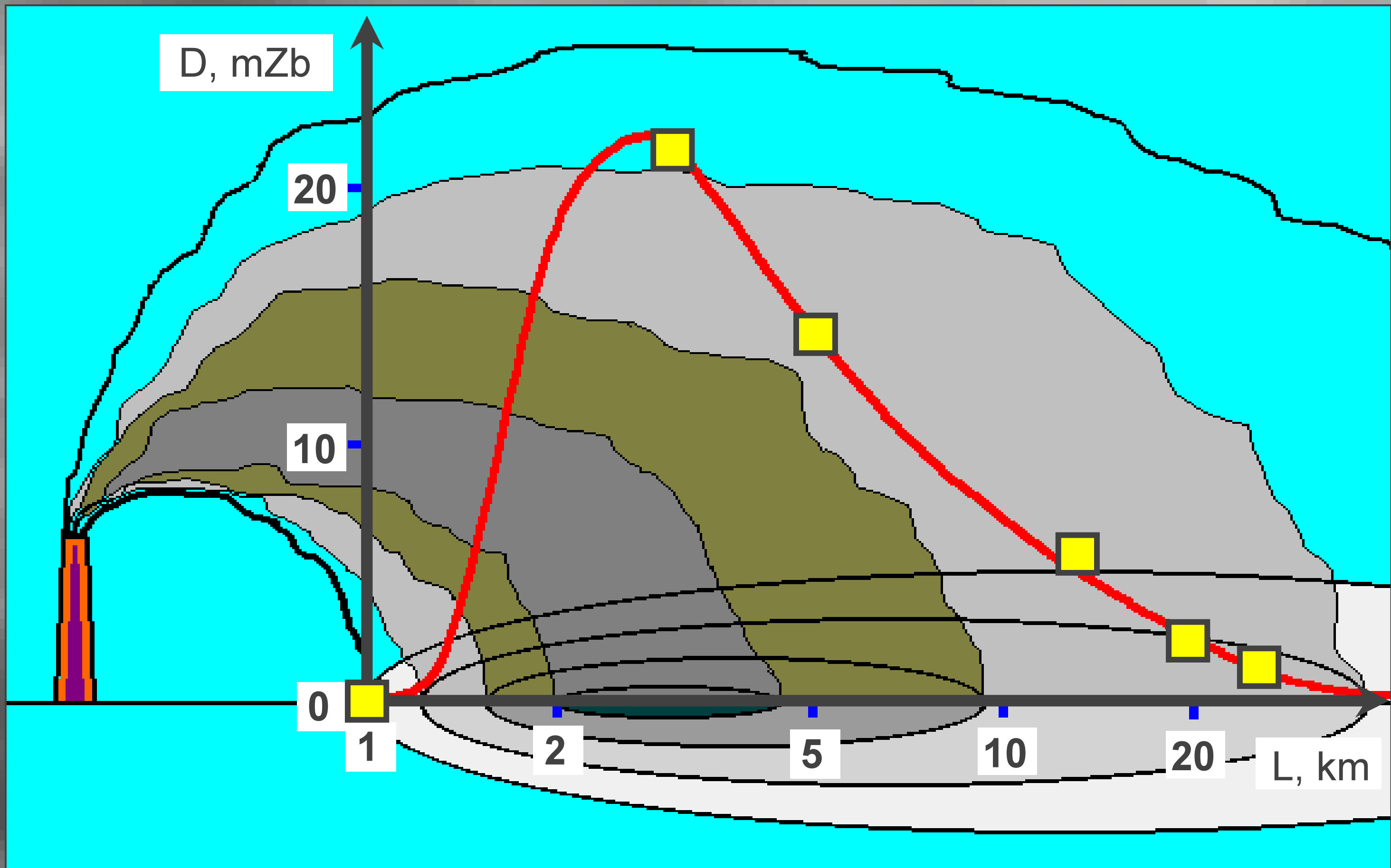
Sodium combustion is associated with a rise of local temperature and generation of aerosols



	Sodium	Benzine
Burning rate, kg/m²h	35	120
Burning heat, MJ/ kg	10	44
Evaporation heat, MJ/ kg	3,8	0,35
Height of flame, m	отс	до 4
Temperature in 0,8 m of the surface, ° C	<100	800
Components disposable into atmoshere	Na_2O Na_2O_2 $NaOH$	CO_2 CO N_2O

Effective yearly dozes in BN-800 beyond of design accident

(*surge ~2,7 t of aerosols under the worst weather conditions*)



Alkaline liquid metal leakage

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Investigations of sodium leakage from fast reactor contours have shown that internal reasons for prompt large defects are absent.
This is confirmed by many years' operation experience

The systems of early detection of sodium leakage, quick stoppage, localization of escaped sodium, equipment for extinguishing of sodium fire, for prevention of hit of combustion products into atmosphere, methods and techniques for cleaning and deactivation of facilities after sodium fire

Investigations into heavy metal technology (Pb-Bi, Pb)

1959 – start of overland prototype of nuclear submarine in IPPE

1963 – nuclear submarine Project 645 is placed into operation

1968 – nuclear submarine accident

Exciting event was a deficiency in the knowledge of coolant properties, an absence of control and cleaning techniques

Impurities was accumulated in the contour that resulted in deterioration of heat transfer in reactor core

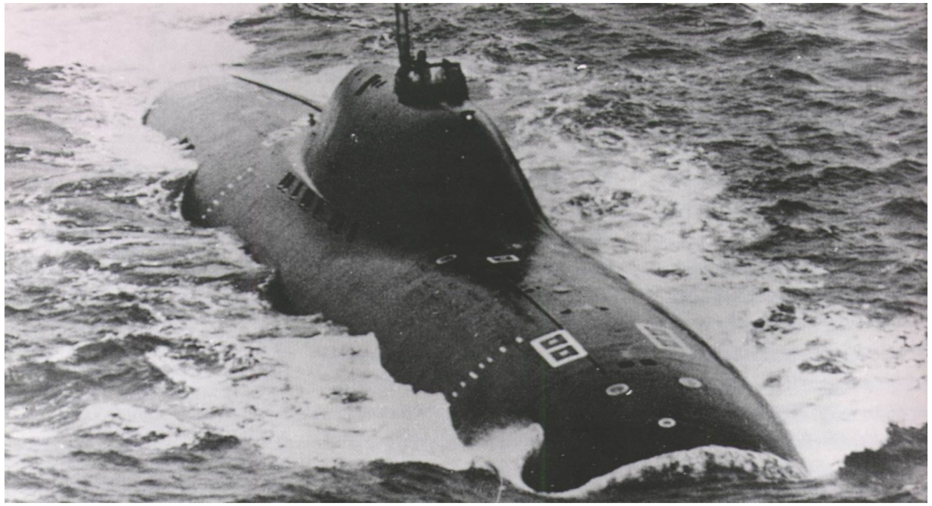
At the first stage of Pb-Bi assimilation these factors resulted in:

- shortening of operation resource of the first nuclear facilities in Russia
- Pb-Bi program was finished in USA

Investigations into heavy metal technology (Pb-Bi, Pb)

Technology of Pb-Bi eutectic was carefully developed in experimental studies on many test facilities, on-ground prototype of full-scale transport NPP and adopted in special NPP designed in the USSR for Projects 645 and 705 nuclear submarines having no analogs on international scale

6-th division of Northern fleet: atomic submarines of the design 705 with the Pb-Bi coolant at a mooring



Atomic submarine with a reactor cooled by Pb-Bi alloy in a campaign

Tasks for Pb-Bi and Pb technology

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Pb-Bi alloy properties,which can negatively influence on NPP capacity for work:

- Pb-Bi is aggressive to structural materials
- when interacts with structural materials and oxigen during campaign Pb-Bi can become dirty by solid impurities

For long accident-free operation two main problems have to be solved

- to provide the needed purity of the coolant and circulation contour surface
- to provide corrosion resistance for structural materials contacting with the coolant

The following processes have been investigated

- physical-chemical processes in non-isothermal contours
- corrosion resistance of materials
- impurity sources and their influence on facility operation

Content and mass of impurities in heavy liquid metal coolants

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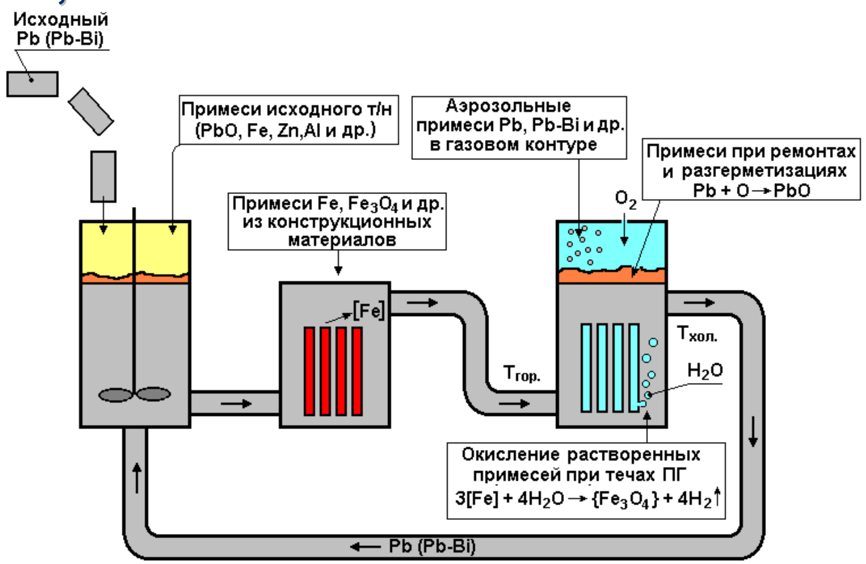
Content and mass of impurities depend on the usable structural materials, mode of operation, design and destination of nuclear facility

During operation the impurities are generated due to diffusive departure of structural components through the protective oxide covers, due to corrosion and erosion, when a coolant effect structural materials, due to new elements formation when irradiated by neutrons and protons

The impurities being basically composed of oxides as of coolant component and structural materials interact with each other, with the coolant and contour materials

Practically, for all LMC the impurities may enter a contour jointly with initial coolant, from protective gas, at gas contour depressurization, when reactor core elements are reloaded, during repairing works, in case of steam generator leakages, as a result of corrosion and erosion of structural materials, in case of nuclear reactions with the coolant and other materials, at depressurization of fuel rods



Basic procedures of coolant technology

On the base of the obtained experience it is proposed to use the following processes of coolant technology for stationary NPP

- hydrogen purification of the loop from the impurities based on the lead oxide
- filtering of the coolant for its purification from the suspended impurities
- enrichment of the coolant with oxygen to maintain the given level of its oxidative potential
- purification of the cover gas from the aerosols
- control of coolant characteristics

HLMC quality control

- Samplers for coolant and protective gas. The samples are taken periodically with sequent analysis with the use of different methods in laboratory
- The continuously acting impurity analyzers in protective gas
- The developed in the IPPE sensor of thermodynamic activity of oxygen (activemeter), based on the principle of galvanic cell with solid electrolyte for control the oxygen dissolved in the melt

Purification of HLMC and contour surface based on hydric gas mixtures

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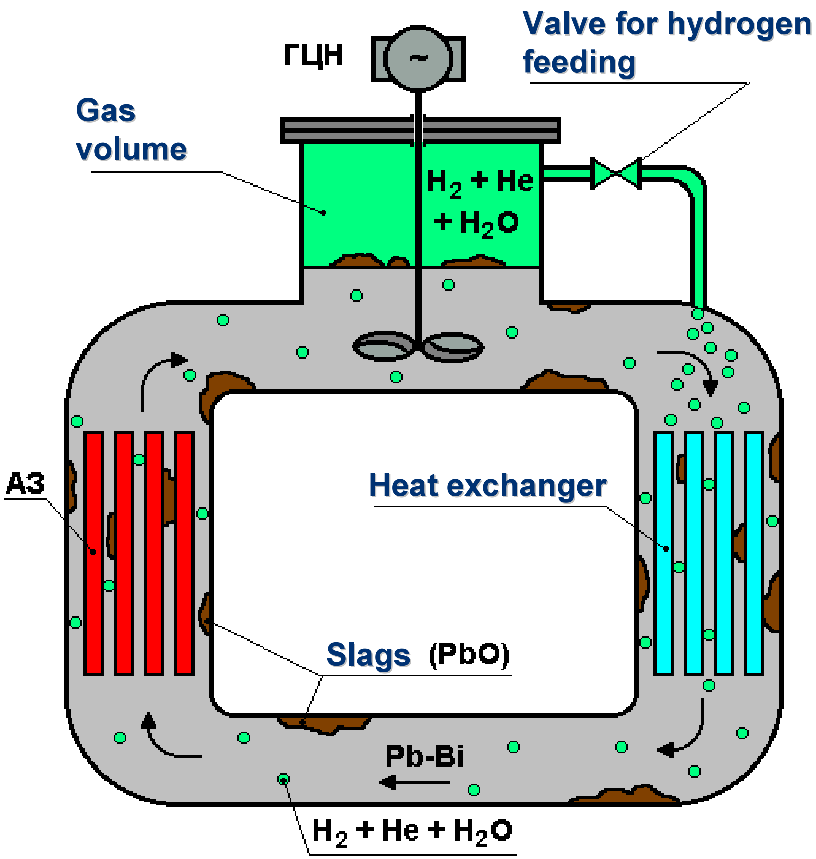
The bubbles of the introduced into the flow gas mixture (mixture of hydrogen, water vapor and inert gas) are transported by the coolant to the place of impurity gathering, where solid-phase lead oxides are reduced up to pure lead, which then returns to the coolant

The possibility to reduce oxides underlying in protective covers is excluded

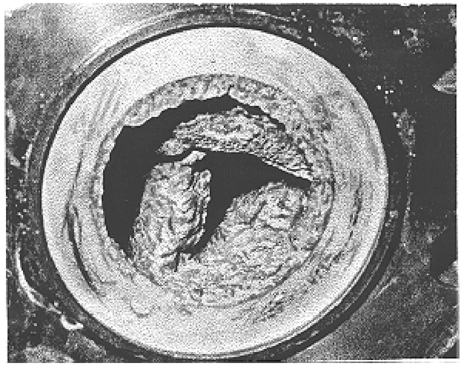
Circulation of flow “liquid metal-gas” is produced by dispergators, which create fine-dyspersated gas mixture with the bubble size up to 10-100 mcm. This mixture is transported by the coolant even in downflow with small velocities (0,2-0,3 m/s)

Initial purification of coolant and contour surfaces from deposits by gas mixtures with hydrogen (τ = 100-200 hour)

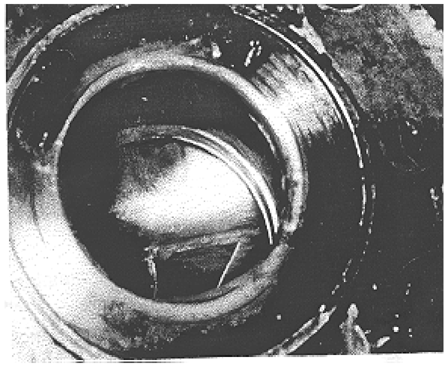
$(H_2) + \langle PbO \rangle \rightarrow (H_2O) + [Pb]$ $(H_2)+[O] \rightarrow (H_2O)$



Efficiency of hydrogenous purification of a contour



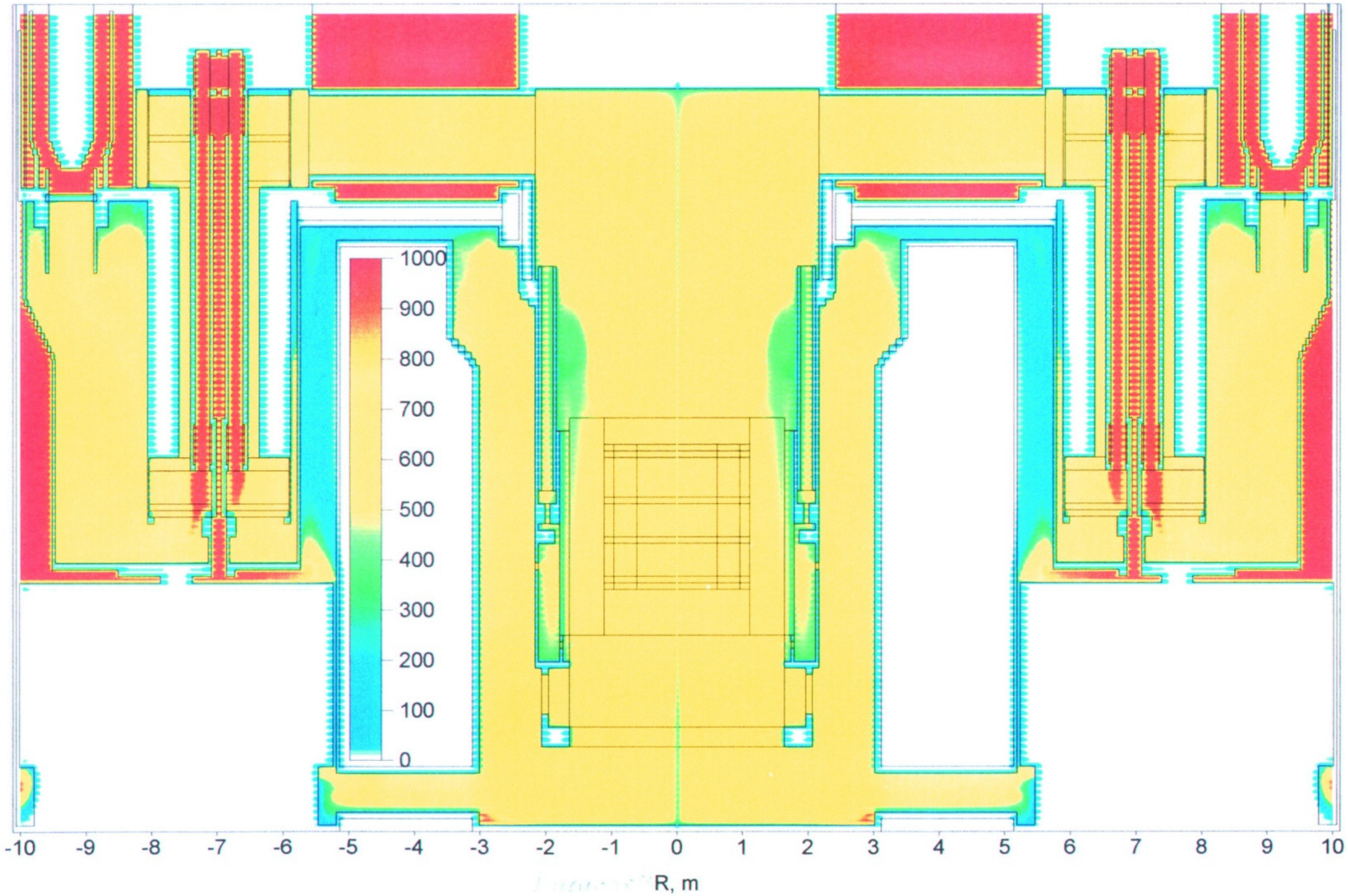
Contaminated loop section before purification



The same section after purification

It is have to make periodic purification of coolant and contour surfaces from deposits by gas mixtures with hydrogen (1 time at 5-10 of years)

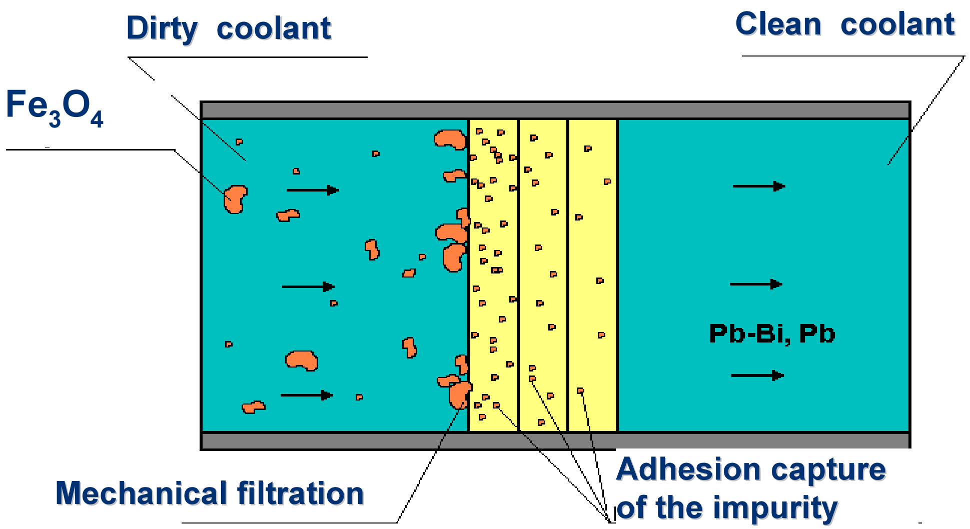
Distribution of oxygen concentration 300 seconds after hydroygen injection (code PORT3D)



HLMC filtration

Two basic processes are realized

- mechanical keeping of impurity particles from alloy flow
- adhesion capture of the impurity by the whole volume of filtrating material



Bubbles of hydric gas mixture enter the filter with coolant flow and reduce lead oxides to pure lead and cleans the filter

Admixture remainders, which do not reduced by hydrogen (iron oxides, particles of structural materials generated in abrasion, welding etc.)

Filtering of coolant

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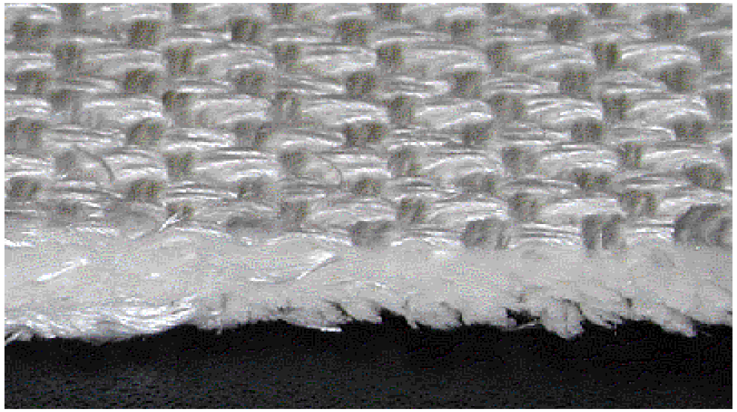
The comparative tests of three filter materials for coolant purification from suspended impurities have been fulfilled

- **the needle-punched fabric made of metal fiber by d=40 μm**
- **the granules made of electrocorundum Al_2O_3 (grinding grains) by 0.6–1.0 mm**
- **the glass tissue MKTT-2.2 A**

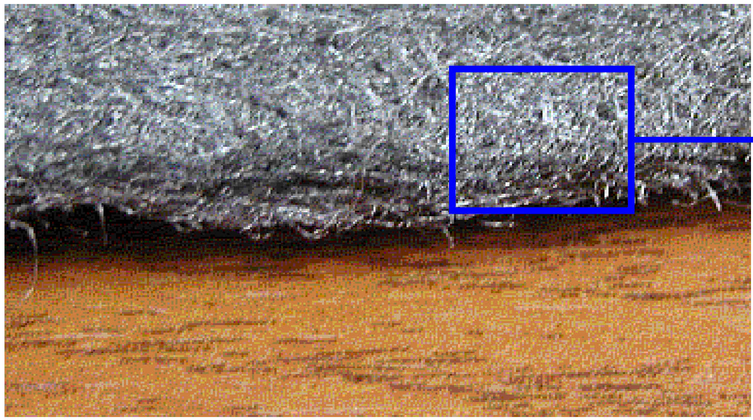
The best results, taking into account the basic characteristics of the filtering materials that meet the requirements of the purification and durability effectiveness, were obtained when using the needle-punched fabric made of metal fiber

Filtering materials for Pb-Bi and Pb coolants

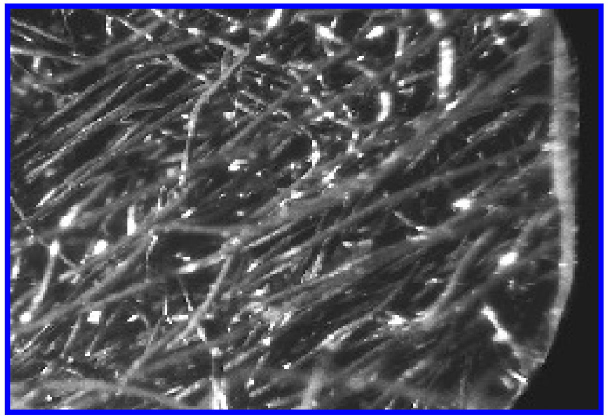


MKTT-2.2A multilayer silica structurized fabric (fibre d=6 μm, t≤450°C)

Metallographic specimen grain Al_2O_3 (granule size d=0.8-1.0 mm, t≤800°C)



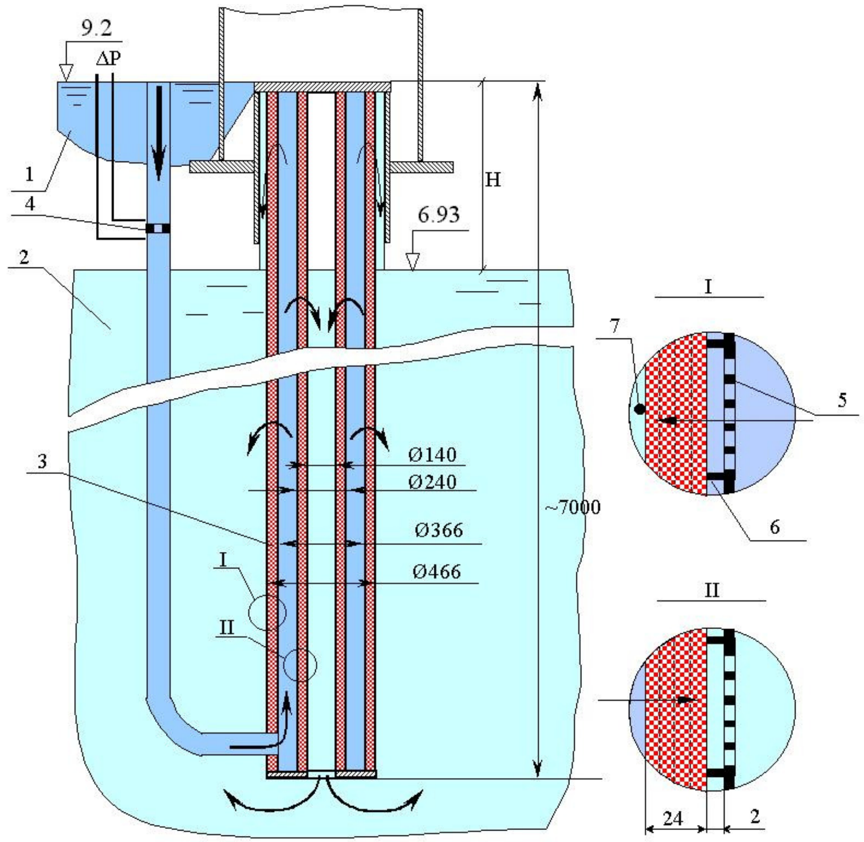
Pin-perforating canvas of metal fibres (fibre d=30 μm, t ≤ 800°C)



Structure of pin-perforating canvas of metal fibres

Scheme of filter section for coolant purification

The filter was developed that can provide the lifetime of continuous operation for ~ 5years at intensity of feeding iron into the coolant equal to ~ 50kg/year



1 – coolant at the filter inlet

2 – purified coolant

3 – needle-punched fabric made of metal fiber, d=40 μm

4 – flowmeter

5 – perforated ring

6 – spacer ring

7 – retainer ring

Purification of loop gas volume from lead aerosols

The dispersed composition and concentration of the formed lead aerosols at different temperature modes (t = 450-600° C) have been found

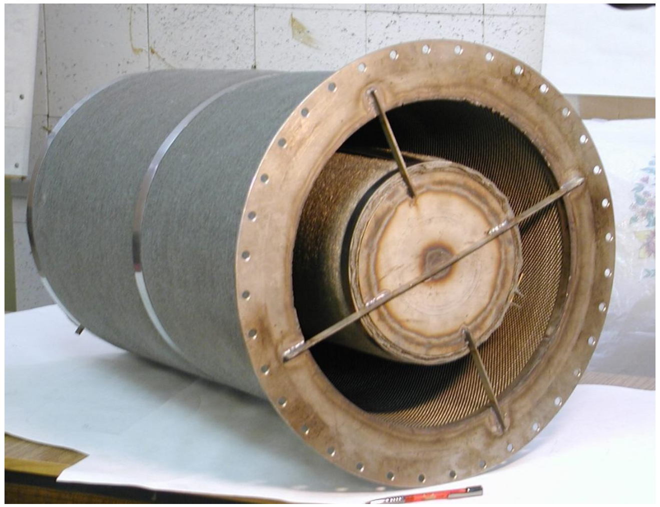
Filtering material – the needle-punched fabric made of metal fiber by d = 40μm have been chosen and its long-duration (~1000 hours) tests have been fulfilled in gas having lead aerosols.
The durability characteristics of the filtering material and its capacity for impurities were obtained

The prototype design of the filter with capacity of 50 m^3/h was developed and tested

Lifetime of the aerosol filter applied to the gas loop of reactor plant of BREST-OD-300 is approximately 6 years

Model of filter for high temperature coolant with efficiency of 50 m^3/h

Filter element and housing before tests



Filter element after tests

Maintenance of optimum concentration of dissolved oxygen in HLMC

Specific feature of Pb-Bi (Pb) loops is a decrease of concentration of the dissolved oxygen in the coolant due to departure of structural materials components (Cr, Fe etc.) and generation of oxides during operation

In this case the processes of mass transfer become more intensive that may results in blockage in cold sections or dissociation of protective cover on the structural materials within hot sections

With the purpose to control concentration of dissolved oxygen in the coolant the technique was developed, which feeds the dissolved oxygen or a mixture of water vapor and hydrogen into the loop and dissolves hard oxides of lead or bismuth

Regulation of dissolved oxygen concentration in Pb-Bi и Pb coolants

For the concentration regulation of oxygen dissolved in coolant the following processes are used:

- **the feeding of gaseous oxygen into the loop**

  $$O_2 + 2Pb \rightarrow 2<PbO>$$

  $$<PbO> \rightarrow Pb + [O]$$

- **the oxidation of the coolant by H_2O and H_2 mixtures**

  $$H_2O + Pb(Pb\text{-}Bi) \rightarrow Pb(Pb\text{-}Bi) + [O] + H_2$$

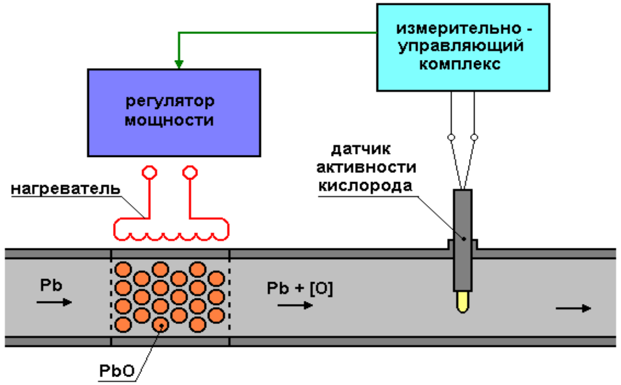
- **the dissolution of solid-phase lead oxide (PbO) in the coolant after special technological processing**

  $$<PbO> \rightarrow Pb + [O]$$

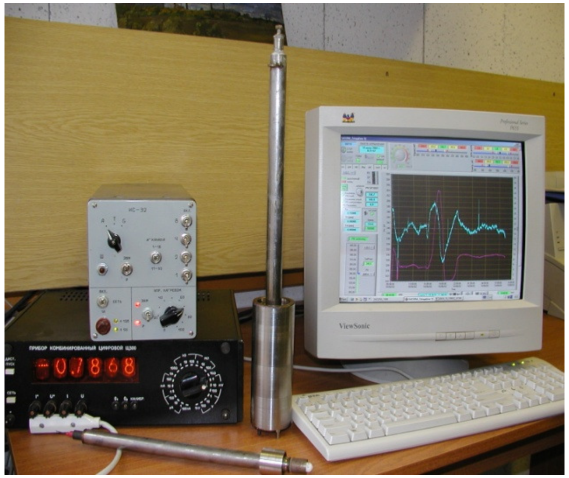
The method based on the using of solid-phase oxides of coolant components for the oxidation is the most effective

Adjustment of oxygen concentration

$<PbO> \rightarrow \{Pb\} + [O]$



Types of hard-phase mass transfer devices



System of automatic adjustment of oxygen concentration “SACURA”

SSC RF IPPE,

2002-2004

New generation of the sensors controlling thermodynamic activity of dissolved oxygen

Having measured temperature and flow rate of the coolant in the vessel it is possible to regulate the rate of lead oxide dissolution

Peculiarities of coolant technology for accelerator-driven systems with Pb and Pb-Bi

POCATOM

The new elements generated by a proton beam in the coolant can take part in different chemical reactions breaking chemical equilibration in the loop

- **the elements having an oxygen affinity less than lead will dissolve without the oxides formation (Au, Ag, Pt, Hg, Os, Cu, Tl, Pb, Bi)**
- **the elements having an oxygen affinity between the values for lead and iron will dissolve or oxidize in dependence on the oxygen thermodynamic activity (Re, As, Te, Sb, Co, Ni, Mo, Sn, Fe)**
- **the elements (lanthanides, halogens, alcaline elements, Be, Y, Sc, Al, Ge, Ti, Hf) having an oxygen affinity higher than iron will be able to deoxidize Fe_3O_4 and under some conditions to destroy the protective film**

Peculiarities of coolant technology for accelerator-driven systems with Pb and Pb-Bi

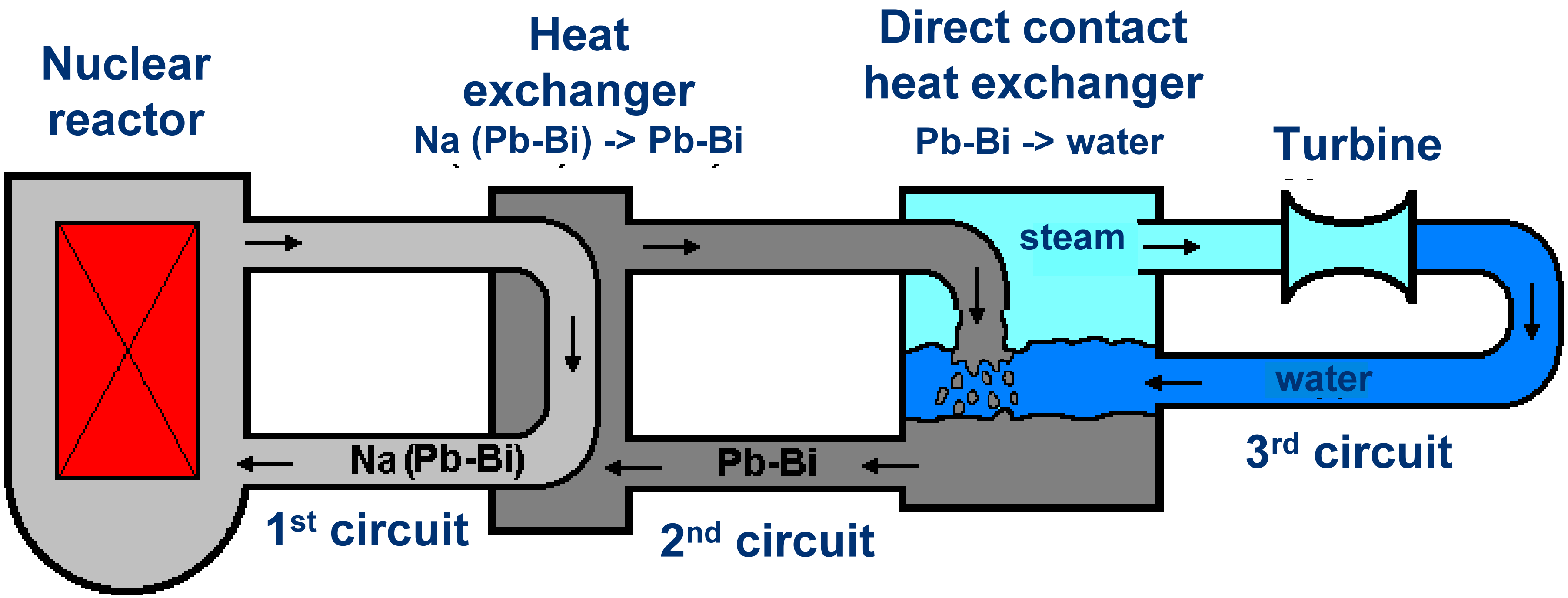
POCATOM

The oxidation-reduction reactions that can take place with the formation of indissoluble oxides with reduction of Fe_3O_4, that are the base of the protective film on the structural materials are the most important

In the whole the analysis has revealed that for the targets by 10 MW power and higher the influence of the impurities generated by the proton beam in the loop on the mass transfer processes can be considerable and requires special study

Variant of NPP with different liquid metal coolants

(Na, Pb-Bi → Pb-Bi + water)



Further investigations

Development of fast reactors with Na as a coolant requires an additional complex of researches to be performed:

- Study of fundamental characteristics defining behavior of impurities in the loops taking into consideration the selected structural materials
- Development of advanced inspection tools, methods and means of Na cleaning
- Development of methods and codes for modeling of admixtures and tritium mass transfer
- Improvement of technology for cleaning, processing and annihilation of sodium coolant
- Scientific substantiation of technology in Na contours at higher coolant temperatures

Scale, design, regime parameters and resource define new tasks to be fulfilled on HLMC technology

An intensity of impurity sources rises by hundreds times, but sinks - by dozens times

A great volume of R&D works are required, first of all about protective covers for structural materials and on development of liquid metal technology providing conditions for steel passivation