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WATER TREATMENT AND WATER CHEMISTRY

Calculation and Visual Displaying of the Water Chemistry Conditions in Return Cooling Systems at Thermal Power Stations

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Abstract—Matters concerned with treatment of cooling water at thermal power stations are addressed. Problems arising during operation of return cooling systems equipped with cooling towers are analyzed. The software used for monitoring, control, and indication of the hydraulic and water chemistry operating conditions of the circulation system at the Yaivinsk district power station is considered.

Keywords: service cooling water supply systems, thermal power station, scale formation, Excel spreadsheets
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The major part of natural water consumed by thermal and nuclear power stations (NPSs and TPSs) is used in their cooling systems for condensing steam. The main requirements imposed on the quality of cooling water can be summarized as follows: this water must have a temperature that allows the required depth of vacuum to be obtained in the condenser; in being heated, this water must not lead to formation of mineral deposits and biofouling, nor must it give rise to corrosion processes in the equipment and pipelines.

The condensers are cooled using either once-through systems (if water streams with a sufficient flowrate are available) or two types of return systems: (i) with cooling ponds and (ii) with cooling towers or spray ponds [1].

In the case of using a once-through cooling system, water passes through the turbine condenser only once. It is important to note that water from a river is in all cases taken from a section located upstream along the flow with respect to the section at which spent water is discharged. Huge quantities of heat are discharged with spent cooling water from thermal power stations into water bodies. Thus, the specific quantity of heat removed with cooling water as it is heated in turbine condensers by 8–10°C at TPSs amounts to around 4.3 kJ/(kW · h) with a consumption of water equal to 100–130 kg/(kW · h). For the influence of discharged heat not to upset the situation with natural environment in a water body, the relevant sanitary standards demand that heat discharges must not cause the water body's own temperature to increase by more than 5°C in winter and by 3°C in summer. These norms can be complied with only if the specific thermal load on a water basin does not exceed 12–17 kJ/m^3.

Until recently, the use of once-through systems has not give rise to any serious difficulties. However, the growth of capacities installed at TPSs and limited amounts of available water flowrates have led to a situation in which the possibilities of using such systems have been exhausted almost completely, due to which the fraction of return systems has become much larger.

In a return cooling system, water passes through a condenser several times. Heated water leaving the condenser is cooled by partially evaporating it. The use of natural water reservoirs is economically more profitable; however, their drawback is that in many cases it is not possible to set up normal thermal conditions in them.

In this paper, we consider the most widely used type of a cooling system, namely, a return cooling system (RCS) equipped with cooling towers in which the same volume of wat6er is used many times, and only a small addition of water is required for replenishing the losses in cooling devices.[1]

Biofouling and formation of mineral deposits are the main problems that arise during operation of RCSs. The following methods are used to prevent biofouling in cooling systems and to remove deposits formed in them.

Cleaning of condenser tubes with rubber balls. For removing soft, silt-like biological deposits (fouling) from condenser tubes, their continuous cleaning by means of solid rubber balls with a density of 1 g/cm^3 and diameter equal to the condenser tube inner diameter can be used.

[1] Dry cooling towers that are constructed in locations with acute scarcity of water resources are not considered in this paper.

Treatment of water with strong oxidizers. To control biofouling, which leads to enhancement of corrosion processes and degradation of vacuum in the condensers, cooling water is subjected to treatment with strong oxidizers, such as chlorine and its derivatives, as well as copper-containing salts.

The following methods are used to prevent formation of mineral deposits in the condensers of return systems:

(i) blowing down the system;

(ii) subjecting circulation water to stabilization treatment with different reagents; and

(iii) subjecting water to physical treatment in a magnetic or an acoustical field [1].

In what follows, some methods used to prevent the formation of mineral deposits are considered.

Acidification of circulation water is carried out for partially decreasing the carbonate hardness H_c to a value equal or somewhat lower than the maximum admissible carbonate hardness $H_{c.max}$ with the use of H_2SO_4 as the cheapest and readily available reagent.

Recarbonization of water. Hydrolysis of hydrocarbonates entailing the formation of a CO_3^{2-} ion can be prevented by replenishing the content of CO_2 desorbed in the cooling tower to its equilibrium value in cooling water. This process is called recarbonization of water because the water is in this case stabilized as a result of saturating it with carbon dioxide,. Fuel combustion products are used at TPSs as a source of CO_2. Recarbonization does not entail any noticeable increase in the content of salts in water, due to which less problems are encountered in fulfilling the environmental requirements when discharging RCS blowdown water into natural water basins.

Magnetic treatment of water is carried out in apparatuses the flow of cooling water in which intersects the force lines of magnetic field with an intensity of up to 10^5 A/m produced by an electromagnetic coil or permanent magnets. Despite the fact that theoretical principles behind the effect exerted by magnetic field on water and its admixtures have not been elaborated as yet, the following fact has been established experimentally: Application of magnetic field on water unstable with respect to carbonates and containing ferromagnetic admixtures (Fe_3O_4 and γFe_2O_3) slows down the formation of deposits on heat-transfer surfaces.

Deposits formed on condenser tubes are removed from them in the course of equipment repairs using chemical washing methods or by means of drawbar tubes fitted with roller cutters or hoses, via which high-pressure water is supplied to special heads with holes arranged so that water flows out from them in directions facilitating the removal of deposits and motion of the heads along the condenser tube [1].

Phosphatization. At present, technologies central to which is the use of phosphonates (OEDF, NTF, IOMS, and others) are the most efficient means to control scale formation. Cooling water in an RCS is prosphatized to slow down the formation of solid phase $CaCO_3$; phophates impede further growth of deposits, increase the permissible extent to which the solution can be oversaturated, thus stabilizing the composition of water. In the case of using oxyethylidene diphosphone acid (OEDPhA), stable scale-free operation of a return system is retained to the values of $H_c = 7.5$ mg-equiv/dm^3. All these technologies rest on certified regulatory documents, such as GOSTs (Russian State Standards), SNiP (Construction Codes), guiding documents, methodical recommendations, and so on. For more details about guiding documents on water treatment, see [2].

Blowing down the system. Blowing down an RCS, i.e., removing part of circulating water and replacing it by fresh water is a universally used method for decreasing the content of mineral substances in cooling water. During blowdown operations, the concentrations of all admixtures, including those of Cl^- and SO_4^{2-}, ions decrease in general, which helps to slow down the corrosion processes in a return system. Salts contained in the return system water are removed from it during the blowdown operations and with droplets entrained from the cooling tower. Since the main intent with which blowdown operations are performed is maintaining the carbonate hardness of circulation water below the maximum admissible level ($H_{c.max}$), the required blowdown flowrate can be determined from the following equations:

$$H_{c\,max}(G_{ent} + G_{bld}) = H_{c\,mkp}(G_{ev} + G_{ent} + G_{bld}),$$

$$G_{bld} = \frac{G_{ev} H_{c\,max}}{H_{c\,max} - H_{c\,mkp}} - G_{ev},$$

where $H_{c\,mkp}$ is the carbonate hardness of water added for replenishing losses in the RCS, mg-equiv/dm^3, G_{ent} is the fraction of the loss of water in cooling towers due to droplet entrainment, %, G_{ev} is the fraction of the loss of water in cooling towers due to evaporation, %, and G_{bld} is the fraction of blowdown, %.

For natural waters with oxidability up to 25 mgO_2/l in the temperature interval 30–65°C, the maximal stable carbonate hardness is found from Krushel's formula

$$2.8 H_{c\,max} = 8 + \frac{Ox}{3} - \frac{t - 40}{5.5 - \frac{Ox}{7}} - \frac{2.8 H_{nc}}{6 - \frac{Ox}{7} + \left(\frac{t - 40}{10}\right)^3},$$

where Ox is the oxidability of water, mg O_2/l; H_{nc} is the noncarbonate hardness of water, mg-equiv/kg; and t is the water temperature, °C.

Blowdown is the simplest method for preventing scale formation and makes it possible to decrease the evaporation ratio; however, its use is worthwhile only if the costs for pumping water and for the blowdown equipment do not exceed the expenditures for other return water correction methods.

Generally, stabilizing treatment of cooling water combines a set of measures including both blowdown and treatment of water with chemical agents. The Yaivinsk district power station uses an RCS with cooling towers. To prevent formation of mineral deposits, blowdown and correction treatment of cooling water with a solution of OEDPhA are used at this power station. This acid belongs to the class of diphosphonous acids, substances that have a high ability to generate complexes and high resistance to hydrolysis; it is readily dissolved in water, acids, alkalis, methanol, and ethanol.

In the course of treating water oversaturated with calcium carbonate, OEDPhA produces a strong complex with Ca^{2+} ions, which is sorbed on the surface of previously formed crystals and crystallization nuclei and impedes their further growth and agglomeration. Since there are no efficient and active crystallization nuclei due to the surface of crystals kept blocked, the solution is maintained in supersaturated state without release of scale [3].

The turbine condenser cooling system used at a power station is one of the least stable and most difficult to control ones in terms of maintaining the optimal water chemistry [4]. It is rather difficult to manually select the optimal operating mode of an RCS without using a dedicated mathematical model. Specialists of the Trieru Company (www.trie.ru), working jointly with specialists of the All-Russia Thermal Engineering Institute, (www.vti.ru) have developed software for monitoring, control, and indication of the hydraulic and chemical parameters characterizing the operation of the circulation system used at the Yaivinsk district power station (DPS). Specialists of the chemical department who are in charge for organizing the optimal water chemistry of return cooling systems often encounter difficulties in their work stemming from insufficient information available in the relevant guiding documents. Such documents contain elements for carrying out calculations, like tables, formulas, and graphs, the manual handling of which is labor- and time consuming. At present, dedicated computation programs have been developed that allow the recommendations of regulatory documents to be taken into account. Such computer programs are developed for particular problems; they contain calculations of technical and economic indicators and provide very exhaustive and user-friendly information. What is most important, specialists who carry out calculations using such computer programs need not to refer to the regulatory documents.

For the Yaivinsk district power station, the hydraulic and chemical operating conditions of its circulation system were calculated, including calculations of water utilization technologies carried out in the environment of the Excel and Mathcad software packages. Figures 1a and 1b show the schematic diagrams of cooling water treatment systems reflected in the Excel computer program, in which all input and calculated data are indicated. The specialist in charge for the circulation system's water chemistry can use them to monitor and control the circulation system's operating conditions. The mathematical model laid down in the computer program makes it possible to trace critical operating modes in which the "balance" in the system will be upset. For example, the program will inform the operator that the dose of OEDPhC introduced into the circuit is exceeded, that the operation with the current parameters may lead to scale formation, etc.

Control boxes are available on the virtual mimic diagram using which the operator can change the following parameters of system operation from the keyboard:

(i) indicators characterizing the quality of makeup water;

(ii) flowrate of water through a circulation pump;

(iii) concentration of OEDPhC working solution; and

(iv) costs of makeup water and OEDPhC chemical agent.

In addition, the operator can change the following parameters of system operation using a mouse manipulator:

(i) the temperature of

outdoor air,

water at the condenser outlet,

water at the circulation pump outlet, and

makeup water;

(ii) blowdown flowrate of the system; and

(iii) throughput capacity of the OEDPhC working solution metering pump.

Once a change occurs in at least one of the abovementioned parameters, the program automatically recalculates the composition of water and produces recommendations on the optimal dose of the correcting chemical agent, i.e., OEDPhC (whether its dose should be increased or decreased) and determines the

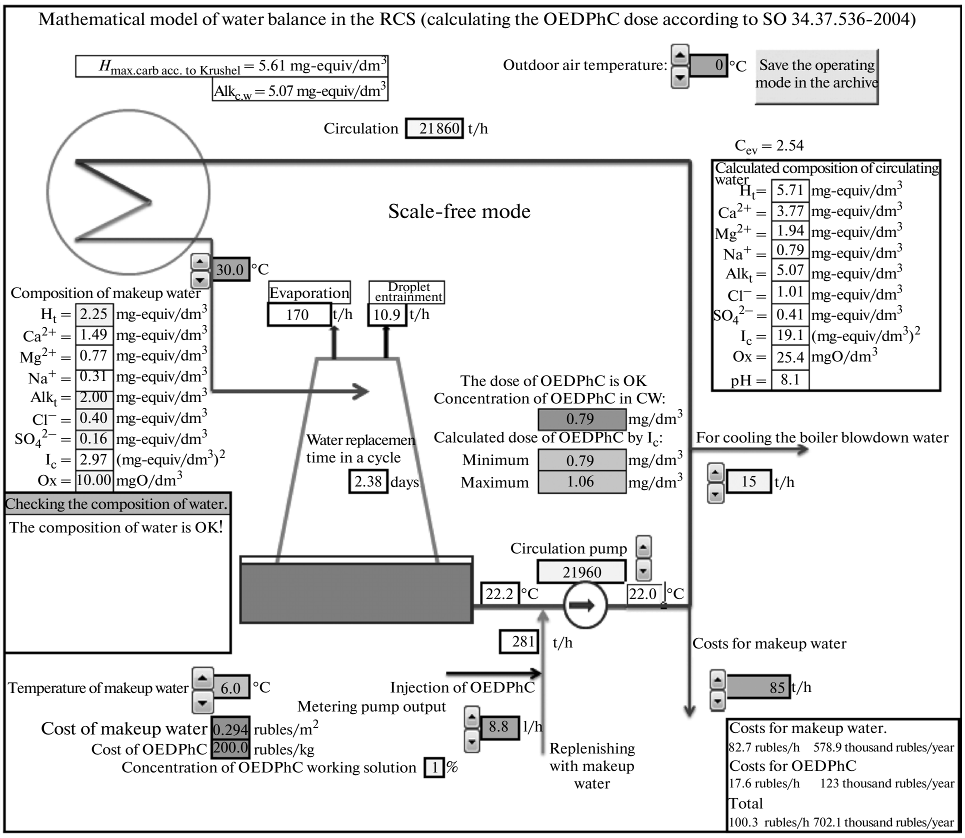
Data on the operating modes of the return cooling system (CS)

Indicator	Mode number		
	1	2	3
Blowdown flowrate of the CS, t/h	85.00	70.00	79.00
Flowrate from the OEDPhC metering pump, L/h	8.80	8.80	9.40
Operating mode	Scale-free	With scale formation	Scale-free
Costs, rubles/h:			
total	100.29	95.99	99.77
for water	82.69	78.39	80.97
for OEDPhC	17.60	17.60	18.80
Composition and indicators of circulation water			
Hardness, mg-equiv/dm^3:			
total calculated H_t^{des}	5.71	6.25	5.91
maximum permissible carbonate hardness according to Krushel H_{max}	5.61	5.82	5.69
Content, mg-equiv/dm^3, of:			
Ca^{2+}_{calc}	3.77	4.13	3.90
Ìg^{2+}	1.94	2.13	2.01
Na^+	0.79	0.86	0.81
Cl^-_{calc}	1.01	1.11	1.05
SO^{2-}_{4calc}	0.41	0.44	0.42
Alkalinity Alk_t^{calc}, mg-equiv/dm^3	5.07	5.56	5.25
Carbonate index I_c, (mg-equiv/dm^3)^2	19.09	22.94	20.46
Oxidability Ox_{calc}, mgO/dm^3	25.36	27.79	26.25
Calculated value of evaporation ratio C_{ev}^{calc}	2.54	2.78	2.62
pH	8.12	8.16	8.14

circulation system operating mode (with or without scale formation).

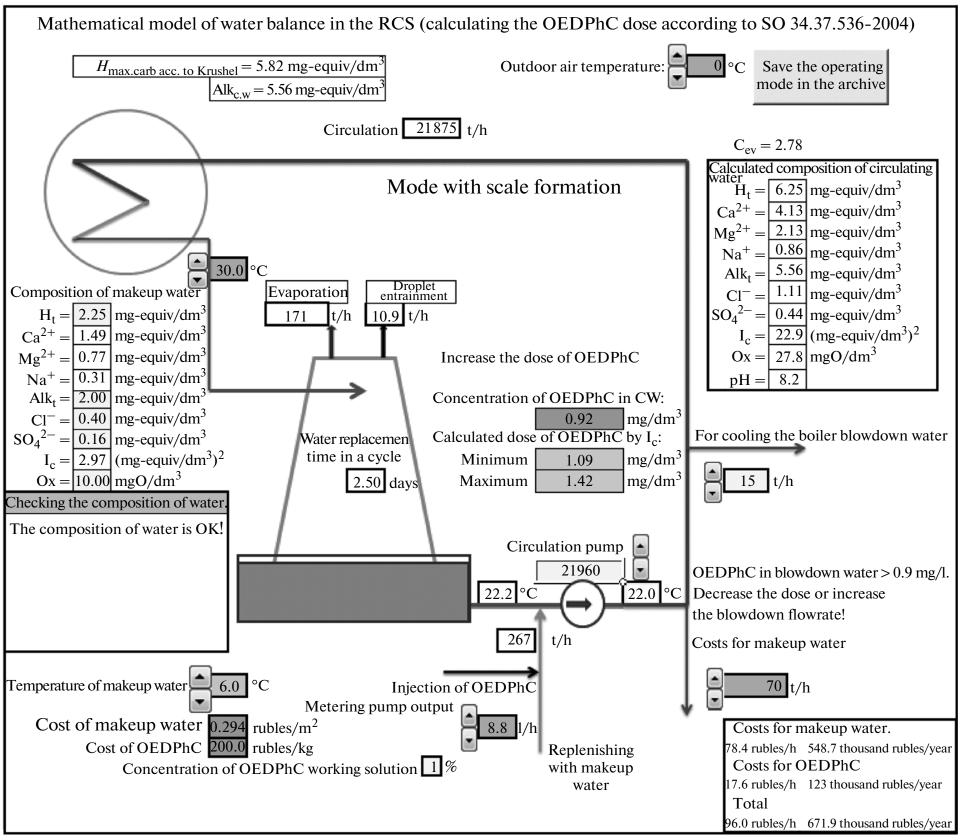
The program processes the parameters entered into it and prints out data on the composition of makeup and return water, on the temperature of circulating water at the cooling tower outlet, on water flowrates (for circulation, evaporation, droplet entrainment, and replenishing with makeup water), on economic

Fig. 1. Mathematical model of water balance in the return cooling system in the Excel software package (calculating the OEDPhC dose according to SO (Industry Standard 34.37.536-2004). (a) Scale-free mode and (b) mode with scale formation. CW is circulating water.



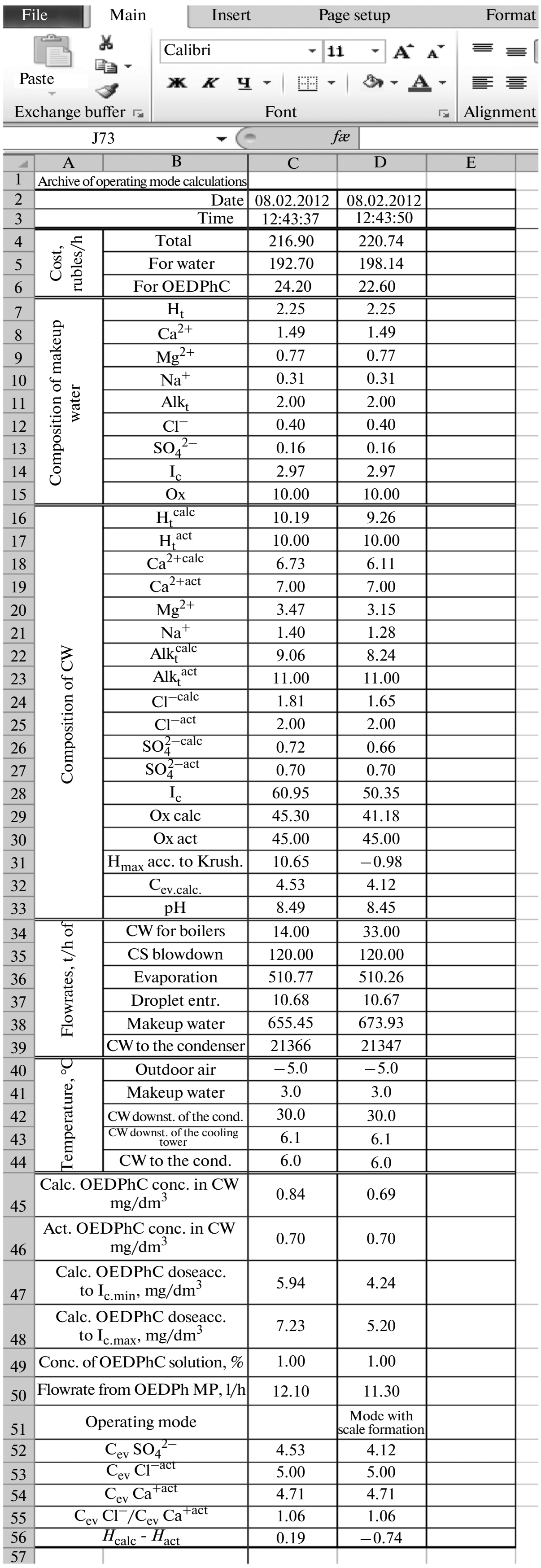
Mathematical model of water balance in the RCS (calculating the OEDPhC dose according to SO 34.37.536-2004)
$H_{max.carb\ acc.\ to\ Krushel}$ = 5.61 mg-equiv/dm^3
$Alk_{c.w}$ = 5.07 mg-equiv/dm^3
Outdoor air temperature: 0 °C
Save the operating mode in the archive
Circulation 21860 t/h
C_{ev} = 2.54
Scale-free mode
Calculated composition of circulating water
H_t = 5.71 mg-equiv/dm^3
Ca^{2+} = 3.77 mg-equiv/dm^3
Mg^{2+} = 1.94 mg-equiv/dm^3
Na^+ = 0.79 mg-equiv/dm^3
Alk_t = 5.07 mg-equiv/dm^3
Cl^- = 1.01 mg-equiv/dm^3
SO_4^{2-} = 0.41 mg-equiv/dm^3
I_c = 19.1 (mg-equiv/dm^3)^2
Ox = 25.4 mgO/dm^3
pH = 8.1
30.0 °C
Composition of makeup water
H_t = 2.25 mg-equiv/dm^3
Ca^{2+} = 1.49 mg-equiv/dm^3
Mg^{2+} = 0.77 mg-equiv/dm^3
Na^+ = 0.31 mg-equiv/dm^3
Alk_t = 2.00 mg-equiv/dm^3
Cl^- = 0.40 mg-equiv/dm^3
SO_4^{2-} = 0.16 mg-equiv/dm^3
I_c = 2.97 (mg-equiv/dm^3)^2
Ox = 10.00 mgO/dm^3
Evaporation 170 t/h
Droplet entrainment 10.9 t/h
The dose of OEDPhC is OK
Concentration of OEDPhC in CW:
0.79 mg/dm^3
Calculated dose of OEDPhC by I_c:
Minimum 0.79 mg/dm^3
Maximum 1.06 mg/dm^3
Water replacemen time in a cycle 2.38 days
For cooling the boiler blowdown water
15 t/h
Checking the composition of water.
The composition of water is OK!
Circulation pump
21960
22.2 °C
22.0 °C
281 t/h
Costs for makeup water
Temperature of makeup water 6.0 °C
Injection of OEDPhC
Metering pump output
85 t/h
Cost of makeup water 0.294 rubles/m^2
Cost of OEDPhC 200.0 rubles/kg
Concentration of OEDPhC working solution 1 %
8.8 l/h
Replenishing with makeup water
Costs for makeup water.
82.7 rubles/h 578.9 thousand rubles/year
Costs for OEDPhC
17.6 rubles/h 123 thousand rubles/year
Total
100.3 rubles/h 702.1 thousand rubles/year

(a)



Mathematical model of water balance in the RCS (calculating the OEDPhC dose according to SO 34.37.536-2004)
$H_{max.carb\ acc.\ to\ Krushel}$ = 5.82 mg-equiv/dm^3
$Alk_{c.w}$ = 5.56 mg-equiv/dm^3
Outdoor air temperature: 0 °C
Save the operating mode in the archive
Circulation 21875 t/h
C_{ev} = 2.78
Mode with scale formation
Calculated composition of circulating water
H_t = 6.25 mg-equiv/dm^3
Ca^{2+} = 4.13 mg-equiv/dm^3
Mg^{2+} = 2.13 mg-equiv/dm^3
Na^+ = 0.86 mg-equiv/dm^3
Alk_t = 5.56 mg-equiv/dm^3
Cl^- = 1.11 mg-equiv/dm^3
SO_4^{2-} = 0.44 mg-equiv/dm^3
I_c = 22.9 (mg-equiv/dm^3)^2
Ox = 27.8 mgO/dm^3
pH = 8.2
30.0 °C
Composition of makeup water
H_t = 2.25 mg-equiv/dm^3
Ca^{2+} = 1.49 mg-equiv/dm^3
Mg^{2+} = 0.77 mg-equiv/dm^3
Na^+ = 0.31 mg-equiv/dm^3
Alk_t = 2.00 mg-equiv/dm^3
Cl^- = 0.40 mg-equiv/dm^3
SO_4^{2-} = 0.16 mg-equiv/dm^3
I_c = 2.97 (mg-equiv/dm^3)^2
Ox = 10.00 mgO/dm^3
Evaporation 171 t/h
Droplet entrainment 10.9 t/h
Increase the dose of OEDPhC
Concentration of OEDPhC in CW:
0.92 mg/dm^3
Calculated dose of OEDPhC by I_c:
Minimum 1.09 mg/dm^3
Maximum 1.42 mg/dm^3
Water replacemen time in a cycle 2.50 days
For cooling the boiler blowdown water
15 t/h
Checking the composition of water.
The composition of water is OK!
Circulation pump
21960
22.2 °C
22.0 °C
OEDPhC in blowdown water > 0.9 mg/l. Decrease the dose or increase the blowdown flowrate!
267 t/h
Costs for makeup water
Temperature of makeup water 6.0 °C
Injection of OEDPhC
Metering pump output
70 t/h
Cost of makeup water 0.294 rubles/m^2
Cost of OEDPhC 200.0 rubles/kg
Concentration of OEDPhC working solution 1 %
8.8 l/h
Replenishing with makeup water
Costs for makeup water.
78.4 rubles/h 548.7 thousand rubles/year
Costs for OEDPhC
17.6 rubles/h 123 thousand rubles/year
Total
96.0 rubles/h 671.9 thousand rubles/year

(b)



	A	B	C	D	E
1	Archive of operating mode calculations				
2		Date	08.02.2012	08.02.2012	
3		Time	12:43:37	12:43:50	
4	Cost, rubles/h	Total	216.90	220.74	
5		For water	192.70	198.14	
6		For OEDPhC	24.20	22.60	
7	Composition of makeup water	H_t	2.25	2.25	
8		Ca^{2+}	1.49	1.49	
9		Mg^{2+}	0.77	0.77	
10		Na^+	0.31	0.31	
11		Alk_t	2.00	2.00	
12		Cl^-	0.40	0.40	
13		SO_4^{2-}	0.16	0.16	
14		I_c	2.97	2.97	
15		Ox	10.00	10.00	
16	Composition of CW	H_t^{calc}	10.19	9.26	
17		H_t^{act}	10.00	10.00	
18		Ca^{2+calc}	6.73	6.11	
19		Ca^{2+act}	7.00	7.00	
20		Mg^{2+}	3.47	3.15	
21		Na^+	1.40	1.28	
22		Alk_t^{calc}	9.06	8.24	
23		Alk_t^{act}	11.00	11.00	
24		Cl^{-calc}	1.81	1.65	
25		Cl^{-act}	2.00	2.00	
26		SO_4^{2-calc}	0.72	0.66	
27		SO_4^{2-act}	0.70	0.70	
28		I_c	60.95	50.35	
29		Ox calc	45.30	41.18	
30		Ox act	45.00	45.00	
31		H_{max} acc. to Krush.	10.65	−0.98	
32		$C_{ev.calc.}$	4.53	4.12	
33		pH	8.49	8.45	
34	Flowrates, t/h of	CW for boilers	14.00	33.00	
35		CS blowdown	120.00	120.00	
36		Evaporation	510.77	510.26	
37		Droplet entr.	10.68	10.67	
38		Makeup water	655.45	673.93	
39		CW to the condenser	21366	21347	
40	Temperature, °C	Outdoor air	−5.0	−5.0	
41		Makeup water	3.0	3.0	
42		CW downst. of the cond.	30.0	30.0	
43		CW downst. of the cooling tower	6.1	6.1	
44		CW to the cond.	6.0	6.0	
45	Calc. OEDPhC conc. in CW mg/dm³		0.84	0.69	
46	Act. OEDPhC conc. in CW mg/dm³		0.70	0.70	
47	Calc. OEDPhC doseacc. to $I_{c.min}$, mg/dm³		5.94	4.24	
48	Calc. OEDPhC doseacc. to $I_{c.max}$, mg/dm³		7.23	5.20	
49	Conc. of OEDPhC solution, %		1.00	1.00	
50	Flowrate from OEDPh MP, l/h		12.10	11.30	
51	Operating mode			Mode with scale formation	
52		C_{ev} SO_4^{2-}	4.53	4.12	
53		C_{ev} Cl^{-act}	5.00	5.00	
54		C_{ev} Ca^{+act}	4.71	4.71	
55		C_{ev} Cl^-/C_{ev} Ca^{+act}	1.06	1.06	
56		H_{calc} - H_{act}	0.19	−0.74	
57					

Fig. 2. Archiving the operating data in the Excel software environment. CW is circulating water, CS is the circulation system, and MP is the metering pump.

indicators (hourly and average annual costs for makeup water and OEDPhC), and on the concentration of OEDPhC in the circulating water.

Figures 1a and 1b show the operating modes without and with scale formation. The latter is caused by changing the blowdown flowrate from 85 to 70 t/h with the OEDPhC flowrate remaining unchanged. The program warns the user that in the given case the OEDPhC concentration in the circulating water is below the minimal calculated dose. To correct the situation, the program suggests to increase the flowrate produced by the OEDPhC metering pump and then to increase the blowdown flowrate to set up a scale-free operating mode. The program incorporates the possibility to select the most optimal operating mode depending on the external conditions with due regard to the economic indicators of the particular selected mode (the operating costs for makeup water and chemical agents). Consideration of the economic component is a very important issue because it allows the costs for consumption of makeup water to be minimized, which are quite high. The table gives the data on three modes of operation at different flowrates of OEDPhC and blowdown. In mode 3, scale-free operation and minimization of costs have been achieved with the initial parameters kept unchanged.

After selecting the optimal mode, the operator can print out the results of calculations or save them in the archive in tabular form. The system makes it possible to save the data of a particular operating mode, to automatically store them in an archive, and to write them in a column with the data and time of accessing the program. The results from archiving the data are shown in Fig. 2 in tabular form.

The same mathematical model was constructed in the Mathcad environment, some fragments of which are presented in Fig. 3, which shows the result from calculations of the economic component. The Mathcad environment has its own advantages: a specialist can see the calculation formulas (which are usually hidden in the Excel environment) and get an insight into the essence of the problem. In addition, not only does the Mathcad environment allow the specialist to use the model, but also to place the results of calculations in the Internet, thus sharing his or her experience with other specialists working in this field. Specialists of the Moscow Power Engineering Institute (www.mpei.ru) and Trieru (www.trie.ru) have developed a technology for publishing technical information with the possibility to directly carry out calcula-

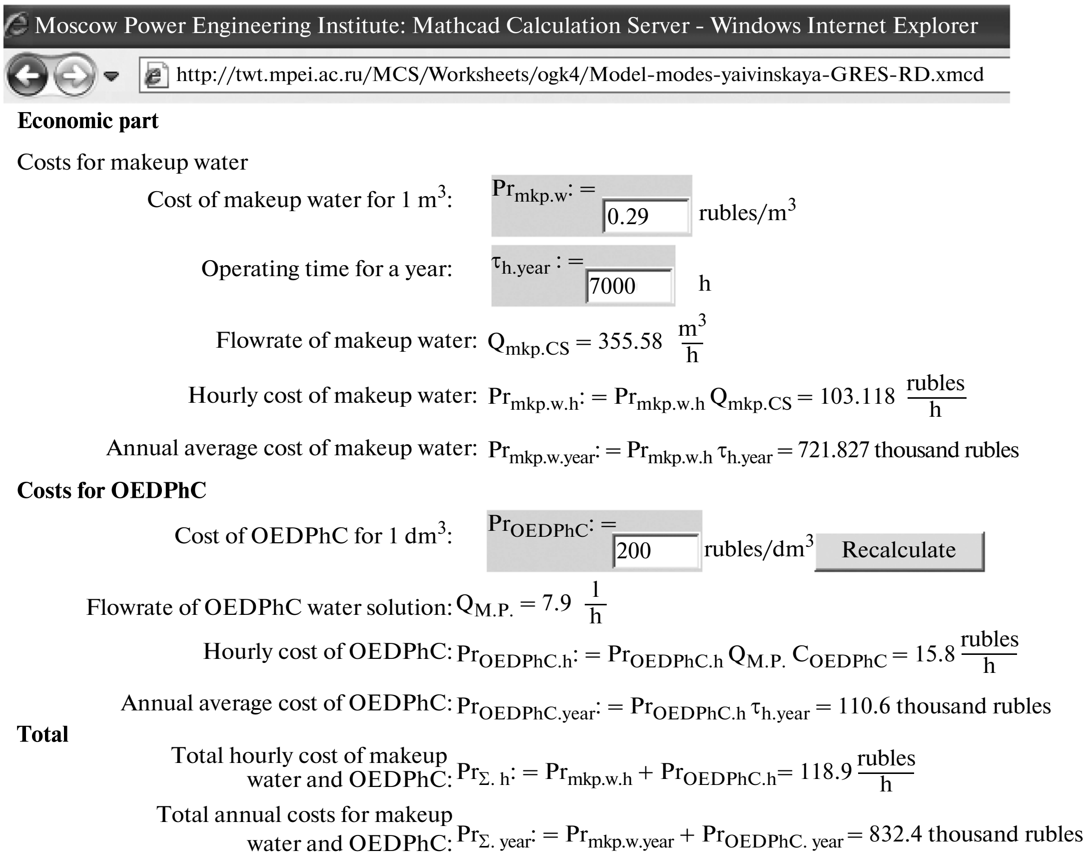


Fig. 3. Fragment of calculation by a mathematical model in the Mathcad environment (the economic part).

tions using this information. The computation server is accessible on www.vpu.ru.mas. The Mathcad environment allows the user to add or correct some calculation components on his or her own, without the need to contact with the software developers, due to which it becomes possibly to promptly respond to certain changes.

On the other hand, the use of the Excel package makes it possible to considerably relieve the burden from the personnel of chemical departments, because this package has been widely used and is familiar to the majority of PC users.

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SPELL: 1. Kopylov, 2. Makushin, 3. Kishnevskii