High-temperature service life tests of full-size thermosyphons

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Abstract. During past two decades, at temperature 240-265°C, resource tests were carried out on 19 thermosyphons of full-scale sizes: 45x4 mm in diameter, 4.92 m in length. The thermosyphons were prepared with varying preliminary surface treatment methods, composition of the aqueous solution to be poured into the thermosyphons, location of titanium chips in the perforated capsules under the lid of the thermosyphons. With a period of 1 to 3 years, thermosyphons were removed from testing system for 30 hours to control the vacuum by thermal method that does not require depressurization. At the last control experiment, four thermosyphons are depressurized for the following purposes: to check the condition of their internal surface in different zones along the length; for the chemical analysis of the aqueous solution poured from them; to determine the structure and characteristics of the mechanical properties of the thermosyphon metal. The main aim of the tests is to justify maintaining the structure and mechanical properties of the metal for a long time, keeping a vacuum of 90-95% inside the thermosyphon, ensuring high heat transfer characteristics of the boiling operating mode of thermosyphons.

1 Introduction

Thermosyphons are hollow tube, sealed from both ends and partially filled with boiling medium, mostly water [1–6]. Their work is based on the gravitational principle with counter-current motion of the steam flow up from the heating zone and the reverse motion of the wall film of the condensate of the vapor.

Thermosyphons have a simple design. Their autonomy and the presence of a double high-heat-conductive barrier between the heated and cooled medium increase the reliability of the heat exchangers consisting of thermosyphons. The depressurization of a small part of the thermosyphon present in the heat exchanger has practically no effect on its productivity.

In gas-and-gas heat exchangers with low external heat output and high values on the inner surface of pipes, use of thermosyphon slightly increases the overall surface compared to traditional heat exchangers [7]. In this case, temperature of the pipes is close to the saturation temperature of two-phase medium in the thermosyphon and is practically the same in length [8–11]. By varying the ratio of the lengths of the heating and cooling zones, it is possible to vary this temperature in the range between the temperatures of the heat-exchanging gaseous media. This increases the corrosion resistance of the heat exchanger when working with aggressive gas.

In works [12, 13], based on experiments with thermosyphons at angles of inclination to the horizon β=1.5–90°, the following is shown:

– high specific axial heat transfer across the thermosyphon section up to 3–4 MW/m^2, independent of the length of the transport section between the heat transfer zones,

– displacement of air remaining in the thermosyphon to its upper end by a steam flow having a velocity exceeding the boundary value of 0.75±0.01 m/s.

The authors [12, 13] proposed relationships for calculation of the intensity of thermal-hydraulic processes in thermosyphons, which are used in the conventional method of thermal-hydraulic calculation of heat-exchange equipment [14].

Up to now, determination of durability of maintaining the high intensity of thermal-hydraulic processes in thermosyphons and their strength characteristics due to the corrosion process.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2 \tag{1}$$
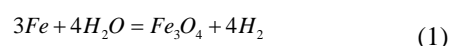
occurring inside the thermosyphon with the evolution of hydrogen. Its accumulation reduces the intensity of steam condensation and the power of the thermosyphon. The diffusion of hydrogen through the steel of the thermosyphon wall can reduce its mechanical properties.

Based on the resource tests conducted lasting for 1.5–36 thousand hours, [15–18] it is shown:

– high intensity of diffusion of hydrogen through the wall of thermosyphon from carbon steel and its low intensity through austenitic steel;

– reduction of the intensity of the corrosion process in the first test 1–1.5 thousand hours due to the

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formation of Fe_3O_4 protective oxide film on the inner surface of thermos background. The film leads to a dynamic equilibrium between the rates of hydrogen accumulation in the volume and diffusion through the wall.

At present, there are no reliable recommendations for calculating the intensity of these mutually compensating processes.

In the given works, the dimensions of the thermosyphons tested are miniaturized. The period of their tests is much lower than the accepted operating life of the heat exchange equipment.

2 Methods

2.1 Technology for manufacturing testing thermosyphons

Joint-Stock Company "I.I. Polzunov Scientific and Development Association on Research and Design of Power Equipment" in 1996, when designing a heat exchanger for the central aeration station of SUE "Vodokanal of St. Petersburg" (heat exchange media – aggressive gases), suggested to use 3400 thermosyphons: pipe diameter 45×4 mm; length 4.92 m, volume 5.25 l, material – steel 20, TU 14-3-190.

For the preparation of thermosyphons were analyzed:
– the optimal variant for passivation of the inner surface of the thermosyphon
– passivation additive to water, poured into thermosyphon
– degree of evacuation
– features of the introduction of the material (getter) that binds the hydrogen formed in thermosyphon under its lid (in the region with the largest hydrogen content).

The analysis was accompanied by short-term (1121–1507 hours) tests of 35 thermosyphons having different manufacturing techniques. In 1996–97, with an interval of 5 months, Joint-Stock Company "I.I. Polzunov Scientific and Development Association on Research and Design of Power Equipment" manufactured two batches of such heat exchangers for various technologies. After putting them into operation, in order to analyze the effect of in-tube factors on the durability of the work of thermosyphons, stand-by resource tests were continued with an increase in the number of thermosyphons under test. These thermosyphons, respectively, on 05.02.1997 and 16.07.1997 were attached to three thermosyphons of the search party, put for testing on 09.10.1996.

Assuming an increase in the intensity of corrosion processes with increasing temperature, the temperature range of the steam-water mixture in the thermosyphon 240–265°C (saturation pressure 3.3–5.1 MPa, abs) is chosen.

Taking into account the tests of the vacuum of the vapor-gas medium in the cooled thermosyphons using the thermal method (see below), which do not require depressurization and carried out with a period of 1–3.5 years, the test duration at 240–265°C at the date of the last inspection is 20.4–21.1 years.

The difference in the technology of thermosyphon manufacturing for heat exchangers of the second batch (installation 16.07.1997) consisted in the build-up of the protective film – dense magnetite Fe_3O_4 on the internal surface of thermosyphons when they were placed for 8 hours in the atmosphere of superheated steam (P=0.11 MPa, abs) at temperature 550–565°C. The thermosyphon blanks for the first batch heat exchangers were only blown with saturated steam to remove transport dust.

For both batches of heat exchangers
– 2 liters of an aqueous solution containing in addition to the turbine condensate (specific electrical conductivity at 25°C not more than 3 μS/cm), potassium chromate K_2CrO_4 – 0.5 g/l and NH_3 ammonia – 1 mg/l were filled into each thermosyphon;
– under the lid of thermosyphons, steel porous containers filled with titanium shavings (getter) were introduced to bind hydrogen ($Ti+H_2=TiH_2$) formed during the corrosion process. To assess the need for introducing a getter, some of the thermosyphons for testing were installed without it.

When determining the vacuum value by the thermal method, the lower part of the thermosyphon filled with the solution was placed in an open vessel tilted (β=8°) with heated water. The temperature of this water increased, and it was determined at what its value (T_b) the boiling of water in the thermosyphon under test would begin. This was associated with the beginning of heating the wall above the water level in the thermosyphon at a distance of 0.2–0.3 m. Prior to the experimental sample of the thermosyphon, under the vacuum gauge cover, the method was calibrated to the actual duration (less than 20 minutes) of finding the bottom of the thermosyphon in a vessel with water heated to T_b. Based on the calibration, accompanied by a vacuum measurement in the thermosyphon (P_0), the dependence $P_0=f(T_b)$ was found.

Three thermosyphon were manufactured at the stage of technology development. She was not pulled out; during the secondary sealing of the upper plug of the thermosyphon No. 24, in addition to the thermal seal, vacuum control was also carried out by the gravitational method with the depressurization of the thermosyphon. Both methods gave identical results. The remaining 15 thermosyphons were made at the end of the waste technology.

2.2 Measurements and testing

Two thermocouples, chromel-alumel, are welded to the thermosyphons under test in the vicinity of the steam-water mixture level and at the upper end of the thermosyphon. The thermosyphons equipped with thermocouples were folded into a bundle, which was installed at an angle β=8°. Around the lower part of the beam, an electric heater with a power of 2 kW of nichrome wire in the insulation of porcelain beads was spiraled. The outer surface of the beam is covered with thermal insulation. Every day, the thermocouple readings on thermosyphons were monitored, and the temperature

Table 1. Results of long-term resource tests of thermosyphons as of 7.12.2017.

Test Start Date	Thermosyphon number	Presence of a getter	Water regime	vacuum, %			Wall thickness of thermosyphon, mm, 7.12.2017 at a distance					Average thick-ness diffe-rence top bottom, mm
							From the bottom end			From the top end		
				ini-tial	7.12.17	cha nge	1 m	1.9 m	2.2 m	1 m	0.5 m	
16.07.97	21	there is	Chro-mate	95	97	2	3.74	3.68	3.73	3.84	3.83	0.125
	22				90	−5	3.76	3.80	3.80	3.86	3.83	0.065
	25				97	2	3.88	3.79	3.86	3.88	3.81	0.01
	28				96.5	1.5	3.90	3.87	3.80	3.82	3.92	−0.015
	23				94	−10	3.74	3.76	3.83	3.73	3.89	0.03
	24				73	−22		3.98	3.91	3.84	3.90	−0.05 0.03
	31	there is not			97	2	3.77	3.80	3.77	3.84	3.78	0.025
	33				97	2	3.82	3.75	3.79	3.80	3.99	0.01
	32				97	2	3.88	3.86	3.86	3.81	3.88	−0.025
	34				97	2	3.72	3.79	3.80	3.70	3.96	0.08
5.02.97	2			92	89	−3	3.80	3.84	3.79	3.98	3.97	0.15
	6			96.5	97	0.5	3.70	3.94	3.86	3.83	4.03	0.11
	3			93	96	3	3.82	3.92	3.81	3.90	3.90	0.03
	13			95	87.5	−7.5	3.88	3.91	3.90	4.01	3.94	0.08
	16			97	96	−1	3.77	3.80	3.87	3.79	3.96	0.09
	14	there is		95.5	97	1.5	3.91	3.98	4.0	4.02	3.97	0.05
9.10.96	8	there is	phos-phate	89	78	−11	3.87	3.86	3.91	3.96	4.00	0.115
	12			91	89	−2	3.76	3.72	3.77	3.76	3.94	0.11
	11	there is not	conde nsate	89	87.5	−1.5	3.94	3.80	3.88	3.96	3.96	0.06

of the thermosyphons was corrected when it reached the accepted range T_{out}=240–265°C.

Table 1 shows the characteristics of processing and filling of the tested thermosyphons, the presence of a getter in them, data on the vacuum value both after the manufacture of thermosyphons, and the last test on 7.12.2017, data on the change in vacuum over the twenty-year test period. Wall thicknesses are also given in different sections along the length of thermosyphon at the last inspection. Measurements were made in the upper and lower parts of the water volume, as well as in the region of the water level in the thermosyphons at T=250°C, i.e. in 2/2 m from the bottom end of the thermosyphon, in the upper part of the steam volume (0.5 m and 1 m from the upper end). After that, the thermosyphons No. 8, 24, 28, 32 were prepared. Of these, a solution for characterization was poured, see Table 2. Samples of 0.2–0.5 m in length were cut from the pipes where the thicknesses of their walls were measured. Samples are longitudinally cut to inspect their inner surface. From the top of the steam volume of 0.05 m and 1 m from the upper end of the thermosyphon No. 32, samples were obtained for estimating the structure and characteristics of the mechanical properties

Table 2. The results of analysis of the composition of water in thermosyphons taken off the test 7.12.2017.

Thermo-syphon number	pH	Colour	Electrical Conductivity, μS/cm	Fe, mkg/l	Transparency, cm
8	5.2	Yellowish	302	> 10000	<40
24	11.3	Transparent	797	442	>40
28	9.6	Transparent, slightly clouded	1100	2160	>40
32	11.6	Transparent, slightly clouded	1450	1180	>40

of the pipe material during diffusion of hydrogen through it. The remaining 15 thermosyphons were re-installed for testing.

3 Results

Analysis of the data presented in Tables 1 and 2 showed

1. Over the twenty-year test period, eight thermosyphons that do not contain a getter co-stored the initial vacuum: an average change of +0.9%, with a maximum decrease of 3%. Among them is a prepared thermosyphon No. 32. Its inner surface has a dense, smooth protective layer along the entire length with a finely dispersed, easily removable deposit of magnetite-type deposits. Compared to the solution fused from the remaining thermosyphons but containing the getter, the solution from thermosyphon No. 32 had fewer insoluble solid inclusions of the same nature as the deposits on its inner surface. Thus, the 8 thermosyphons listed have retained their heat transfer characteristics, i.e. boiling operation at a water temperature in thermosyphons exceeding 50°C. Boiling regime realizes the positive properties of the thermosyphon work: high intensity of axial heat transfer along the length of all zones of the thermosyphon, high heat transfer at boiling of water and film condensation of steam.

A small increase in the vacuum, at level of 2%, for thermosyphons No. 31–34 is associated with a high air temperature in the room T_{int}=31–33°C for the initial determination of the vacuum. At these temperatures, the maximum determined value by the thermal method is 95%, which was the case for these thermosyphons. The last check was carried out at T_{int}=13°C. In addition, the corrosive processes that took place also captured the air oxygen remaining in the thermosyphon after it was evacuated. So after 1507 hours of search tests in one of the thermosyphons, initially not evacuated, the final value of the vacuum was 18%.

2. 11 thermosyphons containing the getter during the first 13–14 years of testing also kept the initial vacuum well: an average change of –0.3% with a maximum decrease of 5%. But over the next 7 years, thermosyphon No. 8 and No. 24 had a sharp decrease in vacuum – by 11% and 22%. The remaining 9 thermosyphons had an average vacuum reduction of 1.4%, which is slightly higher than the value for a thermosyphon without a getter. This circumstance is associated with an electrochemical reaction between the wall of a tube made of steel 20 and a capsule of stainless steel with a getter and, to a lesser extent, the titanium getter itself contained in grids made of carbon-bearing steel for thermosyphons established on July 16, 1997.

For the seven thermosyphons that do not contain the getter, both the past passivation of the internal surface (thermosyphons No. 31–34) and those that did not pass through it (thermosyphons No. 2, 3, 6), there is no noticeable change in the vacuum. The resulted, and also small thinning of the walls of thermosyphons during the testing period, indicates that there is no need to use expensive technology of preliminary passivation of the internal surface of pipes and the insertion of a getter under the lid of a thermosyphon made of carbon steel.

The electrical conductivity of the solution in the thermosyphon increased by a factor of 100 as compared with the turbine condensate, which was 99.95% of the volume of the solution poured. The content of dissolved iron in the solution is also very high. Thermosyphon No. 11, filled only with a turbine condensate, practically retained the initial vacuum. The thickness of its wall decreased by less than 0.2 mm compared with the nominal value. The above calls into question the need for passivating additives to water, which is poured into thermosyphons. Sufficient is only high requirements for water being poured – the specific electrical conductivity is not more than 3 μS/cm.

The absence of data on the initial thickness of the walls of the thermosyphon tubes and the measured significant difference in the wall thickness along the perimeter of the cut samples, reaching up to 0.1 mm, makes it possible to determine only the thickness of the corroded wall layer at the level of the evaluation. It probably averaged about δS=0.02 mm. This value should correspond to the mass of the iron reacted (1), i.e. $\delta m_{Fe} = \pi dL(\delta S)\rho_{Fe}$=87 g and the mass of hydrogen formed m_{H2}=3.12 g.

4 Discussion

Under the level of boiling water, almost complete degassing takes place. Here one can neglect the diffusion of hydrogen through the wall of the tube. In studies [15, 16], the dynamic equilibrium between the rates of hydrogen accumulation in the bulk of the thermosyphon and its diffusion through the thermosyphon wall is characterized by a hydrogen content in the thermosyphon of 0.6–1.2 mg per m² of its entire internal surface. This for the tested thermosyphon corresponds to the mass of hydrogen above the water level m_{H2}=0.33–0.66 mg. That is, 99.98% of the hydrogen formed diffused through the wall of the thermosyphon. During testing, the height of the zone above the water level is L_{steam}=2.6 m, and its volume is 2.8 l, which corresponds to its concentration C_{H2}=0.118–0.236 mg/l. In view of the clearly larger wall thickness of the thermosyphons under consideration, in comparison with those tested in [15, 16], we take only the second value C_{H2}=0.236 mg/l=0.236 g/m³.

Assuming an analogy of the processes of heat and mass transfer and neglecting, due to the smallness of the content of hydrogen in the external air, the specific consumption of hydrogen, which diffuses through 1 m² of the inner surface of the wall of the steam volume of the thermosyphon (j_{H2}, g/m²s) is determined by the relation:

$$j_{H2}=2D_{dif.H2}\cdot C_{H2}/[d_1 \ln(d_2/d_1)], \qquad (2)$$

where $D_{dif.H2}$ – the diffusion coefficient of hydrogen through the wall of a pipe made of carbon steel, m²/s; d_1 и d_2 – outer and inner diameters of thermosyphon, m.

In the case of mass transfer, the relation (2) is neglected, due to the smallness of the diffusion

resistance of the inner and outer wall boundary layers of the medium inside the thermosyphon and the surrounding air.

According to the data [19] at T=300°C for diffusion of hydrogen through steel 12H18N10T $D_{dif.H2}$=3.8·10^{-14} m^2/s. According to the data [20] increase in chromium content in steel from 1% to 6% reduces the value $D_{dif.H2}$ 10^3 times at temperature 400°C and 45 times at 600°C. Hence we can assume the fourth order of difference of the above value $D_{dif.H2}$ for steel 12H18N10T and steel 20, at testing temperature 240–265°C, and take the value for calculation $D_{dif.H2}$=2.6·10^{-10} m^2/s.

With the above assumptions, calculation by (2) gives j_{H2}=1.72·10^{-8} g/m^{2}s,

hydrogen diffusion rate G_{H2}=$j_{H2}\pi d_1 L_{steam}$=0.5·10^{-8} g/s=0.156g/year.

In 20 years m_{H2}=3.12 g. This corresponds to the given value of the mass of hydrogen formed.

For all the roughness of the assumptions adopted, the result of the calculation probably reflects the order of the values taken δS; $D_{dif.H2}$ and C_{H2}.

The systematic excess of the wall thickness in the vapor zone above its value in the water zone (at a level of 0.01 mm) is associated with the dissolution of iron in water.

5 Conclusions

1. The results of twenty-year bench high-temperature resource tests of 19 thermosyphons of full-scale dimensions made of carbon steel are presented.

2. The permissibility of their long-term operation was demonstrated while maintaining high intensity of heat-transfer in-tube processes, as well as the structure and characteristics of the mechanical properties of the thermosyphon metal.

3. The received high indicators are reached also at application of economic methods of manufacturing of thermosyphons:

– cleaning of the internal surface of pipes – billets of thermosyphons – steam flow;

– partial filling of thermosyphons with an aqueous condensate having a conductivity at 25°C of less than 3 μS/cm;

– evacuation of the volume of thermosyphons above the water level to create in it at operating temperatures the boiling operating and a small effect of non-condensing gases on the isothermicity of the surface of thermosyphons in the cooling zone and the heat transfer rate in this zone. For industrial heat exchangers, normally, 90% of vacuum is sufficient.

– sealing of thermosyphons: high-quality argon-arc electric welding;

– control of vacuum not lower than the required value as described in the article by thermal or other method, not requiring depressurization of thermosyphons.

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