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Experience of Implementing the Scheme of Final Cooling of Coke Gas at PJSC "Arcelormittal Kryvyi Rih"

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Technology of the final cooling of coke gas, its ecological and technological aspects is viewed. The ways of reduction in the quantity of ejections into the atmosphere are represented. The experience of closing cycle in different coke-chemical enterprises is analyzed. Results on an improvement in the quality of the circulating water of the closed cycle are examined via the scavenging of cycle and processing of water on the ammonium column with the transfer to the biochemical effluent plant. Conclusions about the need of closing of aqueous cycle and control of salinity in the recirculation water of final gas cooler are made.

Keywords: COKE GAS, FINAL COOLING, EJECTIONS INTO THE ATMOSPHERE, CLOSED WATER CYCLE, CYCLIC WATER, AMMONIA COLUMN.

Introduction

An indispensable condition for the effective absorption of benzene hydrocarbons from coke oven gas is a low temperature process. According to the rules of technical operation [1], the temperature of the gas after the end of gas refrigerators before the benzene scrubbers should be in the summer period not exceeding 30 ° C in winter - when operating scrubbers on tar oil - not below 20 ° C.

To reduce the temperature of the coke oven gas, after separation from the sulfate 50-55 to 20-30 ° C an extended scheme of finite cooling of coke oven gas from the open water cycle was obtained, providing a direct contact with the gas cooling circulating water in the shelf or packed scrubbers.

This, along with heat transfer mass transfer occurs as well; as a result water absorbs hydrogen cyanide, hydrogen sulfide, benzene, hydrocarbons, phenols [2]. Upon cooling circulating water in cooling towers most of these components is desorbed, causing corrosion of metal structures and polluting the environment. To solve this problem, there are two options:

- Closing the loop by avoiding contact with the coke oven gas circulating water, i.e. to cool in the refrigerator by indirect heat transfer through the dividing wall;

- Closing the water cycle the water back end of the gas appliance direct action, i.e. cooling it in a shell and tube, plate or spiral heat exchangers.

Results and Discussion

The positive experience of the plants final cooling of coke oven gas with a closed water cycle is available on the Altai, Makeevka, Zaporizhzhya, Kharkiv coke chemical plants, coke production of the Nizhny Tagil Metallurgical Combine [3].

The final cooling of coke oven gas in refrigerators of indirect action (with a horizontal pipe still) realized on AZOVSTAL IRON & STEEL WORKS (JSC "Markohim") [4]. The structure of the closed loop consists of four end-gas refrigeratori with horizontal tubes with a cooling surface 2900 m2, two volumes of aqueous resin emulsion volume of 50 m3 pump. Cooling of coke oven gas is carried out recycled process water. Process water passes through pipes, coke oven gas - on annulus, according to the scheme shown in **Figure 1**.

The use of gas refrigerators with horizontal tubes for optimum temperature control and cleaning of gas from naphthalene, according to the norms of operational regulations does not result in the accumulation of oil in the ballast of salt absorption and significantly reduces emissions. Disadvantages include increased water consumption (2.5-fold compared to the direct action of refrigerators) [4], high metal content, significant capital expenditures for construction and repair [5].

For modernization of workshops to capture the closing of the water cycle, the final cooling of coke oven gas without stopping the process more useful is the second option of installing additional heat exchangers, resulting in liquidated largest source of harmful emissions into the atmosphere - cooling tower circulating water [6].

Such a scheme (see figure) is implemented on the project at Conservative Christian Giprokoks PJSC "ArcelorMittal Krivoy Rog" and involves the use of spiral self-cleaning heat exchangers of the company "Alfa Laval" [5] to cool the circulating water, refrigerators of direct action with a naphthalene washer at the bottom.

Significant problem in the final cooling with a closed water cycle is an increase in concentration of hydrogen cyanide in coke oven gas, which is caused by the redistribution of chemical desorbed earlier in the cooling tower circulating water absorption oil. As a result, this leads to increased corrosion of equipment in benzene separation, the absorption of oil deterioration, increased consumption of soda in the shop desulfurization.

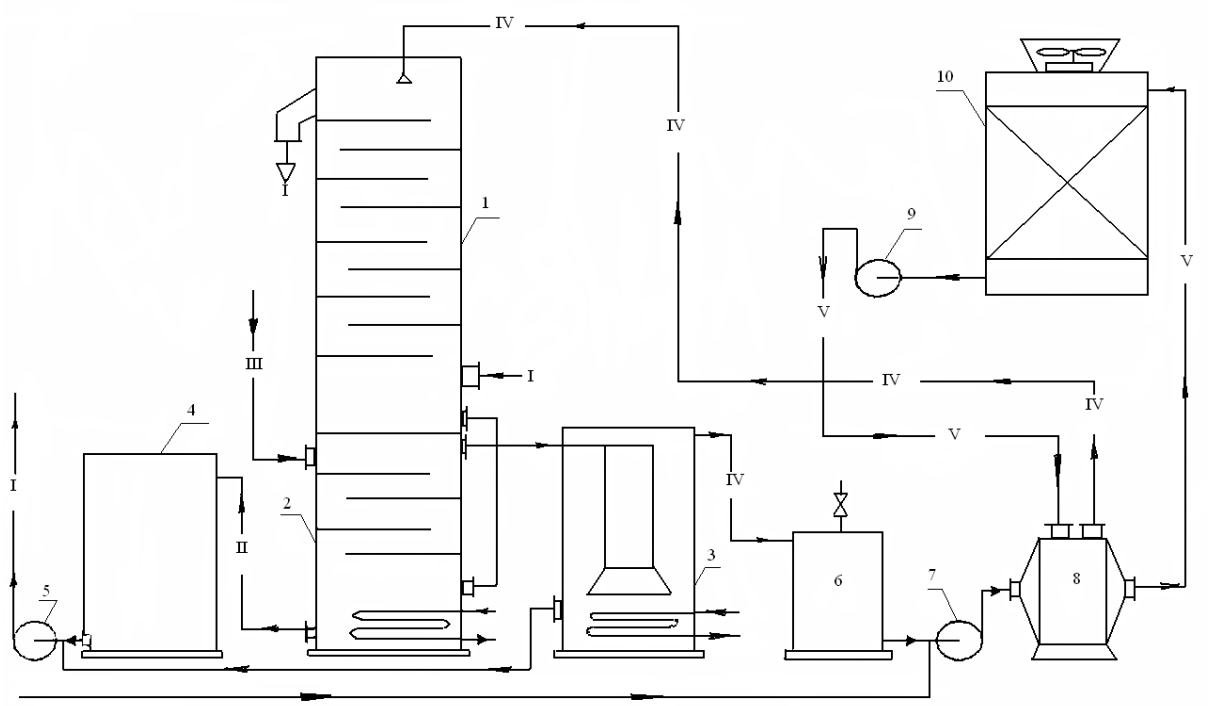

Figure 1. Flow sheet of the final cooling with a closed water cycle: 1 - the final gas refrigerator, 2 - naphthalene washer 3 - water tank; 4 - resin collector, 5 - resin pump, 6 - collector, 7, 9 - pumps, 8 - spiral heat exchanger of the company "Alfa Laval"; 10 - cooling tower; I - coke oven gas; II - resin to the warehouse; III - department of condensation of the resin; IV - circulating water; V - recycled water.

Increasing the concentration of hydrogen cyanide at the closing of the water cycle in the gas can be avoided by changing the existing scheme of trapping chemicals coking. Thus, when placed after the desulfurization of primary gas refrigerators or sulfate separation of the problem does not arise, because the efficiency of the vacuum carbonate desulfurization under very low degree of temperature-dependent process (in the range of 35-50 ° C). In this case the coke oven gas from the separation of sulfate enters the absorber for removal of hydrogen sulfide without intermediate cooling. Absorbed during this process naphthalene can be almost completely removed from the cycle in the tanks, "barometric" condensate formed by cooling gas in the regenerator-capacitors refrigerators. This scheme is applied in the desulfurization shop number 2 Avdeyevka Coke Plant [7].

For successful operation of the closed cycle final cooling of coke oven gas at the enterprises, having in its composition desulfurization, located after the separation of benzene a necessary condition is to extract hydrogen cyanide from the back final gas refrigerator water.

There are a lot of decisions based on the removal of the circulating water cycle of the final gas refrigerator hydrogen cyanide by stripping with inert gas or steam, or by binding of cyanide-ion reagents (iron sulfate, formaldehyde).

Formaldehyde method for treatment of the final final cooling of circulating water was investigated in industrial conditions at on one of factories in Ukraine. Due to the formation of stable aqueous

emulsion resin in the final cooling of the gas in the extraction of naphthalene from the water study was discontinued [8].

Technological scheme of a closed cycle final cooling of hydrocyanic acid from the stripping of recycled water under vacuum provides for decyanisator, which creates a deep vacuum with vacuum pumps. Disposal of uncondensed gases was supposed to decide by transferring them to the regenerative gas desulfurization, or installation receipt thiocyanate salts [8].

Successful implementation of these methods is difficult because of high capital investment, the problem with the further utilization HCN after desorption of the recycled water, which is due to the lack of sales. [3]

In the investigation of employees and specialists of Ukrainian State Research Institute for Carbochemistry and PJSC "ArcelorMittal Krivoy Rog" [9] the quality of water circulating in the closed water cycle at the enterprise established an increased concentration of volatile and total ammonia, hydrogen sulfide, cyanide (**Table 1**).

Table 1. Quality parameters of the chilled water cycle for final cooling during open and closed cycle

Final cooling mode of operation	Determined concentrations, mg/dm^3										Hatdness, meq/dm^3
	NH3	NH3	CNS$^-$	CN$^-$	H2S	Phenols	SO4^{2-}	Cl$^-$	Salts	resinous substance	
1	2	3	4	5	6	7	8	9	10	11	12
Open cycle	155	833	563	109	188	481	558	678	2097	60	3.02
Closed cycle	433	855	461	369	294	469	370	589	1820	370	4.71

Reducing the concentration of cyanides, thiocyanates, hydrogen sulfide, ammonia, and other closed water cycle in the CCP PJSC "ArcelorMittal Krivoy Rog" is carried out by the withdrawal of water through the installation of a biochemical blowing column ammonia plant. Stripping of volatile substances is produced by water vapor, desorbed gases are transferred to the coke oven gas pipeline to the primary gas refrigerators. Refreshing the reverse cycle was carried out technical water. As a result of installing quality of circulating water of final cooling was improved (**Table 2**).

When blowing recycled water in the ammonia distillation columns to reduce the concentration of ammonia and hydrogen cyanide in coke oven gas, which has a positive impact on the quality of the absorption of oil, decreased its consumption per ton of produced benzene, as well as consumption of soda in the shop desulfurization.

In order to reduce the overall hardness of recycled water refreshment cycle (recharge), the reverse process water was replaced with replenishment scheme defective steam condensate formed in chemical plants. This greatly affected the quality of water, which illustrate the data in **Table 3**.

Table 2. Water-quality closed-cycle of final cooling when entering installation of ammonium

Determined concentrations, mg/dm^3									
NH_3 volatite	NH_3 general	CNS^-	CN^-	H_2S	Phenols	SO_4^{2-}	saults	CL^-	Hardness meq/dm^3
240	490	230	190	90	520	120	950	220	4.1

Table 3. The quality of the water cycle after the change of process water by vapor condensation

Determined concentrations, mg/dm^3									
NH_3 volatite	NH_3 general	CNS^-	CN^-	H_2S	Phenols	SO_4^{2-}	saults	CL^-	Hardness meq/dm^3
100	1700	180	100	70	230	40	510	100	0.41

According to the environmental services of the company in the open circuit of final cooling air emissions from the cooling tower for 2-4 quarters of 2005 totaled 377.122 tons. With closed cycle cooling the final air emissions were reduced to 0.037 tons / year [9].

Thus, closing the water cycle of the final cooling substantially reduces the amount of harmful emissions into the atmosphere, which favorably affects the working conditions and health of staff, residents of nearby communities.

Conclusions

Improvement of technology and the elimination of negative factors arising from the closure of the final cooling cycle is possible with the use of integrated measures to eliminate the accumulation of corrosive components in the circulating water of a closed cycle.

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Опыт внедрения схемы конечного охлаждения коксового газа на КХП ПАТ «АрселорМиттал Кривой Рог»

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Рассмотрена технология конечного охлаждения коксового газа, ее экологические и технологические аспекты. Представлены пути снижения количества выбросов в атмосферу. Проанализирован опыт закрытия цикла на различных коксохимических предприятиях. Рассмотрены результаты по улучшению качества циркулирующей воды закрытого цикла путем продувки цикла и переработки воды на аммиачной колонне с передачей на биохимическую установку. Сделаны выводы о необходимости закрытия водного цикла и контроля солесодержания в оборотной воде конечного газового холодильника.