Environment Protection Engineering

Vol. 11 1985 No. 3–4

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USAGE OF PURIFIED WASTEWATER IN REFINERY CIRCULATING WATER SYSTEMS

The quality of fresh and circulating water is briefly discussed. Specific consumptions of water by refineries are also given. Characteristics of circulating water supply systems and the main approaches to their improvement are presented: maximum use of air coolers, conditioning of circulating water and development of systems without bleeding.

Technological properties (actual and standard ones) of circulating water are presented and the limitations of its stabilization treatment mentioned. A recommended scheme for complex treatment of circulating water in water systems is described.

It has been shown that mechanical treatment of industrial and strom runoffs is insufficient for water reuse. Results of pilot plant investigations show that the biochemically treated industrial and storm runoffs as well as municipal sewage can be used in refinery circulating water systems.

Closed-loop systems provide the water for its primary and secondary crude distillation as well as for some petrochemical processes taking place in petroleum refineries.

These systems are largely supplied by river water, ground water being used in insignificant amounts. In most petroleum refineries the amounts of suspended solids in fresh water range from 10 to 70 mg/dm^3. The BOD$_5$ value varies within 3 and 22 mg O_2/dm^3. The total salt content in fresh sweet water ranges from 80 to 770 mg/dm^3 (fry residue).

The quality of circulating water in various plants is characterized by the following parameters:

suspended solids	10–90 mg/dm^3,
oil products	15–50 mg/dm^3,
BOD$_5$	15–60 mg O_2/dm^3,
total salts	200–1000 mg/dm^3.

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In modern petroleum refineries with a high rate of circulating water, specific consumption of fresh sweet water averages 0.25–0.5 m^3 and 0.6–1.2 m^3/t of crude processed, according to fuel and fuel-lubricating oil schemes, respectively. For the above types of refineries specific consumption of circulating water is 13 and 21.5 m^3/t, respectively, its utilization being 92% and 96%. The consumption largely depends on the quality and conversion level of crude oils.

Circulating water systems, widely applied in petrochemical and petroleum refinery plants, contribute substantially to the reduction of industrial pollutants in natural water sources. The efficiency of this method in environmental pollution abatement is, however, lowered by some specific factors:

1. Cooling by evaporation (chiefly in cooling towers), due to which salt and nonvolatile matter are concentrated in circulating water, while dissolved gases and organics boiling at low temperature are emitted to the atmosphere.

2. Increasing concentrations of salt and foreign matter in circulating water intensity corrosion, scale-and-sludge formation in heat exchangers.

3. Large discharge of circulating water to industrial sewers (bleeding).

The main trends for the improvement of circulating water supply in the USSR petroleum refineries are: maximum use of air cooling, fresh and circulating water pretreatment as well as development of circulating water systems without bleeding.

Over the past ten years, air coolers have found wide application in all plants in order to reduce circulating water consumption.

In order to forecast the future water consumption, it has been assumed that 60–70% of the circulating water used at present for cooling petroleum products, heated to at least 50–60°C, could be substituted by air cooling; the remaining 30–40% of the recycle being used for aftercooling the air-cooled petroleum products.

It is known that the consumption of circulating water for cooling depends on the condition of heat transfer surfaces which, in turn, depends on the technological (service) characteristics of the above water. The studies have shown that non-treated circulating water has the following technological properties:

corrosion rate 0.2–1 mm/y,

scaling rate 3000–6000 g/m^2.y,

biological growth rate 8–25 g/m^2.d.

According to the USSR standards, corrosion rate should not exceed 0.1 mm/y, scaling rate 2200 g/m^2.y, biological growth rate 1.7 g/m^2.d. The desired technological properties of the circulating water can be obtained by its conditioning. In some petroleum refineries suspended solids are removed from fresh water by applying pressure or gravity-type sand filters which prevent the inflow of large amounts of river silt (especially over high water periods) into the circulating system.

Until recently, acidification, phosphatization, chlorination, and the addition of blue vitriol were considered to be the main methods of circulating water treatment.

As experience has shown, water stabilization does not sufficiently protect coolers and condensers against corrosion and scaling. Besides, phosphatization intensifies biological growth in circulating water systems and necessitates its bleeding.

Thus, no-bleeding conditions should be created for the operation of circulating systems. However, in this type of operation the concentrations of salts in circulating water incsease and corrosion and scaling processes are intensified. Therefore a more efficient method should be developed for the complex treatment of circulating cooling water. The scheme of such a complex treatment developed in BashNII NP is now used in the designs of new and modified water systems. In addition to oil traps, cooling towers and pump stations, these systems include filtration, inhibition, and chlorination plants.

To remove suspended solids from the fresh water in high water periods as well as suspended solids and petroleum products from a portion of circulating water (10% of an hourly flow-rate), quartz sand or petroleum coke pressure filters are used (filter bed depth 1 m, particle size 0.5–1 mm, filtration rate 7–8 m/h). Other types of filters can be also used.

As a corrosion inhibitor the IKB-4 is recommended as it makes it possible to reduce corrosion and scaling rates in heat exchangers by 80% on the average.

As a rule, chlorine is introduced into the cooled water in summer. Its dose during the operation is established with due regard to fact that the residual chlorine content after the most remote heat exchanger should not exceed 0.2 mg Cl_2/dm^3. Simultaneously blue vitriol is introduced into the hot water (once per 7 to 10 days), the dose of 4 mg Cu/dm^3 is based on an hourly circulating water flow rate.

It should be noted that even in the absence of chlorine, in inhibited water biological growth rates are 50–70% lower than those without IKB-4, which is attributed to detergency of this inhibitor.

Such a complex water treatment provides normal heat exchange and reduces cooling water consumption to nearly a theoretical value.

The non-bleeding operation of water circulating systems necessitates the standardization of water qualities. According to the recently developed standards the admissible salt concentrations (up to 2000 mg/dm^3) in such water are higher compared to the present level (700–1000 mg/dm^3).

Over the past 10 years, in order to reduce the intake of bleeding and fresh water, both in operating plants and those under construction, the maximum use of the treated industrial and storm runoffs has been observed.

The former practices have shown that when using mechanically treated industrial and storm runoffs, the circulating water is largely contaminated with dissolved biodegradable organics, BOD_{total} reaching 100–180 mg mg O_2/dm^3. Cooling towers as well as heat exchangers silted due to an intensive biological growth should be frequently shut-down for cleaning. Therefore, most refineries gave up the idea of using mechanically treated wastes and changed to a fresh water make-up.

As the results of pilot plants investigations in BashNII NP have shown, one-stage activated sludge treatment of industrial and storm runoffs originating from petroleum refineries makes it possible to reduce BOD_{total} to 10–15 mg O_2/dm^3. The biochemical treatment of industrial and storm runoffs proceeds without dilution with municipal wastes, the aeration period being 6 h. Activated sludge concentration ranges within 2–3 g/dm³, oxidation capacity of air tanks being 900–1000 g/m³.day. As a nutrient phosphorus (up to 3 mg/dm³) is added. There is no need to add ammonia nitrogen as its salts are present in wastes. Biochemical treatment of effluents fully meet the standardized circulating water quality.

As it has been found during the pilot plant investigations, the biochemical treatment of reusable industrial and strom runoffs improves considerably technological properties of the circulating water. It reduces the corrosion and scaling rates by 33% and 66%, respectively, if compared to the mechanical treatment.

A valuable experience in the biochemical treatment and reuse of industrial and storm runoffs in the Novopolotsk refinery confirmed the validity of our recommendations. At the same time it has been established that under large-scale conditions, suspended solids (over 25 mg/dm³) are brought out from secondary settling tanks. Hence the treated wastewaters should be subject to aftertreatment before being recirculated. For this purpose granular or drum microscreen filters may be used.

Sand filters with filtration rates of 10 m/h are most efficient in aftertreatment operations (70–80% removal of activated sludge).

A progressive biological growth observed during filtration decreases filtration rates. To prevent this biological growth, filter beds should be periodically treated with chlorine water.

Table

Quality of municipal sewage in the USSR
Właściwości ścieków miejskich w ZSSR

Quality	Min	Max	Mean
Oil products, mg/dm³	3.5	24	11.7
Suspended solids, mg/dm³	6.3	46	29.3
Chlorides, mg Cl^-/dm³	14	244	120
Sulphates, mg $SO_4^{=}$/dm³	22	314	135
Phosphates, mg $P_2O_5^{=}$/dm³	1	25	4.2
Nitrates, mg NO_3^-/dm³	0.02	6.5	1.97
Ammonia nitrogen, mg/dm³	1.6	37	12.9
Total salt content, mg/dm³	323	1180	645
Carbonate hardness, mg-eq/dm³	2.4	6.8	3.4

The recirculation of biochemically treated industrial and storm runoffs makes it possible to reduce considerably the fresh water intake which, however, cannot exclud it completely at the current circulating water flow rates.

In some areas because of the lack of fresh water other sources, such as municipal sewage, should be used for the industrial water supply.

Table shows that concentrations of salts in treated municipal sewage vary within wide ranges. High salt concentrations are characteristics of the cities where industrial wastes are discharged into the municipal sewers. The municipal runoffs may be used in refinery circulating water systems after they have been aftertreated to remove suspended solids. If salt concentrations of municipal runoffs do not exceed 500 mg/dm^3, they may be used instead of fresh water.

Pilot-scale investigations performed by BashNII NP have shown that corrosivity and scale formation ability of biochemically treated municipal runoffs used as make-up water for circulating systems are somewhat higher than those of industrial and storm runoffs treated biochemically.

However, the treatment methods for circulating water are almost the same if the treated municipal sewage or industrial-storm runoffs are used as make-up.

In the U.S.A. and the USSR the compositions of salts in municipal runoffs are almost the same. In the USSR the average phosphate concentration in biochemically treated municipal sewage (4 mg P_2O_5/dm^3) is 8 times lower than in that the U.S.A., therefore, in this country the problem of phosphate removal is not so urgent as it is in the U.S.A.

However, the use of these wastewaters requires an industrial experience since they contain small quantities of aluminium, phosphorus, and silicon salts, which being concentrated in the circulating water, may interact to form compounds of low solubility.

By applying biochemically treated municipal sewage as make-up of circulating systems, it will be possible to build a petroleum refinery not consuming fresh water and, therefore, independent of natural water sources.

In the future, application of make-up water from the out-side will be diminished because of the decreasing circulating water flow rates. It is due to the fact that one half of refinery industrial and storm runoffs consists of oil processing effluents (technological condensate flows, industrial and storm runoffs) and of wastes from outside sources (oily wastes — heat and power plants, steaming units, garages, laboratories, etc). The application of these wastewaters makes it possible to meet fully refinery make-up water requirements with much lower circulating water flow rates.

As the salt composition of the circulating waters with no bleeding depends on quantity of dropwise carry over in the cooling towers, the use of improved cooling towers may result in a higher equilibrium of salt contents in the circulating water which exceed the standards. In the future, complex treatment of water may be improved by its partial desalination.

WYKORZYSTANIE OCZYSZCZONYCH ŚCIEKÓW W SYSTEMACH CYRKULACJI WODY W RAFINERIACH PETROCHEMICZNYCH

Omówiono w skrócie jakość wody świeżej i cyrkulowanej w rafineriach ropy naftowej oraz wielkość jej zużycia. Scharakteryzowano systemy cyrkulacji wody i wskazano główne kierunki ich usprawnienia: maksymalne wykorzystanie chłodnic powietrznych, kondycjonowanie cyrkulowanej wody i likwidacja przecieków. Przedstawiono własności technologiczne (rzeczywiste i standardowe) wody cyrkulowanej oraz występujące ograniczenia metod jej stabilizacji.

Opisano zalecany schemat kompleksowej obróbki takiej wody. Stwierdzono, że mechaniczne oczyszczanie ścieków przemysłowych i odpływów burzowych jest niewystarczające. Wyniki badań w skali pilotowej wykazały natomiast, że zarówno ścieki przemysłowe i komunalne jak i odpływy burzowe poddane biologicznemu oczyszczaniu mogą być stosowane w systemach cyrkulacji wody w rafineriach petrochemicznych.

DIE NUTZUNG VON GEREINIGTEN ABWÄSSERN IN WASSERKREISLÄUFEN DER ERDÖLRAFFINERIEN

In kurzer Weise wird auf den Wasserbedarf und auf die Qualität des Frischwassers und der im Kreislauf von Erölraffinerien geführten Wässer hingewiesen. Charakterisiert werden die Wasserkreisläufe und die entsprechenden Verbesserungsmaßnahmen. Zu den letztgennanten gehören u.a.: die maximale Ausnutzung der Luftkühlung, die Aufbereitung des Kreislaufwassers und die Elimination von Leckagen. Aufgezählt werden die technologischen Eigenschaften (reale und normative) des Kreislaufwassers sowie die bestehden Beschränkungen der Stabilisierungsverfahren.

Mehr eingehend wird ein Schema der Wasseraufbereitung erörtert. Aus ihm folgt, daß eine mechanische Vorreinigung der Industrieabwässer und der Regenwässer nicht genügt. Aufgrund von Versuchen im Pilotmaßstab geht jedoch hervor, daß die biologische Vollreinigung von Industrie-, Kommunalabwässer und Regenwässer vollkommen ausreicht und die auf diese Weise gereinigten Abflüsse in den Wasserkreislauf der oben genannten Werke, eingespeist werden können.

ИСПОЛЬЗОВАНИЕ ОЧИЩЕННЫХ СТОЧНЫХ ВОД В СИСТЕМАХ ЦИРКУЛЯЦИИ ВОДЫ НА НЕФТЕХИМИЧЕСКИХ ЗАВОДАХ

Обсуждено качество свежей и циркулируемой воды на нефтеперерабатывающем заводе, а также описана величина её использования. Охарактеризованы системы циркуляции воды и указаны главные направления их улучшения: максимальное использование воздушных холодильников, кондиционирование циркулируемой воды и устранение утечек. Представлены технологические (действительные и стандартные) свойства циркулируемой воды, а также существующие ограничения методов её стабилизации.

Описана рекомендуемая комплексная схема обработки такой воды. Отмечено, что механическая очистка промышленных сточных вод и стоков дождевой воды является недостаточным. Результаты же исследований в полузаводском масштабе показали, что как промышленные и коммунальные сточные воды, так и стоки дождевой воды, подвергнутые биологической очистке, могут применяться в системах циркуляции воды на нефтехимических заводах.