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## LABORATORY STUDIES ON APPLICABILITY OF BIOLOGICAL EFFLUENTS IN CLOSED COOLING CYCLES

Results of initial preliminary laboratory studies on treatment of biological effluents for cooling purposes in closed cooling systems of a coking plant are presented. The studies included coagulation, decarbonization and filtration of the effluent. As a result industrial water has been obtained with pH 8.0–9.0, organics content expressed as permanganate oxygen consumption and BOD<sub>5</sub> — respectively 4–7 g/m<sup>3</sup>O<sub>2</sub> and 8–20 g/m<sup>3</sup>O<sub>2</sub>, and carbonate hardness equal to 60–85 g/m<sup>3</sup> CaCO<sub>3</sub>. Concentration studies on the recovered water have also been conducted in a model cooling system. Due to the precipitation of carbonates from wastewater post coagulation the concentration index obtained was equal to 1.5; the index after coagulation and decarbonization was equal to 2.0.

### 1. INTRODUCTION

A continuous increase in potable and industrial water consumption results in a depletion of available clean water resources. This deficiency in some geographical regions has produced the problem of water renewal or renovation. The problem is successfully solved in some cases in highly industrialized countries. The United States exhibits the greatest experience in this field, where about 501 mln m<sup>3</sup> per year of the treated wastewaters were used for agricultural, industrial, recreational and household purposes in 1971 [1]. The annual quantities of reused water were as follows:

irrigations — 291.0 mln m<sup>3</sup>,

industry — 202.0 mln m<sup>3</sup>,

recreation — 7.5 mln m<sup>3</sup>

(households water not included) — 0.5 mln m<sup>3</sup>.

Of the 202.0 mln m<sup>3</sup> of wastewaters used annually in industry, 98.5% was destined for cooling in the open and closed cycles. The largest quantities of cooling water reclaimed from municipal sewage are actually used by the steelworks in Baltimore (USA) [1] and industrial plants localized in the Suisun Bay (USA) [2].

The same methods allowing the compensation of water deficiencies in cooling systems might be also applied in this country. This problem is illustrated by water supply design for a coking plant planned in the vicinity of Wałbrzych, which is the subject of our analysis.

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This new coking plant might be also supplied with water from a reservoir located about 20 km below the plant. This, disadvantageous from economical point of view location of the reservoir raised interest in the effluent from the combined wastewater treatment plant — situated at a distance of about 3 km — as a possible source of industrial water required by the cokery. The combined mechanical-biological wastewater treatment plant, operated since 1973, is equipped with screens, grit chamber, activated sludge tanks aerated with compressed air, and secondary settling tanks.

The municipal treatment plant influent contains 30% of industrial wastewaters, originating chiefly from the food industries such as breweries, malt plants, confectioneries, meat and dairy plants. Moreover, small amounts of wastewaters are discharged by glass and porcelain works, linen industry and the gas works.

The purpose of the present work was to determine the applicability of biologically treated effluent as a make-up water in cooling system of the coking plant.

## 2. THE PARAMETERS REQUIRED FOR THE MAKE-UP WATER

The cooling water parameters such as pH, carbonate hardness, salinity and concentration of some metal ions depend primarily on the characteristics of the cooling cycle and the temperature. The requirements set to cooling water for the designed coking plant as well as Polish, Soviet, and American standards — are given in Table 1. From the data it follows that values of the parametrs vary in a broad range.

Analyses of cooling water taken from 11 closed cooling systems [6] supplied with treated surface water or with potable water from the municipal supply system, have the following concentrations of amonium and nitrate nitrogen, phosphorus and phosphates.

	Make-up water	Water in cycle
$N_{NH_4}$ —g/m <sup>3</sup>	0.02–1.60	0.17–2.65
$N_{NO_3}$ —g/m <sup>3</sup>	0.10–2.80	0.12–6.60
P—g/m <sup>3</sup>	0.01–0.80	0.25–6.01
$PO_4^{3-}$ —g/m <sup>3</sup>	0.01–0.45	0.98–2.32

Of various industrial branches using water for cooling purposes, the coking industry has one of the more complex cooling systems. Thus the system maintenance costs depend chiefly on the quality of the cooling water.

If the wastewater treatment plant effluent is to be used as make-up water in the coking plant cooling system, attention should be given to the content of nutrients since the presence of nitrogen and phosphorus compounds promotes the development of microorganisms in the cooling system. According to the studies carried out by the Iron Metallurgy Institute [7] the concentration of ammonia nitrogen is an important factor determining the applicability of water for cooling purposes, because of its corrosive properties. The corrosivity results from the oxidation of ammonia to nitric acid.

Table 1

Requirements for quality of cooling water in closed cycle

Parameters	Units	According to the coke plant specs <sup>xx</sup>	Accord. to Polish data [3]	Accord. to Soviet data [4]			Accord. to US data [5]
Determined for cooled surface temperature	K	≤ 333	≤ 333	≤ 353	353-673	≥ 673	—
pH		7.0-9.5	7.2-9.5	7.2-8.5	7.2-8.5	7.2-8.5	×
Total hardness	g/m <sup>3</sup> CaCO <sub>3</sub>	—	< 1429	—	—	—	< 130
Calcium	g/m <sup>3</sup> Ca	—	—	—	—	—	< 50
Magnesium	g/m <sup>3</sup> Mg	—	—	—	—	—	×
Total alkalinity	g/m <sup>3</sup> CaCO <sub>3</sub>	< 214	< 71-250	< 175-200	< 150-175	< 100-125	< 20
Free CO <sub>2</sub> —agressive	g/m <sup>3</sup> CO <sub>2</sub>	—	< 3	—	—	—	—
Thermostability index	in 333 K	1.0	—	—	—	—	—
Chlorides	g/m <sup>3</sup> Cl	< 400	< 600	< 350	< 250	< 150	< 500
Sulphates	g/m <sup>3</sup> SO <sub>4</sub>	< 400	< 500	< 500	< 350	< 250	< 200
Silica	g/m <sup>3</sup> SiO <sub>2</sub>	< 200	< 200	—	—	—	—
Total iron	g/m <sup>3</sup> Fe	< 2.0	< 1.0	—	—	—	< 0.5
Manganese	g/m <sup>3</sup> Mn	< 0.5	< 0.15	—	—	—	< 0.5
Aluminum	g/m <sup>3</sup> Al	—	—	—	—	—	< 0.1
Dissolved solids	g/m <sup>3</sup>	< 3000	—	—	—	—	< 500
Total suspend. solids	g/m <sup>3</sup>	< 40	< 5	< 20-30	< 20-30	< 20-30	< 100
Permanganate demand	g/m <sup>3</sup> O <sub>2</sub>	—	—	< 10-15	< 10-15	< 10-15	—
BOD <sub>5</sub>	g/m <sup>3</sup> O <sub>2</sub>	—	—	< 15-20	< 15-20	< 15-20	—
COD	g/m <sup>3</sup> O <sub>2</sub>	—	—	—	—	—	< 75
Fats	g/m <sup>3</sup>	—	—	< 10-20	< 10-20	< 10-20	—
Heavy metals ions	g/m <sup>3</sup>	—	—	×	×	×	—
Total nutrients	g/m <sup>3</sup> P <sub>2</sub> O <sub>5</sub> + +N	—	—	< 0.5	< 1.5	< 2.0	—
Surfactants	g/m <sup>3</sup>	—	—	×	×	×	—

x - parameters not included in criteria

xx - quality of water in the cooling cycle, the concentration index n = 3

Furthermore, the presence of the surfactants, fats and microorganisms in treated wastewaters may cause difficulties in the maintenance of the cooling system.

These pollutants occur also in natural waters, their concentrations are however much lower.

### 3. QUANTITY AND PHYSICO-CHEMICAL CHARACTERISTICS OF THE BIOLOGICAL EFFLUENT FROM THE COMBINED WASTEWATER TREATMENT PLANT

Considering the possible reuse of the effluent from the combined treatment plant, the observations performed included changes in quantity and quality of treated wastewater. The latter covered the whole year.

Twenty four hour effluent flow rate from the treatment plant, ranged from 17.3 to 25.9 thousand m<sup>3</sup>/d (averaging 21.9 thousand m<sup>3</sup>/d). Considerable hourly variations of the effluent flow rate were also observed. The minimum and maximum irregularity coefficients being equal to 0.52 and 1.35, respectively, for minimum and maximum flows.

Characteristics of the biologically treated wastewater changed according to the efficiency of activated sludge and its BOD loading. The minimum, mean and maximum values of the effluent parameters are presented in Table 2.

Table 2

Physicochemical characteristics of biological effluent for the period  
April 1, 1974-May 31, 1975

Parameters	Units	Biological effluent		
		minimum 10%	average 50%	maximum 90%
pH		6.50	7.10	7.65
Total hardness	g/m <sup>3</sup> CaCO <sub>3</sub>	220	245	290
Calcium hardness*	g/m <sup>3</sup> CaCO <sub>3</sub>	140	155	200
Magnesium hardness*	g/m <sup>3</sup> CaCO <sub>3</sub>	30	70	85
Total alkalinity	g/m <sup>3</sup> CaCO <sub>3</sub>	75	130	220
CO <sub>2</sub> free	g/m <sup>3</sup> CO <sub>2</sub>	5	13	21
Thermostability index*	333 K	1.00	1.02	1.06
Chlorides	g/m <sup>3</sup> Cl	70	94	119
Sulphates	g/m <sup>3</sup> SO <sub>4</sub>	40	88	320
Silica*	g/m <sup>3</sup> SiO <sub>2</sub>	4	46	70
Total iron*	g/m <sup>3</sup> Fe	0.01	0.15	0.40
Manganese*	g/m <sup>3</sup> Mn	0.00	0.05	0.20
Dissolved solids	g/m <sup>3</sup>	450	580	730
Total suspended solids	g/m <sup>3</sup>	6	71	150
Permanganate demand	g/m <sup>3</sup> O <sub>2</sub>	7	16	27
BOD <sub>5</sub>	g/m <sup>3</sup> O <sub>2</sub>	16	32	60
COD	g/m <sup>3</sup> O <sub>2</sub>	30	46	65
N-NH <sub>4</sub>	g/m <sup>3</sup> N	0.4	6	16
N-NO <sub>3</sub>	g/m <sup>3</sup> N	7	9	19
P-total	g/m <sup>3</sup> P	3.7	5.9	8.4
Phosphates	g/m <sup>3</sup> P	2.3	4.0	8.1
Fats*	g/m <sup>3</sup>	3	6	12
Nonionic detergents*	g/m <sup>3</sup>	4	5	6.5

\* - extremal and average values

During the trouble-free periods of operation of activated sludge at the loadings below  $0.3 \text{ kg O}_2/\text{kg MLVSS}$ , the effluent  $\text{BOD}_5$  and COD, ranged within  $8.5\text{--}20 \text{ g/m}^3\text{O}_2$ , and  $30.0\text{--}40.0 \text{ g/m}^3\text{O}_2$ , respectively.

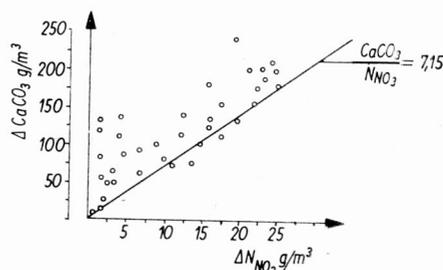
Under these conditions due to the efficient nitrification the effluent ammonia nitrogen has not exceeded  $1 \text{ g/m}^3\text{N}_{\text{NH}_3}$ . At the same time the pH values, and carbonate hardness decreased. Although the phenomenon, called biodecarbonization, seems to be advantageous, it nevertheless may increase the corrosive properties of the recovered water.

Fig. 1. Intensity of nitrification versus the decrease of carbonate hardness

$\Delta\text{CaCO}_3$  — carbonate hardness decrease;  $\Delta\text{NNO}_3$  — increase of nitrate nitrogen concentration

Rys. 1. Zależność między intensywnością procesu nityfikacji ścieków a obniżeniem ich twardości węglanowej

$\Delta\text{CaCO}_3$  — ubytek twardości węglanowej;  $\Delta\text{NNO}_3$  — przyrost stężenia azotu azotanowego



The relation between the degree of biodecarbonization and the intensity of the nitrification process, is shown in Figure 1. From the data presented it follows that, the total alkalinity of biologically treated wastewater decreases with the increase of nitrate nitrogen concentration.

In most cases the weight ratio of carbonate hardness loss to the increase of nitrate nitrogen concentration ( $\text{CaCO}_3/\text{N}_{\text{NO}_3}$ ), obtained from the measurements, was higher than the theoretical value being equal to 7.15.

As a result of biodecarbonization the values of total alkalinity of the wastewater were lower than  $100 \text{ g/m}^3 \text{CaCO}_3$ , being as low as  $80 \text{ g/m}^3\text{CaCO}_3$ . However, these results were obtained, when part of the primary effluent was by-passed directly to the river. On the other hand during the winter period as well as during the biological plant operation under full hydraulic loading, due to inhibition of the nitrification the effluent ammonia nitrogen varied from  $3$  to  $16 \text{ g/m}^3\text{N}$ , and the carbonate hardness ranged within  $120\text{--}180 \text{ g/m}^3 \text{CaCO}_3$ . The effluent  $\text{BOD}_3$  and COD amounted to  $60 \text{ g/m}^3\text{O}_2$  and  $65 \text{ g/m}^3\text{O}_2$ , respectively.

The effluent salinity varied within  $346\text{--}791 \text{ g/m}^3$  of dissolved solids; the mean value being equal to  $559 \text{ g/m}^3$ .

In order to observe changes in the wastewater characteristics during the cooling process a laboratory model of the closed cooling system was constructed, as presented in Fig. 2.

A continuous partial evaporation of the circulating and introducing the make-up water, results in a gradual increase of the dissolved solids concentration in the water.

The so-called solids concentration index  $n$  is defined as a ratio of the initial concentration of a given compound to its concentration after a definite retention time in a cooling system. In our experiments this index was determined by the ratio of chlorides because

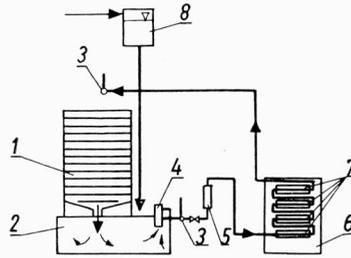


Fig. 2. Closed cooling cycle model

1 – fan cooling tower, 2 – water reservoir, 3 – thermometers, 4 – pump, 5 – rotameter, 6 – heater, 7 – heater tubing, 8 – make-up water tank  $n_x = \frac{c_{xk}}{c_{xp}}$ ;  $n_x$  – concentration index of  $x$  parameter,  $x$  – parameter (chlorides, sulphates, total alkalinity)  $c_{xp}$  and  $c_{xk}$  – initial and final concentrations of parameters

Rys. 2. Schemat modelu zamkniętego obiegu chłodzącego

1 – chłodnia wentylatorowa, 2 – zbiornik wody, 3 – termometry, 4 – pompa, 5 – rotometr, 6 – nagrzewnica, 7 – przewody nagrzewnicze, 8 – zbiornik wody dodatkowej  $n_x = \frac{c_{xk}}{c_{xp}}$ ;  $n_x$  – stopień zagęszczenia wg wskaźnika  $x$ ,  $x$  – wskaźnik (chlorki, siarczany, zasadowość ogólna),  $c_{xp}$  – wartość początkowa stężenia wskaźnika;  $c_{xk}$  – wartość końcowa stężenia wskaźnika

of their high solubility. The concentrations of chlorides, sulphates, carbonates and other salts in wastewater with thermostability equal to 1 should increase proportionally during the cooling process, and satisfy the following rule:

$$n_{Cl} = n_{SO_4} = n_{ZM},$$

where:

$n_{Cl}$ ,  $n_{SO_4}$  and  $n_{ZM}$  are the indices of water solids concentration determined from concentrations of chlorides, sulphates and total alkalinity, respectively.

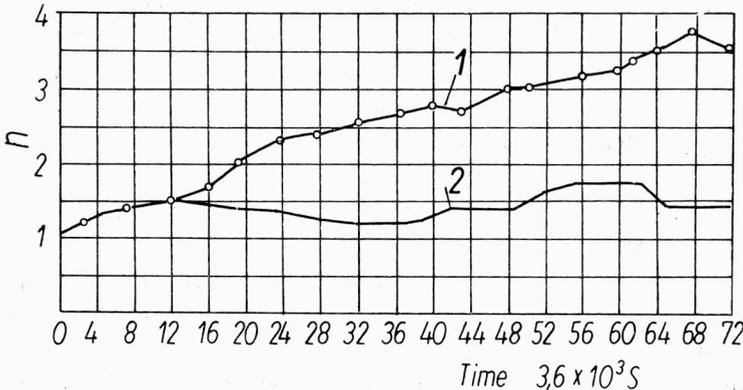


Fig. 3. Concentration curves of biological effluent after filtration

1 – sulphates, chlorides, 2 – total alkalinity

Rys. 3. Przebieg zagęszczenia ścieków oczyszczonych biologicznie, filtrowanych

1 – siarczany, chlorki, 2 – zasadowość ogólna

At 333 K the degree of solids concentration of biologically treated and filtered wastewater, with carbonate hardness equal to  $155 \text{ g/m}^3 \text{ CaCO}_3$ , was equal to 1.15 (Fig. 3). The precipitation of carbonates and other salts observed during further evaporation of wastewater was confirmed by the increase of mass of the laboratory heat exchanger tubing.

#### 4. REQUIREMENTS OF THE COOLING WATER QUALITY IN COMPARISON TO THE TREATED WASTEWATER QUALITY

The physico-chemical analysis of the secondary effluent allowed to state that it does not meet the requirements set for the make-up water, assuming that in the cooling system the solids concentration will be three times higher.

In view of the above, the minimum pH value should be raised to 7.0 and the carbonate hardness lowered to  $71 \text{ g/m}^3 \text{ CaCO}_3$ . The water thermostability index at 333 K should be equal to 1.

The wastewater salinity as well as chlorides and silica concentrations are lower than the admissible ones, while the concentration of sulphates exceeds the admissible value only during about 30 days in a year.

The suspended solids should be lowered to  $13 \text{ g/m}^3$ , because of the possible formation of deposits. The amounts of iron and manganese in the wastewater do not exceed the admissible values specified by the coke plant. According to the Polish standards, organics are not limited; permanganate COD and  $\text{BOD}_5$  exceed however the permissible values specified by the Soviet standards (Table 1).

The nutrients content (as a sum of  $\text{P}_2\text{O}_5$  and N), defined only by Soviet standards, should not exceed  $0.5 \text{ g/m}^3$ . Evidently, in case of secondary effluent this value is much higher.

#### 5. PRELIMINARY TECHNOLOGICAL LABORATORY STUDIES

With the purpose of hardness, free carbon dioxide, phosphorus and suspended solids removal from make-up water the following processes were applied:

- a) coagulation — chemical precipitation,
- b) decarbonization,
- c) filtration.

##### 5.1. COAGULATION

During trouble-free operation of the treatment plant, at low organics and suspended solids (SS) concentration of the secondary effluent contact coagulation alone might be applied. Considering however, periodical deterioration of the wastewater quality, the volumetric coagulation is indispensable.

The latter process was studied using both jar-tests and the continuous system, consisting of an accelerator and sand filter (Fig. 4).

Aluminium sulphate, aluminium chloride, and ferric chloride were employed as reactants. Optimal doses of the coagulants, determined in jar-tests, based on colour removal and oxygen consumption, were the following:

- $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$  – from 40 to 70  $\text{g}/\text{m}^3$ ,
- $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  – from 20 to 30  $\text{g}/\text{m}^3$ ,
- $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  – from 40 to 60  $\text{g}/\text{m}^3$ .

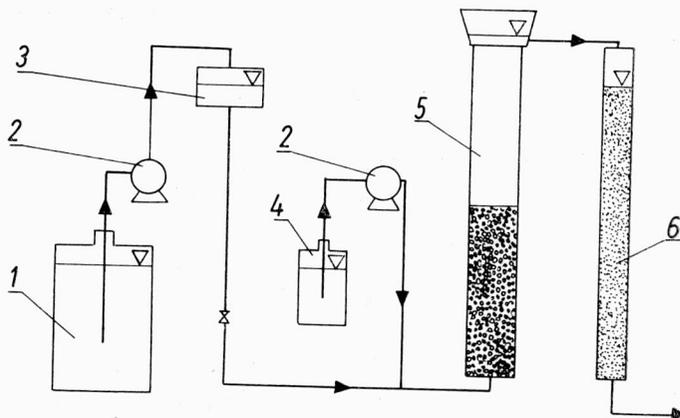


Fig. 4. Model installation for coagulation, decarbonization, and filtration

1 – wastewater tank, 2 – pumps, 3 – equalizing tank, 4 – reagents tank, 5 – accelerator, 6 – filter

Rys. 4. Schemat instalacji modelowej procesu koagulacji, dekarbonizacji i filtracji

1 – zbiornik ścieków, 2 – pompy, 3 – zbiornik wyrównawczy, 4 – zbiornik z reagentem, 5 – akcelerator, 6 – filtr

The effect of the separate reactant on the permanganate COD removal during the coagulation process is presented in Fig. 5.

Considering the fact that optimal aluminium and iron doses caused the substantial decrease if the water pH (alume – to pH 6.20; ferric chloride to pH 6.10 and aluminium chloride to pH 5.6) then to correct it the lime doses of 30–40  $\text{g}/\text{m}^3$  CaO in case of alume and ferric chloride and 60–80  $\text{g}/\text{m}^3$  CaO for aluminium chloride had to be applied in coagulation process.

Colour removal and permanganate COD reduction obtained, due to coagulation ranged within 30–60%. In order to improve the treatment efficiency coagulant aid doses of 0.2–12  $\text{g}/\text{m}^3$  were employed. Their trade names were Zetag 51, Praestol 444 K, Magnafloc 351 and Rokrysol WF-1, WF-2 and WF-3. The flocculants caused a 10–20% increase in permanganate COD removal on an average. The increase of floc size was observed beginning with a dose of 0.4  $\text{g}/\text{m}^3$ . As the optimal flocculants Rokrysol WF-3 and Zetag 51, were chosen.

The following reactants were used in the studies of continuous coagulation and filtration process

- $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  – 60  $\text{g}/\text{m}^3$ ,
- CaO – 40  $\text{g}/\text{m}^3$ ,
- Rokrysol WF-3 – 1  $\text{g}/\text{m}^3$ .

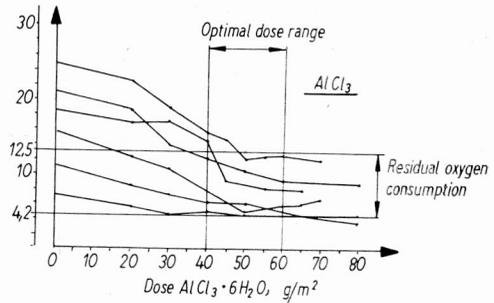
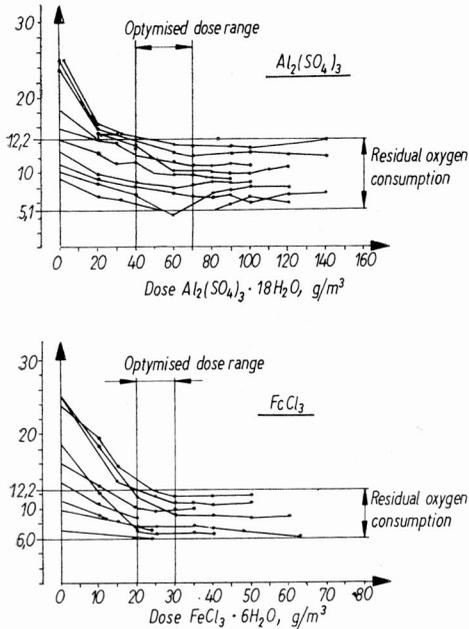


Fig. 5. Results of coagulation jar tests  
 Rys. 5. Wyniki badań procesu koagulacji prowadzonego metodą testu naczyniowego

Grain size of the filtration medium was equal to 0.2–0.3 mm, and an applied overflow rate was 0.00833 m/min.

Permanganate COD, dichromate COD and suspended solids of wastewaters after treatment amounted to 5.2–9.1 g O<sub>2</sub>/m<sup>3</sup>; 38.0–44.0 g O<sub>2</sub>/m<sup>3</sup> and 8–11 g/m<sup>3</sup>, whereas their removal efficiencies ranged within 70–75%, 10–22%, and 78–85%, respectively.

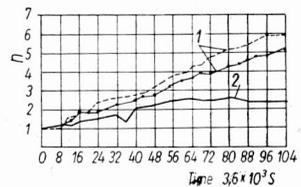
After partial evaporation of wastewater, coagulated with a dose of 70 g/m<sup>3</sup> Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 18 H<sub>2</sub>O coupled with 40 g/m<sup>3</sup> of CaO, the concentration index in the model cooling system (Fig. 2) was equal to 1.5 and water total alkalinity 300 g/m<sup>3</sup> CaCO<sub>3</sub>. The latter parameter decreased in course of further evaporation. The solids concentration curve is presented in Fig. 6.

Fig. 6. The course of concentration of biological effluent after coagulation

1 – chlorides, 2 – total alkalinity

Rys. 6. Przebieg zagęszczania ścieków oczyszczonych biologicznie, koagulowanych

1 – chlorki, 2 – zasadowość ogólna



### 5.2. DECARBONIZATION

Lime decarbonization of the make-up water reduces the carbonate hardness and allows to increase the concentration index in the cooling system.

The feasibility of the wastewater decarbonization was studied initially, by adding theoretical dose of lime to the sample, and leaving it for 12 hours at constant temperature.

Chemical characteristics of the decarbonized wastewater was the following: pH 6.2–7.7, total alkalinity 90–170 g/m<sup>3</sup> CaCO<sub>3</sub>, permanganate COD 7–26 g/m<sup>3</sup> O<sub>2</sub> and dichromate COD 30–70 g/m<sup>3</sup> O<sub>2</sub>. Two temperature ranges 277–281 K and 285–289 K, at lime dose of 25–130 g/m<sup>3</sup> CaO, were covered in the preliminary tests.

Fig. 7 presents the changes in carbonate hardness depending on the temperature and initial wastewater hardness. As the relationship: 2 Ph. alk. = M alk. was fulfilled in the tests with the accuracy to 10 g CaCO<sub>3</sub>, the conclusion might be drawn that calcium hydroxide doses had been optimum.

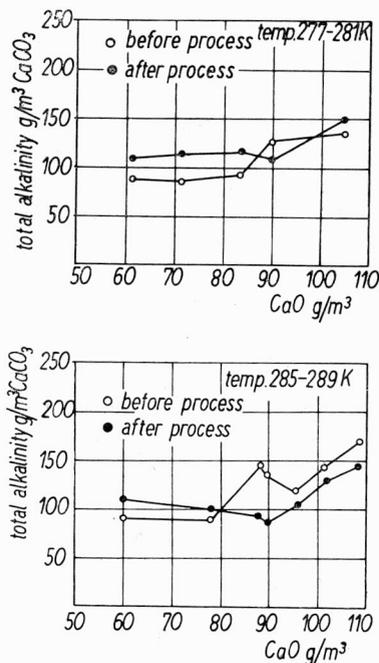


Fig. 7. Applicability of wastewaters after decarbonization

Rys. 7. Wyniki badania podatności ścieków na dekarbonizację

The tests displayed some increase of carbonate hardness in most cases, particularly at low temperatures, the lowest value being 80 g/m<sup>3</sup> CaCO<sub>3</sub> (temperature 289 K). These preliminary results are in agreement with the earlier statement on strong stabilization of calcium carbonate crystallization in supersaturated solutions containing significant quantities of organics resulting from biochemical decomposition [3].

Further decarbonization tests were conducted in a continuous flow system (presented in Fig. 3) including sludge blanket reactor. The wastewaters treated with the dose of 709/m<sup>3</sup> CaO had the following characteristics: pH 7.3; permanganate COD 13.8 g/m<sup>3</sup> O<sub>2</sub>; dichromate COD — 32.0 g/m<sup>3</sup> O<sub>2</sub>; ammonium nitrogen — 0.4 g/m<sup>3</sup> N—NH<sub>3</sub>; total alkalinity — 95 g/m<sup>3</sup> CaCO<sub>3</sub>; total hardness — 250 g/m<sup>3</sup> CaCO<sub>3</sub>; magnesium hardness 46 g/m<sup>3</sup> CaCO<sub>3</sub>, and temperature — 289 K.

The suspended sludge blanket in the column was yellowish and had a spongy character. The water carbonate hardness increased to  $100 \text{ g/m}^3 \text{ CaCO}_3$  in the experiment. Suspecting that a contact time between wastewater and the sludge blanket (450 seconds) is too short the additional softening tests were carried out on the same sample by mixing it for two hours with a varying dose of calcium hydroxide and  $10 \text{ cm}^3/\text{dm}^3$  of the contact mass extracted from the column. In the samples for which the relationship:  $2 \text{ Ph alk.} = \text{M alk.}$  was fulfilled, the carbonate hardness was equal to  $120 \text{ g/m}^3 \text{ CaCO}_3$ .

### 5.3. THE COAGULATION AND DECARBONIZATION PROCESS

In all further experiments the coagulation process combined with decarbonization was performed by jar-test method using ferric chloride, alum and lime. The tests were carried out at the fixed coagulant dose optimum for permanganate COD removal and at varying lime dose, in temperatura range 277–288 K.

The following coagulant doses were used:  $40\text{--}70 \text{ g/m}^3 \text{ Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and  $20\text{--}30 \text{ g/m}^3 \text{ FeCl}_3 \cdot 6\text{H}_2\text{O}$ .

The optimum lime dose was  $50\text{--}105 \text{ g/m}^3 \text{ CaO}$  and pH range 8.6–9.0 depending on the total alkalinity of the sample.

The residual total alkalinity was equal to  $60\text{--}85 \text{ g/m}^3 \text{ CaCO}_3$  (Fig. 8) and total hardness  $120\text{--}210 \text{ g/m}^3 \text{ CaCO}_3$ . In contrast to the decarbonization process alone, in each sample reduction of total alkalinity was observed. The decarbonization process, preceded by coagulation was found to be more efficient, nevertheless, the decrease of carbonate hardness below  $50 \text{ g/m}^3 \text{ CaCO}_3$  was not attained.

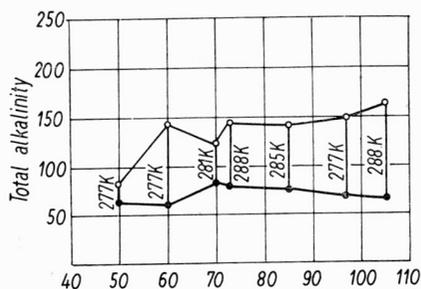


Fig. 8. The course of coagulation and decarbonization

Rys. 8. Przebieg procesu koagulacji i dekarbonizacji

The wastewater concentration index based on carbonates and obtained from concentration by means of evaporation at 335 K, was equal to 2.0. When one half of the sample volume was evaporated the carbonate hardness increase from  $60$  to  $120 \text{ g/m}^3 \text{ CaCO}_3$  was accompanied by a simultaneous increase of chlorides from  $100$  to  $200 \text{ g/m}^3 \text{ Cl}$ . In a sample from which two-thirds of the volume were evaporated the carbonate hardness was equal to  $132.5 \text{ g/m}^3 \text{ CaCO}_3$ .

It should be expected that the use of complexions preventing precipitation of carbonates will result in an increased concentration index of the wastewater dissolved solids.

## 5.4. REMOVAL OF PHOSPHORUS COMPOUNDS

The necessity of phosphorus removal from cooling water excludes also the use of phosphates as the inhibitors of calcium carbonate precipitation. The phosphates might be rather easily and inexpensively eliminated during chemical precipitation, and other scaling inhibitors can be used. For this reason phosphorus concentration was also determined during the coagulation and decarbonization tests.

The tests included lime coagulation followed by the decarbonization with carbon dioxide. Treated wastewater samples contained 4.25–7.9 g/m<sup>3</sup>P — the orthophosphate level being equal to 0.82–6.93 g/m<sup>3</sup>P. Depending on the degree of phosphate hydrolysis and on the type of reagent used, the total phosphorus reduction was in the range of 64–99%, while the orthophosphates removal was equal to 93–99%. The remaining quantity of total phosphorus amounted to 0.09–1.15 g/m<sup>3</sup>P — the orthophosphate residual being 0.03–0.07 g/m<sup>3</sup>P (Table 3).

Table 3

Elimination of the phosphorus compounds

$\text{Al}_2(\text{SO}_4)_3 \times 18\text{H}_2\text{O}$ Dose	CaO dose	Rokrysol WF-3 Dose	pH	Per- mang. de- mand	Total P	% remo- val of P — total	Dissolved phos- phates	% PO <sub>4</sub> = remo- val	Com- ments
g/m <sup>3</sup>	g/m <sup>3</sup>	g/m <sup>3</sup>	pH	g/m <sup>3</sup>	g/m <sup>3</sup> P	%	g/m <sup>3</sup> P	%	
—	—	—	7.30	17.5	7.90	—	6.93	—	
40	—	—	6.10	8.7	0.42	94.7	0.10	98.5	
40	20	1.0	7.15	6.9	0.09	98.9	0.05	99.2	
—	—	—	7.40	14.0	4.75	—	3.61	—	
70	40	—	7.25	7.5	0.42	89.0	0.06	98.3	
70	40	1.0	7.25	5.1	0.10	97.0	0.07	98.4	
—	—	—	7.40	14.0	4.75	—	3.88	—	
—	120	—	10.80	9.3	0.56	88.1	0.05	98.4	
—	120	1.0	10.80	7.0	0.32	93.3	0.05	98.4	
—	120	1.0	17.90	7.0	0.32	93.3	0.05	98.4	
—	—	—	6.85	20.0	4.25	—	0.82	—	Sample after re-carbo- nation
—	140	—	10.95	9.8	1.52	64.2	0.05	92.9	
—	140	1.0	10.95	8.3	1.15	72.0	0.03	95.7	

As follows from the initial runs, the coagulation with aluminium sulphate combined with decarbonization result in a significant elimination of phosphorus compounds. The use of high lime doses, requires however, additional recarbonation measures, and in full scale, may increase the carbonate hardness of wastewaters — this effect being undesirable as far as the cooling system is concerned.

## CONCLUSIONS

1. The proposed technological layout of the water reuse system includes coagulation, decarbonization and filtration processes. The system yields water of carbonate hardness equal to 60–85 g/m<sup>3</sup>, CaCO<sub>3</sub> effluent suspended solid content below 11 g/m<sup>3</sup>, and pH range 8–9. At the same time organics are reduced to 4–7 g/m<sup>3</sup>O<sub>2</sub> of permanganate COD; 8–20 g/m<sup>3</sup>O<sub>2</sub> BOD<sub>5</sub>; Phosphorus being equal to 0.1 g/m<sup>3</sup>P.

2. The process yields water of a quality corresponding to cooling water standards in all parameters, except for the required concentration index which should be  $n = 3$ . The obtained concentration index  $n = 2$  calls for an increased consumption of make-up water.

3. The combined process of aluminium sulphate coagulation and decarbonization results in an increase of wastewater pH, related to the solubility of aluminium. For this reason the two processes should be conducted in separate reactors; the alternative solution is the use of ferric chloride as the coagulant.

4. The main factor influencing the concentration ability of wastewaters in cooling system is the presence of carbonates. In case of the wastewaters examined, where high salt content inhibits the use of ion exchange, carbonates removal through decarbonization is the most suitable method.

5. During decarbonization with calcium hydroxide some problems were encountered due to the increase of carbonate hardness after the application of the proper dose of calcium hydroxide (Fig. 7). The attempts to combine the coagulation and the decarbonization processes yielded positive results (Fig. 8); terminal carbonate hardness was of the order 60–85 g/m<sup>3</sup> CaCO<sub>3</sub>.

6. The biodecarbonization process observed during the nitrification in activated sludge tanks results in the decrease of total alkalinity and pH, and may occur also in the cooling towers. This phenomenon is unfavourable because of corrosion of equipment in the cooling system. For this reason, to prevent the occurrence of nitrification in the cooling tower in case of low carbonate hardness water, the ammonium nitrogen should be removed.

BADANIA LABORATORYJNE NAD ZASTOSOWANIEM ŚCIEKÓW BIOLOGICZNYCH  
W ZAMKNIĘTYCH UKŁADACH CHŁODZENIA

Przedstawiono wyniki wstępnych badań laboratoryjnych nad oczyszczaniem ścieków biologicznych do celów chłodniczych w zamkniętych układach chłodniczych koksowni.

Badania obejmowały: koagulację, dekarbonizację i filtrację ścieków. W wyniku otrzymano wodę przemysłową o pH 8.0–9.0. Zawartość związków organicznych wyrażona przez utlenialność i BZT wynosiła odpowiednio 4–7 g/m<sup>3</sup> i 8–20 g/m<sup>3</sup> O<sub>2</sub>; twardość węglanowa 60–85 g/m<sup>3</sup> CaCO<sub>3</sub>.

Badania stężenia odzyskanej wody przeprowadzono w modelowym układzie chłodzącym. Ze względu na strącanie się węglanów ze ścieków po koagulacji wskaźnik stężenia wynosił 1.5, a po koagulacji i dekarbonizacji 2.0.

## LABORFORSCHUNGEN ÜBER DIE ANWENDUNG BIOLOGISCHER ABWASSER IN DEN GESCHLOSSENEN KÜHLSYSTEMEN

Es wurden Ergebnisse der Laborvorprüfungen bezüglich der Reinigung biologischer Abwasser für Abkühlung in geschlossenen Kühlsystemen der Kokerei dargestellt. Die Untersuchungen umfassten: Koagulation, Entkarbonisierung und Abwasserfiltration. Als Ergebnis wurde das Industrierwasser mit pH in Grenzen 8,0–9,0 erreicht.

Der durch Oxydierung und BZT ausgedrückte Gehalt organischer Verbindungen betrug entskreichend: 4–7 g/m<sup>3</sup> und 8–20 g/m<sup>3</sup> O<sub>2</sub>; Karbonathärte 60–85 g/m<sup>3</sup> CaCO<sub>3</sub>. Die Forschungen der Wasserkonzentration wurden im Modellkühlsystem durchgeführt.

In Hinsicht auf die Tatsache der Karbonatausfällung von Abwasser betrug der Konzentrationsindikator nach der Koagulation 1,5 und nach der Koagulation und Entkarbonisierung 2,0.

## ЛАБОРАТОРНЫЕ ИССЛЕДОВАНИЯ ПО ПРИМЕНЕНИЮ БИОЛОГИЧЕСКИХ СТОЧНЫХ ВОД В ЗАКРЫТЫХ СИСТЕМАХ ОХЛАЖДЕНИЯ

Представлены результаты вступительных лабораторных исследований по очистке биологических сточных вод для холодильных целей в закрытых холодильных системах коксового завода.

Исследования касались коагуляции, декарбонизации и фильтрации сточных вод. В результате получили промышленную воду с pH в пределах 8,0–9,0. Содержание органических соединений, выраженное окисляемостью и ВТ, составляло соответственно 4–7 г/м<sup>3</sup> и 8–20 г/м<sup>3</sup> O<sub>2</sub>; твердость карбоната 60–85 г/м<sup>3</sup> CaCO<sub>3</sub>.

Исследования концентрации полученной воды проводились в модельной системе охлаждения. Учитывая осаждение карбоната из сточных вод после коагуляции, показатель концентрации составлял 1,5, а после коагуляции и декарбонизации — 2,0.