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# INDUSTRIAL WASTEWATER TREATMENT WITH THE HELP OF STRONG OXIDIZING AGENTS

The paper deals with the method of chemical treatment of wastewaters coming from copper mill and produced during wet dedusting of gases in a closed cycle. Ozone and perhydrole were used as oxidizers. Higher treatment efficiency was obtained with perhydrole, whereas ozone appeared to be more efficient with respect to its consumption for a unit of pollution indexes. No close correlation between BOD and TOC has been stated both in reaction of wastewaters with ozone and perhydrole.

## 1. INTRODUCTION

The purpose of the investigations was to determine the efficiency of the treatment of industrial wastewaters of a specific composition. They are produced in a closed cycle of wet dedusting of pyrometallurgical gases characterized by high concentrations of organic and inorganic pollutants (phenols, amines, amides, ketones, chlorides, sulphites, sulphides, salts of alkaline earth metals, alkali metals and heavy metals) [1].

As it has been shown in the previous investigations, these scrubbing wastewaters are exceptionally resistant to conventional treatment methods [2]. Biological treatment yielded only 30% to 40% removal of organics determined as dichromate COD, provided that they had been subject to primary alkalization and dilution with municipal sewage.

In the studies reported the method of chemical oxidation was applied, using ozone and 30% hydrogen peroxide solution. Chlorination method, being previously examined, has been rejected because of the increasing amounts of chlorides and chloroorganic compounds present in wastewaters. Ozone was employed in treatment of phenol wastewaters [3], petrochemical [4] and photographic processing wastes [5], whereas 30% hydrogen peroxide was used as an additional source of oxygen in activated sludge process [6–9] or as an oxidizing agent in chemical oxidation of phenol wastewaters [10, 11].

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## 2. METHODS

The wastewaters investigated were of dark brown colour and odour of phenol. They were characterized by the following parameters: pH 4.4, permanganate value — 13800 g $O_2/m^3$, dichromate COD — 38200 g $O_2/m^3$, total organic carbon — 10500 g $C/m^3$. The raw (pH 4.4) and primarily alkalized (pH 9.8) not diluted wastewaters were subject to oxidation. Ozonation performed on a laboratory scale was conducted in a flow-through reactor [12]. Oxidation with 30% hydrogen peroxide was performed by the method of jar tests, the following doses of the oxidizing agent being used: 20, 40, 60, 100, 200 and 400 g/dm³.

The investigations were carried out in the time interval ranging from 0 to 300 h. The initial pH of wastewaters was 5.4, being elevated to 9.1 and measured by pH-meter. Total organic carbon was determined in Beckman Total Organic Carbon Analyser, colour was measured spectrophotometrically at the wavelength $\lambda = 700$ nm. Ozone [13] and $H_2O_2$ [14] were determined iodometrically. The excess of $H_2O_2$ (non-reacted) was decomposed catalytically, using battery manganese.

## 3. DISCUSSION OF RESULTS

### 3.1. OZONATION

The course of ozonation depends on the initial pH of wastewater. The permanganate value, pH value and total organic carbon as functions of ozone consumption are shown in fig. 1A, B and C, respectively, for the initial pH 4.4 and 9.8. The relationship between the amounts of the consumed and residual ozone is illustrated by the curves 1' and 2'. With the same amount of ozone consumed the reduction of permanganate value was

Table 1

Permanganate value (PV) reduction at the break
through point at a constant pH value
Obniżenie utlenialności w punkcie przebicia ozonowa-
nia przy stałym pH

| pH | Ozone consumption at break through point | PV removal |
|---|---|---|
| | g/dm³ | % |
| 4.2 | 2.54 | 58 |
| 9.8 | 2.00 | 66 |

higher at pH 9.8 (fig. 1A), no distinct effect of pH being stated with respect to TOC (fig. 1C).

At the break through point (the final stage of the quantitative ozone-wastewater reaction) the permanganate value removal amounted to 65% at pH 9.8 and to 42% at pH 4.4, whereas in both cases the TOC removal did not exceed 50% of the initial concentrations of organics in wastewaters. While introducing ozone into wastewaters, their initial pH decreased continuously to pH 2.
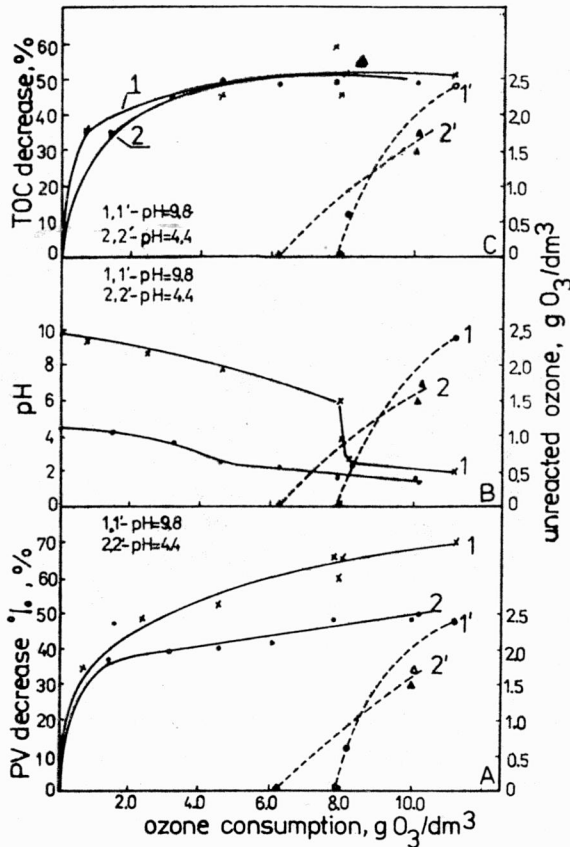


Fig. 1. TOC, pH and permanganate value versus ozone consumption for initial pH 4.4 and 9.8
Rys. 1. Zmiany utlenialności, odczynu i CWO podczas ozonowania ścieków przy początkowym pH 4,4 i9,8

Some additional investigations during which the pH values were kept constant (9.8 and 4.2) confirmed the influence of pH on the efficiency of ozonation. A higher permanganate value removal was achieved at lower ozone consumption (tab. 1).

Table 2

Unit ozone consumption required for the reduction of pollution indices at the ozonation break through point

Jednostkowe zużycie ozonu potrzebne do obniżenia wskaźników zanieczyszczenia ścieków w punkcie przebicia ozonowania

| Initial pH | $O_3$ consumption at break through point | $O_3$ consumption for removal of 1 g of TOC | $O_3$ consumption for the PV removal by 1 g | Reduction of TOC | Reduction of PV |
|---|---|---|---|---|---|
| | $g/dm^3$ | $g/g$ | $g/g$ | % | % |
| 4.4 | 6.2 | 1.5 | 1.05 | 50 | 42 |
| 9.8 | 7.9 | 1.5 | 0.90 | 50 | 65 |

### 3.2. OXIDATION WITH HYDROGEN PEROXIDE

Different effects have been obtained when wastewaters were oxidized with hydrogen peroxide. The efficiency of wastewater oxidation, depending on the initial dose of hydrogen oxide at pH 5.4 and 9.1, is presented in figs. 2 and 3, respectively, the influence of time on the oxidation course being illustrated in figs. 4 and 5. It has been stated that oxidation time and initial pH influence distinctly the reduction of TOC value and additionally affect the decrease of the pH solution preliminarily alkalized (figs. 2–5). Longer reaction time and elevated pH value led to higher organic carbon removal, no effect of pH value being stated on the permanganate value removal. Very high indices of pollutant removal could be achieved solely at high excess of hydrogen peroxide. Introduction of 200 g $H_2O_2/dm^3$ of hydrogen peroxide resulted in 90% removal of permanganate value, 70% removal of TOC and almost 100% decolourization of the oxidized wastewaters.

### 4. INTERPRETATION OF RESULTS

The results obtained from the ozone and hydrogen peroxide reactions with wet dedusting wastewaters have been described in the former sections. The wastewater discussed contained large number of reduced compounds, hence hydrogen peroxide manifested first of all its oxidizing properties both in acid and alkaline solutions. Some small amounts of oxygen bubbles appearing during reaction gave, however, the evidence to some reactions with the pollutants in which hydrogen peroxide occurred as a reducing agent. During ozonation ozone acted as: oxidizer in reaction with reduced compounds and agent attacking double bonds in organic compounds. Effect of ozone (or the products of its decomposition) depended additionally on the pH of the medium.

Both the reagents applied (ozone and perhydrole) lowered the concentration of pollutants in the wastewater investigated (decrease of permanganate value and TOC as well as discolouration of wastewater). Since both the reagents act according to different mechanisms and the latter depends on other conditions, the results obtained are also diffe-
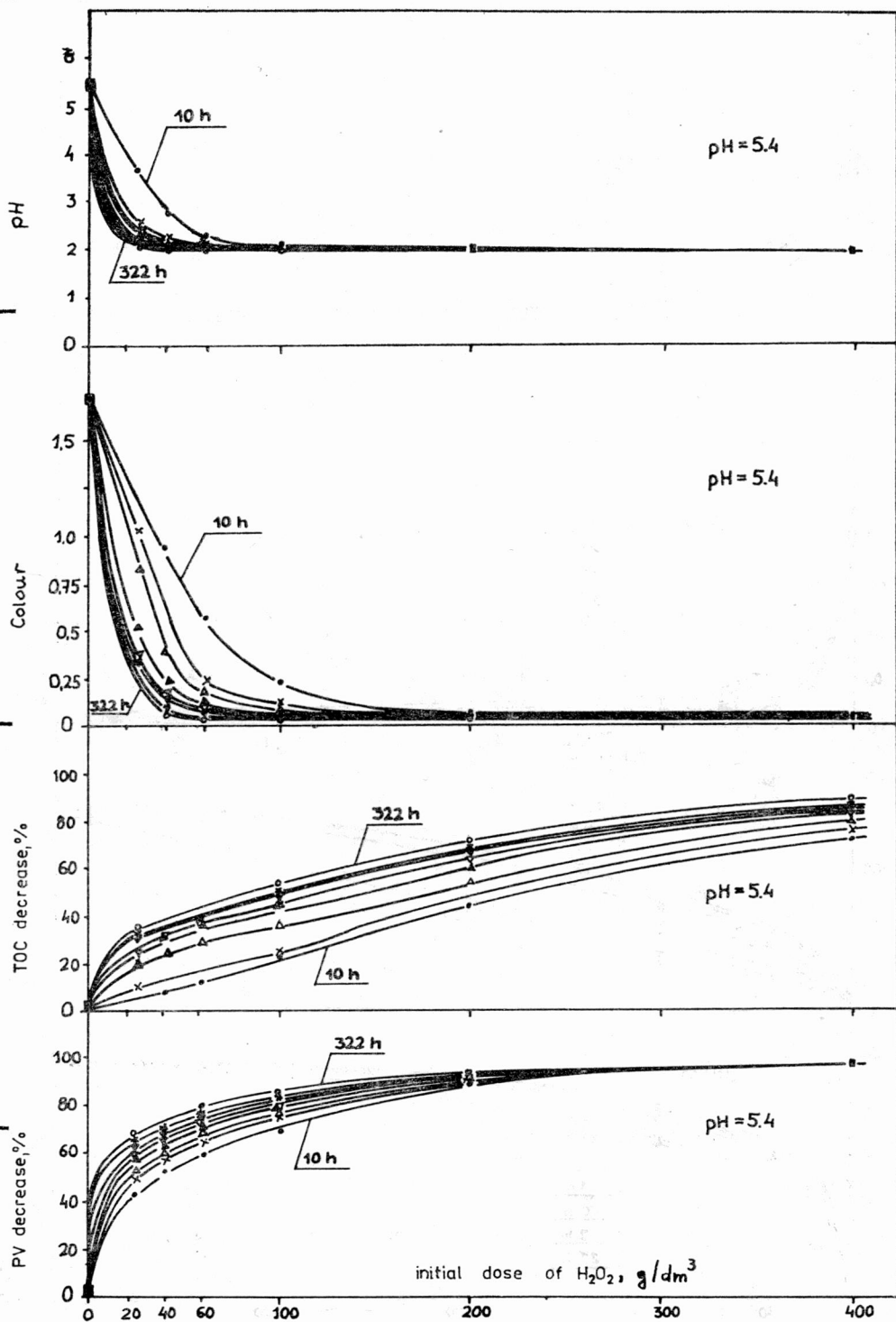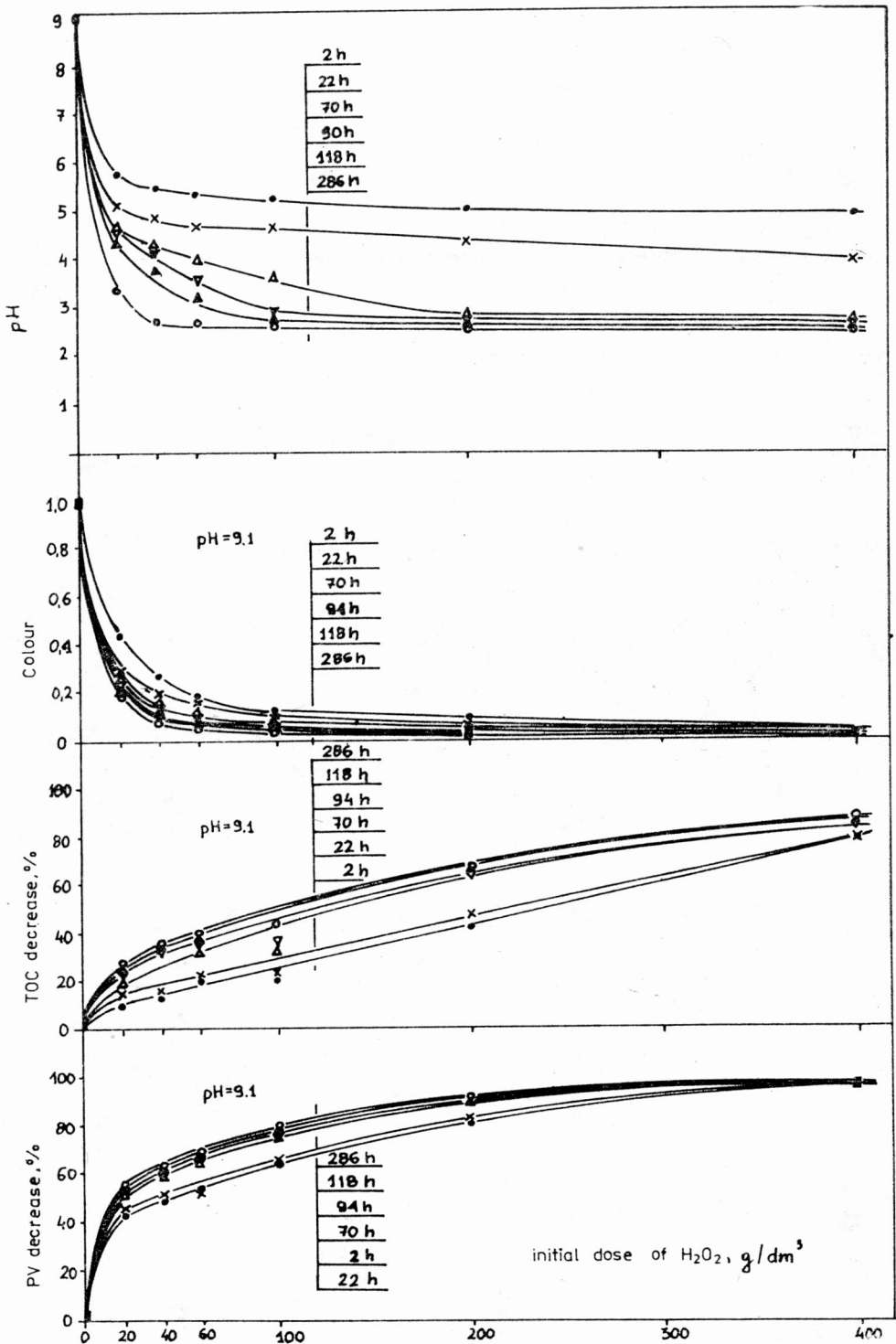
Fig. 2. TOC, permanganate value, pH and colour versus initial $H_2O_2$ dose for initial pH 5.4

Rys. 2. Efektywność utleniania perhydrolem zanieczyszczeń w ściekach przy początkowym pH 5,4

Fig. 3. TOC, permanganate value, pH and colour versus initial $H_2O_2$ dose for initial pH 9.1

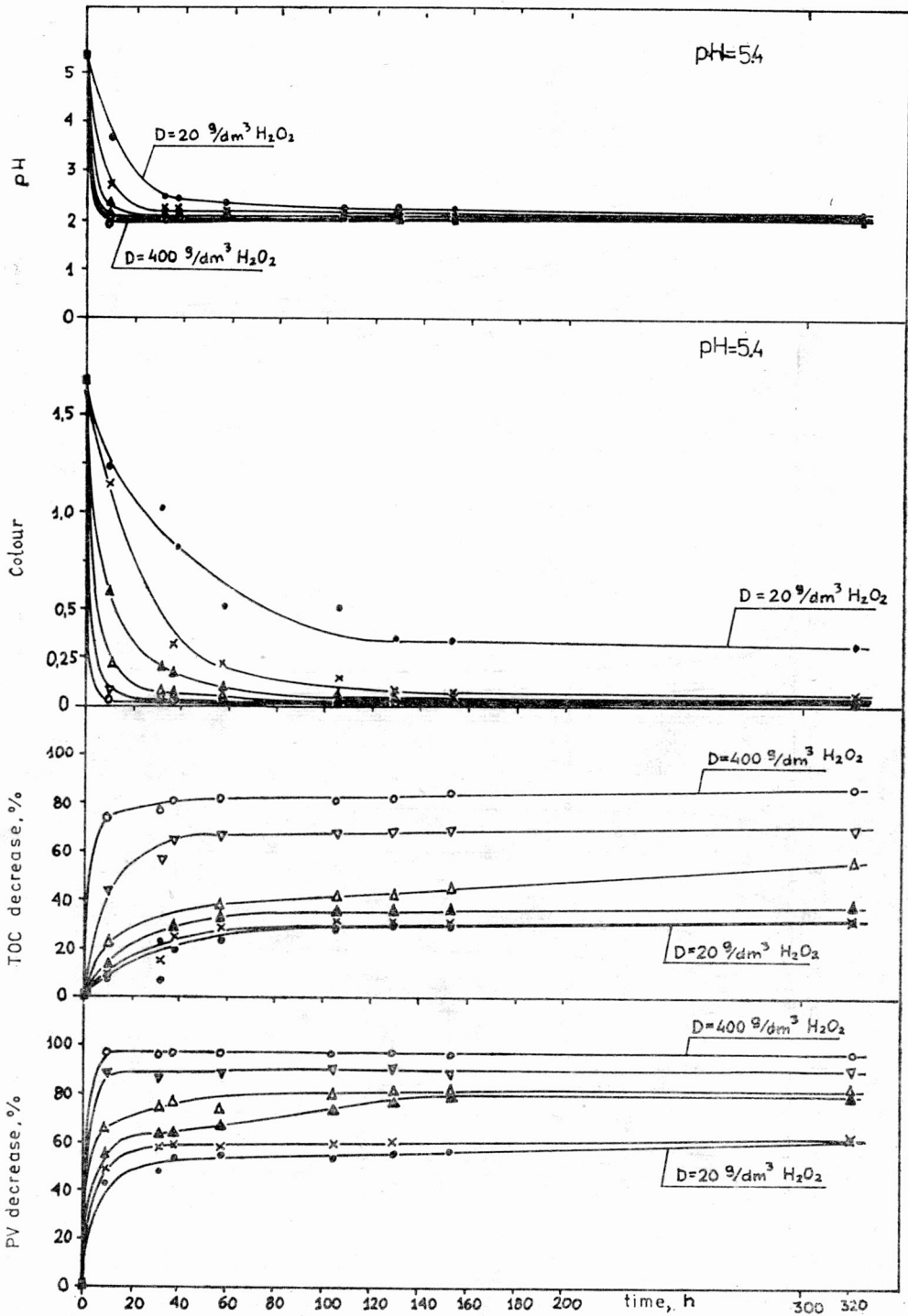Rys. 3. Efektywność utleniania perhydrolem zanieczyszczeń w ściekach przy początkowym pH 9,1

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Fig. 4. TOC, permanganate value, pH and colour versus reaction time for initial pH 5.4

Rys. 4. Efektywność utleniania perhydrolem zanieczyszczeń w ściekach w zależności od czasu przy początkowym pH 5,4
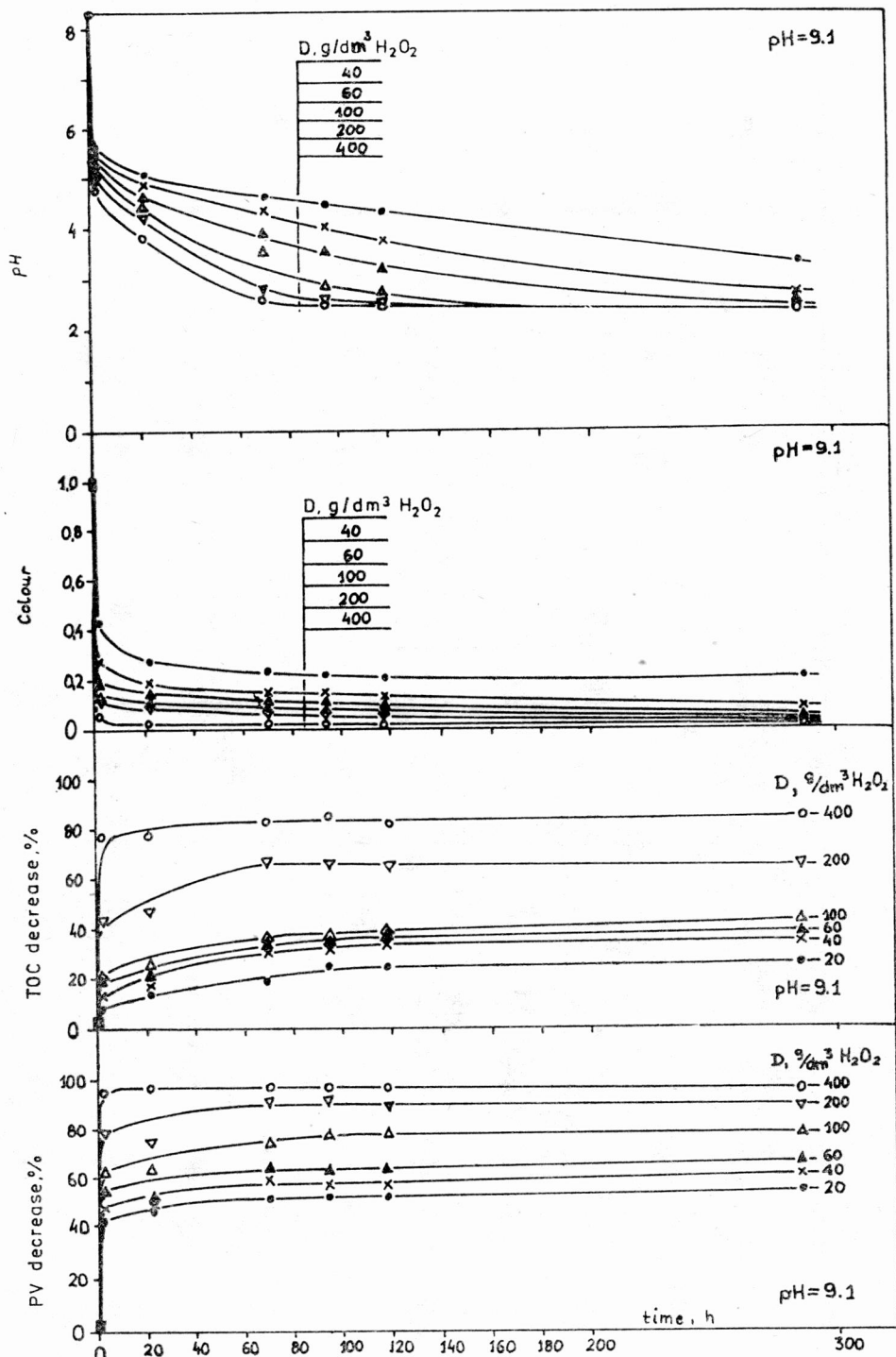
Fig. 5. TOC, permanganate value, pH and colour versus reaction time for initial pH 9.1

Rys. 5. Efektywność utleniania perhydrolem zanieczyszczeń w ściekach w zależności od czasu przy początkowym pH 9,1

rent. For the final stage of qualitative reaction of ozone with wastewater, ozone consumption was equal to 6.2 g $O_3/dm^3$ and 7.9 g $O_3/dm^3$ at pH 4.4 and 9.8, respectively, and 1.5 g of ozone was required to remove 1 g of TOC. At the above dosage TOC removal amounted to 50% (fig. 6, tab. 3). Reactions leading to the removal of a part of organic compounds (reduction of TOC) did not depend on the pH of the solution.
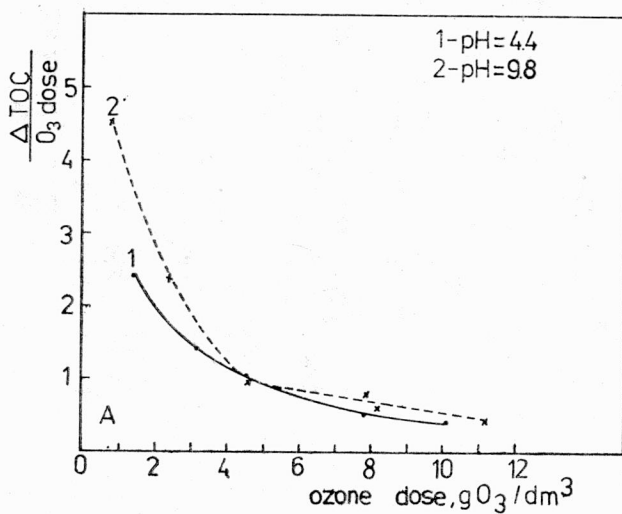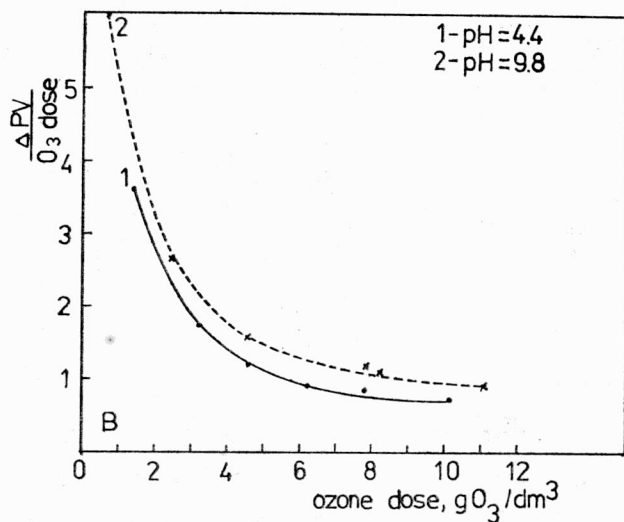
Fig. 6. Unit ozone consumption per unit removals of permanganate value and TOC for initial pH 4.4 and 9.8

Rys. 6. Porównanie jednostkowego zużycia ozonu potrzebnego do obniżenia utlenialności i CWO w zależności od dawki ozonu przy początkowym pH 4,4 i 9,8

Reduction of permanganate value followed a different pattern. The results obtained depended on the pH value; its increase enhanced the reaction (fig. 6, tab. 3). At the ozonation break through point 1 g $O_3$ had to be used to decrease the permanganate value by 1 g.
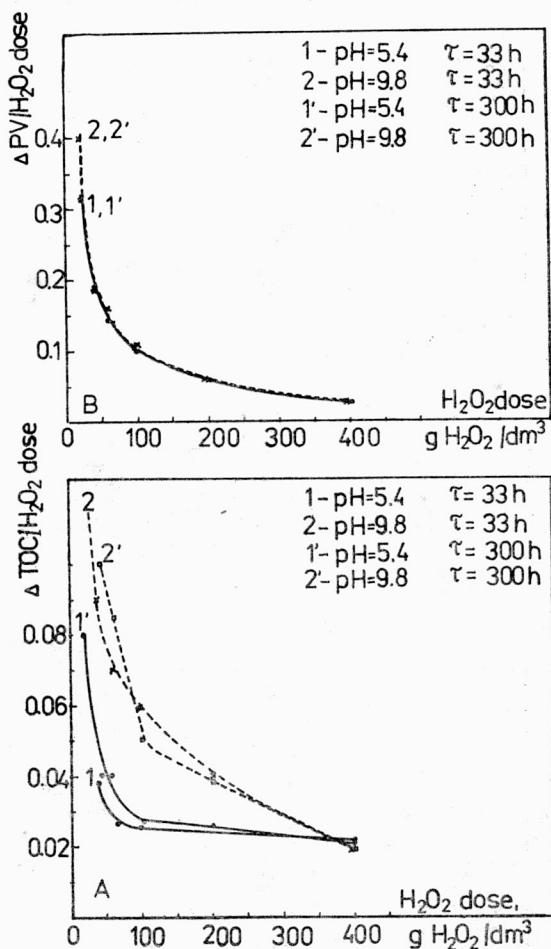


Fig. 7. Unit perhydrole consumption per unit removal of permanganate value and TOC for initial pH 5.4 and 9.1

Rys. 7. Jednostkowe zużycie nadtlenku wodoru potrzebne do obniżenia utlenialności i CWO w zależności od dawki $H_2O_2$ przy początkowym pH 5,4 i 9,1

Different relations have been obtained if perhydrole was used for ozonation. It has been stated that the effect of TOC removal depends on the pH of the medium and to a small degree on the reaction time (fig. 7), whereas reduction of permanganate value depends neither on reaction time nor on pH (fig. 7).

Consumption of hydrogen peroxide ($100 \text{ g/dm}^3$ of wastewater) required for the reduction of pollution indices is given in tab. 3 for two initial pH values and two reaction times. Since only 20–50% of the oxidizer came into reaction with wastewater, its consumption with respect to 1 g of the TOC or PV removal was substantially higher (tab. 3).

Table 3

Unit consumption of perhydrole required for reduction of pollution indices of wastewater examined
Jednostkowe zużycie perhydrolu potrzebne do obniżenia wskaźników zanieczyszczenia ścieków

| Perhydrole dose | Initial pH | Reaction time | Perhydrole consumption for the removal of 1 g of TOC | Perhydrole consumption for the removal of 1 g of PV | Reduction of PV | Reduction of TOC | $H_2O_2$ consumption |
|---|---|---|---|---|---|---|---|
| $g/dm^3$ | — | h | g/g | g/g | % | % | % |
|  | 5.4 |  | 40 | 7 | 74 | 23 | 35 |
|  |  | 33 |  |  |  |  |  |
|  | 9.1 |  | 17 | 7 | 73 | 24 | 20 |
| 100 |  |  |  |  |  |  |  |
|  | 5.4 |  | 40 | 7 | 82 | 56 | 55 |
|  |  | 300 |  |  |  |  |  |
|  | 9.1 |  | 20 | 7 | 81 | 45 | 32 |

In order to decrease the amount of unreacted perhydrole, the reaction course should be controlled, e. g. by successive perhydrole proportioning in time, thus maintaining its indispensible quantities without introducing the excess of this oxidizer.

## 5. SUMMARY AND CONCLUSIONS

Ozonation of wastewater led to the following conclusions:
reduction of PV of wastewaters depends on the pH of the medium, at higher pH the PV removal is also higher,
final TOC value does not depend on initial pH,
constant pH during ozonation allows us to decrease ozone consumption (3 times at pH 4.4 and 4 times at pH 9.8),
at ozone break through point wastewater decolourization reaches almost 100%.
Treatment of wastewater with perhydrole led to the following statements:
reduction of wastewater PV depends on the initial pH of the medium,
reduction of TOC depends on the pH and reaction time,
in the system investigated only 20–50% of perhydrole came into reaction with wastewater (this percentage being lower for higher initial value of the oxidizer),

under the given condition perhydrole acted as oxidizer, its reducing activity was very slight.

No close correlation between PV and TOC, stated in reaction ozone or perhydrole with wastewaters, is probably due to the presence of inorganics of reductor types (sulphides, sulphites, nitrogen compounds) that increase PV and are not manifested when TOC is determined. It has been found that, as far as the consumption of oxidizer for a unit removal of pollution index is concerned, ozonation process is more efficient. A higher removal efficiency has been obtained with perhydrole, though its consumption was also higher than that of ozone. Treatment of industrial wastes (strongly concentrated) with ozone and perhydrole is very expensive. Such processes may be taken into account if waste oxidizers are at ones disposal.

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## OCZYSZCZANIE ŚCIEKÓW PRZEMYSŁOWYCH
### PRZY UŻYCIU SILNYCH UTLENIACZY

Przedstawiono metodę chemicznego utleniania ścieków pochodzących z obiegu zamkniętego mokrego odpylania gazów z hut miedzi. Zastosowano ozon i nadtlenek wodoru. Wyższy stopień oczyszczania ścieków uzyskano stosując nadtlenek wodoru, natomiast bardziej efektywne pod względem zużycia utleniacza na

jednostkę zużytego wskaźnika było utlenianie ozonem. Nie stwierdzono ścisłej korelacji między utlenial-
nością a zawartością całkowitego węgla organicznego, zarówno podczas reakcji zanieczyszczeń ścieków
z ozonem, jak i nadtlenkiem wodoru.

## ANWENDUNG VON STARKEN OXYDATIONSMITTELN ZUR ABWASSERREINIGUNG

Dargestellt wird die Oxydation von Abwässern die aus der Waschanlage von Kupferabgasen stammten.
Angewandt wurden Ozon und Wasserstoffperoxyd. Einen höheren Reinigungsgrad erzielte man durch
den Einsatz des Wasserstoffperoxyds, mehr effektiv zeigte sich jedoch die kleinere spezifische Dose des
Ozons. In beiden Fällen konnte eine exakte Korrelation zwischen der Oxydierbarkeit und dem Gehalt
am gesamten organischen Kohlenstoff (TOC) leider nicht erffasst werden.

## ОЧИСТКА ПРОМЫШЛЕННЫХ СТОЧНЫХ ВОД
## ПРИ ИСПОЛЬЗОВАНИИ СИЛЬНЫХ ОКИСЛИТЕЛЕЙ

Предложен метод химического окисления сточных вод от замкнутого цикла мокрой очистки
газов от пыли из медеплавильных заводов. Был применён озон и перекись водорода. Высшая сте-
пень очистки сточных вод была достигнута при применении перекиси водорода, более же эффек-
тивным по расходу окислителя на единицу отработанного индикатора было окисление озоном.
Не отмечено тесной корреляции между окисляемостью и содержанием полного органического
углерода, как во время реакции загрязнений сточных вод озоном, так и перекисью водорода.