

THERMOCATALYTIC TREATMENT OF HAZARDOUS INDUSTRIAL WASTEWATERS

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Industrial wastewaters containing high concentrations of chemical substances were treated using a method of thermocatalytic oxidation. A number of selected examples of the application of this method have been presented. Wastewaters containing non-ionic detergents were oxidized in the presence of catalyst. High degrees of oxidation over 97% were obtained. The consumption of electrical energy, was 10 kWh/kg COD under optimum conditions. Exhausted cooling oil-emulsions, were treated autothermically in the presence of catalyst. A high degree of oxidation of organic substances over 99% was obtained. Copper was recovered from the wastewaters electrochemically with an efficiency of 90%. The wastewaters from the production of phenol-formaldehyde resins, were treated in the presence of catalysts. High degrees of oxidation over 99% were obtained. In each of examples presented copper-zinc catalyst was used at a temperature of 400-700 °C. The examples testify to very high efficiency of the method for thermocatalytic oxidation of industrial wastewaters hazardous for the aqueous environment.

INTRODUCTION

Industrial wastewaters containing toxic and resistant to biochemical decomposition substances are very noxious for natural environment and besides they cannot be treated in commonly used biochemical plants. This type of wastewaters containing high concentrations of organic substances can be treated using a method of thermocatalytic oxidation (1-3). A number of selected examples showing the application of this method have been presented.

TREATMENT OF NON-IONIC DETERGENTS

Detergents belong to a group of organic materials which can pose a great threat to the aqueous environment. Their use is continually increasing making necessary more and more effective methods of waste disposal. A prototype installation for the thermal-catalytic oxidation of used wastewaters containing non-ionic detergents from washing baths was constructed in Factory of Transport Equipment in Kalisz (4). The baths are used in this plant for washing metal parts. They contain surface-active substances of the ethoxylated type, and also both anticorrosive and antifoaming agents. Used baths contain, in addition, considerable amounts of oils and greases removed from the metallic parts. The wastes treated in the installation were characterized by great variations in composition. The concentration of non-ionic surface active substances (NSAS) ranged from 5,000 to 70,000 mg/dm³. The concentration of organic substances measured as chemical oxygen demand (COD) ranged from 8,500 to 123,000 mg O₂/dm³ and the residue after calcination at 550⁰C was from 1.5 to 15 mg/dm³. The installation is shown in Fig.1.

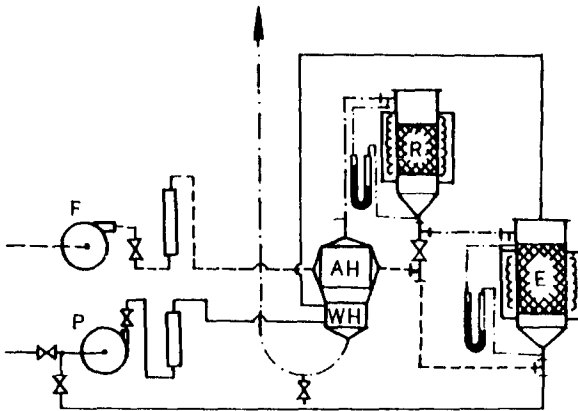


Fig. 1. Schematic diagram of the installation for the thermal-catalytic destruction of detergents

According to the design specification the maximum values of the parameters were: flow rate of the wastewaters 50 dm³/h, air flow rate 35 m³/h, temperature of the evaporator 500⁰C and temperature of the reactor 400⁰C. The major items of the waste treatment installation are:

- evaporator made of acid-proof pipe 450 mm in diameter filled with Raschig rings, heated by an electric furnace of 52 kW power,

- reactor made of acid-proof pipe 250 mm in diameter, containing 75 kg of Cu-Zn catalyst, heated electrically by a furnace of 35 kW power (an oxide catalyst containing 49% Cu and 20% Zn in the form of tablets 6x8 mm was used),
- air heater constructed as a cross-flow heat exchanger with a heat exchange area of 2,7 m²,
- wastes heater built of a ribbed pipe placed inside the duct through which the waste gases flow (heat exchange area was 3,4 m²).

The rig is operated in the following way (Fig.1). The air, heated in the air heater AH, is passed to the evaporator E. Simultaneously the wastes, heated in the heater WH, are delivered to the upper part of the evaporator E. The evaporated wastes, together with the air, flow through the reactor R. The waste gases leaving the reactor heat the air and the wastes in the heaters AH and WH, and then are discharged outside through the chimney. The main problem of the method described is high energy consumption caused by the necessity of evaporating the water contained in wastes. The specific energy consumption decreases with increasing flow rate of the wastes, as shown in Fig.2.

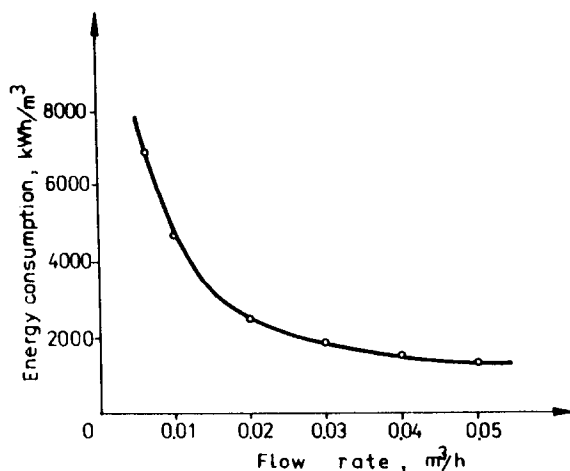


Fig.2. Dependence of the specific energy consumption on the flow rate of the wastes

It follows that it is desirable to deliver as much of the wastes per unit of time as can be evaporated in the evaporator. At a flow rate of 50 dm³/h, the energy consumption was 1440 kWh/m³. Further increase in the flow rate would result in lowering the temperature of the evaporator and then in flooding the packing. The energy consumption is also affected by the concentration of organic substances in the wastes. Fig.3 presents the

dependence of electrical energy demand on the COD of the delivered wastes. As the

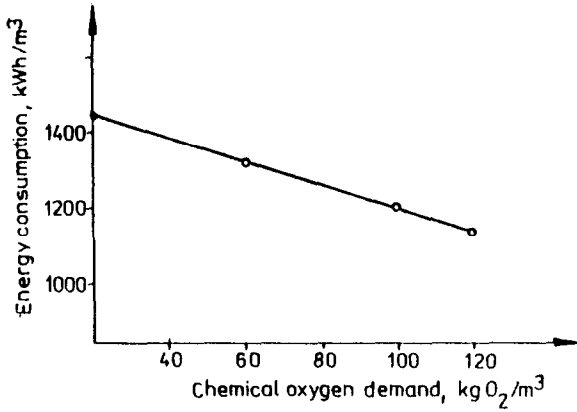


Fig.3. Dependence of the electrical energy demand on the concentration of organic substances in the wastewaters.

COD increases from 20,000 $\text{mg O}_2/\text{dm}^3$ to 120,000 $\text{mg O}_2/\text{dm}^3$ the energy consumption decreases by about 25%. With higher concentrations of organic substances greater amounts of energy are produced in their oxidation, and thus there is a lower consumption of electrical energy. Fig.4 presents the specific energy consumption expressed as

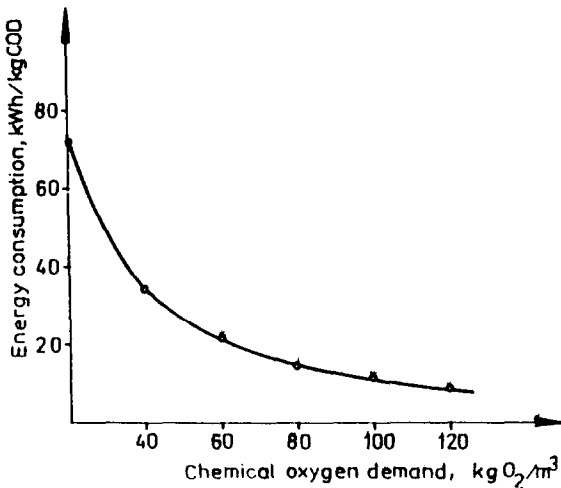


Fig.4. Specific consumption of electrical energy as a function of the concentration of organic substances in the wastewaters

$\text{kWh}/\text{kg COD}$ as a function of the COD of the wastes from the baths. For adequately high concentrations of organic substances the energy consumption decreases to about

10 kWh/kg COD. The process of catalytic oxidation is stable even when substantial changes occur in the composition of the wastes to be treated. The degree of reduction of the impurities obtained in the installation, expressed as the change of NSAS and COD values, is 97% on the average. It seems interesting that slightly higher degrees of conversion were obtained for greater initial concentrations of organic substances in the used baths and for higher flow rates of the wastes. Thus it seems advantageous to use high flow rates of the wastes containing organic substances in high concentrations.

TREATMENT OF COOLING OIL-EMULSIONS

Cooling oil-emulsions are commonly used in the metal industry. Exhausted cooling oil-emulsions also contain metallic particles coming from treated metals. In order to prolong the working time of the emulsion, its purification and recycling are applied. However, after some time the concentration of treated metal ions increases too. The recycled emulsion loses the required technological features and changes into wastewaters, containing considerable amounts of organic substances resistant to biochemical decomposition and ions of heavy metals as well. Therefore it becomes noxious industrial wastewaters, polluting water environment and soil. Its treatment is a necessity. The simplest way of treatment would be to send exhausted emulsion to the refinery after its eventual separation. However, refineries do not want to accept such oil in consideration of content of sulfur organic compounds and other compounds which cause deterioration of final product quality. Costs of transport are important too. Investigations of exhausted cooling oil-emulsion treatment have been carried out. Complete neutralization aims at isolation of the components, which can be repeatedly utilized, and at conversion of the remaining substances into nontoxic compounds. This aim can be achieved by complete oxidation, following the pretreatment of the exhausted emulsion (5). During the experiments, exhausted cooling oil-emulsions used in the process of copper wire drawing in cable factories were treated. The dispersed phase was sulphonated natural oil. The colour of emulsion was beige or green-beige. Its COD values were from 200 to 300 g O₂/dm³, copper content was from 0.33 to 6.63 g/dm³, including 0.3 to 4.0 g/dm³ of dissolved copper. The amount of postsintering residue was from 4.0 to 8.0 g/dm³. Elementary composition of organic phase of emulsions was 50.50% C, 10.56% H, 1.01% N, and 0.75% S. Decomposition of toxic organic substances by oxidation should be highly efficient, with possible low consumption of energy. This assumption requires the necessity of application of a catalyst allowing a decrease in temperature of the reaction. In order to avoid evaporation of high quantities of water, separation of emulsion is necessary. The oil phase is subjected to catalytic oxidation, while the aqueous phase is sent to the process of removal of heavy metal ions. The

exhausted emulsions were treated according to the concept presented in Fig.5. The separation (stage 1) was carried out with the periodic method. Phases were separated

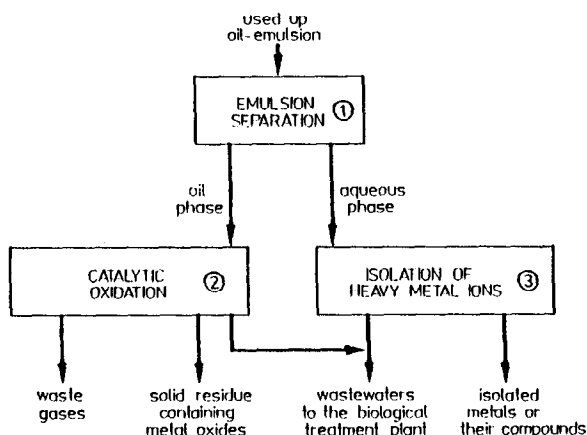


Fig.5. Schematic diagram of treatment of exhausted cooling oil-emulsions

by out-salting with inorganic compounds, as well as with electroflotation or thermic method accompanied by centrifuging. The oxidation (stage 2) was carried out with continuous method over wide range of basic parameters such as: temperature, air excess, concentration of organic substances, and reactor loading. Exhausted emulsions without pretreatment, and emulsions with adding of oil phase isolated from process presented in Fig.5, were sent to oxidation process also. The COD value of these concentrated emulsions increased to about $500 \text{ g O}_2/\text{dm}^3$ allowing the oxidation process to occur in an autothermic way. Periodic and flow electrolyzers with current density control were used in order to minimize energy consumption in stage 3. Various doses of inorganic out-salting substances were added to $100\text{-}1000 \text{ cm}^3$ samples. Among them were sulphuric acid, sodium carbonate, and chloride. This mixture was stirred for one hour and left for phase separation. The separation process was characterized by measuring of volume of isolated oil layer and estimation of COD of aqueous layer. Separation of phases with electroflotation method was carried out in a 200 cm^3 electrolyser, containing polymer diaphragm, with copper as cathode and platinum as anode, and using a current density of $0.22\text{-}0.28 \text{ A}/\text{cm}^2$. Thermocatalytic oxidation of organic substances was carried out in a reactor made of a pipe of acid-proof steel of 2.0 cm diameter and heated electrically using an intensity of emulsion flow $15\text{-}28 \text{ cm}^3/\text{h}$ and air flow $80\text{-}120 \text{ dm}^3/\text{h}$. The reactor consisted of two segments. The first one (vaporizer), kept at a temperature of 800°C , was not paced. Here the emulsion was evaporated, the organic substances were partially

oxidized, and the dry residue was isolated. The other segment contained a copper-zinc catalyst TMC-2 and was kept at a temperature of 510-640⁰C. Quantitative relationships between the oxidation degree of organic substances and also the concentration of sulphur and nitric oxides in combustion gases on temperature and initial concentration of organic substances were investigated. Initial concentration of organic substances ranged from 200 to 500 g O₂/dm³. Dry residue containing cupric oxide, obtained in the oxidation process, was dissolved in 25% sulphuric acid. Electrochemical isolation of copper from the aqueous phase was carried out in a 350 cm³ electrolyzer with copper cathode and lead anode. Current densities of 0.35 A/dm³ and 0.14 A/dm³ were applied for concentrations of copper ions 0.5 g/dm³ and lower than 0.5 g/dm³, respectively. The problem of isolation of emulsion with inorganic substances was considered from the viewpoint of the influence of a dose on the effect of phase separation. From the data shown in Fig.6, which presents the dependence of COD of the aqueous layer on the dose of 25% sulphuric acid, it can be seen that optimum separation takes place at the 2.5 vol.% acid dose for the separated emulsion. The COD of the isolated aqueous phase was about 1.5 g O₂/dm³. Optimum dose of crystalline sodium carbonate or sodium chloride was respectively 10% and 5% of emulsion. In both cases COD of the aqueous phase after separation was about 2.5 g O₂/dm³. Fig.7 presents the data of the

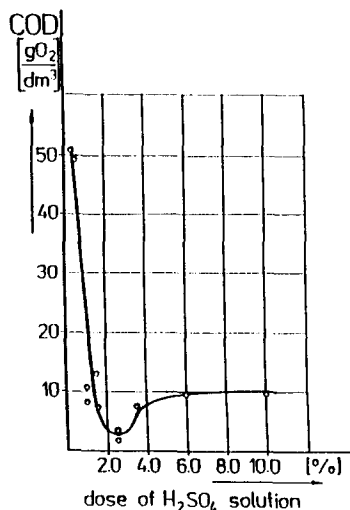


Fig.6. Dependence of COD of the aqueous phase on the dose of 25% sulphuric acid

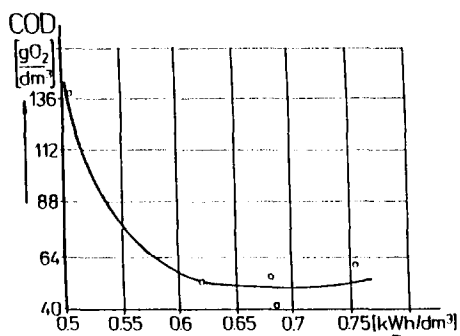


Fig.7. Dependence of COD of the aqueous layer on the energy consumed in the electroflotation process

electroflotation process. Minimum COD values of the aqueous phase (about 45 g O₂/dm³) were achieved with energy consumption of about 0.6 kWh/dm³. For thermocatalytic oxidation it was found that the catalyst was not poisoned during its more than six month's work. Such parameters as the temperature 600⁰C for the catalyst and 800⁰C for the vaporizer, air excess coefficient 2, contact time one second, allows of a yield of oxidation of organic substances from 99.7 to 99.93%. Treatment of emulsions (initial COD values 200-500 g O₂/dm³) carried out under these conditions results in formation of a condensate of COD, value 300-800 mg O₂/dm³ and pH 6.0. As a result of electroreduction, concentration of copper ions in the aqueous phase decreased from 1.27 g/dm³ to 40 mg/dm³, with energy consumption of 2.2 kWh/kg of the recovered copper. Application of electrolysis allowed separation of about 97% of initial contents of copper dissolved in the aqueous solution. As a result of neutralization of exhausted cooling oil-emulsions, the following wastewaters were obtained:

1. Wastewaters after electrolysis with COD value of about 1500 mg O₂/dm³, and the contents of dissolved copper about 40 mg/dm³.
2. Copper-free wastewaters after thermocatalytic oxidation with COD value of 500 mg O₂/dm³.

Therefore, a summary degree of oxidation of organic substances and the degree of copper separation from wastewaters exceed 99%. Organic substances are oxidized to carbon dioxide, water vapour, and trace amounts of sulphur dioxide and nitrogen oxides. Reaction heat is emitted. Energy consumption in the process is decreased by combustion heat of emulsion organic components. Copper is isolated partly in metallic form (from stage 3) and partly in the form of sediment containing CuO (from stage 2). The sediment can be sent to a special plant for further treatment. It is also possible to dissolve it in 25% sulphuric acid and recover metallic copper with an electrochemical method. In this way, about 90% of copper contained in emulsions can be recovered in metallic form. However, in order to achieve the above yield, individual operations must be carried out with great precision. It is particularly important to separate precisely the oil phase from the aqueous one. The electrochemical separation of copper runs without any disturbances in the aqueous layer containing no oil phase. Therefore, emulsions separation by inorganic agents is now regarded as the optimum method. Application of the solution of sulphuric acid is particularly purposeful if a plant possesses waste acid, e.g. from the pickling process. Addition of inorganic agents to emulsion causes an increase of salinity of water reservoirs. In the electroflotation process this disadvantage does not occur. However, at the present stage of investigations the phase separation with this method is insufficient and energy consumption is still too high. Energy consumption is the basic problem in this method of treatment, specially at the stage of thermocatalytic

oxidation. Balance calculations indicate that the concentration of treated emulsion corresponding to COD value of about $500 \text{ g O}_2/\text{dm}^3$ allows realization of the catalytic oxidation process in an autothermic way. Investigation has shown that increase of concentration of treated emulsion does not cause deterioration of the obtained condensate. It also does not cause the increase in concentration of toxic components in waste gases from the process of thermoatalytic oxidation. Concentration of sulphur dioxide was $0.002\text{-}0.02 \text{ mg}/\text{dm}^3$, nitric oxides $0.002\text{-}0,01 \text{ mg NO}_2/\text{dm}^3$. These values were independent from the initial COD (200 to $500 \text{ g O}_2/\text{dm}^3$) of the emulsion. Decrease of energy consumption was the main criterion of choice of copper electroreduction method. For each kilogram of the recovered copper, 2.2 kWh of energy was used up and concentration of copper ions decreased to $40 \text{ mg}/\text{dm}^3$. Futher decreased of the concentration is possible at higher energy consumption. However, it is not necessary because of very high dilution (about 1000 times) of the obtained aqueous phase in biological treatment plant.

TREATMENT OF PHENOL-FORMALDEHYDE WASTEWATERS

The wastewater from the production of phenol-formaldehyde resins, containing: phenol at concentration 5.5 up to $75 \text{ g}/\text{dm}^3$, formaldehyde at concentration up to $12 \text{ g}/\text{dm}^3$, and with COD value 48 up to $172 \text{ g O}_2/\text{dm}^3$, were treated. Investigations without using any catalyst were carried out under the temperature 615 to 1050°C with application of reactor direct heating by gas. Increase of temperature in the above mentioned range caused the decrease of phenol concentration from 4470 down to $11.6 \text{ mg}/\text{dm}^3$ in the obtained condensate. The COD value in the condensate was $46 \text{ mg O}_2/\text{dm}^3$ under the highest temperature and the factor of excess air 1.5 . Investigations with using some catalysts were carried out, too. The best results were obtained using copper-zinc catalyst. These experiments were carried out under the catalyst temperature 550 up to 700°C . The weight of used catalyst was changed in the range of 100 up to 6000 g , the factor of excess air in the range 1.05 to 2.0 and the rate of wastewater flow in the range 40 up to $2000 \text{ cm}^3/\text{h}$. The treatment of wastewaters with the initial value of COD - $172 \text{ g O}_2/\text{dm}^3$ and phenol concentration - $32000 \text{ mg}/\text{dm}^3$, caused the decrease of these parameters values in the condensate under increase of temperatur. COD value decreased from 2340 down to $15 \text{ mg O}_2/\text{dm}^3$ and phenol concentration from 220 to $0 \text{ mg}/\text{dm}^3$. Obtained results were more satisfactory than results obtained during experiments without any catalyst, while three times lower consumption of gas was observed. Investigations in the large laboratory scale indicates that the factor of excess air should reach the value of 1.5 and the catalyst load for wastewater should be about $1 \text{ m}^3/\text{m}^3\text{h}$. Under these conditions and catalyst temperature about 500°C , colourless and transparent condensate with COD

value of several $\text{mg O}_2/\text{dm}^3$ and pH about 6, was obtained from wastewaters very noxious for environment. Decrease of that process costs may be caused by next decrease of catalyst load in spite of controlled increase of COD value in the condensate.

CONCLUSIONS

As it results from the presented examples, the employed method of treatment of non-ionic detergents, cooling oil-emulsions and phenol-formaldehyde wastewaters based on thermocatalytic oxidation of organic substances and electrochemical recovery of heavy metals, allows achievement of 97-99% degree of oxidation of organic substances. Use of copper-zinc catalyst enables to obtain that high yield of process in lower temperature and in consequence of this enables to reduce the energy consumption.

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