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NEUTRALIZATION OF WASTEWATERS FROM WET DEDUSTING OF THE PYROMETALLURGIC SMELTER GASES FROM COPPER WORKS

The wastewaters coming from wet dedusting of the pyrometallurgic smelter gases from copper works were subject to biological treatment, chemical oxidation (with O_3 , NaOCl and 30% solution of H_2O_2), sorption on activated carbon and extraction with benzene. It appeared that only 40–50% of the organic impurities might be removed in each of the above processes. In such a situation the attempts at incineration of sewage were made and successful results obtained. In practice the utilization of wastes as a binding agent in briquetting the fine coal and combustion of the obtained product in furnaces have been recognized as the best ones.

1. THE CHARACTERISTICS OF THE WASTEWATERS

Copper ore, when smelted in shaft furnaces, is usually accompanied with emission of dusts and gases containing CO, CO_2 , SO_2 , SO_3 , CS_2 , H_2S , COS, NH_3 , aromatic hydrocarbons, with 1–6 atoms of carbon in one molecule. To reduce the emission of the noxious chemical compounds to atmosphere, dusts and smelter gases are subject to wet dedusting, products of which are wastes and sludges. The first contain large amounts of the organic impurities, mostly benzene derivatives, mainly phenols, amines and amides and smaller amounts of aromatic and aromatic-aliphatic ketons, aliphatic hydrocarbons and mixed ethers.

Sorption of volatile sulphur compounds (H_2S , COS, SO_2 , CS_2) in water and secondary reactions of these compounds occurring in the liquid phase yield: sulphides, sulphates and sulphites. Besides chlorides, rhodanates, ammonia salts, alkali metal salts and alkaline earths they constitute the basic inorganic elements of wastes. Heavy metals (Zn, Pb, Cu), cyanides and phosphates are in lower concentrations.

The detailed data on the chemical composition of wastes are presented in tab. 1. Two kinds of wastewaters coming from the same plant were taken into account: "wastes 1"

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Table 1

Chemical composition of wastes from wet dedusting of smelter gases from copper works
Skład chemiczny ścieków z mokrego odpylania gazów odlotowych z hut miedzi

Parameter	Unit	"wastes 1"	"wastes 2"
pH		4.7	4.4
Permanganate value — PV (COD)	g O ₂ /m ³	4625	13800
BOD ₅	g O ₂ /m ³	4100	12840
COD	g O ₂ /m ³	8050	38200
TOC	g C/m ³	—	9800
Volatile phenols	g/m ³	464	480
Total phenols	g/m ³	—	800
Sulphides	g S ⁻² /m ³	92	450
Sulphites	g SO ₃ ⁻² /m ³	282	850
Sulphates	g SO ₄ ⁻²	1951	16200
Rhodonates	g SCN ⁻ /m ³	380	—
Chlorides	g Cl ⁻ /m ³	2430	5600
Phosphates	g PO ₄ ⁻³ /m ³	15.6	19.3
Cyanides	g CN ⁻ /m ³	3.7	8.6
Ca	g Ca/m ³	500	720
Mg	g Mg/m ³	200	350
Na	g Na/m ³	890	—
K	g K/m ³	540	—
Fe	g Fe/m ³	109	128
Cu	g Cu/m ³	1.7	15.0
Pb	g Pb/m ³	1.2	8.0
Zn	g Zn/m ³	6.8	18.2
Ammonia nitrogen	g H/m ³	203	1750
Nitrate and nitrite nitrogen	g N/m ³	0	74
Total dissolved solids (TDS)	g/m ³	14280	95 357
Volatile TDS	g/m ³	6360	45765

from not modified wet dedusting processes and "wastes 2" from the modified, more efficient process. Within 24 hours about 50–100 m³ of these wastes (2) were discharged from the water circulation.

Because of large amounts of impurities, including toxic compounds and those harmful for microorganisms (hydrocarbons, heavy metals, sulphides, rhodonates and cyanides), the treatment of wastes before their recycling or disharing was necessary. The investigations so far have shown that physical and physical-chemical methods based on alkalization, sorption, aeration and extraction are of no practical use [3]. Extraction of wastes with benzene lowered the COD to only 40%. The recovery of the organic compounds was unprofitable in that process. The aeration of wastes did not change the content of the organic impurities, there occurred only an intense oxidation of sulphides to sulphites, the latter being slowly oxidized to sulphates. This last process proceeded much more rapidly in the presence of catalytic agents (ferros, Co-Mo). After alkalization with Na OH or Ca(OH)₂ to pH 9 the wastes contained less than 1g of heavy

metal ions (Fe, Pb, Zn, Cu) per m^3 . Alkalinization of wastes did not, however, influence significantly the concentration of organic compounds. Sorption on activated carbon (Carbopol Z-4), though, assured 60% removal of TOC but only at 10 kg dose of activated carbon per m^3 . The activated carbon once used could not be regenerated.

The purpose of further investigation was to state the usefulness of methods based on chemical oxidation (with O_3 , NaOCl and 30% solution of H_2O_2) and biodegradation (with activated sludge). If it appears that the above methods are insufficient or their application, because of other reasons, impossible, the incineration of wastes is to be analyzed. This expensive, energy consuming process is applied in practice only in special, economically justified cases.

2. BIODEGRADATION OF WASTES

In order to determine the biodegradability of wastes, they were subject to long-time aeration with nonadapted activated sludge. Oxygen consumption (OC), amount of released CO_2 and changes in chemical composition of wastes occurring with time have been determined. The analyses were performed using "wastes 1" and "wastes 2", alkalinized

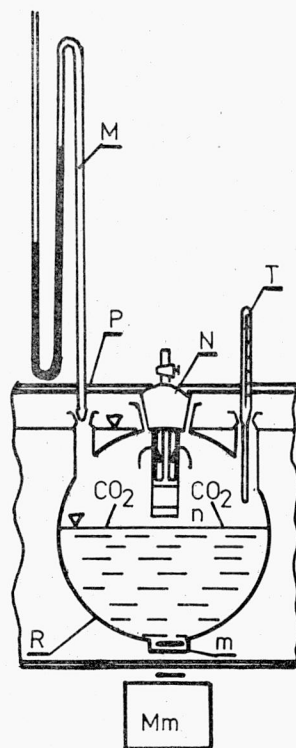


Fig. 1. Respirometer

M — manometer, T — thermometer, R — reactor, N — cap with valve, n — vessel with KOH solution, m — magnetic mixer, Mm — magnetic stirrer, P — tank with water

Rys. 1. Respirometr

M — manometr, T — termometr, R — reaktor, N — nasadka z zaworem, n — naczynie z roztworem KOH, m — mieszalnik magnetyczny, Mm — mieszadło magnetyczne, P — zbiornik z wodą

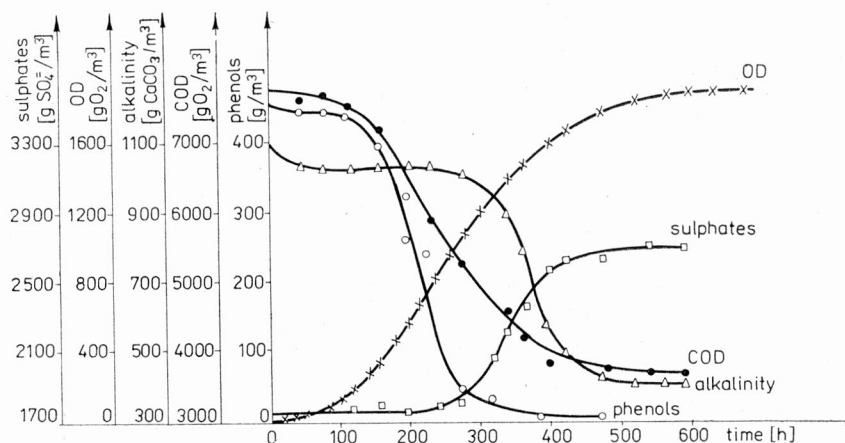


Fig. 2. Biodegradation of wastes
Rys. 2. Biologiczne oczyszczanie ścieków

with NaOH to pH 9, and activated sludge from municipal sewage. The concentration of sludge was equal to about 1 kg of dry MLVSS. The process was carried out in the respirometer, shown in fig. 1, under static conditions [1].

Biodegradation of "wastes 1" was a selective process with respect to the given chemical compounds (fig. 2), being initiated by the adaptation of activated sludge. That process was characterized by slight COD removal and small oxygen consumption due to biodegradation of the compounds easily assimilated by microorganisms. With the adaptation of activated sludge the whole biodegradation process was accelerated. The rates of COD removal and oxygen consumption increased, and the removal of phenols, their derivatives and of other compounds more resistant to biodegradation were initiated. The subsequent process initiated by the degradation of most phenols was characterized by reaction of inorganic sulphur compounds yielding sulphuric acid. The production of the latter influenced the increase of the sulphate ion concentrations and the decrease of basicity in the treated wastewater. The increment of sulphates ($924 \text{ g SO}_4^{2-}/\text{m}^3$) was approximately equal to the decrement of sulphides, sulphites and rhodanates ($893 \text{ g SO}_4^{2-}/\text{m}^3$). At the final stage of the process the rate of oxygen consumption decreased and COD decrement was inhibited. Most of the compounds assimilated by microorganisms were biodegraded. This fact was also confirmed by high, almost total removal of BOD_5 . The treated wastewaters contained only substances resistant to biodegradation, constituting 50% of pollutants determined as COD.

The more detailed studies [2] allowed to formulate the following statements:

1. "wastes 1" affected negatively nonadaptive microorganisms and impeded the activated sludge adaptation and biodegradation of the compounds easily assimilated by microorganisms,
2. wastewaters were lethal for *Nitrosomonas* and *Nitrobacter*,
3. phenols inhibited biochemical degradation of rhodanates and oxidation of sulphites.

In "wastes 2", more concentrated than the "wastes 1", biochemical processes were completely inhibited. The influence of toxic compounds was lethal for most of microorganisms. Although a slight oxygen consumption was stated and small removals of COD (12%) and BOD (13%) took place, these reactions were chiefly due to chemical processes and sorption of impurities on the the activated sludge floccules. Biodegradability of "wastes 2" occurred only when they were diluted with the municipal sewage in the ratio 1:4. Under these conditions the COD removal amounted only to about 40%. Biochemical decomposition of the pollutants proceeded analogically to "wastes 1". The remaining compounds were resistant to biodegradation.

Wastes from wet dedusting are characterized by a low biodegradability. This process is impeded by toxic compounds lethal for microorganisms, and the removal of impurities is limited to 40–50% of COD by the substances resistant to biochemical decompositions. To improve the results of wastewater treatment, more efficient methods should be applied.

3. OXIDATION OF WASTEWATERS

Such oxidants as O_3 , NaOCl and H_2O_2 may be used for treatment of wastes coming from wet dedusting provided that most organic impurities will be oxidized to CO_2 or to other inorganic products. Otherwise, satisfactory results will not be obtained.

The investigations comprised the ozonation and chlorination of wastewaters as well as their oxidation with 30% solution of H_2O_2 . The first process consisted in passing the air and O_3 mixture through raw "wastes 2" and alkalized ones with NaOH to pH 10 and determining the amounts of the reacted and unreacted O_3 , COD, permanganate COD, TOC, phenols and pH.

The influence of O_3 dose on changes in chemical composition of alkaline wastewaters is shown in fig. 3. It appeared that some organic compounds were oxidized to organic products, others were decomposed and generated CO_2 . The last process proceeded actively until the O_3 consumption amounted to about 2 kg/m³ yielding 45%, 65% and 50% removal of TOC, COD and permanganate COD, respectively. Further ozonation had no significant effect on the total content of the organic compounds. The removals of TOC, COD and permanganate COD were almost completely inhibited, one observed only the degradation of the remaining organic compounds decomposed to well dissociated organic acids (pH of wastewaters decreased from 10 to 2.6) or to other organic products. The above process was completed when at least 8 kg O_3 /m³ was introduced into wastewaters. Then the pH of wastewaters feared to decrease and gases leaving the reactor contained the unreacted O_3 , the amount of which rapidly increased with the dose of O_3 . Most of impurities were oxidized to final products. The compounds resistant to O_3 remaining in wastewater constituted 55% TOC and 35% COD of raw wastewaters.

The efficiency of acid wastewater ozonation was much lower. Permanganate value — PV (COD), TOC and COD values decreased by 45%, 40% and 55%, respectively. This

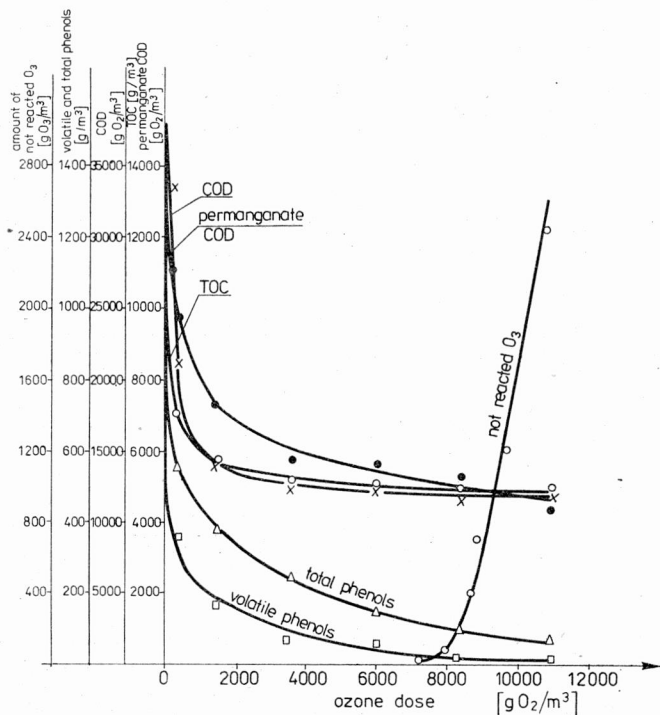


Fig. 3. Effect of ozone dose on chemical composition of wastewater
Rys. 3. Wpływ dawki ozonu na zmiany w składzie chemicznym ścieków

treatment required consumption of about 2 kg O₃/m³. Further ozonation was characterized by decomposition of the organic impurities to organic acids (pH decreased from 4.4 to 1.6) and to other organic compounds. This process, however, had no influence on COD, PV and TOC.

Treatment of wastes with sodium hypochlorite required the usage of 10 kg Cl⁻/m³. Oxidation resulted in 40% removal of organic compounds determined by TOC. Reaction of remaining compounds with hypochlorite resulted in stable organic products including also organic halogen derivatives. Large amounts of hypochlorite used for oxidation resulted in undesirable increase in wastes salinity.

Oxidation of wastewaters with 30% solution of H₂O₂ proceeded very slowly. Not earlier than 2 hours after introduction of 10, 100 and 200 kg H₂O₂/m³ of raw "wastes 2", the respective values of TOC and permanganate COD removal amounted barely to 13%, 30% and 35% of TOC and 35%, 60% and 65% (fig. 4). Efficiency of the reaction slightly increased (in about 10%) after preliminary alkalization of wastewaters to pH 9 or after extending the reaction time to 20 hours.

Intensive oxidation of wastewaters with O₃, NaOCl or 30% solution of H₂O₂ does not assure suitable conditions for the total decomposition of some organic compounds.

After ozonation, chlorination and oxidation with H_2O_2 the percent of TOC in wastes amounts to 55–60, 60 and 55–65, respectively. These amounts are too large to consider the chemically oxidized wastes as being sufficiently treated.

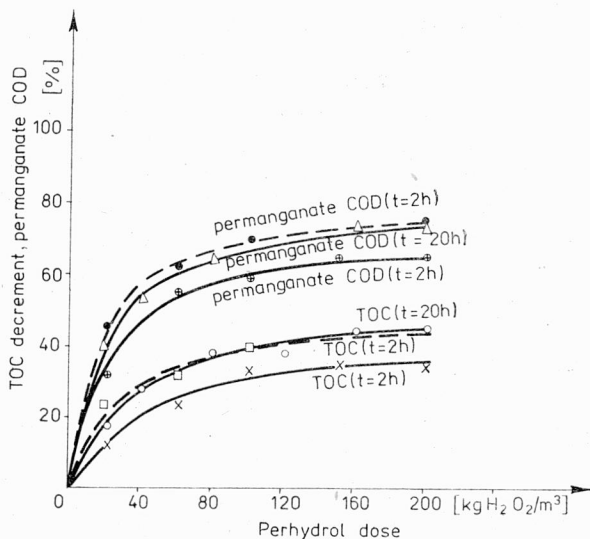


Fig. 4. Effects of 30% solution of H_2O_2 dose and reaction time on TOC and permanganate COD removal in wastewater for pH 4.4 (—) and 9 pH (---)

Rys. 4. Wpływ dawki perhydrolu oraz czasu reakcji na ubytek CWO i utlenialności w ściekach o odczynie pH 4.4 (—) oraz pH 9 (---)

4. INCINERATION OF SEWAGE

Since so far none of the processes examined has given satisfactory results the attempts of the incineration of sewage were made. It has been expected that this process will assure a complete thermal decomposition of the organic pollutants in organic products and, despite, high costs connected with energy, consumption will be competitive with other processes.

Incineration was conducted with the concentrated wastewaters ("wastes 2") coming from wet dedusting. They were let together with air through granular catalyst placed inside the quartz tube heated in the furnace. The gases leaving the reactor were cooled. The condensed products were collected in the receiver, the remaining ones being absorbed in the washers. The process was carried out at 673–973 K and in the presence of cupric, nickelic, ferric and cobalt-molybdenic oxides produced by Chemical Establishment "Oświęcim". In order to compare the effects of temperature and catalyst on the process efficiency, the rates of wastes and air flows through the reactor were always the same and amounted to $0.1 \text{ dm}^3/\text{h}$ and $4 \text{ dm}^3/\text{h}$, respectively.

Table 2

Incineration of sewage in the presence of catalysts
Spalanie ścieków w obecności katalizatorów

Kind of catalyst	Temperature	Amounts of organic compounds incinerated to final products		Amounts of organic compounds incinerated to pyrolysis products		Chemical composition of condensate				
		K	g C/m ³	%	g C/m ³	%	g Cl ⁻ /m ³	g SO ₄ ⁻² /m ³	g NO ₃ ⁻ /m ³	TOC pH
Cobalt-molybdenic	673	4942	50.4	4858	49.6	620	720	730	2330	2.6
	773	7050	71.9	2750	28.1	790	2120	1580	1820	2.3
	873	9776	100.0	0	0	1580	5400	1340	0	1.6
	973	9810	100.0	0	0	—	—	—	0	1.4
Iron	673	5863	59.8	3937	40.2	840	980	990	1020	2.6
	773	7173	73.2	2627	26.8	1120	1330	1011	520	2.1
	873	9883	100.0	0	0	1420	4210	1380	0	1.7
	973	9790	100.0	0	0	2230	—	1578	0	1.2
Copper	673	6043	61.6	3757	38.3	684	1130	975	1160	2.1
	773	6777	69.1	3023	30.8	742	1380	1083	672	1.8
	873	9876	100.0	0	0	1980	4511	1518	0	1.4
	973	9860	100.0	0	0	1710	5321	112	0	1.3
Nickel	673	5215	53.2	4585	46.8	680	911	706	1510	2.6
	773	6321	64.5	3479	35.5	—	2080	911	982	1.7
	873	9812	100.0	0	0	1530	3421	—	0	1.4
	973	9885	100.0	0	0	1780	4812	1230	0	1.1

TOC of raw wastes — 9800 g/m³.

Incineration of the organic impurities of wastes to the final products such as inorganic acid anhydrides (SO₂, SO₃, NO₂, CO₂), HCl and H₂O was conducted at temperature ≥ 873 K (tab. 2). The amount of CO₂ produced in such conditions was equivalent to that of TOC in raw wastewaters. At temperatures ranging from 673 to 873 K the amount of CO₂ was smaller and gases, leaving the reactor, contained some products of pyrolysis. The latter constituted 40–50% and 25–35% of TOC in raw wastewaters at the temperatures of 673 K and 773 K, respectively.

After cooling the gaseous products of strong mineral acid anhydrides (SO₃ and NO₂) and of HCl were dissolved in water. In this way gaseous solutions of H₂SO₄, HCl and HNO₃ were obtained. Their concentrations in the condensate increased with the incineration temperature. At 673 K it was equivalent to 700–1 100 g SO₄⁻²/m³, 600–850 g Cl⁻/m³, 700–1 000 g NO₃⁻/m³, and to pH 2.1–2.6. At the temperature of 873 K it was equivalent to 3 400–5 400 g SO₄⁻²/m³, 1 500–2 000 g Cl⁻/m³, 1 300–1 500 g NO₃⁻/m³, and to pH 1.4–1.7.

The condensate contained not only mineral acids but also liquid organic compounds (products of pyrolysis) provided that combustion occurred at temperature < 873 K. At 673 K the amount of pyrolysis products ranged within 10–20% with respect to TOC in raw wastewater, at temperature higher by about 100 K it decreased by about 5%.

Weak, mineral acid anhydrides (CO_2 , SO_2) were not condensed and remained in gaseous products together with volatile organics. The latter constituted 15–20% and 10–15% of TOC in raw wastewaters at the respective temperatures of 673 K and 773 K.

Fe_2O_3 , Ni_2O_3 , MoO_3 and CuO catalyzed the process. In their presence the incineration of organic compounds to final products occurred at 773 K. In the absence of catalyst the pyrolysis products were formed even at temperature > 873 K, and at 1 173 K the amount of formed organics constituted about 20% of TOC content in raw wastewaters.

Long-lasting incineration of sewage had a disadvantageous effect on the activity of the catalyst. The amount of organic compounds in final products increased with the time due to exhaustion of catalyst. To regenerate the catalyst it was heated at the temperature of 873–1 173 K after the wastewaters inflow to the reactor had been closed.

Of the so far examined methods, the incineration should be appreciated as being the best one. In contrast to chemical oxidation biological treatment, sorption and extraction, this process assures a complete removal of the organic pollutants. High efficiency of this process gives the possibility of its application, despite high costs.

In technology of wastewater incineration a method of acid anhydride removal from smelter gases should be included. This problem may be conveniently solved by sprinkling smelter gases with ammonia water in columns to get the solution of ammonia salts which may be utilized in agriculture as a liquid nitrogen fertilizer.

Incineration of wastewaters may be successfully performed after their condensation. This method was confirmed by experiments made on technological scale. Wastewaters, chemical composition of which was similar to that of "wastewaters 2", were concentrated to 1/4 of their volume in the evaporator with the submerged flame burners, then they were mixed with waste sulphite cellulose lyes which so far have been used in copper works to briquette solid fuel. It was found that the product obtained after mixing waste sulphite cellulose lyes with the condensed wastewaters in voluminous ratio 3:1 had approximately the same density and viscosity as well as the same ability of binding fine coal, as those of waste sulphite cellulose lyes. Fine coal moistured with such a mixture of wastewater was briquetted in the hydraulic presses. Briquettes used as fuel in mill furnaces were burned together with organic impurities.

Wastewater condensation in the evaporator requires a high gas consumption. To reduce its amount, it has been suggested to restrict the amount of wastewater from several hundred to 50–100 m^3 per 24 h by improving the process of wet dedusting. This effect was obtained by reducing the make up water in the system of wet dedusting and by increasing the rate of water circulation. In this way the amount of wastewaters was several times reduced, increasing, however, its concentration (tab. 1). The gas consumption may be also reduced when the hot steam leaving the evaporator is utilized in the

initial heating of the wastewaters flowing into the evaporator. Water from the steam may be employed for wet dedusting.

Satisfactory results and practical reasons speak for the implementation of the discussed process to the copper works.

5. CONCLUSIONS

1. In view of large amounts of impurities present in wastewaters from wet dedusting of smelter gases from copper works and toxic properties of these wastewaters, it is obvious that an efficient method for their neutralization ought to be developed and implemented.

2. Extraction of wastes with benzene gives only a 40% removal of COD. The recovery of the organic compounds in this process is not efficient economically.

3. Activated carbon (Carbopol Z-4) may adsorb about 60% of waste impurities determined as TOC, when at doses in excess of 10 kg/m³. After sorption the activated carbon cannot practically be regenerated.

4. Biodegradability of wastewaters is low. This process is impeded by the compounds toxic and noxious for microorganisms, while the substances resistant to biochemical decomposition limit the removal of impurities to 40–50% of COD. Biodegradation may occur not earlier than after preliminary alkalization and dilution of wastewaters.

5. Chemical oxidation of wastewaters with O₃, NaOCl or 30% solution of H₂O₂ may decrease COD by 40–45% provided that O₃, Cl and H₂O₂ are used in amounts of 2 kg/m³, 10 kg/m³ and 100–200 kg/m³, respectively.

6. Incineration of sewage in the presence of the catalyst at the temperature of 873 K guarantees the removal of all the organic impurities exceeding by 40–70% that resulting from biological treatment, chemical oxidation, sorption or extraction. High efficiency of this method creates the possibility of its practical application. Gaseous products of the process can be used for production of liquid nitrogenous fertilizers.

7. Wastewaters may be incinerated together with coal in the furnaces. To this end they should be first concentrated in the evaporator to 1/4 of their volume, and the obtained product utilized for briquetting the fine coal in the hydraulic presses. Numerous practical advantages of this process speak for its implementation in copper works.

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UNIESZKODLIWIANIE ŚCIEKÓW Z MOKREGO ODPYLANIA PIROMETALURGICZNYCH GAZÓW ODLOTOWYCH Z HUT MIEDZI

Ścieki z mokrego odpylania pirometalurgicznych gazów odlotowych z hut miedzi poddano biologicznemu oczyszczaniu, chemicznemu utlenianiu (ozonem, podchlorynem sodowym, perhydrolem), sorpcji na węglu aktywnym i ekstrakcji benzenem. Okazało się, że tylko 40-50% zanieczyszczeń organicznych można usunąć w każdym z wymienionych procesów. W tej sytuacji podjęto próby spalania ścieków. Wypadły one pomyślnie. Za najbardziej przydatne w praktyce uznano wykorzystanie ścieków jako spoiwa w procesie brykietowania mialu węglowego i spalanie otrzymanego produktu w piecach hutniczych.

REINIGUNG DER GASWASCHWÄSSER AUS KUPFERHÜTTEN

In der Kupfererzverhüttung entstehen Abgase die im Naßverfahren gereinigt werden müßen. Die dabei entstehenden Abwässer wurden versuchsweise biologisch gereinigt, chemisch oxydiert (mittels Ozon, Natriumhypochlorid, konzentriertem Wasserstoffperoxyd), auf Aktivkohle sorbiert und mit Benzol extrahiert.

Mit Hilfe eines jeden der genannten Einzelverfahren lassen sich nur 40-50% der organischen Verunreinigungen beseitigen. Positive Ergebnisse lieferten Versuche über Abwasserverbrennung. In der Praxis könnte man die Gaswaschwässer als Bindemittel bei der Herstellung von Preßkohle nutzen; der Kohlenstein wird anschließend im Hütteverfahren verbrannt.

ОБЕЗВРЕЖИВАНИЕ СТОЧНЫХ ВОД ИЗ МОКРОЙ ОЧИСТКИ ОТ ПЫЛИ ПИРОМЕТАЛЛУРГИЧЕСКИХ ОТХОДЯЩИХ ГАЗОВ С МЕДЕПЛАВИЛЬНЫХ ЗАВОДОВ

Сточные воды из мокрой очистки от пыли пиromеталлургических отходящих газов с медеплавильных заводов были подвергнуты биологической очистке, химическому окислению (озоном, гипохлоритом натрия, пергидролем), сорбции на активированном угле и экстракции бензолом. Оказалось, что только 40-50% органических загрязнений можно удалить в каждом из перечисленных процессов. В этой ситуации были предприняты попытки сжигания сточных вод. Эти попытки оказались благоприятными. Наиболее пригодными в практике было признанным использование сточных вод в качестве вяжущего вещества в процессе брикетирования штыба и сжигания полученного продукта в металлургических печах.