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REMOVAL OF HEAVY METALS CONTAINED IN THE WASTEWATER FROM GLASS-MAKING INDUSTRY

The physicochemical composition of wastewaters generated by crystal-glass and glass-ware manufacturing plants was investigated. Special interest has been focussed on the concentrations of heavy metals and their removal efficiencies. Wastewaters from the chemical processing of glass were subject to chemical precipitation and 2 hours sedimentation in order to determine the removals of low soluble heavy-metal compounds. Another kind of wastewaters, namely those from the grindery department, were treated in alum and ferric sulphate coagulation processes followed by sedimentation and filtration.

For acidic wastewaters generated in the chemical processing of glass the best results were obtained by chemical precipitation (at pH between 9.5 and 10.0) followed by 2 hours sedimentation. The wastewaters from the grindery department, which contain organic complexes of heavy metals, should be treated by coagulation with ferric sulphate (at pH = 6.0), 2 hours sedimentation, and filtration through a sand bed.

1. INTRODUCTION

Glass-manufacturing plants are among those pollution sources that create the most serious environmental hazards. This is because the stock material used in glass-making contains a number of toxic substances. These are combinations of heavy metals such as lead, zinc, nickel, cobalt, copper, chromium, cadmium, silver, selenium, and arsenic. The kind and quantity of heavy metal compounds used in the glass-making process depend on the method employed and the end product required. Heavy metal compounds are generally applied to produce household glass-ware and lead crystal. They may also be employed in manufacturing window or bottle glass, etc.

Manufacturing of glass involves consumption of various quantities of heavy metals ranging yearly from trace amounts to several dozen tons (domestic glass-ware producing plants) or even several hundred tons (lead-crystal making plants). Among heavy metals

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present in the stock material red lead takes the most important part. It is also worth emphasizing that, despite the quantity of heavy metals used, the wastewaters generated in glass-making processes are highly hazardous to natural environment.

2. CONCENTRATION OF HEAVY METALS IN THE WASTEWATER

The experiments were carried out for wastewaters generated by crystal-glass and glass-ware manufacturing plants. Earlier investigations of heavy metal behavior [1] show that the highest average concentration of the total heavy-metal content (81.76 mg/dm^3) is found in the effluent from the galvanizing department. In the wastewaters from grinders, chemical polishing, and acid embossing processes the average concentrations are 43.75 mg/dm^3 , 23.81 mg/dm^3 , and 2.75 mg/dm^3 , respectively. The percentage of zinc, nickel, lead, chromium, and copper is listed in table. Wastewaters generated in the che-

Table

The percentages of zinc, nickel, lead, chromium, and copper in the wastewaters from glass-ware and crystal-glass manufacturing plants

Procentowy udział cynku, niklu, ołowiu, chromu i miedzi w ściekach z zakładów wyrobów szkła i kryształów

Wastewater	Zinc	Nickel	Lead	Chromium	Copper
Galvanizing department	0.848	97.024	0.962	0.124	1.042
Grindery	4.497	0.210	94.733	0.080	0.480
Chemical polishing	6.160	4.860	15.360	5.900	67.720
Acid embossing	35.170	2.060	15.470	0.000	47.300

mical processing of glass are characterized by low pH and a very high concentrations of heavy-metal ions, as well as by very high contents of sulphates, suspended solids, fluorides, and silica. There is a strong relationship among zinc concentration, sulphate content, and suspended solids (figs. 1 and 2). Lead concentration follows a different behavioral pattern (fig. 2). Sulphate concentrations in the wastewater amounting to several score thousands of mg/dm^3 are sufficiently high for precipitation of PbSO_4 . The concentration of the latter is, however, substantially higher than it might be expected from the solubility product. Thus, it can be concluded that the precipitation of this compound is not the only factor affecting the concentration of lead. The correlation between suspended solids and heavy-metal concentrations indicates that suspended matter present in the wastewater has the ability to adsorb heavy metals.

Another type of wastewaters carrying very high concentrations of heavy metals are those generated in the grinding process. The effluent from the grindery is additionally characterized by a very high pH value (10–11), an intense turbidity (which is due to the

presence of dispersed suspended matter), an opalescent grey and white colours, and by a high concentration of organics (measured in terms of permanganate COD). At a pH as high as 10–11, copper and nickel should occur in trace amounts, whereas lead and zinc should not exceed the conventional level resulting from the dissolution of plumbate and zincate. This was not stated in our study, in which heavy-metal concentrations were

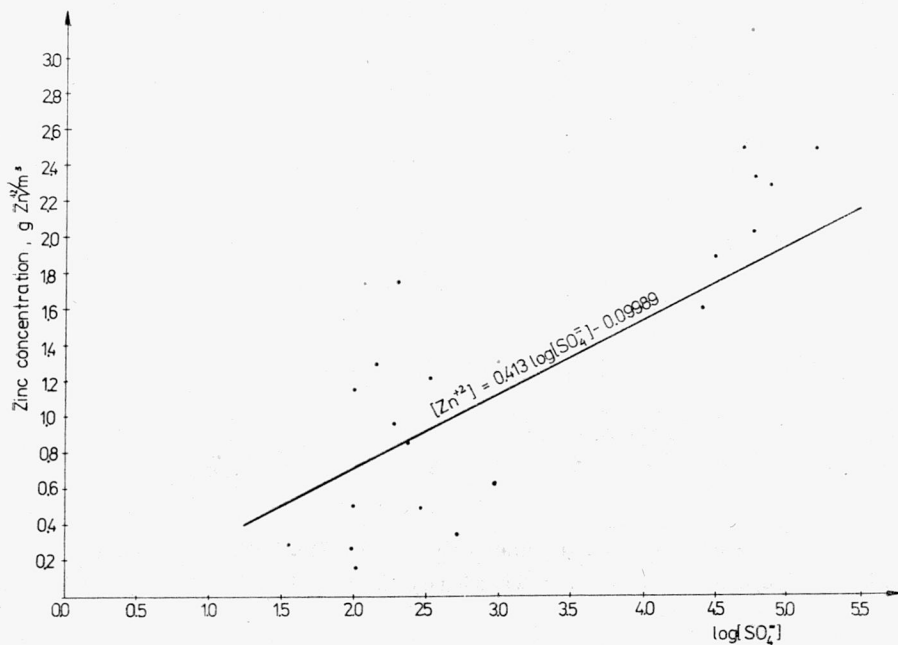


Fig. 1. Correlation between zinc and $\log[\text{SO}_4^-]$ in wastewater generated in chemical processing of glass

Rys. 1. Korelacja między stężeniem cynku a $\log[\text{SO}_4^-]$ w ściekach pochodzących z chemicznej obróbki szkła

always higher than the theoretical values calculated for a pH between 10 and 11. The increased heavy-metal concentrations can be attributed to the presence of water-soluble organic complexes of metals.

Since lead and zinc were present in all the wastewater samples, these two metals were selected as the examples to study correlation between lead and zinc concentrations and permanganate COD. The results are plotted in figs. 3 and 4, respectively, the strong correlation is quite apparent. The correlation between heavy-metal concentration, suspended solids, and sulphates is not so evident for this type of wastewater. To avoid environmental contamination by heavy metals all of the wastewaters generated in glass-making processes should be subjected to a thoroughly selected sequence of treatment processes before being discharged into a watercourse.

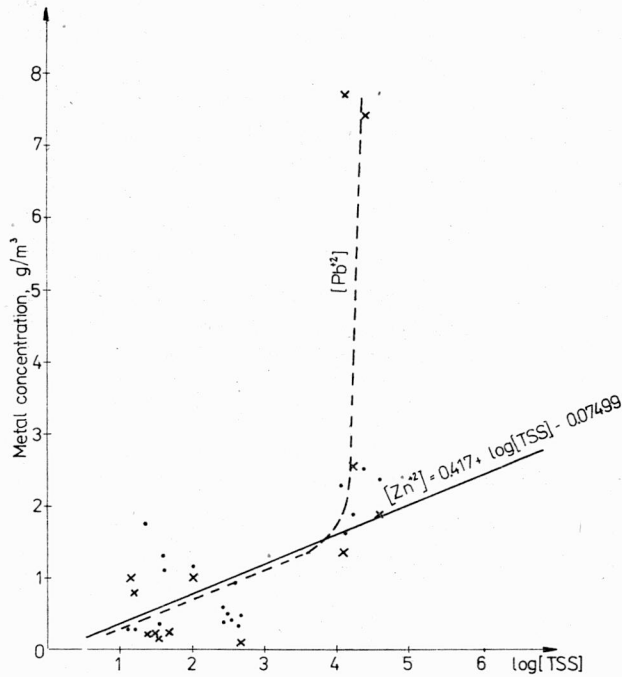


Fig. 2. Zinc and lead concentrations versus log TSS in acidic wastewaters

Rys. 2. Stężenie cynku i ołowiu w zależności od logarytmu zawiesin ogólnych w ściekach kwaśnych

3. REMOVAL EFFICIENCIES

The lab. experiments on lead, zinc, copper, and nickel removals were carried out over a period of one year. Wastewaters generated in the chemical processing of glass were subject to chemical precipitation alone, in order to determine the removals of low soluble heavy-metal compounds. Grindery wastewaters were subject to alum and ferric sulphate coagulation, sedimentation, and filtration processes in order to remove heavy metals.

3.1. WASTEWATERS FROM CHEMICAL PROCESSES

Precipitation process involved lime treatment which enabled both the adjustment of pH to the required value and achieving high degrees of removal. Residual metal concentrations were measured in the effluent from the precipitation and sedimentation processes. The removals of lead, zinc, copper, and nickel as a function of pH are plotted in figs. 5, 6, 7, and 8, respectively. From fig. 5 it follows that with the increasing pH value

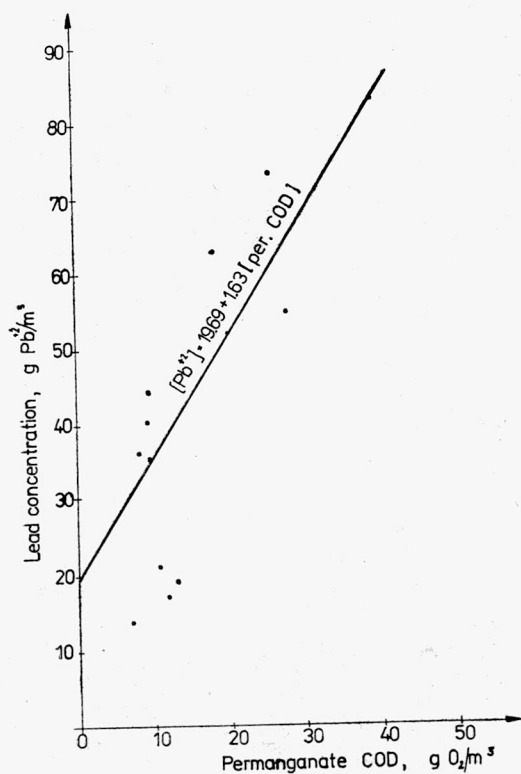


Fig. 3. Correlation between lead and permanganate COD in wastewaters from grindery department

Rys. 3. Korelacja między stężeniem ołowiu a utlenialnością nadmanganianową w ściekach z wydziału szlifowania szkła

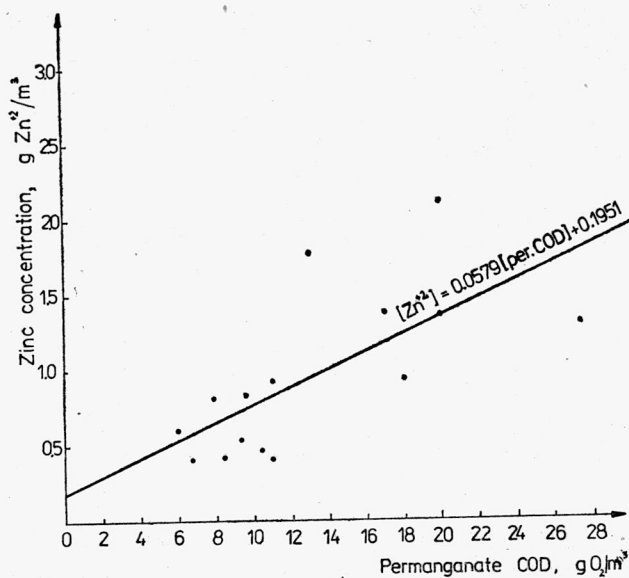


Fig. 4. Correlation between zinc and permanganate COD in wastewaters from grindery department

Rys. 4. Korelacja między zawartością cynku a utlenialnością nadmanganianową w ściekach z wydziału szlifowania szkła

to about 10, the lead removal efficiency increases. Further pH increase above 10 leads to the formation of plumbates increasing the concentration of residual lead.

After completion of the precipitation process which was carried out at pH between 9.5 and 10.0 the high lead removal efficiency resulted in the low metal concentrations in the effluent varying from traces to $0.25 \text{ g Pb}^{+2}/\text{m}^3$, whereas theoretical values for identical process conditions ranged from 10^{-6} to 10^{-7} moles/ dm^3 , i.e. 0.207 to 0.0207 $\text{g Pb}^{+2}/\text{m}^3$. The theoretical residual lead concentrations were calculated according to the formula

$$\log[\text{Me}^{n+}] = n(14 - \text{pH}) - pK_{so}, \quad (1)$$

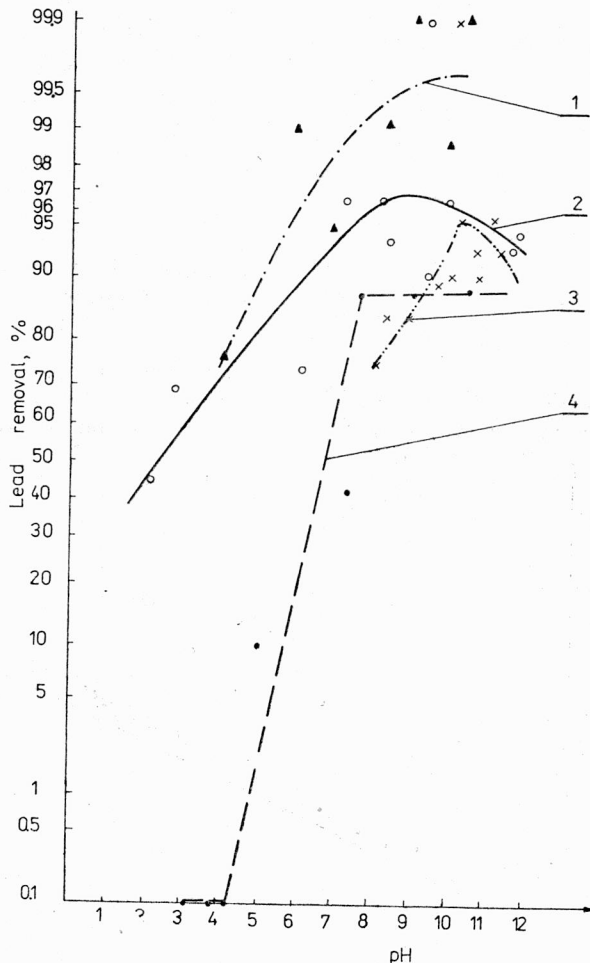


Fig. 5. Lead removal by chemical precipitation

1 and 2 – wastewaters from chemical polishing, 3 – wastewaters from galvanizing, 4 – wastewaters from acid embossing

Rys. 5. Usuwanie ołowiu w procesie chemicznego strącania

1, 2 – ścieki z chemicznego polerowania, 3 – ścieki po galwanicznej obróbce szkła, 4 – ścieki po matowaniu szkła

where: Me^{n+} is residual concentration of heavy metal in moles/dm³, n denotes valency, and $pK_{so} = -\log K_{so}$.

The comparison of both theoretical and experimental results shows that, if pH is kept within the optimum range, i.e. between 9.5 and 10.0, the high removal efficiency is due to the precipitation process solely. At pH of about 6.0 or less, the precipitation efficiency is influenced by presence of sulphates. Curves 1 and 2 in fig. 5 represent lead removals from wastewaters characterized by very high sulphate concentrations (max. 61 000 g SO₄⁻²/m³). At pH values not exceeding 6.0 the efficiency of lead removal is contributed by the co-precipitation of lead sulphate and calcium sulphate. The concentration of residual lead at pH = 6.0 varies from 0.45 to 0.55 g Pb⁺²/m³ and is consistent with the theoretical

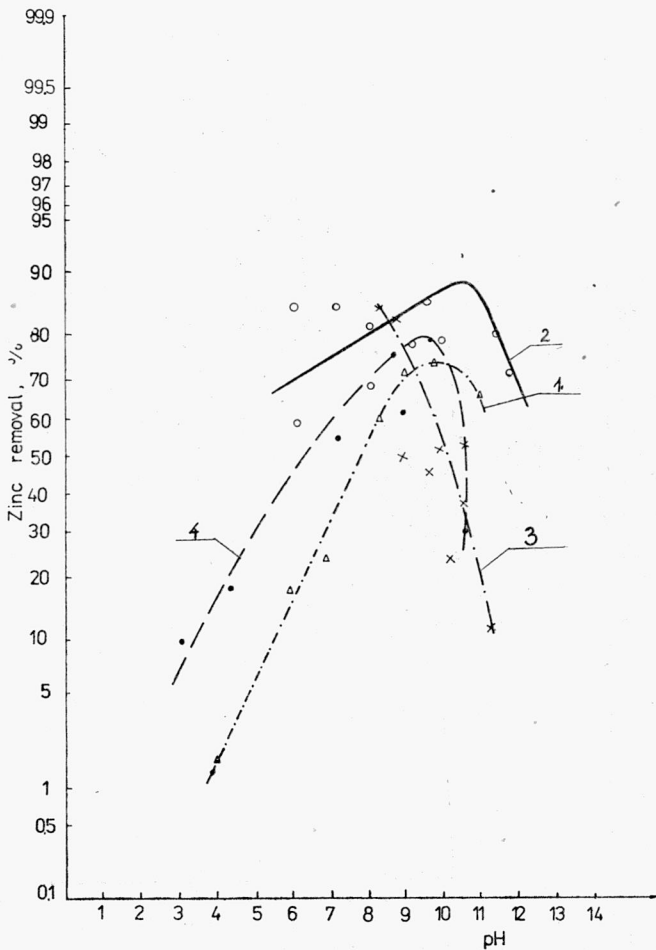


Fig. 6. Zinc removal by chemical precipitation

For explanations see fig. 5

Rys. 6. Usuwanie cynku w procesie chemicznego strącania

Objaśnienia jak na rys. 5

values resulting from the solubility product for PbSO_4 . Curves 3, 4 in fig. 5 shows lead removals from wastewaters with low sulphate concentrations (at the most $200 \text{ g SO}_4^{-2}/\text{m}^3$). The shape of this curve is typical of lead removal from low sulphate solutions.

The relationship between pH and zinc removal is illustrated in fig. 6. Of all the heavy metals tested, the percentage of zinc removal is the lowest. The latter is strongly influenced by the concentration of hydrogen ions. For acidic wastewaters the optimum pH values vary from 9.5 to 10.0. For the galvanizing department effluent which is characterized by higher initial pH the best removal efficiencies are obtained at pH of about 8.0. Further increase in pH leads to the formation of zincates and to the increased residual zinc con-

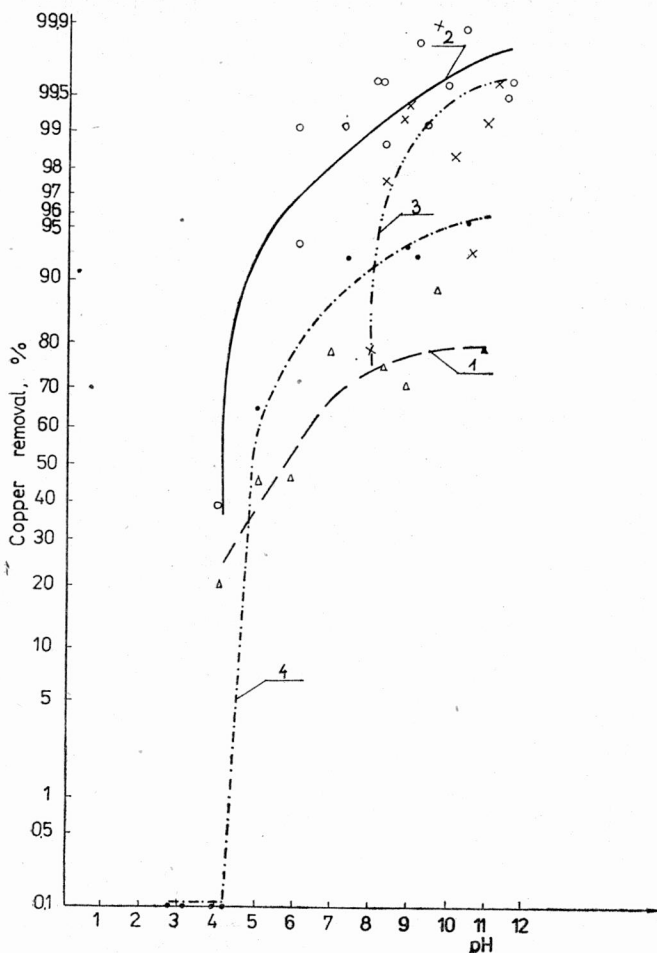


Fig. 7. Copper removal by chemical precipitation

For explanations see fig. 5

Rys. 7. Usuwanie miedzi w procesie chemicznego strącania

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centrations. After completion of the precipitation process at optimum pH the concentration of residual zinc was from 0.16 to 0.37 g Zn^{+2}/m^3 , whereas the theoretical value calculated from the formula (1) amounted to about 0.65 g Zn^{+2}/m^3 .

Copper removals are shown in fig. 7 from which it follows that the copper removal efficiency increases with raising pH. The concentration of residual copper at pH 10.0 is below 0.1 g Cu^{+2}/m^3 , whereas the theoretical value calculated for pH 10.0 from the formula (1) approaches zero. Further increase in pH was without any effect.

The relationship between nickel removal and pH is presented in fig. 8. Nickel removal proceeded in a similar manner as that of copper and was directly proportional to hydrogen ion concentration. The residual concentrations of nickel amounted to about 0.1 g

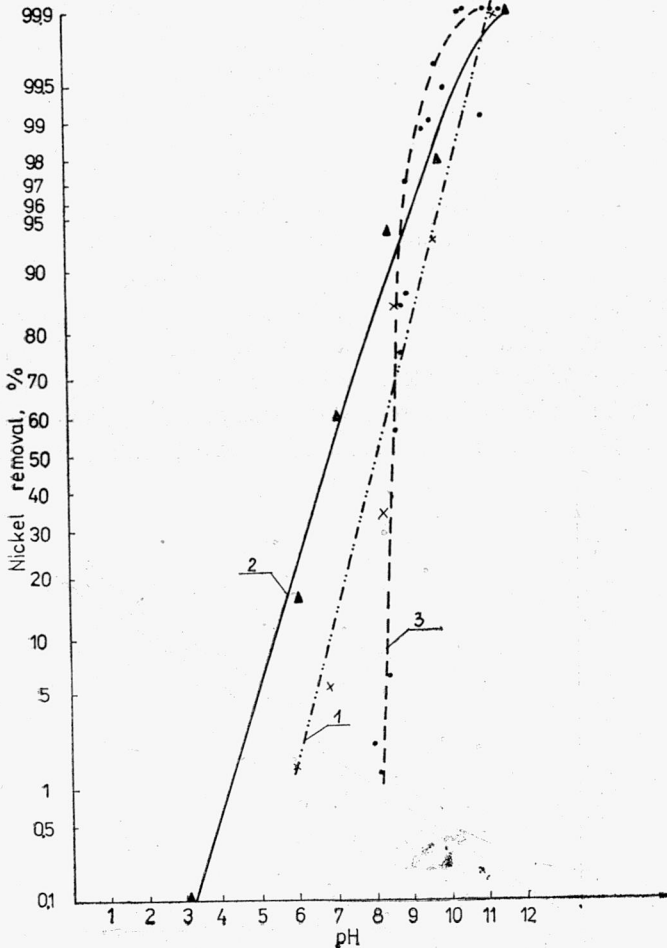


Fig. 8. Nickel removal by chemical precipitation

For explanations see fig. 5

Rys. 8. Usuwanie niklu w procesie chemicznego strącania

Objaśnienia jak na rys. 5

$\text{Ni}^{2+}/\text{m}^3$ and $0.28 \text{ g Ni}^{2+}/\text{m}^3$ after precipitation at pH 11 and pH 10.0, respectively; pH 10.0 being optimal for lead, zinc, and copper removals.

These investigations have shown that if the precipitation process is conducted at pH between 9.5 and 10, the concentrations of lead, zinc, copper, and nickel will decrease to a level which is tolerable in natural waters.

3.2. GRINDERY WASTEWATERS

Wastewaters generated in the grinding process were subjected either to sedimentation alone in order to determine the removal of heavy metals together with settleable solids or to coagulation process followed by 30 min sedimentation in order to establish the removal of lead along with colloidal matter. The removals of the remaining metals could not be determined because their concentrations in raw wastewaters were too low to prevent analytical errors. In the coagulation process alum and ferric sulphates were dosed either separately or jointly as mixed coagulants. Efficiency of lead removal was established for different pH ranges. The results obtained indicate that it is primarily pH and not type or dose of the coagulants which influences the removal efficiency of the metals. pH is also a basic factor affecting organics removal determined as permanganate COD. This relationship indicates that lead present in the wastewaters from grinding processes occurs in the form of an organic lead complex. Lead concentration versus permanganate COD is plotted in fig. 9. The highest lead removal efficiency (95%) from secondary effluents by coagulation and sedimentation processes was achieved at ferric sulphate dose of $150 \text{ g}/\text{m}^3$,

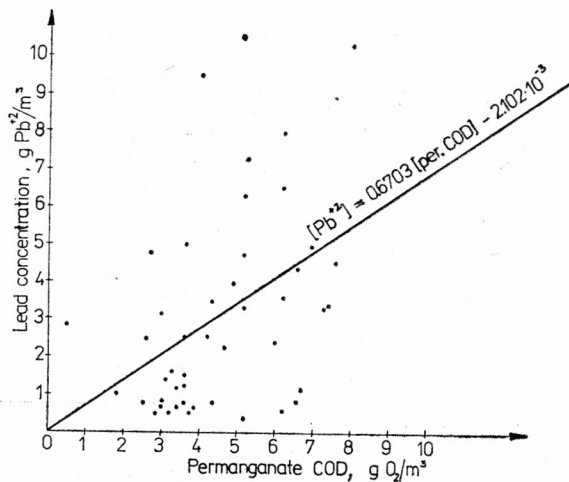


Fig. 9. Correlation between lead concentration and permanganate COD in wastewaters from grinding processes (after completion of treatment)

Rys. 9. Korelacja między stężeniem ołowiu a utlenalnością nadmanganianową w oczyszczonych ściekach poszlifierskich

pH 6, and settling time 30 min. The optimum pH for alum and ferric sulphate ranged from 5 to 6. It also provided the highest removal efficiencies of organics. A high removal of lead was also obtained by coagulation with ferric sulphate at pH ranging from 10.0 to 10.5 (which is close to raw wastewaters pH) followed by 30 min settling. Under these conditions $Pb(OH)_2$ was removed together with $Fe(OH)_3$ flocks. A further increase in lead removal resulting in trace amounts of lead in the effluent was achieved in the following system: coagulation at optimum pH, settling during 2 hours and filtration on a sand bed characterized by effective diameter of grains $d_{60} = 0.75-1.2$ mm and $d_{10} = 0.5-0.8$ mm, at filtration velocity 5 m/h.

For wastewaters carrying large amounts of suspended solids, experiments were run to remove heavy metals together with the suspended solids. The latter were clarified either by sedimentation or by filtering through filter a paper. The results are given in fig. 10.

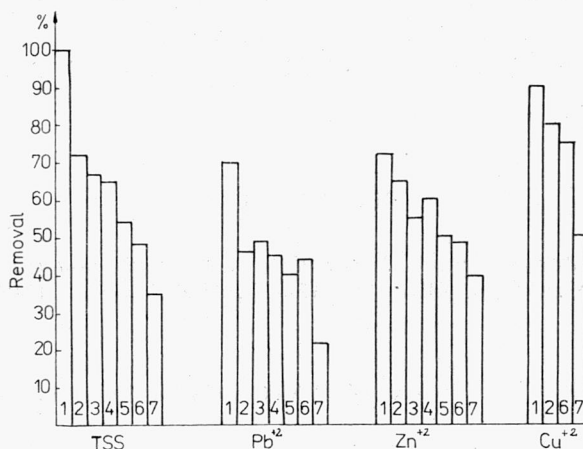


Fig. 10. Removal efficiencies for TSS, lead, zinc, and copper contained in wastewater from grinding processes

Rys. 10. Efektywność usuwania zawiesiny ogólnej, ołowiu, cynku i miedzi ze ścieków poszlifierskich

Removals of heavy metals achieved in this way justify the use of such a treatment method. The highest removal efficiencies were obtained for copper, zinc, and lead. The experimental results indicate also that in order to reduce the concentration of pollutants (especially heavy metals) and make the wastewater treatment both simpler and cheaper it is reasonable to employ sedimentation prior to other treatment processes.

4. CONCLUSIONS

1. Wastewaters generated both in the chemical processing of glass and in the grinding operations are characterized by high concentrations of heavy metals.
2. Wastewaters produced in glass-making processes are toxic. They cannot be discharged into natural water streams or sewerage systems without adequate treatment.

3. There is a strong relationship between lead or zinc and organic matter (permanganate COD) present in the wastewater from grinding processes. This indicates that heavy metals contained in the wastewater form water-soluble complexes with organic matter, thus they should be removed jointly.

4. For zinc present in acidic wastewaters (from chemical processing) two linear relationships were established. These relationships are not so evident for lead.

5. If heavy metals occur in highly turbid wastewaters with high TSS, they are attached to the available surface area of suspended matter. In that particular case the treatment process should be preceded by sedimentation.

6. To remove lead, copper, nickel, and zinc from acidic wastewater generated in chemical processing of glass, it is advisable to employ chemical precipitation at pH between 9.5 and 10 followed by settling for 2 hours.

7. Heavy metals occurring in highly turbid wastewaters from the grindery department form complexes with organic matter. The treatment process for those wastewaters should include ferric sulphate coagulation at pH 6.0, sedimentation for 2 hours, and filtration through a sand bed.

REFERENCES

- [1] KOWAL A. L., ŚWIDERSKA-BRÓŹ M., *Investigations on wastewater treatment technology from glass processing industry*. Stage II, part I. Report of I-15 of Technical University of Wrocław, Wrocław 1980.

USUWANIE METALI CIĘŻKICH ZAWARTYCH W ŚCIEKACH Z HUT SZKŁA

Zbadano skład fizykochemiczny ścieków powstających w hutach szkła. Szczególną uwagę zwrócono na stężenia metali ciężkich i skuteczność ich usuwania. Ścieki z chemicznej obróbki szkła poddano strącaniu chemicznemu i 2-godzinnej sedymentacji w celu wyznaczenia stopnia usunięcia trudno rozpuszczalnych związków metali ciężkich. Ścieki poszlifierskie oczyszczano w procesie koagulacji siarczanem glinowym i żelazowym, a następnie poddawano sedymentacji i filtracji. Najlepsze wyniki dla kwaśnych ścieków z chemicznej obróbki szkła otrzymano przez strącanie chemiczne (przy pH zmieniającym się od 9,5 do 10) z następującą po tym 2-godzinną sedymentacją. Ścieki poszlifierskie, zawierające kompleksy organiczne metali ciężkich, powinny się oczyszczać w układzie technologicznym: koagulacja siarczanem żelazowym (przy pH = 6,0), 2-godzinna sedymentacja i filtracja przez złoża piaskowe.

ELIMINIERUNG VON SCHWERMETALLEN AUS DEN ABWÄSSERN DER GLASHÜTTEN

Anhand von umfangreichen, physikalisch-chemischen Abwasseranalysen aus Glashütten (Glas- und Kristallglaswerke), besonderer Augenmerk wurde den Schwermetallen und deren Eliminierung gewidmet.

Die Abwässer aus der chemischen Glasbearbeitung wurden chemisch gefällt und anschließend zwei Stunden sedimentiert. Den Abwässern aus Kristallschleifereien werden im Koagulationsverfahren Aluminiumsulfat und Ferrosulfat zugegeben; dann folgt Sedimentation und Filtration.

Beste Ergebnisse bei der Reinigung der ersten Abwasserart lieferte die chemische Fällung im Bereich $9,5 < \text{pH} < 10$ plus Sedimentation. Abwässer aus dem Schleifprozeß, die Metalle auch in der Form von organischen Komplexverbindungen beinhalten, sollte man mit Ferrosulfat bei $\text{pH} = 6,0$ ausfällen; es folgt Sedimentation und Filtration in einem Sandbettfilter.

УДАЛЕНИЕ ТЯЖЁЛЫХ МЕТАЛЛОВ, СОДЕРЖАЩИХСЯ В СТОЧНЫХ ВОДАХ СТЕКОЛЬНОЙ ПРОМЫШЛЕННОСТИ

Был исследован физикохимический состав сточных вод, происходящих от завода, изготовляющего стекла и хрустали. Особое внимание уделено концентрации тяжёлых металлов и эффективности их удаления. Сточные воды от химической обработки стекла были подвергнуты химическому осаждению и двухчасовой седиментации для определения степени удаления труднорастворимых соединений тяжёлых металлов. Сточные воды другого вида (происходящие от механического шлифования) очищались в процессе коагуляции с сульфатом железа (III) и алюминия, а затем подвергались седиментации и фильтрации. Наилучшие результаты для кислых сточных вод от химической обработки стекла были получены путём химического осаждения (при pH изменяющемся от 9,5 до 10) с последующим после этого двухчасовой седиментацией. Сточные воды от процессов механического шлифования, содержащие органические комплексы тяжёлых металлов, должны очищаться с помощью коагуляции с сульфатом железа (III) (при $\text{pH} = 6,0$), двухчасовой седиментации и фильтрации через песчаные слои.