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## TREATMENT OF WASTEWATER RESULTING FROM STEEL PHOSPHATIZING PROCESS

Physical-chemical characteristics of the wastewater from steel-phosphatizing process has been presented and the results of the wastewater treatment by chemical coagulation with lime milk. Optimum precipitation of heavy metals occurred at pH range from 6.5 to 7 whereas effluent concentration of phosphates was equal to about 100 g/m<sup>3</sup>. The pH increase resulted in better phosphate removal and in the higher sludge volume.

### 1. INTRODUCTION

The 19th century discovery of excellently preserved steel objects dating back to the Roman times drew attention to the possibility of protecting the surfaces of steel products against corrosion by artificially formed coating, the composition of which is similar to that of corrosion products. At the beginning of the 20th century a number of methods were developed for coating steel with a thin layer of phosphates. However, this coating was too thin to protect sufficiently from corrosion. It was only the use of monosubstituted zinc phosphate instead of ferrous phosphate that enabled a wide use of phosphate coating for anti-corrosive protection against corrosion. Further progress was recorded when phosphatizing process was shortened from 30-40 min to 1-5 min by the addition of the so-called accelerators to the bath and appeared possible to be conducted at room temperature. In many cases phosphate coatings supplement perfectly metallic coatings and improve the properties of other protective coatings.

A certain amount of wastewater resulting from phosphatizing processes contains rinsing water and exhausted phosphatizing baths. However, it is rinsing water that is the major wastewater source, since a complete exchange of bath takes place not more often than several times a year. The amount and composition of wastewater from phosphatizing depends on the bath type and details of the technological process. Phosphates and ions of heavy metals (Fe, Cr, Zn, Mn, and Ni) belong, as a rule, to the most

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troublesome pollutants. Because of a distinct acid reaction and the presence of phosphates and heavy metal ions, wastewater must be treated before being discharged into a receiving water body.

The studies on the removal of heavy metal ions and phosphates, described herein, were carried out using the wastewater from an existing plant producing 3–4 m<sup>3</sup>/d of wastewater of pH 4–4.5. Its average composition is the following:

phosphates	—	775 mg of P <sub>2</sub> O <sub>5</sub> /dm <sup>3</sup> ,
Zn	—	120 mg/dm <sup>3</sup> ,
Cr	—	50 mg/dm <sup>3</sup> ,
Mn	—	0.89 mg/dm <sup>3</sup> ,
Fe	—	0.53 mg/dm <sup>3</sup> ,
Ni	—	0.68 mg/dm <sup>3</sup> .

## 2. METHODS

Various volumes of 15% lime milk solution introduced into beakers (each containing 500 cm<sup>3</sup> of wastewater from phosphatizing) were intensively stirred for 10 min. Then the contents of the beakers were transferred into the calibrated 500 cm<sup>3</sup> cylinders (of 6 cm in inner diameter). The height of the precipitated sludge was measured every half an hour. After 4 hr a sample of clarified supernatant was analyzed for its pH, phosphates, heavy metals and calcium ions. The concentrations of phosphates were determined colorimetrically using ammonium molybdate [1], while heavy metal and calcium ions were determined by atomic absorption spectroscopy (AAS). Thereupon the course of SS sedimentation was studied by measuring the height of the sludge layer every 1 hr. The amount of sludge as the function of time with respect to the total wastewater volume was determined in percent of the wastewater volume. Next, the optimal sedimentation time and percent volume of the sediment precipitated were determined from the plotted sedimentation curves by Rich's method [2].

## 3. RESULTS AND DISCUSSION

The time-depending characteristics of sedimentation for pH range from 6.6 to 7.6 are presented in fig. 1. At lower pH values sedimentation proceeds faster, e.g. at pH 6.6 the suspended solids are precipitated as soon as after 2 hr, while at 7.6 the precipitation occurs after 5 hr. The precipitation rate of ions versus pH is presented in table from which it can be concluded that practically total precipitation of heavy metal ions occurs at pH 6 (the detectable level for AAS method was achieved). At the same time calcium ion concentrations increase continuously with the increasing pH values from about 124 mg Ca/dm<sup>3</sup> at pH 6 to 440 mg Ca/dm<sup>3</sup> at pH 12.6.

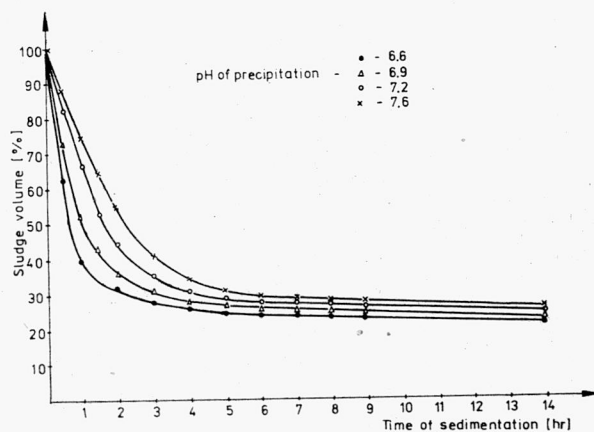


Fig. 1. Sedimentation process as the function of time at pH ranging within 6.6–7.6

Rys. 1. Proces sedymentacji jako funkcja czasu przy pH 6,6–7,6

Table

Effect of pH value on concentrations of heavy metal ions in clarified wastewater

Wpływ pH na stężenie jonów metali ciężkich w sklarowanych ściekach

No. of sample	pH value	Concentration of individual metal ions in the supernatant [mg/dm <sup>3</sup> ]					
		Ca	Fe	Mn	Ni	Zn	Cr
0	4.1	88.0	0.5	0.9	0.7	120	50
1	4.7	102.5		0.7	0.5	110	45
2	5.3	112.0		0.5	0.4	60	32
3	5.7	120.0		0.3	0.4	3.7	6.3
4	6.2	127.5			0.3	0.4	0.8
5	6.8	132.0				0.3	
6	7.3	144.0					
7	7.7	153.0					
8	8.0	168.0					
9	8.3	189.0					
10	8.7	200.0					
11	9.1	213.0				below 0.2	
12	9.5	239.0					
13	10.0	248.0				1.12	
14	10.6	264.0				2.01	
15	10.8	278.0				1.95	
16	11.0	290.0				2.20	
17	11.1	302.0				2.41	
18	11.5	330.0				2.39	
19	12.0	380.0				2.54	
20	12.2	410.0				2.68	
21	12.6	440.0				3.37	
			below 0.5	below 0.2	below 0.2		below 0.2

The influence of pH on the removal rate of phosphates is illustrated by figs. 2 and 3. The removal of phosphates below the limit of  $1 \text{ mg/dm}^3$  takes place at pH 9.5, while at pH 6 30% of phosphate ions remain still in the solution; their concentration decreases from  $800 \text{ mg/dm}^3$  to  $300 \text{ mg/dm}^3$ . With the increasing pH value, the volume of the precipitated sludge also increases (fig. 3). At pH 6 the amount of the precipitated sludge reaches 20% of wastewater volume and increases with the rising pH value, reaching 35% of the wastewater volume at pH 9.5, i.e. when practically total precipitation of phosphates takes place. This means that precipitation of 35% of phosphates present in the wastewater (i.e. decrease of concentration from  $800 \text{ mg/dm}^3$  to  $300 \text{ mg/dm}^3$ ) results in the increase of sludge volume in wastewater from 20 to 35%. Hence, it can be concluded that the water content of the sludge increases with the increasing pH value. This phenomenon is unfavourable since sedimentation of the sludge proceeds more slowly (fig. 1) and its filtrability is deteriorated.

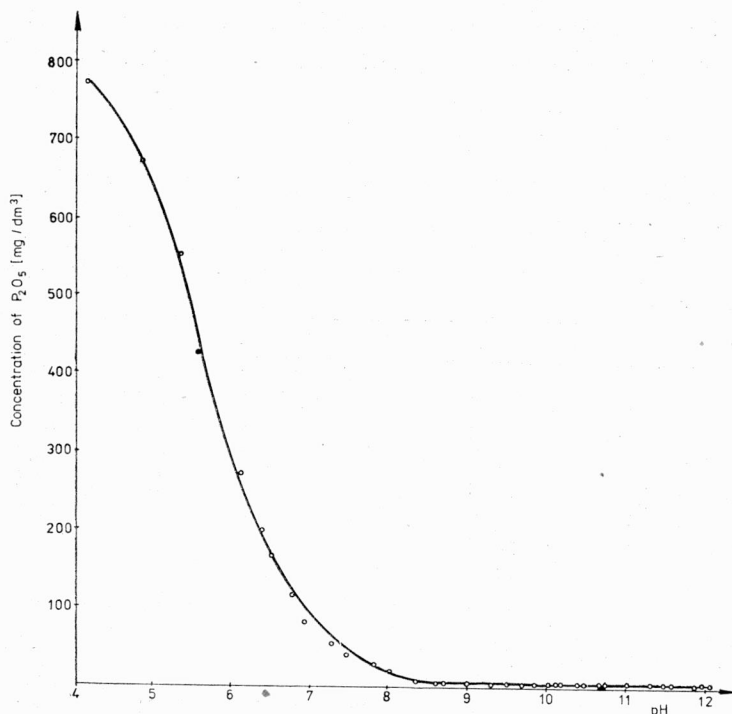


Fig. 2. Effect of pH on the rate of phosphates removal (concentrations up to  $800 \text{ mg P}_2\text{O}_5/\text{dm}^3$ )

Rys. 2. Wpływ pH na szybkość usuwania fosforanów (stężenia do  $800 \text{ mg P}_2\text{O}_5/\text{dm}^3$ )

#### 4. CONCLUSIONS

The results presented allow to formulate a preliminary concept of treatment of wastewater from phosphatizing process. Since, as a rule, the amounts of wastewater of this kind discharged by the plants are small (from a few to a dozen of cubic meters or so per

day), the problem should not be solved from point of view of water recovery but rather with respect to the environment protection via heavy metals removal from wastewaters. In larger plants where dilution of wastewater is possible, optimal precipitation of sediments taking place at pH ranging from 6.5 to 7 comprises a complete precipitation of heavy metal ions, and removal of phosphates is limited to the concentration of about  $100 \text{ mg/dm}^3$ . Volume of the sludge produced will then reach about 25%. If, however, for some reasons higher removal of phosphates is required the wastewater pH should be suitably higher. The adequate values can be determined from figs. 2 and 3. The volume

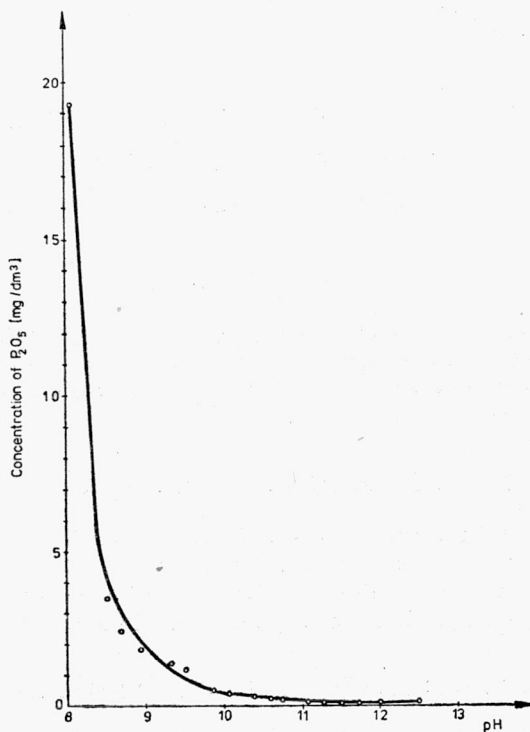


Fig. 3. Effect of pH on the rate of phosphates removal (concentration up to  $20 \text{ mg P}_2\text{O}_5/\text{dm}^3$ )

Rys. 3. Wpływ pH na szybkość usuwania fosforanów (stężenie do  $20 \text{ mg P}_2\text{O}_5/\text{dm}^3$ )

of precipitated sludge increases simultaneously with pH increase (fig. 4). The problem connected with the utilization of sludge should be considered separately. This sludge is practically of no value and cannot be processed into any useful semiproduct. Since, however, it contains heavy metals, its dumping place must be suitably protected. The sludge volume may be in tenfold reduced by filtration on filter presses, which would, however, increase considerably the investment costs and evidently complicate the operation and maintenance of a treatment plant.

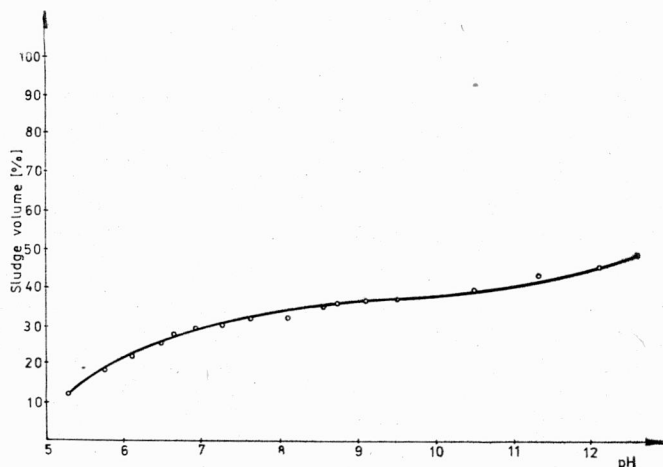


Fig. 4. Influence of pH on the volume of sludge obtained (after optimal time)

Rys. 4. Wpływ pH na objętość otrzymanego osadu (po czasie optymalnym)

#### REFERENCES

- [1] AGRANONIK P. et al., *Thickening and dewatering of wastewater sludges*, WKiC, Warszawa 1976.  
 [2] Polish Standard PN-73/C-4337. *Determination of phosphorus compounds concentration*. Sheet 03. *Determination of the dissolved orthophosphates by extraction-colorimetric method using ammonium molybdenate and stannous chloride as reducing agent*.

#### OCZYSZCZANIE ŚCIEKÓW POCHODZĄCYCH Z PROCESÓW FOSFATACJI

Przedstawiono fizykochemiczne cechy ścieków z procesów fosfatacji stali oraz wyniki oczyszczania ścieków mlekiem wapiennym przez koagulację chemiczną. Optymalne strącanie metali ciężkich stwierdzono przy pH 6,5–7, podczas gdy stężenie siarczanów w odpływie wynosiło około 100 g/m<sup>3</sup>. Przy wyższym pH stwierdzono większą wydajność usuwania fosforanów i większą objętość osadu.

#### REINIGUNG DER ABWÄSSER AUS DER PHOSPHATIERUNG

Dargestellt werden sowohl die physikalisch-chemischen Eigenschaften der Abwässer aus der Stahl-Phosphatierung wie auch die Ergebnisse der Abwasserreinigung im chemischen Fällungsverfahren mittels Kalkmilch. Beste Fällungsergebnisse der Schwermetalle waren bei pH-Werten zwischen 6,5 und 7,0 feststellbar, wobei die Sulphatkonzentration im Abfluß etwa 100 g/m<sup>3</sup> betragen hat. Höhere pH-Werte führen zur besseren Eliminierung von Phosphaten bei größeren, spezifischen Schlammengen.

#### ОЧИСТКА СТОЧНЫХ ВОД, ПРОИСХОДЯЩИХ ОТ ПРОЦЕССОВ ФОСФАТАЦИИ

Представлены физикохимические свойства сточных вод от процессов фосфатации стали, а также результаты очистки сточных вод посредством химической коагуляции известковым молоком. Оптимальное осаждение тяжёлых металлов выявлено при pH 6,5–7, в то время как концентрация сульфатов в стоке составляла около 100 г/м<sup>3</sup>. При высшем pH выявлено большую эффективность удаления фосфатов и больший объём осадка.