Treatment of chromic tannery wastes

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ABSTRACT

The new method for treatment of waste waters from tanneries containing chrome and large amounts of other inorganic compounds has been studied. It was found that the addition of cement at suitable temperature and pH results in a decrease of Cr(III) and Fe(III) contents. The method has been verified in practice in five tanneries. It is very simple, cheap and effective in all cases with very different composition of tannery chrome-containing wastes.

INTRODUCTION

Leather tanning processes by means of chrome agents produce large quantities of waste waters. They contain among others Cr(III) and significant amounts of organic compounds. Current amounts of these waste waters produced Poland is estimated to be 0.5 million of cubic meters per year. This amount was even larger in past years and reached 4 million c.m per year [1]. Decrease of production accompanied by an increase in the utilization rate of Cr(III) during tanning processes from previous 60-70% to current 90% had substantial influence on reduction of the waste water amount.

Generally chrome tannery wastes differ considerably one from another under respect of both chrome and organic compounds concentration. Chrome concentration ranges from 1.0 to 2.0 g/dm^3. Concentration of organic compounds depend mostly on the sort of leather, type of tanning processes and on other conditions. These are reasons for substantial differenties in COD (Chemical Oxygen Demand) and BOD5 (Biological Oxygen Demand) which range for COD from 2000 to 5000 g/m^3 and for BOD from 700 to 2000 g/m^3. Concentration of Fe_2O_3 ranges from 0.2 to 0.3 g/m^3 and the usually high cocentration of chlorides range from 1 to 5 g/m^3. Similar wastes are formed also after utilization of leather scraps. For example after utilizing leather scraps into a fertilizing leather powder about 10000 c.m. per year of waste water is formed containing 0.6-1 g/dm^3 of Cr(III).

Tannery wastes containing Cr(III) according to literature data can be utilized into chrome salts by treating them with sodium lye or sodium chromate [2]. A conventional method of chrome wastes treatment is based on adjusting suitable precpitations conditions for $Cr(OH)_3$ and than filtration of precipitate [3]. Among other methods the extraction of chrome compounds with an excessive amount (17-35% to waste water weight) of sulfuric acid should

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be mentioned [4], as well as the suggestion of plasma burner application for burning the wastes in order to obtain metallic chrome [5].

A basic factor which disturbs the Cr(III) removal from tannery wastes is the high concentration of organic compounds. It precludes the application of conventional methods i.e. $Cr(OH)_3$ precipitation [3] since during neutralization by means of $Ca(OH)_2$ or NaOH a sedimentation of $Cr(OH)_3$ is not observed and its filtration is practically impossible. That is why neutralization of waste waters with $Ca(OH)_2$ mostly applie in polish tanneries was eeffective only partially and only at low concentrations of organic compounds. Neverthless, the method of direct precipitation of $Cr(OH)_3$ from waste waters seemed to be both the cheapest and the simplest way.

The solution of this problem required however reaserch in selecting such precipitation conditions that would make the precipitate of $Cr(OH)_3$ easy for sedimentation and filtration. Beside of that a method for utilization of the obtained precipitate was expected to be suggested.

EXPERIMENTAL PART

Experiments were carried out on waste waters from the utilization of chrome tanned leather at a plant in Tuczno Krajenskie [6]. These wastes represent a brownish liquid with a disagreeable odor and visible suspension. Their temperature is 60-80°C, pH is 4.8 to 5 and density is 1.03 g/cm^3. The investigated waste waters contained (in g/dm^3): Cr(III) 0.6-1 about 0.1 Fe_2O_3 and on the average 0.1-0.3 of Al_2O_3, 0.1 SO_4^{2-}, 4.0-5.0 of Cl^-. Particularly high was the concentration of organic compounds. COD ranged from 30 to 40 g/dm^3 and BOD5 from 10 to 20 g/dm^3. Total suspended solids amounted on the average 11 g/dm^3. The organic compounds concentration was several times higher than is typical for tannery wastes.

First the samples were treated with a NaOH solution (conc. 45%) until pH equal to 8. $Cr(OH)_3$ formed at those conditions did not settle. Various flocculants were used to force its sedimentation, for example: polyacrylamides (Polish "Rokrysole" and American "Separan"), starch (Polish "P-26") or surface-active agents ("Sapogen T"). These means were without effect neither the application of $FeCl_3$. Only the application of $Al_2(SO_4)_3$ showed to some extent to be effective but the waste water had to be previously diluted five times with water. However the obtained slurry was practically unfilterable and the rate of flocculant consumption reached 35 kg per c.m. of diluted waste water.

Surprisingly good results were obtained when about 1% of cement was mixed with fresh waste water and the mixture was boiled. Rapid sedimentation was then observed and after 3 min. the slurry was reduced to 25% of the previous mixture volume. These preliminary results formed a basis for methodical researches. At the same time attention was paid to the fact that precipitation from fresh waste water was easier than from waste stored for 10 days. The reason is known phenomenon aging of colloid. Examined samples contain the major part of hydrated chrome oxides in the form of colloids.

The results of sedimentation researches of waste waters from Tuczno Krajenskie are shown in Fig. 1 and Fig. 2. Coordinates of the system are nf and t, where nf is percent ratio of the thickened suspension volume to suspention initial volume and t is duration line time of the process. The addition of 2.5% cement to the waste water was admitted to be advatageous.

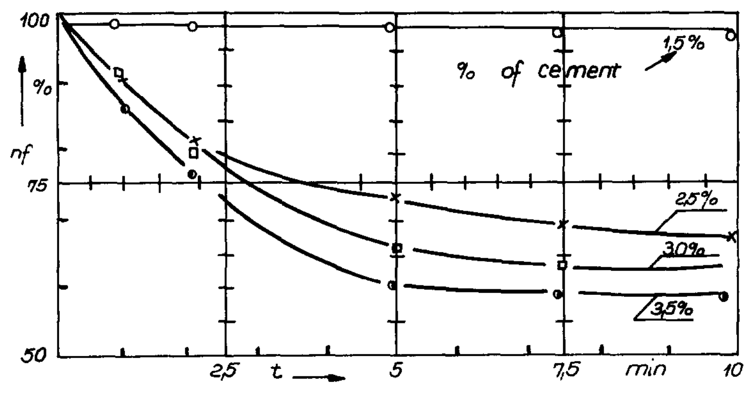

Figure 1. Sedimentation curve of $Cr(OH)_3$ precipitates at various quantities of added cement; 1-1.5%, 2-2.5%, 3-3.0% 4-3.5% of cement

In Fig. 2 the sedimentation curves are shown at various pH and after adding of 2.5% cement. The value of pH 8 was admitted to be most advantageous.

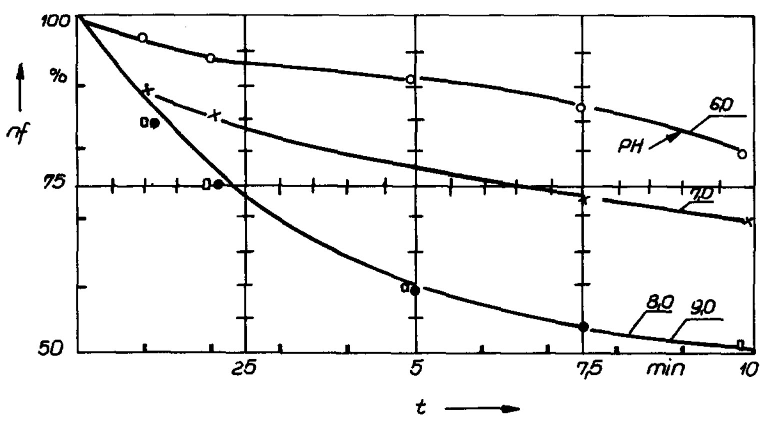

Figure 2. Sedimentation curve of $Cr(OH)_3$ precipitates at various pH and addition 2.5% of cement; 1-pH 6.0, 2-pH 7.0, 3-pH 8.0, 4-pH 9.0

Microscopic examinations showed that the action of cement lies in the aggregetion of solid particles and in the formation of large size agglomerates with an apparently higher sedimentation rate than the initial particles.

The obtained slurry was filtrated with a a laboratory frame press under the pressure of 0.3-0.4 MPa and at temp. of 353-363 K. Filtration curves for filter cloth of type BT-17 and BT-41 are shown in Fig. 3.

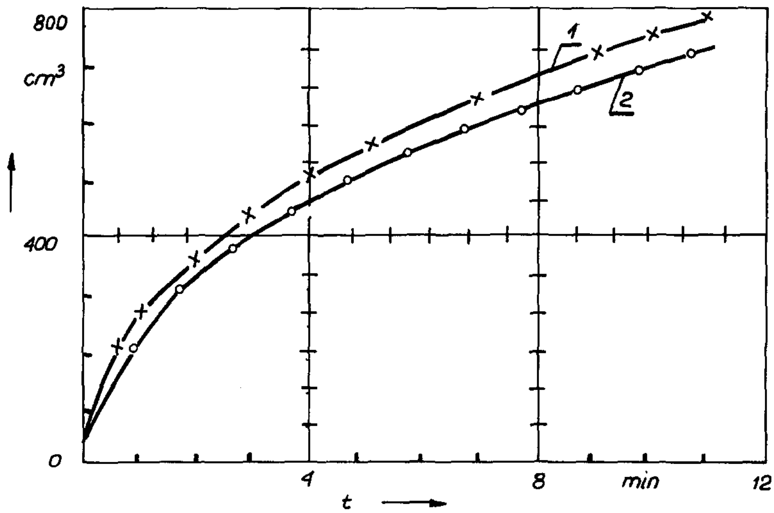

Figure 3. Filtration curve of thickened slurry containing $Cr(OH)_3$ sediments precipitated by addition of 2.5% cement at pH 8; 1-filter cloth BT-17, 2-filter cloth PT-41

Achieved filtration rates (300-350 $dm^3/m^2/h$) should be admitted as relatively high. The filtrate contained less than 0.01 ppm of Cr(III) and Fe_2O_3. COD and BOD5 were reduced by half. The obtained waste water like filtrate can be after dilution with municipal sewage further cleaned in conventional biological treatment plants.

Cakes from the filter press were stored for 14 days and changes in their consistency were examined. A setting process of precipitates was observed which after 7-10 days formed a hard, brittle body (similar a plaster). These precipitates contained in average: 1-1.5% Cr(III), 0.8-1% Fe_2O_3, up to 30% CaO and 30% SiO_2 (of dry solids). H_2O content was from 66 to 72%.

Reaserch on utilization of precipitates were carried out later and took several years. They resulted in developing among others the method of precipitates application as the component for concrete in ratio of 5% to applied cement amount [7].

CONCLUSIONS

On the ground of waste water treatment reaserch results from Tuczno Krajenskie the simple method was developed for treatment chrome wastes containing large amount of organic compounds.

Addition of cement accompanied by suitable process conditions adjustment make possible sedimentation of $Cr(OH)_3$ in the presence of high organic compounds concentrations as well as the good filtration of obtained slurry [8]. Flow diagram of typical chrome tannery waste water treatment plant was shown in Fig.4.

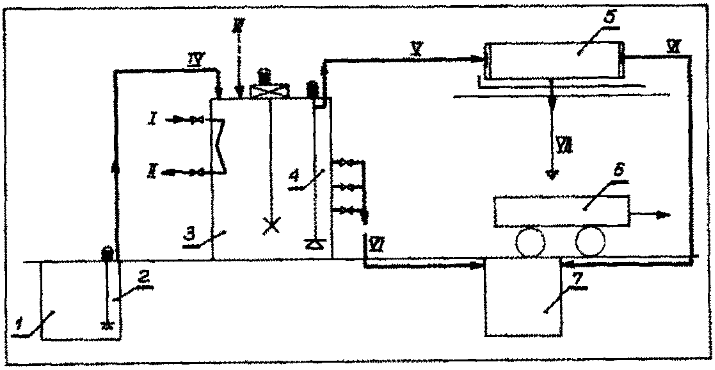

Figure 4. Flow sheet of chrome tannery waste waters treatment plant; 1 - waste water tank, 2, 4 - immersed pumps, 3 - reactor, 5 - filter press, 6 - trailer for cake removal. I - steam, II - condensate, III - cement, IV - waste water, V- thickened slurry, VI- filtrate, VII- cake

First plant running according to developed method was started up in Tuczno Krajenskie in the year of 1988. Then five other various copacity plants were constructed at tanneries in the years of 1989-1992. Currently about 30 000 c.m. chrome tannery waste waters per year can be cleaned using presented method.

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