THE NEUTRALISATION OF WASTE WATERS CONTAINING STRONG INORGANIC TOXICANTS

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ABSTRACT. This paper presents neutralization of residual waste waters containing trivalent iron cyanide complex in alkaline solution by chemical oxidation with hypochlorite. Reactive reagent is sodium hypochlorite with 13% free chlorine and sodium hydroxide, necessary for alkaline pH, 11-12. There are different sources waste waters containing $K_3[Fe(CN)_6]$: like: inorganic industries, thermal steel treatment, pigments, photographic industries. The method is based on decomplexation reaction between trivalent iron cyanide complex potassium salt and sodium hypochlorite at 70°C when $K_3[Fe(CN_6]$ become not dangerous red – brown ferric oxihydroxide in form of α FeO(OH). Residual content of total cyanide was determined photometrical according to SR ISO 8466-1, at 578 nm. Efficiency of chemical oxidation was evaluated by chemical volumetric analysis of iron content in FeO(OH) extracted, in the same time with trivalent iron cyanide complex destruction.

Keywords: oxidation, waste waters, chlorine, cyanide

INTRODUCTION

Electronic, electrotechnics industries, also electroplatings works produce a large variety of waste waters containing heavy metals, toxic anions like F, CN, cyanides complexes with Zn, Cu, Cd, Ag, or Fe, which are strong toxicants. Their constant of stability makes difficult treatment and technological methods for relive or detoxification by chemical, ion-exchange, burning, dilution etc. Simple salt cyanide or complexes cyanides, have an acute toxicity and are poisons for human and other animals exposed to him, via water, air, soils, dusts. These chemicals enter the body by ingestion, inhalation. However, in most cases, the toxic effects only occur after the pollutant entered the bloodstream following absorption through either the gut, the lungs or the skin[1]. Once in the bloodstream the chemicals are circulated around the body and metabolism, usually in the liver, or are stored in various organs (Alloway BJ and Ayres DC, 1993).

Acute toxic effects are quantified by controlled experiments to determine the dose causing the immediate death of 50% of the organisms exposed*LD50 value (50-200mg)[2] .

Examples of critical (trigger) concentration for organic pollutants used in different countries are given below CN (total free) 1µg/g, CN (total complexes) 5µ/g as reference values for standards used in the Netherlands for assessing soil contamination by inorganic and organic substances.

The concentration of cyanides in drinking water is very important sins adults drink on average 1,5L/day and are therefore likely to be more rapidly affected by pollutants from this route than from the diet. A selection of some guideline values currently in use are 100µg/L (Canada Council of Ministers of the Environment), 0µg/L in USA, 200µg/L* in Canada (*=maximum acceptable values).

Among chemical methods – oxidation is a suitable process for cyanides destroying using reagent agents like chlorine, sodium hypochlorite, chlorine dioxide, ozone, $CaOCl_2$., due to their remarkable oxidation potential (1,16V- relative standard potential for ClO_2) assurance high degree of neutralization (Burtică G and Pode R, 2000).

In our country the total cyanides content is determined in accordance with SR ISO 8466-1.

The alkali cyanides, cyanides complexes of zinc cadmium copper, silver and nickel can be treated by chlorine or catalytic action at 20^0 C, but non-decomposable cyanides of di and trivalent iron couldn't be destroyed in these manner.

It was studied a strong oxidation at 70° C with hypochlorite in alkaline solution pH11-12, in the presence of NaOH. 25% solution (Gavriş G and all 2004, Gavriş G 1981).

MATERIALS AND METHODS

All the reactive used for these purpose were analytical pure, Merck, Fluka, Reanal, and deionised water.

The synthetic solution used consisting in 3g/L potassium trivalent iron cyanide complex at pH 12 was treated with NaClO 13% free chlorine, under ventilation. From 10 to 10 minute the FeO(OH) obtained was filtered , washed and dissolved in hydrochloric acid 1:1 vol. Iron was determined in a suitable volume, by volumetrically method using chelating agent ethylenedinitrilotetraacetic acid dissodium salt dihydrates (Titriplex III) 0,05M at pH 2-2,3, using 5-sulfosalicylic acid 5%[5,6]. The iron must be

in trivalent form. Any iron (II) salts which may be present must be oxidized to iron (III) salts by heating with nitric acid .The iron (III) salt solution , which contain up to about 20 mg of iron is diluted to about 100 ml with distilled water. The pH value is adjusted to about 2, 3 with sodium acetate 20% 1 ml of indicator solution is added and the solution is titrated against Titriplex III solution. At the equivalence point, color changes suddenly from red to yellow and the red coloration disappears. If the red color appears again the titration against the Titriplex solution is continued. 1 ml of Titriplex solution= 2,7925mg Fe.

Iron oxihydroxid was determined through thermal analysis using a derivatograph Paulik, Paulik, Erdely – Hungary, when at 350°C the red-brown precipitate of iron oxihydroxide is decomposed to Fe_2O_3.

K 3[Fe(CN)6] became not dangerous by an energetically oxidation reaction at high temperatures (80°C) with sodium hypochlorite 13% chlorine active, according to the reaction equation (Gavriş G et all, 2004).

$$[K_3[Fe(CN)_6] + 15\ NaOCl + 2H_2O = 12NaCl + 3KCl + 3NaOH + FeO(OH) + 6CO_2 + 3N_2 \quad (1)$$
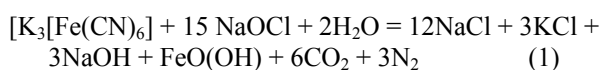
in a well-defined relation to the quantity of trivalent iron cyanide complex present. To an excess of 40-50% sodium hypochlorite it was obtained a counter-poisoning degree of 99.9% of the initial quantity of ferricyanide.

The formula for calculating are presented by relation (1)

$$\alpha,\% = \frac{K_3\left[Fe(CN)_6\right]_i - K_3\left[Fe(CN)_6\right]_f}{K3\left[(CN)_6\right]_i}100$$

(1)

Were:
$K_3[Fe(CN)_6]_i$ = initial quantities of salt in [mg/l]
$K_3[Fe(CN)_6]_f$ = final quantities of salt in [mg/l]
All the concentrations are calculated in [mg/L]

- Determination of the total cyanides (Mogoş G and Sitcai N 1990, Merck E 1988)

All complex cyanide compound including those of di and trivalent iron are decomposed quantitatively to hydrogen cyanide between 0,2 to 1000 mg, concentration suitable for distillation method of the total cyanides, in acid range . The distillation is carried out in the apparatus illustrate on figure1. To the sample is added 2N hydrochloric acid in the presence of methyl orange solution and 10 ml of the acid in excess. Heat up the distillation flask for 5-10 min, then boil for 30 min under reflux.. Then very carefully add 30 ml sulfuric acid, and distill for 90 min. The distillate is obtained in 20 ml 1N alkaline solution of sodium hydroxide and drained into 100-ml volumetric flask for photometrical determination of cyanide.

- Photometric determination of cyanide (Merck E 1988)

The analysis is made at 578 nm by means of barbituric acid and pyridine, suitable for determination of cyanide ions concentration from 0,02 to 2 mg CN/L, against deionised water as blank. Higher concentration require a dilution of the solution.

Reagent preparation barbituric acid/pyridine solution. Slurry 15g barbituric acid with little deionised water, completely dissolved in 75 ml pyridine, and treat with 15 ml hydrochloric acid min 375. After cooling the solution make up to 250 ml with deionised water.

Chloramine T solution: dissolve 1 g chloramines t in 100 ml deionised water.

Cyanide standard solution: dissolve 1, 25 g potassium cyanide in 0,2N sodium hydroxide to make 500 ml. 1 ml = 1 mg CN. The exact content of cyanide ions in the solution is ascertained by a titrimetric determination [5] with silver nitrate solution using 5-(4-dimethylaminobenzyliden) rhodanine as indicator. With standard solution 0,1mgCN/mL, was prepared 0, 01mgCN/L, by dilution with 0,2N NaOH.

Potassium dihydrogen phosphate solution disolve 150 g salt in 850 ml deionised water.

0,2N sodium hydroxide is used to make up the dilution required for preparation of reference curve.

Into 100 ml volumetric flask, pipette an aliquot portion of the distillate, 15 ml potassium phosphate, 1, 5 ml chloramines t and after 3 min reaction add 3 ml barbituric acid/pyridine makes up to the mark with deionised water and mix. The pH value of the solution must be around 6. After 20 min the solution was measured at 570 nm. A pink-violet compound appeared, containing anion $[CN^-]$.

RESULTS AND DISCUSSION

The results of oxidizing process of cyanides trivalent iron is shown in Table 1 and 2.

Table 1

THE QUANTITIES OF FEO(OH) OBTAINED BY CHEMICAL OXIDATION OF K3[FE(CN)6]

Reaction time [min]	0	10	20	30	40	50	60	70
K3[Fe(CN)6],[mg/L]	3000	1765,4	925,8	347,5	82,4	32,7	1,2	0,4
Fe [mg/l]	0	210,566	350,526	449,86	494,82	503,25	508,59	508,72
FeO(OH)extracted[mg/l]	0	335,03	557,71	715,77	787,3	800,71	809,21	809,43
TitriplexIII0.05M[ml]	0	75,4	125,52	161,09	177,19	180,02	182,13	182,18

CN[mg/L]	1421,1	836,269	438,551	164,61	82,4	15,49	0,568	0,189
Time[min]	0	10	20	30	40	50	60	70

After a 70 min treatment the waste solution had a cyanide content of 0,189mg/ mL, corresponding to an absorbance A=0,418, (ten twice diluted). and a maximum content of FeO(OH) extracted 809,43mg/L. For 1 L studied solution, corresponds to 99% efficiency. At "0" moment all the content of trivalent iron cyanide complex are non decomposable compound. At the end of reaction, the quantities remained in waste water is very low value 0,40mg/L $K_3[Fe(CN)_6]$. The total cyanide photometrical determined was $[CN]=0,45\mu g/25ml$, for an extinction: A= 0,42 and ten twice dilution, that is around 0,2mgCN/L.

Excess of sodium hypochlorite might be eliminated using sodium sulfite, 10% solution, pH must be corrected at standard value, all parameters according to NTPA 002 and SR ISO 8644-1.

The thermal analysis are presented in Illustration 1 (Todor DN, 1972).

The quantity of water, theoretically lost is 10.1 % but practical determined is 11%.

Table 2

CONCENTRATIONS AND EXTINCTIONS VALUES FOR CALIBRATION CURVE OF CYANIDE STANDARDS SOLUTIONS

CN[μg/25mL]	0,1	0,2	0,4	0,6	1
A[u.a.]	0,118	0,189	0,368	0,512	0,812
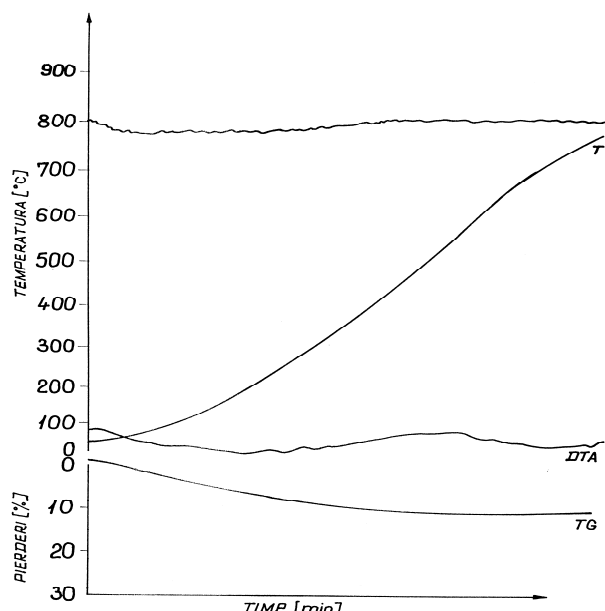
Fig. 1 The T, TG, DTA, DTG curves

The thermal decomposition reaction are:

$$2FeOOH \xrightarrow[-H_2O]{320°C} \alpha Fe_2O_3 \qquad (3)$$
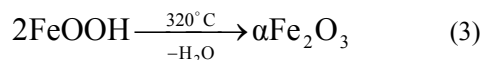
In accordance with the derivatograme obtained at 320°C, the iron oxyhydroxide transforms into iron oxide, form α, and after that the weight loss strives to constant value.

CONCLUSIONS

The chemical oxidation in thermal conditions at 70 C with sodium hypochlorite 13% free chlorine, under strong mechanical stirrer and ventilation could decompose the very stable di and trivalent iron cyanides complexes.

The necessary time is around 70 min, that means the reaction are taken place slowly, and we can obtained a non-dangerous compound of iron oxihydroxide.

Thermal analysis indicated the quality of red - brown compound as well as chemical composition.

The total cyanide content is 0,189 mg/L , all the analysis were made according to SR ISO 8466-1.

The excess of hypochlorite can be eliminated with suitable reduction agent like sodium sulfite.

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