ANNALS of the ORADEA UNIVERSITY.
Fascicle of Management and Technological Engineering, Volume IX (XIX), 2010, NR2

ANALYZE OF SOME PROCEDURES OF ELIMINATION THE POLLUTION FROM THE RESIDUAL WATERS WITH CYANIDES CONTENT

CÎRŢÎNĂ Daniela, MITRAN Ramona
„Constantin Brâncuşi" University, Faculty of Engineering, Tg-Jiu, Romania
e-mail: daniela@utgjiu.ro

Keywords: cyanides, residual waters, oxidative procedures.

Abstract. Waters with cyanides content present the disadvantages of a high toxicity involving special measures of labour security and high costs of the processes to eliminate their poisonous process. These advantages can be alienated or at least diminished by implementing in the processes generating waters polluted with cyanides some specific operations of treatment and neutralizing, aiming the more complete elimination of some very toxic pollutants for the environment. Experiencing some oxidative procedures is based on more profound knowledge of chemical processes taking place, as well as of the particulars of the cyanic substances. In the paper it is presented an analyze of the oxidative procedures that can be used ad eliminating the poisonous aspect of residual waters having a high content of cyanides, through which are underlined the advantages and shortcomings of each exposed procedure, application conditions and realized performances.

1. INTRODUCTION

At the present moment, cyanide is used in thousands of industrial operations in the entire world and at the manufacturing of many large consumption products. It is a unique compound that, due to its special characteristic is used in chemical and metallurgic industry. Many industrial galvanic-technical processes of depositing some singular metals (cooper – plating, golding, zinc plating, cadmium plating) take place in cyanic electrolytes. Large scale usage of these electrolytes in galvanic-techniques is due to multiple advantages that they present: high penetration power, very good tolerance at any technology of surfaces pre-treatment and of impurities, corrosion resistance as well as economic advantages by the reduced cost of afferent equipments. Cyanides reach, commonly, natural waters as a result of some industrial activities. Their toxicity is reflected, first of all, on microorganisms enduring bacterial self- purification and on the totality of fishes not resisting, generally, at doses higher than 0,05 mg/l. It seems that, for bacterial flora, the sulphur-cyanides are less harmful than cyanides. Flora can retake activity, in normal conditions, after the disappearance of the cyanides in the water [1,2].

The compounds entering "cyanides" category are very different from the point of view of the physical - chemical and toxicological properties, so than can be underlined the following categories [5]:

- simple soluble cyanides, *poisonous,* represented by prussic acid and its salts (NaCN, KCN) polluting water with cyanide ions CN^-. The prussic acid is an colourless liquid having a low boiling point (p.f. = 26,5°C), which is mixture with water in all proportions, is very weak, its dissociation constant being of $13,3.l0^{-10}$, it is easily polymerized and enters in different combination reactions.
- simple insoluble cyanides like copper or iron cyanide which might pass in the group of not-toxic ones. Still, due to the fact that can be found in water, in a thin dispersed manner, if reaching the organism, under the action of gastric juice, begin to dissolve, passing in simple poisoning cyanides and provokes its poisoning. In stock piles, simple insoluble cyanides, under the action of rain water, of the sun and temperature oscillations, pass into simple soluble cyanides.

- copper and zinc complex, soluble, poisoning cyanides $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$, $[Cu(CN)_4]^{3-}$, $[Zn(CN)_3]^-$, $[Zn(CN)_4]^{2-}$. In residual waters can highly be found $[Cu(CN)_3]^{2-}$, which is the most stable as its dissociation constant is the greatest, 5.10^{-28}.
- soluble *not-poisoning* complex cyanides, from which are a part ferro- and ferrocyanides of the type: $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$. The solubility of $K_3[Fe(CN)_6]$ in 100 g water at 20°C is equal to 42,9 g, of $K_4[Fe(CN)_6]$ in the same conditions is of 28,9 g and $Na_4[Fe(CN)_6]$ solubility is of 17,9 g. The lack of toxicity of ferro- and ferrocyanides often gave birth to doubts, as well as relative lack of toxicity of simple cyanides. Under certain conditions, these composites can be partially discomposed and give into solution simple poisoning soluble cyanides.
- insoluble cyanide compounds and due to this , not -toxic, for example ferric ferrocyanide (Prussian blue) $Fe_4[Fe(CN)_6]_3$. The solubility product of this salt equals to 3.10^{-4}, which indicates its insolubility in water.

In residual, industrial water whose chemical composition are not a constant one and varies permanently, can be simultaneously contains all forms of cyanide compounds. In this context it was imposed the necessity of treating residual cyanide water with the purpose of neutralising pollutants with high toxicity, the elaboration and experimenting of some lacking toxicity procedures of the waters, with cyanides content, the optimization of the procedures and optimization of its performances. Their majority aims the destruction by oxidation of the cyan ion at the form of less toxic cyanide ion and, moreover, to final inoffensive reaction products, N_2 and CO_2 [7].

Most used oxidation agents are chlorine and sodium hypochlorite, like ozone used on large scale for lacking toxicity from cyanide waters.

2. OXIDATIVE TECHNOLOGIES FOR THE PURIFICATION OF RESIDUAL WATERS POLLUTED WITH CYANIDES

2.1. ELIMINATING TOXICITY WITH CHLORINATED OXIDIZED PRODUCTS

Cyanides chemical oxidation represents the most frequently applied procedure on industrial scale and can be realised by using as oxidation agent, different chlorine salts like: $CaOCl_2$, NaOCl or liquid chlorine.

Reactions taking place instead of simple cyanides oxidation, are presented below:

$$CN^- + OCl^- \longrightarrow CNO^- + Cl^- \qquad (1)$$

$$CN^- + Cl_2 + 2\,OH^- \longrightarrow CNO^- + 2Cl^- + H_2O \qquad (2)$$

The reaction time is of maximum 1 minute, and temperature should not exceed 40°C. Increasing the chlorine quantity and the treatment period, a total decomposition of cyanate happens, according to the reaction:

$$2NaCNO + 4NaOH + 3Cl_2 \longrightarrow 2CO_2 + 6NaCl + N_2 + 2H_2O \qquad (3)$$

The reaction speed, in this case is of 30 minutes (theoretical) and practical, of one hour. The excess of chlorine is alienated with fixing salt:

$$4Cl_2 + Na_2S_2O_3 + 5\,H_2O \longrightarrow Na_2SO_4 + H_2SO_4 + 8\,HCl \qquad (4)$$

Cyanate ions (CNO^-) formed in both cases hydrolyses up to carbonate and ammonium ions. So, as a result of the purification with calcium hypochlorite, sodium hypochlorite or liquid chlorine, the cyanides are destroyed integrally, and hard metals precipitate under form of insoluble combinations (hydrated oxides or carbonates).

The time required for complete destruction of complexes of heavy metals at pH = 12 and 25°C is presented in table 1.

Table 1. The time required for complete destruction of complexes of heavy metals

No.	Complex cyanides	*The time required for complete destruction (minute)*
1	$[Zn(CN)_4]^{2-}$	*1*
2	$[Cd(CN)_4]^{2-}$	*1*
3	$[Ag(CN)_2]^{-}$.	*1*
4	$[Cu(CN)_4]^{2-}$	*40*
5	$[Ni(CN)_4]^{2-}$	*50*

The theoretical quantity of active chlorine that is necessary for the decomposition of simple and complex cyanides that are present in used waters, is computed with the formula:

$$X = 2{,}7A + 3{,}2B + 2{,}7C \qquad (5)$$

in which: A represents the concentration of simple cyanides (recomputed at CN^-), in mg/l; B and C represents the concentration of complex cyanides with Cu and Zn (recomputed at CN^- in mg/l).

The real request of Cl_2 is always higher than the theoretical quantity, due to the presence of other oxidable constituents of the rests with cyanides, like copper -ions, nickel - ions, ammonia and organic substances. The optimal conditions of oxidation of the cyanides are determined by the value of pH, which should be of at least 10-11.

Oxidation starts in an intensely acid environment, when it is formed the greatest capacity of hypochlorous acid, but in this case is also present the molecular ion, which reacts with the cyanides and forms the very toxic chlorine - cyan ($ClCN$).

The toxicity of chlorine-cyan

Formation of chlorine-cyan represents the most critical point of the procedure, this compound, as well as halogen-cyan generally, is a very volatile, lachrymator product, as toxic as prussic acid, but less soluble in water (p.t. -5°C; p.f. 15°C). Chlorine-cyan is formed at any value of pH, but if the values of pH is too low (under 9) or if the concentration of the cyanides in water is too high (over 1g/l), or solution is too warm (over 50°C), there is the danger of volatilization of the chlorine-cyan, dissolved in water. On the other part, speaking bout solutions that are too concentrated in cyanide, the reaction of chlorine combination with cyan being a violent and exothermic one, the solution can be warmed up and encouraging the release of toxic cyan. The most efficient means of volatilization is the rigorous control of pH, before and during the process of lacking toxicity, taking into account the pH dependence of the hydrolyse reaction of chlorine-cyan [3,4].

If as oxidant it is used hypochlorite ion (lime chloride, calcium hypochlorite, free chlorine in alkaline environment), then the oxidation capacity of the compounds that is used can be determined according to the content of so – called „active chlorine" and all doses would be calculated according to this measure. A great disadvantage of using hypochlorite is the great chloride quantity that is formed by oxidation. For example, at the oxidation of 100 kg of cyanide at cyanate, results only from the solution of hypochlorite consumed abut 500kg of sodium chlorine. In the case of complete oxidation, this quantity reaches 1125kg of NaCl. More, to settle and maintain pH, as well as in reaction is consumed a great quantity of NaOH, which in return must be neutralised before release, operation through which is generated such a great quantity of salt.

It must be stated that, in case of treating residual waters with a great content of hypochlorite or oxidant chlorine, only a part of these substances can be consumed by oxidation of the cyanides, the rest oxidises other substances that are present in residual waters.

Because of this, the consumption of chlorine –agents is not calculated but determined in an experimental manner. At the neutralization of the residual waters it is used a solution of 5% reactive.

The chlorine necessary from water represents the difference between the chlorine quantity that is added and the quantity that can be determined in analytical manner as residual chlorine. The residual chlorine includes all forms existing in water: Cl_2, HOCl, OCl^-. For great installations it is recommended to be used liquefies chlorine and for small installations and in unforeseen situations cam be used with satisfactory results: calcium hypochlorite, sodium hypochlorite and lime chloride.

When the existence of the chlorine excess is not allowed in water, it would be realised the purification of chlorine by one of the following methods:

- treatment with reducer agents like ca: sodium sulphite (Na_2SO_3), sodium bi-sulphite ($NaHSO_3$), sulphur dioxide (SO_2), fixing salt (Na_2SO_3);
- introduction in water of dust active coal.

2.2. ELIMINATING THE TOXICITY OF CYANIC RESIDUAL WATERS BY OZONIZATION

One of the oxidants aggravating the ionic composition of residual waters is ozone, used especially for drinkable water purification, but in the past years have been realised researches regarding the use of ozone also for the purification of residual waters. Ozone is an oxidation agent whose usage does not involve the apparition of a secondary toxicity and does not modify the saline load of water. But, a part of ozone is consumed for the oxidation of other substances (especially organic ones) from the water, whose destruction by oxidizing is not necessary for eliminating toxicity. Ozone dissociates especially in aqueous solution as well as in air. In very alkaline solution, the ozone's decomposition is realized rapidly; meanwhile in acid solutions it is more stable. Ozone is a powerful oxidizing character, its normal oxidizing character is E_0 = 2,0 V, and in the alkaline environment E_0 = 1,24 V.

It must be taken into account the fact that ozone is toxic and acts on respiratory organs, also can affect central nervous system. The limit admitted concentration in the air from the rooms where people works is about 0,0001 mg/dm^3 [5,6].

In aqueous solutions, a part of ozone acts directly with water dissolved substances (M), the reaction being a selective and lent ones and another part is transformed in a fast manner in free radicals OH. Transformation in free OH radicals is initiated by OH ions and starts as fast as pH is higher. OH radicals are non selective powerful oxidising elements, being able to act in two modalities.

a) forms water dissolved substances, secondary radicals (R) functioning as promoters of chain reactions;

b) can be captured by some compounds breaking the chain, as for example bicarbonate and carbonate ions, resulting inactive species, retarder of chain reactions.

Cyanide ions are oxidised in the first stage with a fast speed at cyanate ions, less toxic, which at certain values of pH hydrolyzes, resulting CO_2 and N_2, as can be seen from the following:

$$CN^- + O_3 \rightarrow CNO^- + O_2 \qquad (6)$$

$$2CNO^- + 2H_2O \rightarrow 2CO_2 + N_2 + 4H^+ \qquad (7)$$

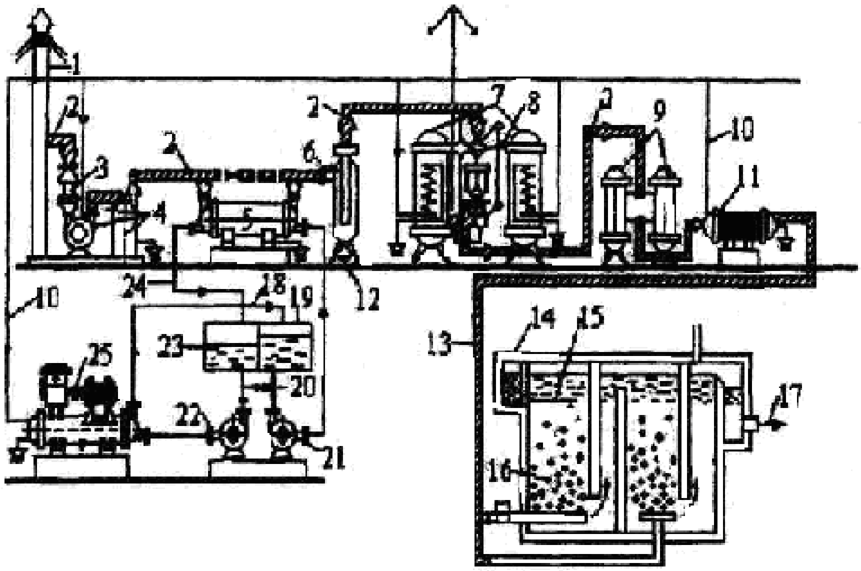

Fig. 1. Technological scheme of an installation for ozone treatment of industrial used waters.
1 – air inlet; 2 – supply of atmospheric air; 3 - filter; 4 - blower; 5 – heat exchanger; 6 – water separator; 7 – air drying installation; 8 – air supply for regenerating absorption; 9 – block of filters; 10 – pipe for drinkable water; 11 – ozone generator; 12 - sewerage; 13 – air- ozone supply; 14 – contact chamber for ozonization of residual waters; 15 – untreated waters supply; 16 – porous tubes for distributions; 17 – exhaustion of purified waters; 18 – supply of solution of cold salted water; 19 – reservoir of cold salted water; 20 – three way mixture vent;- 21 – pump for cold salted water; 22 - pump for warm salted water; 23 – reservoir with warm salted water; 24 – supply of salted warm solution; 25 - refrigerant.

Ozone is completely consumed during first reaction. After the oxidation of the free cyanide, the rhythm of the reaction decreases, as remained cyanide is complex with present metals. In this point the residual cyanide concentration is stoechiometric equivalent with metal content. A second reaction takes place when pH decrease, which is a consequence of the cyanides oxidation in cyanate. The hydrolysis of the cyanate, during the second reaction is accelerated by the presence of the ozone in alkaline solution. For ozonization, the most favourable field of pH is between 9-12. Between these intervals, the influence of pH's size on the oxidation effect is meaningless./ Still, increasing alkalinity provokes the fast decomposition, catalyzed by hydroxyl ions of ozone and because of this it is recommended that the process be realise at pH $\le$ 10. The technological scheme (fig. 1) of ozonization of industrial residual waters is made of two basic ensembles: obtaining ozone and purification of residual waters. The ensemble of obtaining ozone contains four basic block and namely: obtaining and cooling air, drying and filtering air and generating ozone. Dry, purified air is alimented in the blocks of the ozonizers, under the action of electrical discharge it is generated ozone and is pulverized in chamber of contact with water to be treated.

2.3. TREATMENT OF CYANIDE CONCENTRATES BY CATALYTIC COMBUSTION OF HYDROCYANIC ACID

The disadvantages of treating water having a high content of cyanic compounds by chemical methods, for example with sodium hypochlorite, are well-known and are due to forming and release of especially harmful chlorine – cyan. To avoid these inconvenient, in practice, most of times is realised the dilution of cyanic solutions that are used, which is not economic, involving other practical disadvantages. A simple procedure of treating cyanic concentrates is the release of prussic acid from solution and the catalytic burning [3]. The prussic acid is released by the action of the sulphuric acid on simple and complex cyanides, from which is released prussic acid, feeble volatile acid, according to reactions:

$$2\ NaCN + H_2SO_4 \longrightarrow Na_2SO_4 + 2\ HCN \qquad (8)$$

$$Na_xMe(CN)_y + H_2SO_4 \longrightarrow x/yNa_2SO_4 + MeSO_4 + yHCN \qquad (9)$$

Me = Cu, Zn, Cd, Ag etc.

Prussic acid is burnt with air excess:

$$4\ HCN + 5\ O_2 \longrightarrow 4\ CO_2 + 2\ N_2 + 2\ H_2O \qquad (10)$$

In fig. 2. is presented the scheme of the installation for the treatment of cyanic waters by catalytic burning. The cyanic solution is pumped from a collecting reservoir in the superior part of the reaction tower. In the same place, simultaneous with the used solution, it is introduced the acid. The tower is filled with Raschig rings, to increase the reaction surface. By the dilution of the sulphuric acid with the solution to be treated takes place also a weak heating of the solution, fact which influences in a positive manner the release of the Prussic acid. In counter-current with the liquid, at the inferior part of the tower it is blown air, the released prussic acid being mixture and involved with the air that exists at the superior part of the tower. After mixing with acid, the pH of the solution is about 2, and for each litre of cyanic solution is introduced 1m^3 air. In these conditions, cyanides are transformed over 99% in prussic acid. The air released at the superior part of the tower, loaded with prussic acid, is lead to the burning room in which, on a platinum catalyser, takes place the burning of the prussic acid at CO_2 and N_2. By using the catalyser it is lowered the activation energy that is necessary for the reaction, the temperature necessary in these conditions is around 300°C.

As the oxidation reaction of the prussic acid is exothermal during the process, the reaction products and the air in excess are heating. By using exchanger, this heat can be recovered, so that after priming the reaction practically is not anymore consumed energy from outside.

The release of prussic acid from cyanides can be realised with the agency of hydrochloric acid, solution is neutralised with sodium hydroxide or lime. The entire installation forms a closed unit, insulated and works at pressure below the atmospheric one, being avoided this way any release of prussic acid, outside.

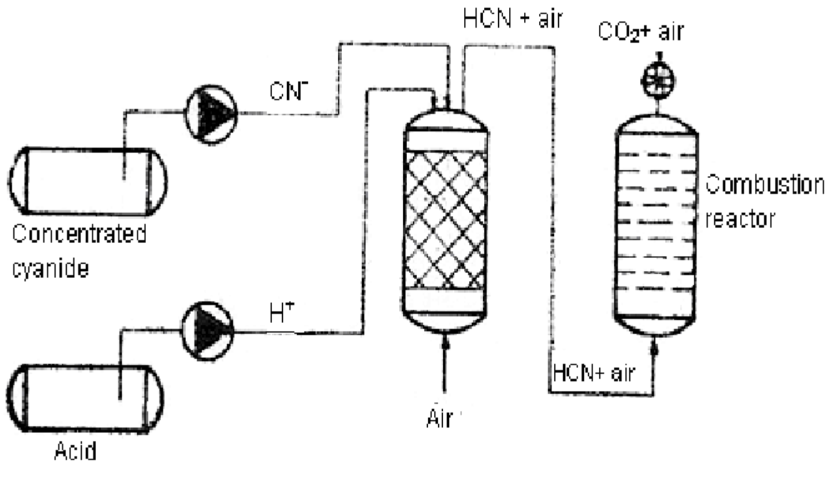

Fig.2. The scheme of the installation for the treatment of cyanic waters by catalytic burning.

3. CONCLUSIONS

Eliminating cyanides from residual waters is a necessity due to especially toxic effects of these pollutants on aquatic environment. From the procedures known and successfully applied for the cyanic waters pollutants elimination, the ones based on chemical and electrochemical oxidising of the cyanide ions are widely applied in practice. In this purpose can be used different oxidising agents who can destroy the cyan ion by oxidation to less toxic cyan ion, from these, a part being the free chlorine or sodium hypochlorite. The disadvantage of the hypochlorite oxidation procedure is first of all that of toxicity of treatment reactive. The concentration of residual chlorine that is admitted in water is limited by legal settlements. As a consequence, the hypochlorite excess that is used must be well settled, by correspondent measurement - regulation devices. Another aspect in the disadvantage of this procedure is connected to water salinization. In case of eliminating toxicity from solutions with small cyanides concentration, by alkalinisation followed by neutralising, in residual water can be reached a salt quantity that is ten times higher than the one resulted from the cyan reaction with the oxidation agent. Also, the use of some old hypochlorite solutions with low content of active chlorine, affects not only treatment costs, but also contributed to significant increase of water salinity degree. By water salinization it is formed a powerfully aggressive environment involving additional expenses for anticorrosive protection of afferent equipments.

Ozonization is a method competitive with chlorination. Using ozone for eliminating toxicity of residual waters having cyanides content was for a period limited due to the absence of some efficient and economic ozone generators, this deficiency was exceeded by constructing such reliable equipments, having substantially reduced energy consumption. Another aspect connected to the elimination of toxicity from waters by treating with ozone is the one connected to the fact that at the destruction of the cyanides complexes, once with the cyanates are formed hydroxides of hard metals being able to cause, by a heterogeneous catalytic action of decomposition of the ozone, fact which involves the increase of agent consumption for the present oxidation in respect to the necessary theoretic one. From this cause, for the fast and total development of the reaction and the maintenance of ozone consumption at a low level, it is useful the continuous alienation of the hard metals' hydroxides, that are formed in reaction environment.

Even if the ozonization method is more expensive than the ones of chlorination, it has a series of advantages. Calculus show that the ozonization method is of great perspective for used waters purification. The ozonization allows the destruction of the pollutants which are not submitted to oxidation by biochemical methods, so that it is ensured the necessary quality of residual waters.

The advantages of the ozone purification method of the residual waters with low content of cyanides are the following:

- possibility of complete automation of the process;
- forming an insignificant deposit quantity;
- lack of foreign impurities in treated water;
- the possibility to obtain oxidising at the present place.

REFERENCES

[1] Gavrilescu, E., (2007), Sources of pollution and environmental pollutants, Sitech Publ., Craiova.

[2] Geamăn, V., and others, (2005), Fundamentals of environmental engineering industry, University Transilvania Publ., Braşov.

[3] Gergely, A., Bay, E., Dumitrescu, M., (1992), Waste water treatment and recovery of electrolytes in galvanotechnics, Ed. Technica, Bucharest.

[4] Ianculescu, O., Ionescu, Gh., Racoviţeanu, R., (2001), Wastewater Treatment, Ed. MatrixRom, Bucharest.

[5] Sârbu, R., (2008), Procedures and equipment for waste water treatment, Ed. Focus, Petrosani.
[6] Szabolcs, S., Constantinescu I., (2000), Technologies, facilities and equipment for water treatment, Ed. Technica, Bucharest.
[7] Rojanschi, V., Bran, F., Diaconu, Gh., (1997), Protection and Environmental Engineering, Economic Publ., Bucharest.