Settlement of cyanide eliminating and monitoring station at the Dunaferr

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Abstract

The article describes the originating of cianide contaminated waste waters originated during the cleaning of the dusty exhaust gases coming from the blast furnaces of the Dunaferr Company Group, moreover presents the environmental protection problems and their solutions arising from this.

1 Introduction

During the analysis of the waste waters of the Dunaferr Company Group, at the middle of the 90's unpredictable cyanide concentration peaks were found in the Bob-upper canal, collecting the industrial waters of the companies, before emptying to the Danube. The effect was manifested more and more sharply and after a period the exceeding of the limit value was also more and more frequent. It has become an urgent task for the management of the Shareholding Company responsible for the waste water quality of the companies, to discover the technological origination and technical reasons of the contamination.

- The reasons of the above mentioned effect were various:
- Inone hand, the HCN in the waste water is not belong to the group of the contaminants, but into the poisoning agents, its toxicity is high.
- The exceeding of the environmental protection limit values implies amercement. The basic value of this is 10 thousand HUF/kg.
- Not in the last place, the emission of such agressive material abates the reputation of the company, too.

Because of the increasing of the contamination and its limit value exceeding the Shareholding Company has got higher and higher amercement from the Environmental Protection authority.

The systematic sampling of the inner canal system, the principles of the forming of HCN compound and its properties has led to that conclusion, that the cyanides with the highest chance are originated within reducing conditions. So we could find relatively soon the cyanides in the scrubbing water of the wet gas-cleaning of the blast furnaces.

The feature of the scrubbing water circuit belonging to the blast furnaces is, that the sludge separated from the scubbing water with a volume flow rate of 600-700 m^3/h gets to the Sludge Valley from the Dorr–agitators and the purified water reaches the aeration basin, where it loses its residual cyanide content, and gets back, after a certain fresh water addition, into the Venturi–scrubber of the blast furnaces. Nevertheless the system is not totally closed, as the water has a segmental flowing over possibility into the Bob–upper canal, from where the HCN reaches the Danube.

The forming of the cyanide concentration shows parallelism in time in the Dorr–agitators and at the Bob–upper. This is illustrated in the table 1.

Year	Dorr	Bob-upper	Kisapostag	Emission
	mg/l	mg/l	mg/l	t/year
1995	5,34	0,100	0,027	3,57
1996	9,37	0,115	0,046	4,04
1997	10,85	0,108	0,035	3,67
1998	2,71	0,059	0,100	2,22

Table 1: The cyanide concentration and cyanide emission of the canal system of the Dunaferr Company Group

2 Possibilities to eliminate of the cyanides

During the hypochloritic oxidation the $2NaCN+2NaOCl+2NaOH=5NaCl+2Na_2CO_3+N_2+H_2O$ reaction is performed with 11-12 pH, after the completion which the pH of the waste water has to be set back with hydrochloric acid. During the hydrogen peroxide treatment the $NaCN + H_2O_2 + NaOH = Na_2CO_3 + NH_3$ reaction is performed, also with around 10 pH, where the neutralization and the releasing ammonia means troubles. A rarely applied method is the treatment with formaldehyde, where differently from the former processes only liquid reaction product (glykol-nitrile) is originating, which is alone a poison. According to our local circumstances the treatment with ferrous sulphate seems to be the most applicable. This reaction is performed according to the $6HCN + 3FeSO_4 = Fe_2[Fe(CN)_6] + 3H_2SO_4$ equation around 7-8 pH. The originating ferricyanide precipitate is thermodynamically stabile, is not toxic. The smooth increasing of acid is favourable, as it reduces the HCN- dissolving capacity of the waste water. Comparing the reagent demands we can find, that the treatment with ferrous sulphate is the cheapest, the cost of the hydrogen peroxide treatment is 35 times, while the hypochloritic treatment is 100 times higher, not speaking about that thing, that in the latter cases the procedure would be solved only in closed storing system.

3 Requirements

We have stated the following requirements against the cyanide-eliminating method and the station solving it:

- in the state of the scrubbing water such changes must not be happened, which would prevent the further realisation of the recycling;
- the treatment must not increase the aggressivity of the scrubbing water, so the corrosion of the structural materials of the scrubbing water circuit;
- during the treatment poisoning agents must not be originated;
- the treating technology has to be well controllable;
- considering the large water circulation, the elimination has to be solved with the most economic way, with on-line analytic and with the automatic charging of the reagents.

4 Execution

The monitoring system and the eliminating station fulfilling the above mentioned requirements has built and was taken over by the spring of 1999. The measurement of the cyanide content is performed at 3 places, from which the sample, taken from the confluence of the Venturi–canals of the I–II. blast furnaces, forms the sign used for the controlling (See Figure 1). The value of the control signal is set by the operators, while the charging of the ferrous sulphate is performed in the form of solution. The bath, which gives the place for the storage and dissolution of the sulphate was settled between the Dorr-agitator and the blast furnaces. The monitor system, belonging to the gas dispatcher service, collects and store on PC the following data:

- the cyanide content of the scrubbing water,
- the pH of the scrubbing water,
- the Na+K content of the scrubbing water,
- the temperature of the blast furnace gas before and after the venturi scrubber,
- the temperature of cooling water after the venturi scrubber.
- We will present the results reached with the monitoring and treating system, which is unique in the country, after collecting and evaluating the necessary amount of data.

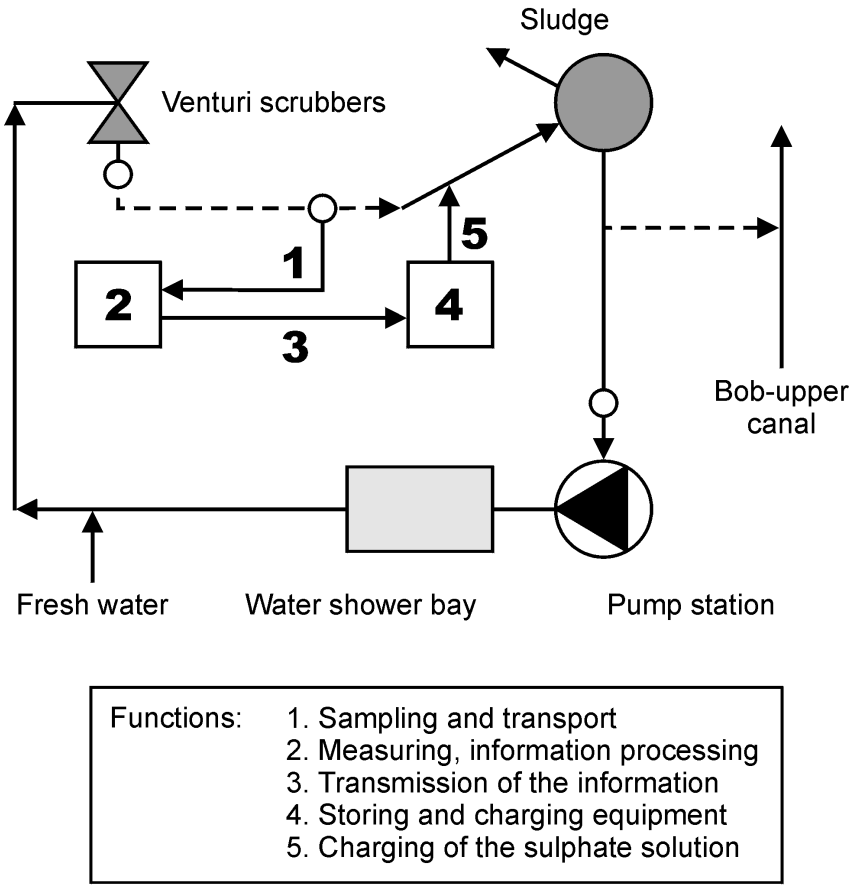

Figure 1: The scheme of the settlement and operation of the cyanide eliminating and monitoring station