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THE REUSE BY RECYCLING OF INDUSTRIAL WASTEWATERS FROM IRON MAKING INDUSTRY

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ABSTRACT:
The technological solution for the pollution diminishing regarding the industrial wastewaters from iron and steel industry are became a necessity in order to harmonized our environmental legislation with Union European environmental acquits.
The paper present the actual status at national and European Union level concerning the treatment of industrial wastewaters from iron making processes.

KEYWORDS:
industrial wastewaters, treatment techniques, best available techniques (BAT), iron and steel industry.

1. EUROPEAN UNION TREATMENT TECHNIQUES FOR WASTEWATERS FROM WET SCRUBBING OF BLAST FURNACE GAS

In order to choose the maximum efficiency for treatment of wastewater from wet Blast Furnace (BF) gas scrubbing of iron making, it is recommended by European Union the best available techniques (BAT), defined as:

- "Technology": the main operations made for obtaining a decrease of the pollutants;
- "Available": indicate the technology with high efficiency at industrial scale, assuring for that the equipment, apparatus, reagents etc, at right prices.
- "The best": refers to the technology efficiency. Though, this is not a complete reduction of the pollutants. This means the accordance with pollutants limits.

This definition was also harmonized by our national legislation with Government Ordinance no. 34/2002 regarding the integrated prevention pollution control (IPPC).

In this context, *BAT (Best available techniques)* represents „the most advanced and efficiently stage of the development registered during the activity of operating and exploitation, being considered, in this way, the reference for the establish the limit values of the emissions, and where is not possible, the reference for the global reduction and for the environment impact assessment as a whole".

These techniques are applied when there is an economical reason or when the chosen technology for the pollution reduction of wastewaters is not become a source of solid wastes or energy consumptions, in this case not being considered as a BAT.

In European Union countries, the wet scrubbing of BF gasses, by help of Venturi Scrubbers, is the most applied technique, being considered a BAT.

The technique is also applied in our country. The gas treatment lead to a high wastewater flow with suspended solids (carbon and heavy metals), cyanides, phenols, nitrogen compounds and others compounds from BF gas.

The compounds from BF raw gas and theirs composition is presented in table 1.

As it is observed, the BF raw gas is exhausted at Blast Furnace top with a high content of suspended solids (7 - 40 kg/to pig iron), cyanides (CN^-), ammonia (NH_3) and sulphur compounds.

Table 1.
Blast Furnace raw gas composition and emission factors

Compounds	Values	U.M.	Emission Factors	U.M.
Raw gas quantity	1 - 7	$1x10^5$ Nm^3/h	1200 - 2000	Nm^3/to pig iron
Suspended solids	3,5 - 30	g/Nm^3	7000 - 40000	g/to pig iron
Hydrocarbons (CxHy)	67 - 250	mg/Nm^3	130 - 330	g/to pig iron
Cyanides (CN-)	0,26 - 1,0*)	mg/Nm^3	0,5 - 1,3	g/to pig iron
Ammonia (NH_3)	10 - 40	mg/Nm^3	20 - 50	g/to pig iron
PAH (polycyclic hydrocarbons aromatic) - benzo(a)pyren - fluoranthen	 0,08 - 0,28 0,15 - 0,56	 mg/Nm^3 mg/Nm^3	 0,15 - 0,36 0,30 - 0,72	 g/to pig iron g/to pig iron
Carbon monoxide	20 - 28	% vol.	300 - 700	kg/to pig iron
Carbon dioxide	17 - 25	% vol.	400 - 900	kg/to pig iron
Hydrogen (H_2)	1 - 5	% vol.	1 - 75	kg/to pig iron

In the first treatment stage of BF gas (dry treatment – bag filters) is removed a high quantity of coarse solids particles are retained, these containing a high quantity by carbon and iron, being suitable for recycling in sinter process.

The fine particles (1 - 10 kg/to pig iron) resulted after the first treatment stages are collected in Venturi Scrubbers.

Thus, a quantity about of 3 - 15 kg sludge /to pig iron is resulted, having a high content with Zinc, being unrecyclabe for sinter process.

After the two stage of treatment, the gas has the composition presented in table 2.

The water necessary for BF gas treatment is between 0,3 - 4 l/Nm^3 BF gas, which represents 0,4 - 8 m^3/to pig iron.

A large quantity from this water can be treated and recycled, the treatment being made into radial settling basins.

The settlement properties for the sludge from the treated water can be improved by adding of coagulants (iron and aluminium salts) and/or floccullants reagents (anionic polyelectrolytes, polymer mix or activated silicic acid).

Table 2.
Blast Furnace gas composition, after the applying of the two treatment stages

BF gas composition after treatment	Concentration	U.M.	Emission factors	U.M.
Treated gas	1 - 7	1 $x10^5$ Nm^3/h	1200 - 2000	Nm^3/to pig iron
Solid particles	1 - 10	mg/Nm^3	1 - 20	g/to pig iron
H_2S	14	mg/Nm^3	17 - 26	g/to pig iron
Heavy metals*): - Mn - Pb - Zn	 0,1 - 0,29 0,01 - 0,05 0,03 - 0,17	 mg/Nm^3 mg/Nm^3 mg/Nm^3	 0,22 - 0,37 0,02 - 0,07 0,07 - 0,22	 g/to pig iron g/to pig iron g/to pig iron
Carbon monoxide	20 - 28	% vol.	300 - 700	kg/to pig iron
Carbon dioxide	17 - 25	% vol.	400 - 900	kg/to pig iron
Hydrogen (H_2)	1 - 5	% vol.	1 - 75	kg/to pig iron

*) also, the others heavy metals could be found.

It is necessary a chemical treatment for wastewater blow downs, especially for cyanides reduction, from time to time.

This treatment consists of formaldehyde add in water circuit, according to Fig. 1.

The wastewaters composition, after chemical treatment, is presented in table 3.

The obtained results in European Union has indicated:

- optimum value for pH have to be between 8 and 9;
- the reaction takes not place at pH below 7;
- at pH higher then 10, glyconitrile formed is not stable and lead to the cyanide and formaldehyde (table 3).

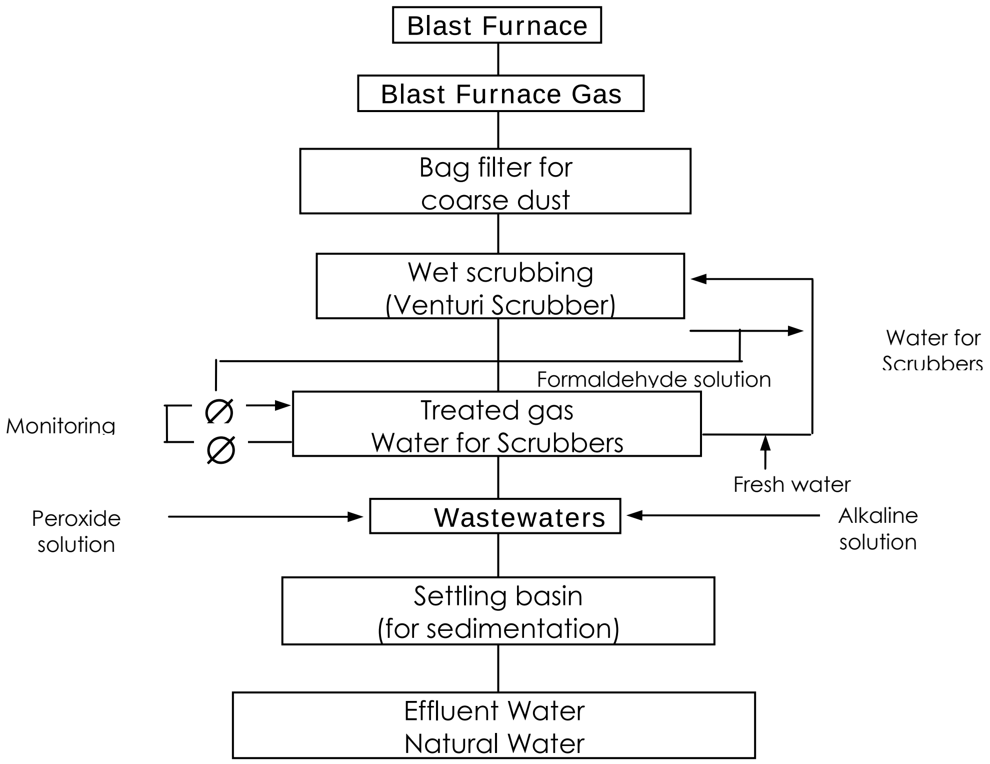

Fig. 1: Cyanide treatment from wet Blast Furnace gas treatment

Table 3.
Discharges for wastewaters from wet BF gas treatment, after treatment

Parameters		Average value	U.M.	Emission factors
Debit	m^3/day	3387	m^3/to pig iron	0,23
CCO	mg/l	51	g/ to pig iron	11,7
CN^{-} *)	mg/l	0,7	g/ to pig iron	0,06
N	mg/l	133	g/ to pig iron	30
H_2S	mg/l	22	g/ to pig iron	0,5
Suspended solids	mg/l	16,1	g/ to pig iron	3,7
Zn	µg/l	1051	mg/ to pig iron	242
Cu	µg/l	12,7	mg/ to pig iron	3,0
Cr	µg/l	33,4	mg/ to pig iron	7,6
Cd	µg/l	0	mg/ to pig iron	0
Ni	µg/l	39	mg/ to pig iron	8,9
Pb	µg/l	89	mg/ to pig iron	18,3
Hg	µg/l	< 0,1	mg/ to pig iron	0,02
As	µg/l	5,7	mg/ to pig iron	1,3
PAH	µg/l	3,1	mg/ to pig iron	0,71

*) free cyanides.

As it is concerned, the resulted sludge from wet BF gas scrubbing, due to the high concentration of zinc content (table 4), it is necessary the hydrocyclonage treatment.

Table 4.
Sludge composition (% mass) from wet BF gas scrubbing

C	Fe	Pb	Zn	Mn	Al_2O_3	S
15 - 47	7 - 35	0,8 - 2,0	1 - 10	0,12 - 0,14	0,8 - 4,6	2,4 - 2,5
SiO_2	P_2O_5	CaO	MgO	Na_2O	K_2O	
3 - 9	0,1 - 0,44	3,5 - 18	3,5 - 17	0,15 - 0,24	0,08 - 0,36	

With the hydrocyclonage treatment, this sludge can be separated into two fractions: one has a high Zn content and the other has a very small content of Zn, this one being recycled in sinter process.

The hydrocyclonage technique can be applied as *"end of pipe"* process, if the wet scrubbing assures a good granulometric distribution leading to a good separation of fractions.

The main features of wet scrubbing treatment, including the sludge hydrocyclonage, are:

- low energy consumption;
- for high quantities of water it is necessary the applying of an efficient system for water treatment, otherwise the clogging of scrubbers might be appeared, leading to the efficiency decreasing;
- for avoiding the high salt contents and deposits on ducts, it is necessary the add of small quantities of fresh water into recycling system;
- the resulted sludge, after water treatment has a high Zn content;
- a very important aspect is coagulant dose;
- this type of technology is applied at: Hoogovens (Ijmuiden), Holland; Thyssen AG, Krupp Hoesch Stahl (Dortmund) and Duisburg, Germany.

The total investment for Blast Furnace wastewater treatment at Hoogovens (Ijmuiden) was at about 18 mil. ECU in 1996, the treatment including also the separation in two fractions of the sludge an pH adjustment, operating costs being very small. The rate of water recycling is about 97%, only 3% being losses and from this percentage only 1,5% being lost by evaporation.

2. ACTUAL STATUS IN OUR COUNTRY

Actual treatment of wastewaters from BF gas scrubbing consists of: radial settling basins, cooling towers and filter plants.

In order to prevent deposits and corrosion is compulsory the add of trisodium phosphate.

The water treatment from our country was designed to assure a rate of recycling at about 90%, but the maximum rate of recycling is 60%.

The treatment of wastewater means:

- the reduction of solids at about 50 mg/l (maximum 100 mg/l) for avoiding the deposits in cooling towers and pipes;
- the cooling at 30 - 35 °C, for the gas cooling;
- the cyanides reduction at maximum 1 mg/l in order to protect the environment.

After treatment, the sludge resulted as waste can be reused due the high content of iron (20 - 40 %) and carbon (10 - 20 %).

The pipes placed at large distances from the sources offers a natural treatment for wastewaters, but rate of recycling is still reduced.

An experimental model consists of the treatment of waters with sodium carbonate and ferrous sulphate lead to a rate of removal for suspended solids at about 50% from an initial rate at 25%, in these conditions, the global efficiency increasing at about 70% (for the whole treatment plant).

3. EXPERIMENTAL DATA

For laboratory experiments a coagulation technique considered as BAT was chosen.

The system sodium carbonate – ferrous sulfate was tested for the removal of the suspended solids, also for cyanides and heavy metals.

The samples were:

- 5 samples from 1,2 Blast Furnaces, point: settling basin;
- 5 samples from 3,4,5 Blast Furnaces, point: settling basin.

For pH adjustment was prepared a 36% Na_2CO_3 solution. The pH value of water, after adding of soda, was 9,5.

The optimum quantity of soda for pH adjustment was 16 mg Na_2CO_3 for 1 l wastewaters from 1,2 BF and 14,5 mg Na_2CO_3 for 1 l wastewaters from 3,4,5 BF.

The samples were tested for medium, minimum and maximum contents for suspended solids and physical-chemical composition of waters was analysed during two months.

The optimum dose for ferrous sulfate was between 30 – 35 mg for 1 l wastewater.

In this case, removal efficiency for suspended solids was about 50%.

Also, for organic matters, the removal, using this system for coagulation, was about 50 - 60%, exprimed as COD (chemical oxygen demand) and oils.

The obtained results are presented in table 5 and 6, and also the method efficiency is presented in fig. 2.

Table 5.
Obtained results after $FeSO_4.7H_2O$ treatment of waters
from 1, 2 Blast Furnaces, optimum dose: 35 mg / l

Parameters	Untreated wastewater	Wastewater treated with coagulant	Efficiency, %
pH	6,8	8,5	-
Suspensii solide	935	460	50,53
CCO	59	20	66,66
Ulei	48	20	58,33

Table 6.
Obtained results after $FeSO_4.7H_2O$ treatment of waters
from 3, 4, 5 Blast Furnaces, optimum dose: 35 mg / l

Parameters	Untreated wastewater	Wastewater treated with coagulant	Efficiency, %
pH	7,6	8,6	-
Suspended solids	650	305	53,07
Ulei	41	16,25	60,36
CCO	38	14,2	62,63

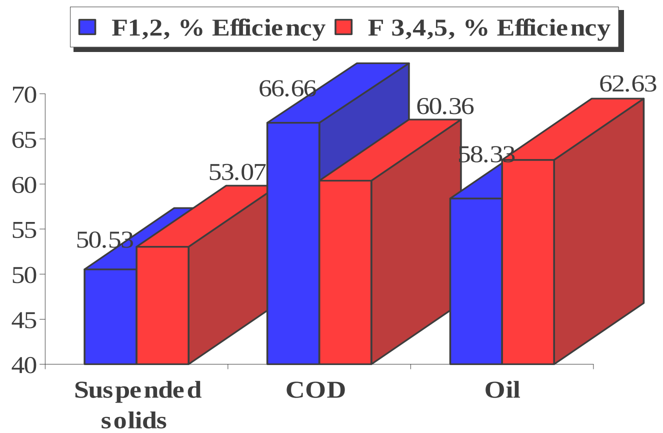

Fig. 2. Efficiency removal for suspended solids and oils
from wastewaters after coagulation treatment

4. CONCLUSIONS ABOUT „BAT” CONCEPT

Considered as “up to date” equipment, the treatment installations applied BAT concept and solved the issues as organic matters and especially anorganic compounds removal (suspended solids, heavy metals, cyanides, etc).

Of course, these installations (the most efficiency tiil now), not solve the hazardous potential for some pollutants as polyciclic aromatic hydrocarbons or even some cyanides.

As a review, the methods and techniques existing in our country are presented in comparison with European Union techniques (BAT), in table 7.

Table 7.
National and European Union techniques applied for wastewaters resulted at Blast Furnaces

Sector	Emission sources	BAT in European Union	Techniques applied at national level
Blast Furnaces	Wet scrubbing gasses (Venturi Scrubbers)	settling + filtration + activated sludge/coagulants adding + reuse of water	settling + filtration + reuse of water
	Indirect Cooling	blow down: settling + sand filtration + reuse of water	blow down: settling + sand filtration + reuse of water
	Slag Granulation	100 % reuse of water: closed system	reuse of water: closed system

From techniques abovementioned, it is observed that in our country, even if the treatment equipment for wastewaters is according to BAT, the actual treatment applied is not properly, comprising only a settling for sedimentation and sometimes the adding of some reagents for avoiding the deposits into pipes.

Of course, for an eficient treatment it is very important the costs aspects, but the environment regulations are more and more restrictived and it is compulsory the applying of some efficient techniques.

The reduction of the expensives and the obtaining of the high rate for wastewaters treatment can be made only at the end of pipe and it is necessary improvements for iron and steel processing in order to diminuiting the pollution from emissions resulted.

BAT concept includes the use of the unpolluted technologies for the main processes from iron and steel industry at low costs and with high efficiency.

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