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Modelling of an Ozonation Process for Cyanide Removal from Blast Furnace Gas-Washing Water and Analyses of Process Behaviour in Different Scenarios

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In the steel sector, the control of cyanide in the wastewater of the gas washing system of blast furnaces is one of the main issues related to the wastewater quality. Although established treatment processes exist, the relevant costs, the stringent environmental regulation and the extremely complex and variable composition of gas washing water lead to investigate modifications of current treatments and to develop new ones. A cyanide treatment based on ozonation is one of the proposed and experimented methods within the European project "DynCyanide". Starting from experimental data, a process model was developed through Aspen Plus® v.8.6, in order to test a wide range of operating conditions and wastewater features and to prove the robustness of the proposed process. The paper focuses on the process modelling and simulation phases. Water stream and ozonation are modelled through a number of theoretical reactors, by considering main and collateral reactions and a genetic algorithm is applied in order to reproduce at best the kinetics of these reactions. The validated model was applied for scenario analyses. Process knowledge was enhanced and, after finding the parameters and the compounds that reduce the ozonation efficiency, suggestions were obtained to improve the treatment performances. A temperature of 30°C and an initial pH value of 10 favour the cyanide ozonation; the batch mode of the treatment allows the removal of cyanide after 4.5 hours (3 cycles) using a limited ozone amount. If the wastewater contamination level is higher, a further cycle or a higher amount of ozone are needed.

1. Introduction

Process industry develops research activities for improving the environmental sustainability of the production, including improvement of wastewater quality. In the steel sector, the control of cyanide content in the wastewater of the Gas Washing (GW) system of Blast Furnaces (BF) is a relevant issue. The BF gases are purified through dry dedusting followed by a washing process, which can release cyanides in the GW Water (GWW). Such water is treated to remove fine particles and the cyanide content by means of well-established treatments, such as the Degussa methods, which adds formaldehyde and hydrogen peroxide by obtaining glycol. However, the related costs, the variable separation efficiencies due to changing BF operational conditions and the ever more stringent environmental requirements could require a modification of existing methods or the development of new approaches. A cyanide treatment process based on ozonation is one of the proposed methods within the European project entitled ''Cyanide Monitoring and Treatment under dynamic Process Conditions'' (DynCyanide). The ozonation is an efficient process to remove cyanide from municipal and industrial wastewater, such as pointed out by Upadhyay and Srivastava (2015), who, despite of the high cost of the treatment, highlight the ozone potentialities in different treatment fields. The adaptability of the ozonation to the treatment of different wastewaters and the growing interest toward this treatment are underlined in several research works. Van Leeuwen et al. (2003) investigate at laboratory scale the possibility to use ozonation to remove cyanides, thiocyanates and color in wastewater coming from coal coking plant. They found that the ozonation process is suitable and more environmental friendly than other treatments, but it is competitive only over a long operational period. Investigations are carried out on the use of an advanced ozone-based treatment of olive mill wastewater obtaining useful information for the treatment design (Lafi et al., 2009). Furthermore, the exemplar study of Derco et al. (2012) is focused on the assessment of the

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degradation of organochlorine pesticides and oil compounds (micropollulants of wastewater) through ozone with/without UV; the investigation results in high removal rate in short treatment times. Finally yet importantly, an ozone-based process is proposed for the treatment of milk-including wastewater (Sato and Saito, 2013): in this case, the efficiency of the process depends on the initial conditions of the wastewater to be treated. As already underlined by the work of Sato and Saito (2013), the ozonation is affected by several factors related to the features of the water to be treated. For this reason also in the case of cyanide removal different studies were carried out. For instance, investigations were performed in order to assess which parameters affect the ozonation of a coke-oven wastewater (Chang et al., 2008). The removal of total cyanide was always obtained in each of the different operating conditions (e.g. pH, ozone/hydrogen peroxide, ozone/UV) explored by Monteagudo et al. (2004) in the treatment of thermoelectric power station waste waters, but different reaction rates were obtained. Finally, Kepa et al. (2007) found that pH has a strong influence on the efficiency of the ozonation process to remove cyanide from water and that best results are achieved with H_2O_2/O_3 system. Despite several research works and applications of ozonation to treat wastewater of different origins and, in particular, to treat cyanide, only recent studies exist related to the cyanide removal through ozone from BF GWW (Luzin et al., 2012), which shows a wide range of varying contaminants that can compete for the ozone consumption. Within the Dyncyanide project, experiments were performed through a pilot plant settled by the process developer to improve understanding the ozonation process, the competing reactions and the cyanide removal efficiency. Ozone is generated and injected into the untreated GWW through a spiral reactor; the GWW goes in a settling reactor to allow the ozonation reactions. The plant can be used in a batch mode, with recirculation of GWW, or in continuous mode, without recirculation. The unreacted ozone is then destroyed. Furthermore, a process model was developed in order to test a wide range of operating conditions and GWW features, which can vary within a single plant or from one plant to another. The importance of process simulation in the steel field through advanced tools such as Aspen Plus® has already been emphasized in many works, such as in the study carried out by Alcamisi et al. (2015) to test options of wastewater blowdown reuse in an Italian steelworks. Another exemplar simulation work was carried out by Matino et al. (2016) in which an electric steemaking route model was presented and used to assess the sustainability of real plants in different scenarios. The paper focuses on the process modelling and simulation phases that were carried out using the specialized commercial software Aspen Plus® and on the application of the validated model for extensive scenario analyses. The aim of the paper is to enhance the knowledge on the cyanide ozonation behaviour in different conditions for this novel application. The paper is organized as follows: Section 2 presents the modelling phase; in Section 3, the achieved results are discussed and a preliminary economic analysis is introduced and Section 4 includes concluding remarks.

2. Materials and methods

A model of the ozonation process was developed through Aspen Plus® v. 8.6 starting from the acquisition of the process know-how and data of experimentation carried out in the pilot plant with GWWs coming from an integrated steel plant. GWWs are complex aqueous mixtures with different kind of cyanide compounds (e.g. KCN, $Zn(CN)_2$, NaCN) and with a lot of chemical complexes that can interfere during the cyanide removal (e.g. $CaCO_3$, NH_3, CaO, MgO, Nitrates, Nitrites, Iron compounds, NaCl, K_2SO_4). For this reason, the modelling of the GWW to be treated was carried out following the indications given in Alcamisi et al. (2014) in order to fill both the fraction of each of the compounds and the pH, conductivity, hardness, etc, that can be found in real GWWs data. Moreover, 59 between equilibrium, salt and dissociation reactions related to the considered/selected chemical compounds were included in the model, in order to consider as much as possible the phenomena that these compounds undergo in aqueous solution. The treatment model is composed of a series of N treatment cycles (e.g. 3) with a specified duration (e.g. 1.5 hours), in the case of batch mode, and of a single continuous stage in the case of continuous mode. Each cycle/stage is modelled in the same way for the batch and the continuous mode. The cycle constitutes the reaction system in which the following main ozone reactions are taken into account in different reactors:

- Cyanide reactions

$$CN^- + O_3 \rightarrow CNO^- + O_2 \quad (1)$$

$$2CNO^- + 3O_3 + H_2O \rightarrow 2HCO_3^- + N_2 + 3O_2 \quad (2)$$

- Side reactions

$$2NH_3 + 4O_3 \rightarrow NH_4NO_3 + 4O_2 + H_2O \quad (3)$$

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \quad (4)$$

In addition, the consumption of ozone due to CaO and MgO that act as radical interceptors is considered. On the other hand, the iron effect on cyanide demand is neglected. The kinetics of the previous reactions are considered through the application of an ad-hoc developed genetic algorithm (GA). Such GA was implemented in the Matlab® simulation environment, in order to find the best fitting parameters of the reaction rate law for each considered ozonation reaction according to experimental data obtained through the analyses that were carried out with DIN 38405 method. The GA is based on the "integral method" standardly exploited to search the chemical kinetic law of a reaction. The GA uses the following data in its computations: discretized treatment time, chemical compounds conversion during the treatment time, estimated ozone concentration during the treatment time, initial chemical compounds concentration, population size, crossover rate and other parameters of the GA. The GA evolves until the mean error between computed kinetic constants (or pre-exponential factor) in each treatment steps and their median was minimized. The obtained chemical kinetic parameters are listed in Table 1, where *a* is the order of reaction with respect to the chemical compounds to be ozonized, *b* is the order of reaction with respect to ozone and K_0 is the pre-exponential factor of the Arrhenius equation and *K* the kinetic constant in the case of ammonia.

Table 1: Kinetic parameters for cyanide and side ozonation reactions

	a (cyanide, nitrite, ammonia)	b (ozone)	K_0 or K	GA Error
Cyanide	$5.4 \cdot 10^{-1}$	$1.3 \cdot 10^{-3}$	$K_0 = 1.5 \cdot 10^{-8}$	0.3%
Nitrite	$5.4 \cdot 10^{-1}$	$3.6 \cdot 10^{-5}$	$K_0 = 9.9 \cdot 10^{-6}$	0.5%
Ammonia	0	$1.5 \cdot 10^{-1}$	$K = 5.1 \cdot 10^{-8}$	12.3%

The GA gives very good results with low errors; only in the ammonia case, the error exceeds the 10 %. The found kinetic parameters were put into the related reactor together with activation energy found in literature (Gottschalk et al., 2009 and Huie and Herron, 1974). The ozone consumption due to the radical sequestration by CaO and MgO are considered through a customized Excel-based calculator block, due to some lack in Aspen Plus chemical compounds database that prevented the use for these of common reactors; however, a sort of "rate law" was found also in this case and it was used in the Excel block. An "auxiliary tuning reactor" was added in the model in order to allow a better management of HCN and CN^- equilibrium in the reactor system. In addition, FORTRAN-based calculator allowed the calculation of electrical conductivity according to the indication given in Matino et al. (2015). Finally, ad-hoc Excel-based calculator blocks were implemented in the model in order to obtain punctual cyanide and other main compounds contents as well as unreacted ozone at each treatment time; these blocks include the found kinetic laws and small tuning parameters in the form of multiplicative correction factors in order to correct the small errors of the kinetic laws. The model was validated comparing different trials and simulation results under the same operating conditions. The model follows very well the cyanide trend as well as the trends of collateral compounds during the ozonation treatment. On the other hand, some little differences were found for the monitored parameters. The drop of pH in the simulation is slightly greater than in the real case: this fact can be due to the software intrinsic management of acid-base equilibria or to the neglecting/consideration of some reactions that affect pH. The simulation conductivity does not undergo a decrease in the first hour of treatment, such as it occurs in the reality, but then they are both stable; the final error for this parameter is between 10 - 15%. The validated model was used to test the behaviour of the proposed ozonation process for different GWW compositions and operating conditions.

3. Results and discussions

The real experimentation trials, which were carried out in a first part of DynCyanide project, were extended exploiting the developed "virtual treatment" in order to consider the variability of the BF GWW composition and to assess the efficiency of ozonation treatment process in different operating conditions.

3.1 Cyanide ozonation behavior starting from different BF GWW compositions

The analyses of the considered steelworks data related to long term GWW sampling allows the definition of the range of the GWW composition and paves the way to the values to be used in simulations; in particular the average values of main compounds are used as starting point and then changes up to the limits in Table 2.

Table 2: Main simulated GWWs compounds range

Contaminant	Average Values [mg/L]	Min Limit	Max Limit [mg/L]
CN^-, free	5	5	20
NH_4^+	100	50	200
CaO	50	50	150

During the simulations, the standard operating conditions were used: batch mode, O_3/GWW ratio of 100 mg/L, pH input value of 10, room temperature and a treatment time of 4,5 h (3 cycles steps).
The simulation shows that with an initial content of 10 mg/L of Weak Acid Dissociable (WAD) cyanide, 100 mg/L of ammonia and 150 mg/L of CaO, the treatment consumes a higher amount of ozone and the cyanide ozonation decelerates with respect to the cases of lower GWW contamination. However, the desired cyanide limit (0.2 mg/L) is reached after 4.5 hours of treatment. On the other hand, the standard operating conditions are insufficient to achieve the desired limit if an amount of 20 mg/L of WAD cyanide is present in the initial GWW although the amount of ammonia and CaO are not very high. Figure 1 shows the results obtained in the case of lowest and highest contaminated GWWs. Simulations provide also further information: ammonia and nitrites show having negligible effects on cyanide ozonation even at higher concentrations while radical sequestrations seem to negatively affect the cyanide removal due to a high ozone consumption; different results were obtained for this aspect in laboratory trials carried out by process developer adding a disturbing compound per test. More investigations are needed to improve the knowledge of collateral reactions and synergies between them.

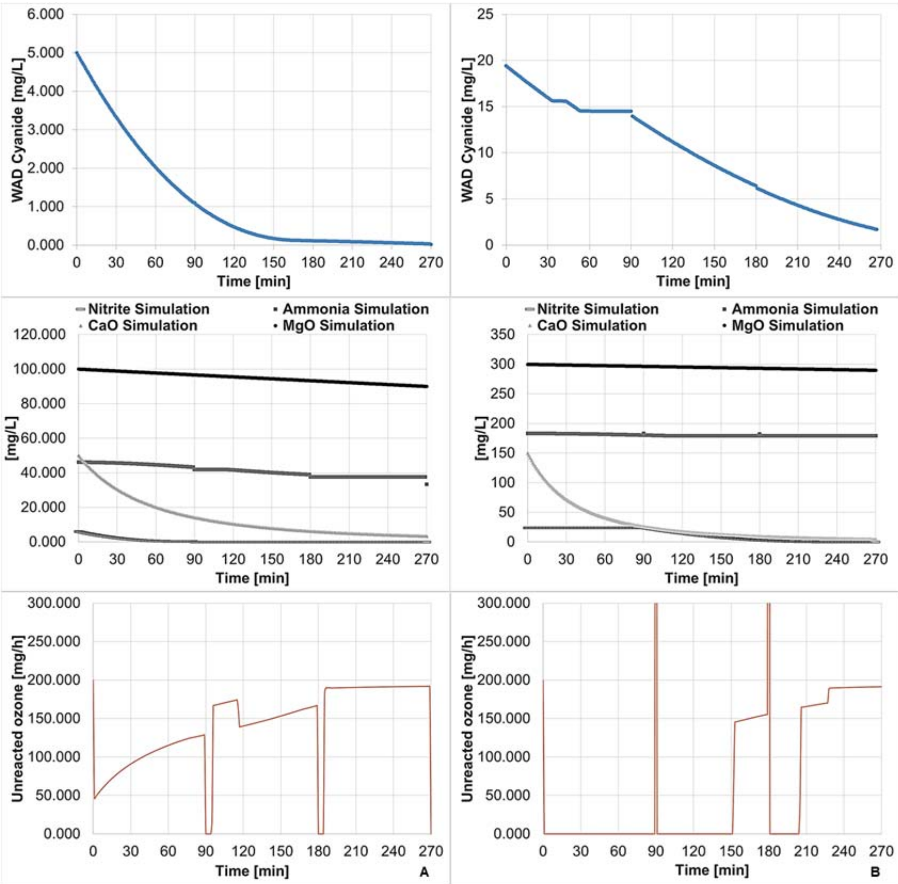

Figure 1: Simulation results in the case of: A. lowest contaminated GWW; B. highest contaminated GWW

3.2 Assessment of different treatment operating conditions

Several operating conditions were evaluated in order to assess the parameters, which mostly affect the process efficiency. To this aim, different simulations were carried out by varying one parameter at a time; the simulated operating conditions are listed in Table 3.

Table 3: Simulated treatment operating conditions (the standard ones are underlined)

Input pH	Temperature [°C]	O_3/GWW ratio [mg/L]	Others	Mode
9	10	50	Without recycle of unreacted O_3	Batch
10	Room temperature	100	With recycle of unreacted O_3	Continuous
12	30	200		
	50			
	80			

The following values of main GWW contaminants were considered in simulations: 12 mg/L of CN^-, 120 mg/L of ammonia, 100 mg/L of CaO. The results are depicted in the radar diagrams in Figure 2.

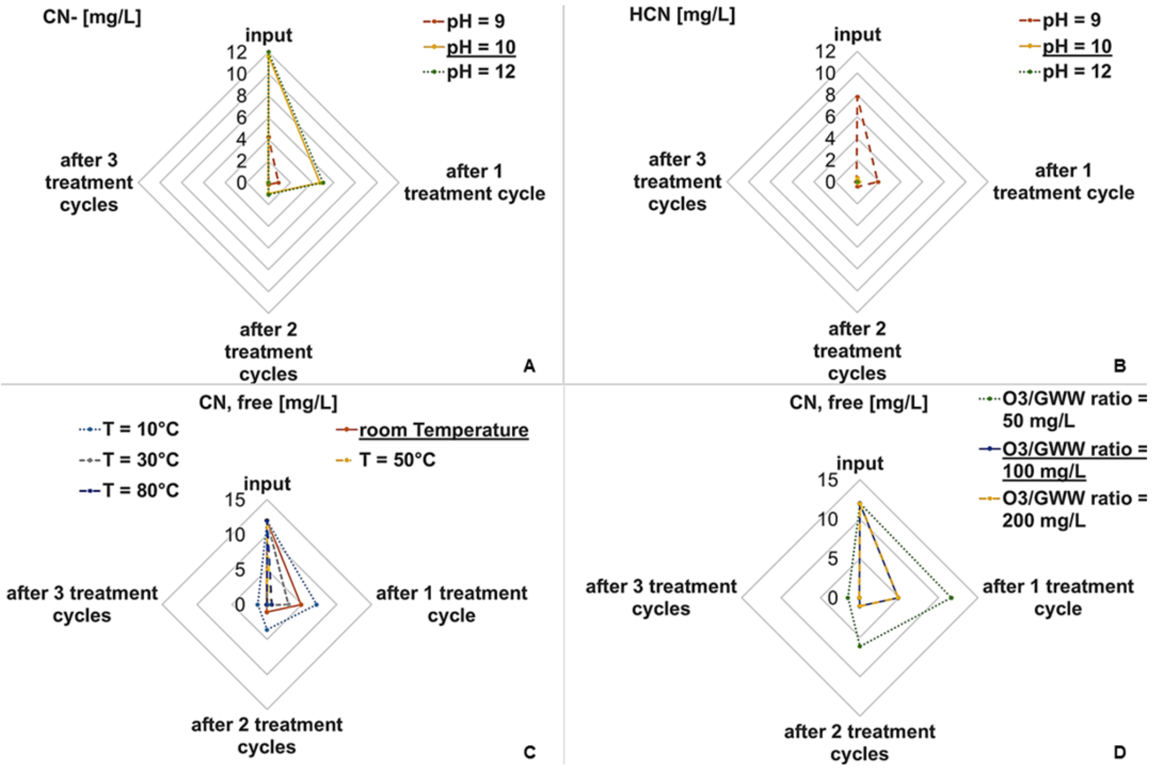

Figure 2: Simulation results in the case of variation of: A and B. pH; C. temperature; D. O_3/GWW ratio

The diagram related to the pH highlights that the lower the input pH, the higher shift of the equilibrium CN^-/HCN toward HCN in each batch treatment cycle, which makes the cyanide ozonation more difficult; the pH value of 10 represents a good compromise.

High temperature implies a significant increase of cyanide treatment rate and a good improvement is achieved with a temperature of 30 °C. On the other hand, a significant decrease of ozonation treatment efficiency was achieved by decreasing the O_3/GWW ratio; the value of 100 mg/L represents a good choice, as, by further increasing the considered ratio, the improvement in cyanide ozonation efficiency is not significant.

Moreover, if a recycle of unreacted ozone is possible, it improves the cyanide ozonation rate and two treatment cycles are almost sufficient to achieve the CN limit.

Finally, the continuous mode allows achieving very low cyanide removal efficiency (24 %) in standard operating conditions and with a residence time of 30 minutes. A temperature of 50°C, a O_3/GWW ratio of 400 mg/L and ensuring a residence time of 3 hours allows obtaining a removal efficiency of about 94 %.

A preliminary economic investigation was carried out through the estimation of Net Present Value (NPV) and the Discounted PayBack Period (DPBP) for the ozonation treatment to compare it with other common ones such as Degussa process, Degussa process followed by aeration (DPA) and alkaline chlorination. Post treatments were taken into account in order to consider the possibility of reuse of treated water. The analysis considered the amount of investment and annual operating costs (i.e. chemicals, energy, maintenance, labor, depreciation) and benefits (e.g. recovered water) in order to compute the discounted cash flows along the operating life (i.e. 20 years). The ozonation treatment and the DPA require the highest investment, but in the long term, they result the most convenient solution, as the NPV is positive and the DPBP is less than 5 years, while in the other cases the operating costs are much higher than the benefits and DPBP is higher than 15 years.

4. Conclusions

The model of a novel BF GWW ozone treatment for cyanide removal is proposed here, whose aim is to extend the experimental campaigns in order to develop a sort of sensitivity analysis taking into account the variability of BF GWW composition and assessing different operating conditions. Useful information was obtained about the chemical compounds that negatively affects the efficiency of cyanide ozonation: CaO and MgO seem the most significant ones according to simulation point of view. However, deeper analyses are needed for this aspect because of different results obtained in laboratory trials carried out adding a collateral compound per test. In particular, the effects of complex reactions with interference and synergies between compounds require more investigations. A pH value of 10, temperature of 30 °C and a O_3/GWW ratio of 100 mg/L appear the best operating conditions in batch mode for a wide range of GWW compositions in order to achieve the cyanide limit of 0.2 mg/L within a reasonable time. However, more ozone and time are required when the GWW contamination is close to the upper bound. On the other hand, the continuous operating mode is possible and suitable, as long as enough O_3 and dwell time are available in relation to the CN content. A preliminary economic analysis showed that the ozonation process is more convenient with respect to other common treatments in terms of NPV and DPBP. Although the achieved results represent only indications and further real tests can be needed before plant implementation for a full assessment of the obtained achievements, the developed model is indeed useful in order to verify the robustness of the process in the proposed highly variable and novel application, by improving the knowledge on the application of the cyanide ozonation process for the treatment of BF GWW.

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