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MODELING AND OPTIMIZATION OF CHLORINE DIOXIDE GENERATION

MODELOWANIE I OPTYMALIZACJA WYTWARZANIA DWUTLENKU CHLORKU

1. Introduction

Chlorine Dioxide (ClO_2), which is widely used for the protection of distribution systems from the regrowth of bacteria, is also used by a big waterworks who supply over 600.000 people with an average of 150.000 cubic meters of high quality drinking water per day. Since recent years, modern standard-compact-units are used for the production of ClO_2 with the conventional Aqueous Chlorine-Chlorite Process. However, the efficiency of this apparatus keeps at about 80 % which is distinctly lower than expected.

It is the objective of the work presented to increase production efficiency and decrease at the same time production of unwanted by-products. In order to achieve this goal, the chemical fundamentals are studied from the literature and transferred into a mathematical model of the chlorine dioxide production process. Model simulations are then carried out to find optimum reaction points.

2. Modeling

In the production unit, chlorine dioxide is produced from gaseous chlorine, acid and dissolved sodium chlorite as shown in Figure 1.

Gaseous chlorine and hydrochloric acid are fed to driving water which is then, together with chlorite solution, fed to a reactor to produce a concentrated solution of chorine dioxide. This solution is further diluted with dilution water and the finished chlorine dioxide solution is stored in a tank to be finally dosed to drinking water.

The process has been thoroughly investigated over the last 30 years. The main reactions in the process are:

$$Cl_{2(aq)} + H_2O \Leftrightarrow H^+ + Cl^- + HOCl_{(aq)} \tag{1}$$

$$HOCl_{(aq)} \Leftrightarrow H^+ + OCl^- \tag{2}$$

$$ClO_2^- + H^+ \Leftrightarrow HClO_{2(aq)} \tag{3}$$

$$2\ ClO_2^- + Cl_{2(aq)} \Leftrightarrow 2\ ClO_{2(g)} + 2\ Cl^- \tag{4}$$

$$2\ ClO_2^- + HOCl_{(aq)} + H^+ \Leftrightarrow 2\ ClO_{2(g)} + Cl^- + H_2O \tag{5}$$

$$ClO_{2(g)} \Leftrightarrow ClO_{2(aq)} \tag{6}$$

$$2\ ClO_{2(aq)} + OH^- \Leftrightarrow HClO_{2(aq)} + ClO_3^- \tag{7}$$

$$2\ ClO_{2(aq)} + HOCl_{(aq)} + H_2O \Leftrightarrow 2\ ClO_3^- + 3\ H^+ + Cl^- \tag{8}$$

$$CO_{2(aq)} + H_2O \Leftrightarrow HCO_3^- + H^+ \tag{9}$$

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \tag{10}$$

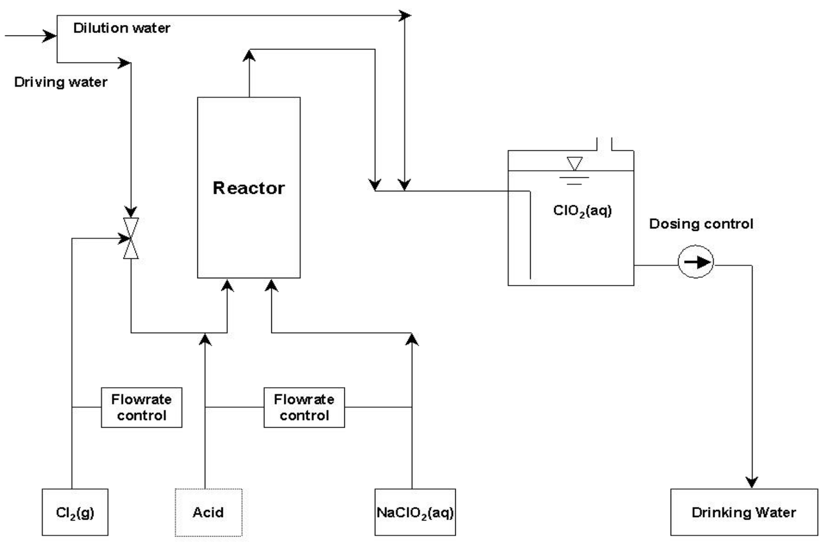

Fig. 1. The process of ClO2 production by aqueous chlorine/chlorite process

A model based on these reactions for simulation of the ClO_2 generation process is established with the software "PHREEQC for windows v.2.11.00" which is a computer program for simulating chemical reactions and transport processes in natural or polluted water. In this model, acid-base reactions such as (2), (3), (9) and (10) are defined with equilibrium constants and enthalpy of reaction and some other redox reactions such as

(1), (4), (5), (7) and (8) are defined with kinetics expression whose rate constants are collected from the literature. Because chlorine dioxide has a high solubility in water, it is assumed that all the chlorine dioxide exists in aqueous phase in this model.

3. Results

With the help of the model, influences of different parameters on the chlorine dioxide production can be investigated theoretically. The influences of temperature and pH value which are usually two main parameters for chemical reactions are investigated firstly. As shown in Figure 2, the temperature has very little influence on the production of chlorine dioxide.

Figure 3 shows that the chlorine dioxide yield is strongly dependent on the pH value in the storage tank which can be used for easy comparison with practical data. It is apparent that when pH in storage tank is below 6, yield of chlorine dioxide can nearly reach 100% and when it is in alkaline solution, there is very little chlorine dioxide produced. The square symbol in pink shows pH measured in the storage tank and chlorine dioxide efficiency measured. As efficiency measured is much lower than expected from theory, the reason for the low efficiency has to be found.

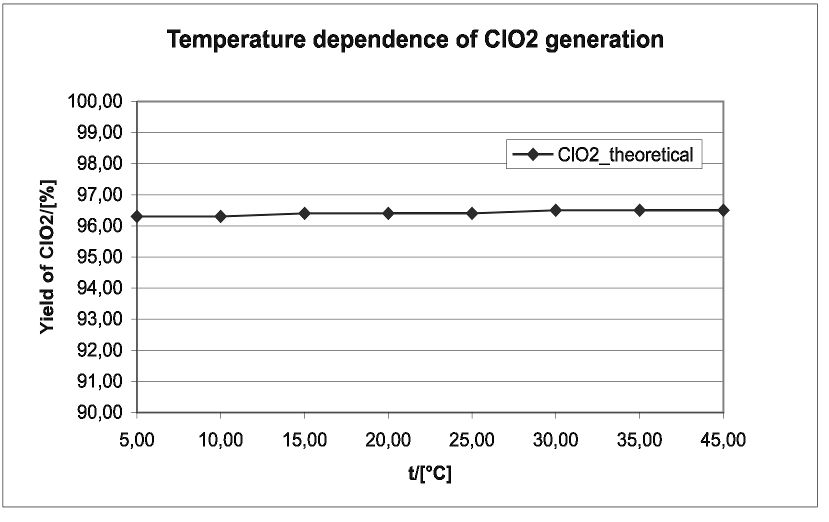

Fig. 2. Theoretical temperature influences on the ClO2 production.

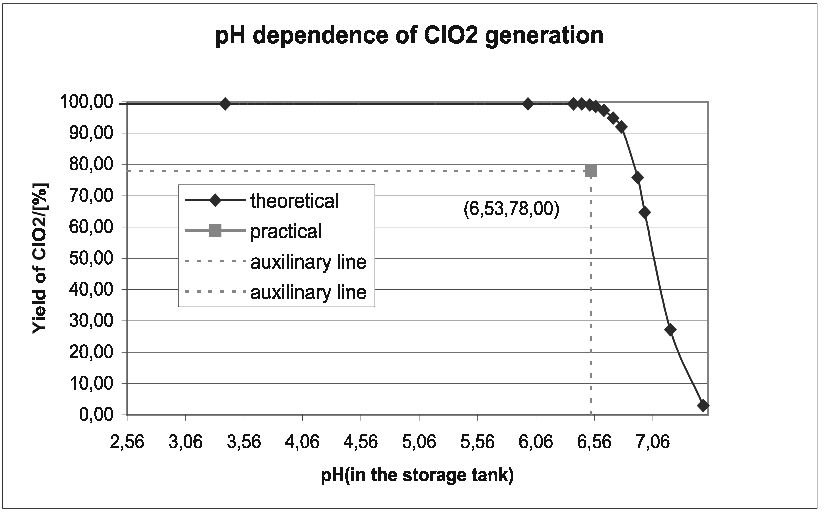

Fig. 3. *Theoretical pH in storage tank influences on the ClO_2 production*

An alkaline pH decreases chlorine dioxide formation efficiency. However, also reactions for byproduct production such as (7) and (8) are favored. So acid environment can improve the production of chlorine dioxide.

For practical process, several measures can be taken for adjusting the pH value in the reactor such as adjusting the pH value of process water, acid capacity of process water, amount of excess Cl_2 dosage and the proportion between driving and dilution water. The investigation of influences of these parameters is shown from Figure 4 through Figure 7.

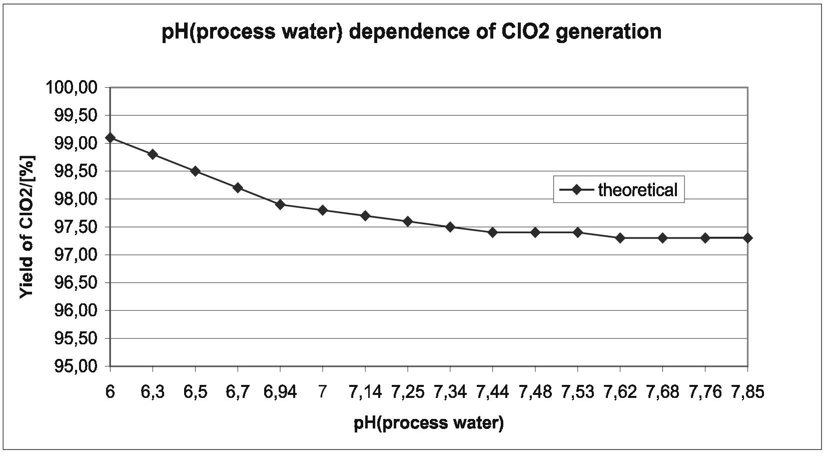

Fig. 4. *Theoretical pH of process water influences on ClO_2 production*

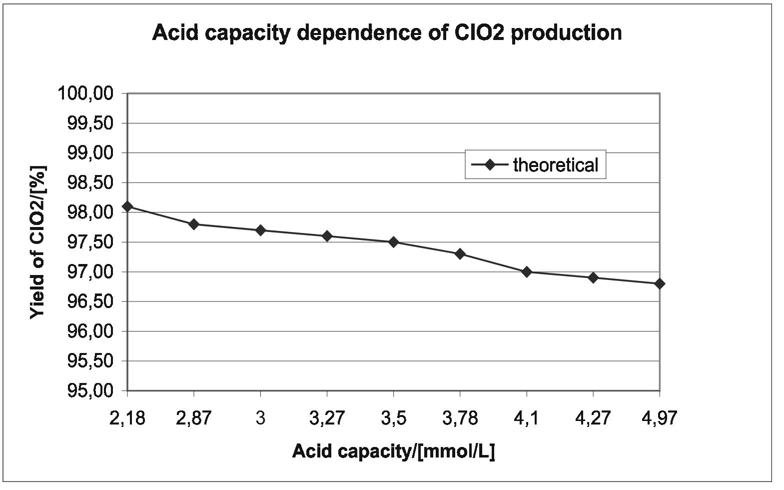

Fig. 5. Theoretical acid capacity influences on ClO2 production efficiency

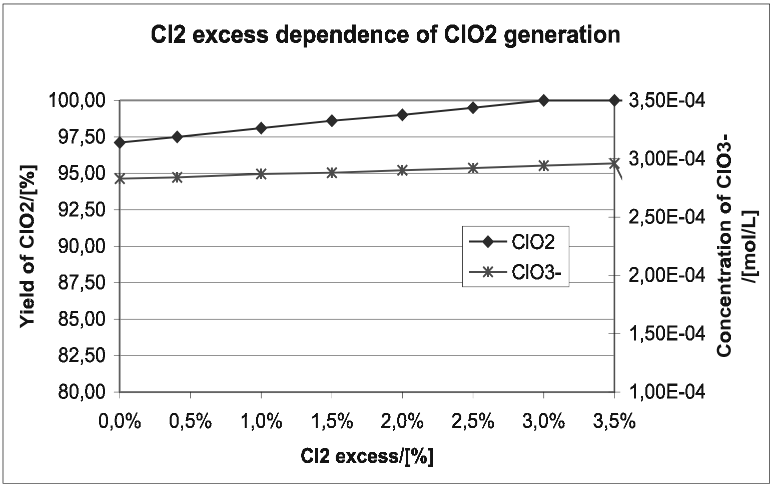

Fig. 6. Excess Cl_2 influences on the production of ClO_2

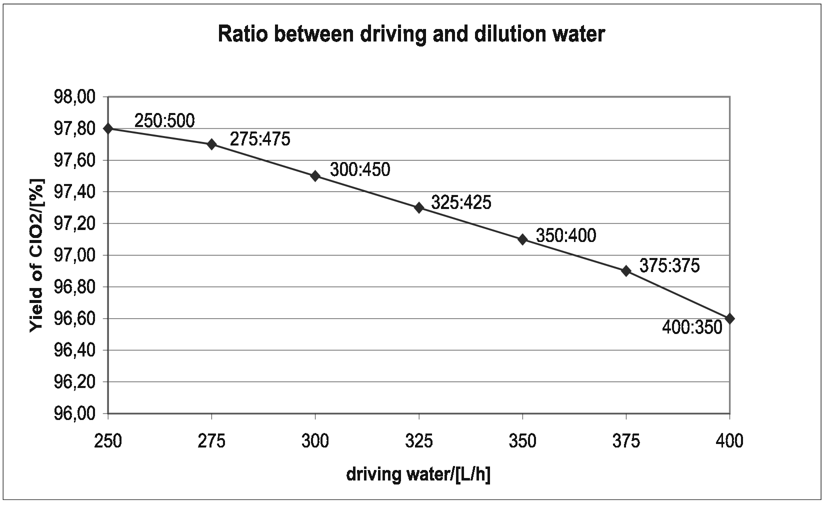

Fig. 7. The proportion between driving and dilution water influences on the ClO_2 production

It can already be seen that, depending on environmental conditions, slight adaptations of the production process can improve the overall yield and minimize by-product formation.

Currently, yields predicted by model simulation and obtained in the full scale plant are compared and consequences for future optimization of the process are derived.