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RESEARCH PAPER

Recovery of High-Purity Magnesium Hydroxide with Self-Tuning PID Control and PID of pH

Yavuz Demirci[1*] and Mustafa Alpbaz[2]

[1] Department of Environmental Engineering, Adiyaman University, P.O.Box 02040, Adiyaman, Turkey
[2] Department of Chemical Engineering, Ankara University, P.O. Box 06100, Tandogan, Ankara, Turkey

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Abstract
The salt obtained from salt sources has a low purity level and contains contaminants. The primary contaminants in the brines were eliminated in this investigation by using analytical separation (titration) techniques. Following the purification method, sodium hydroxide (NaOH) was added to magnesium chloride (MgCl2) to make magnesium hydroxide (Mg(OH)2) coagulate in pH control. This was done by PID and Self-Tuning PID (STPID) Control. Using STPID Control, hydrochloric acid (HCl) at a rate of 20% was employed as an effective acid current, MgCl2 as a coagulant, and NaOH at a rate of 10% as a neutralization base throughout the process. The coagulation technique was carried out with pH values of 7, 9, and 11, respectively. The pH of the medium was adjusted using the PID and STPID algorithms, as well as an on-line computer control system. As the system model, ARMAX was employed. As a forcing function, a pseudo-random binary sequence (PRBS) was used to identify the dynamics of the process to be controlled, and the system output was measured. The Bierman algorithm was used to evaluate the model parameters. The STPID controller's tuning parameters were calculated. Following the coagulation method, an analytical titration procedure was used to find out if there are any trace amounts of Mg(OH)2 in the current environment, and a settlement percentage of 90% to 95% was found. To get the best coagulation, a pH value of 11 was chosen as the optimal value based on the performed calculations.

Keywords: Coagulation, Magnesium Hydroxide, PID, Self-Tuning PID Control, Brine

INTRODUCTION

Crude salt obtained from salt sources has NaCl in concentrations ranging from 94 to 96 %. The rest is made up of $MgCl_2$, $MgSO_4$, $CaCl_2$, and other small things. These chemicals are referred to as soluble or insoluble impurities. In the chemical industry, crude salt dissolves in water or brine with impurities. Therefore, the brine must be purified before being processed. The impurities from the crude salt dissolved in the brine are precipitated with chemicals and removed by various processes.

The most important step in the production of salt is to bring the solution or coarse salt obtained from the existing salt sources to supersaturation by evaporation, then crystallize and subject it to purification. Because these impurities remain in the system indefinitely due to the manufacturing method, time-dependent buildup happens with the raw salt added to increase saturation. Although these salts are not commercially available due to their low concentrations in the environment, they may inhibit a prospective production in terms of energy efficiency and production efficiency over time.

With chemical purification, it is possible to remove these salts without taking them into the

* Corresponding author Email: yavuzdemirci@gmail.com

production line, but if it is done continuously, it negatively affects the competitiveness of the companies economically. For this reason, chemical purification is recommended when these salts reach certain degrees of saturation.

Many research have reported the feasibility of recovering magnesium hydroxide from a saline solution via reactive crystallization, a precipitation process triggered by the addition of an alkaline reactant (Mažuranıć, Bılınskı, & Matkovıć, 1982; Um & Hirato, 2014):

Mg^{2+} (aq) + 2OH(−aq) = $Mg(OH)_2$ (s)

$Mg^{2+} + 2NaOH \rightarrow Mg(OH)_2 + 2Na^+$

Magnesium precipitation begins at approximately pH 9.5, becomes significant above pH 10.5, and is essentially complete at pH 11.0–11.5. Good chemical clarification is usually not achieved until pH 11.0–11.5 is reached (Semerjian & Ayoub, 2003).

There are numerous studies on the recovery of $Mg(OH)_2$ by precipitation with the addition of NaOH. Alamdiri et al. in his study, MgOH was precipitated from brine samples (Alamdari, Rahimpour, Esfandiari, & Nourafkan, 2008). Precipitation was carried out by adding NaOH to the magnesium-containing brine sample. In addition, a mathematical model for the precipitation of $Mg(OH)_2$ has been developed in the study. La Corte et al. showed magnesium recovery from exhausted brines produced by Trapani's saltworks (Italy). These brines contain a high concentration of magnesium ions (approximately 20–30 times higher than seawater), which were recovered as high-purity magnesium hydroxide by adding NaOH to the brine. The reactive crystallization procedure was carried out in a continuous stirred tank reactor (CSTR), and the purity of the $Mg(OH)_2$ crystals was found to vary from 98 percent to 100 percent. Reactants were combined together in reactive crystallization. As a result, high-purity reactants were required for this process to avoid contaminating the final product, although operating costs rose proportionately. Furthermore, because saltwater and brines contain numerous ions, selecting the best alkaline reactant was critical to ensuring high product purity: in the worst-case scenario, undesirable large co-precipitations may occur (La Corte et al., 2020).

Salt production for high-consumption areas will be achievable thanks to a production process that will be handled with modern control elements by combining existing systems. The pH control by adding sodium hydroxide (NaOH) to magnesium chloride ($MgCl_2$) was achieved in a stirred continuous reactor using the self-tuning PID (STPID) algorithm in the current work. As the system model, ARMAX was employed. As a forcing function, a pseudo-random binary sequence (PRBS) was used to identify the dynamics of the process to be controlled, and the system output was measured. The Bierman algorithm was used to evaluate the model parameters. The tuning settings of the STPID controller (for example, t_1) were determined using ISE and IAE criteria (Alpbaz, Hapoglu, Ozkan, & Altuntas, 2006; Altınten, Ketevanlioğlu, Erdoğan, Hapoğlu, & Alpbaz, 2008). pH control is a critical phenomenon in the removal of mainly pollutants from brine. Because of its very non-linear characteristic, pH regulation has been acknowledged as a tough problem in the literature (Alpbaz et al., 2006). One of the goals of this work was to demonstrate that using a linear second order ARMAX model in conjunction with the STPID algorithm giving adequate pH control. The second goal was to keep the running process at the greatest level of coagulation of magnesium hydroxide ($Mg(OH)_2$).

MATERIALS & METODS

Wastewater sampling

The bioreactor with a cooling jacket and a volume of 2 L, used in the experiments, is shown in Fig. 1. There were two pumps, flow meters, pH electrode, A/D converters and a computer in the system. The computer control system was connected online to the reactor where the

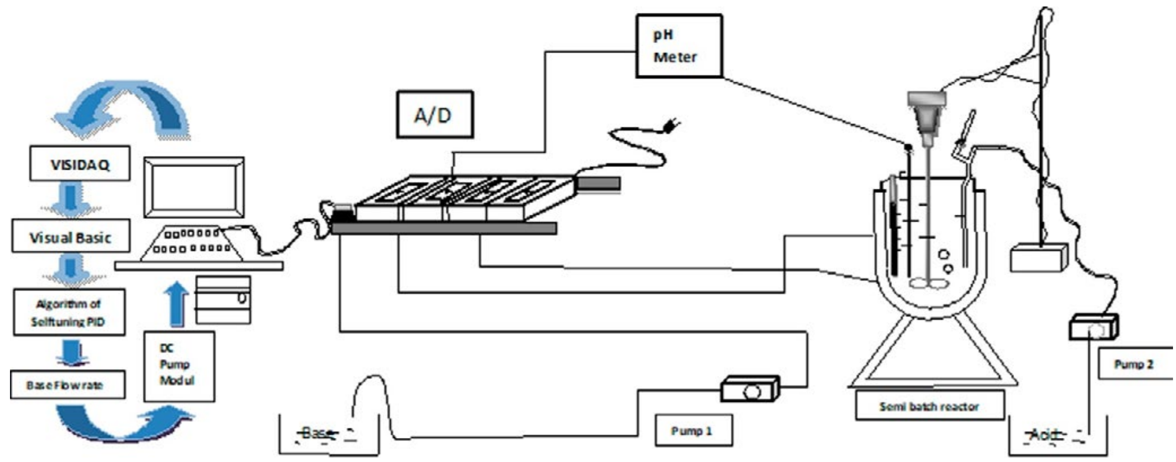

Fig. 1. Experimental set-up.

Table 1. Major elements and their concentrations in brine samples (Bayram, 2018)

Major elements	Brine concentrations
Na^+	111.2
K^+	1.4
Mg^{2+}	3.5
Ca^{2+}	0.85
Cl^-	180
SO_4^{2-}	8.2

precipitation processes were carried out.

Brine samples used in the experimental study were obtained from Salt Lake in Turkey and the concentrations of the main elements in its content are given in Table 1(Bayram, 2018).

Coagulation Process

This experimental study was carried out to evaluate the recovery of high purity magnesium hydroxide at different pH values. In the control experiments, 20% HCl and 10% NaOH solutions were used for both PID control and STPID control. In this part, pH control of a semi-batch reactor was carried out with a self-adjusting PID control system. For this purpose, the process pH was stabilized at 7, 9 and 11, respectively, and negative and positive step effects were given to the HCl flow rate. PID and self-adjusting PID control experiments performed at 25 °C using the same brine samples are compared in this section.

The STPID control algorithm in the computer was operated depending on the system variables. The pH measurements were made from the reactor, and the necessary information was transmitted to the computer, where calculations were made and the pump, which was used for pH control and known as the adjustment variable, sends the NaOH solution to the system. After reaching the appropriate pH, it was operated for a while and the reaction was stopped. Then, by turning the mixer speed to slow, polyelectrolyte was added to the medium.

The precipitation experiments in the chemical treatment system were carried out with PID and STPID control algorithms. The PID control algorithm was carried out using the control parameters obtained by the Cohen-Coon method (Isdaryani, Feriyonika, & Ferdiansyah, 2020).

Cohen-coon tuning parameters were calculated as P=33, I=38, D=6 using "the passing reaction curve method". With the experimental results obtained, magnesium removal, which was one of the major impurities in the brine, was achieved. Appropriate operating conditions were created for the precipitation to be carried out. Appropriate control parameters were found at the beginning of the control studies and preliminary tests were made before the control experiments. The computer control system was connected online to the reactor where the precipitation processes are carried out. The pH values were measured in the reactor, and the necessary data was transmitted to the computer, and the amount of the NaOH solution used for pH control and known as the adjustment variable, and the pump that sends it to the system were adjusted by making calculations.

In the second stage of the experimental study, Self-Tuning was carried out by using PID control algorithm. In order to ensure the best efficiency in the control studies, the control setting parameter in the STPID control algorithm had to be selected in the most appropriate way. Therefore, the setting of the parameter, t_1, from the control studies was very important. In the control experiments, the optimum value of t_1 was used 0.5 to observe the control efficiency (Furqan Aulia, 2010).

A self-adjusting control program was developed in the VISIDAQ programming language and the control algorithm was employed online for control calculations. Under operational settings, the system model was discovered between the base flow rate and pH employed for control purposes. The pH of the brine was managed by a self-adjusting control system using the data received, and the base flow rate was employed as an adjustable variable.

While the system was in dynamic state, the pH was controlled at the desired value with the self-adjusting PID control algorithm. Providing an effective control was possible with the correct determination of the model coefficients that make up the system and the adjustment parameters such as t_1. In order to use the STPID control system effectively, the coefficients of the ARMAX model and the t_1 tuning parameter were used appropriately (Furqan AULIA, 2010). Efficiency was observed in the precipitation process in the salt solutions by using STPID algorithm that used for pH control.

Self-tuning PID control

A generally used process model is a controlled auto regressive moving average model (CARMA) or auto regressive moving average exogenous (ARMAX) model (M. B. Zarrop, 1991; Newell R.B.; Lee, 1989; Seborg, Edgar, & Shah, 1986). ARMAX model is given in the following equation.

$$A\left(z^{-1}\right)y\left(t\right)=z^{-k}B\left(z^{-1}\right)u\left(t\right)+C\left(z^{-1}\right)e\left(t\right) \tag{1}$$

where A, B, and C are polynomials in the backward shift operator z^{-1}, and k is the control input's system time delay. The discrete time system's poles and zeros are represented by A and B, respectively. C comprises process noise zeros, and e(t) is an uncorrected random sequence. At time t, y(t) is the system output, and u(t) is the system input.

The model parameters were estimated on-line in the self-tuning control, and the controller settings were updated based on the current parameter estimator. The self-tuning strategy has gotten the most attention of any adaptive control strategy. CARMA, which uses the least square parameter estimation, is a commonly used process model. The CARMA model can be expressed as

$$y\left(t\right)= x^{T}\left(t\right)Q^{T}+e\left(t\right) \tag{2}$$

Where x is the data vector, the parameter vector is the collection of coefficients from the A, B, and C polynomials, and e is random noise. and x are calculated as follows:

$$Q^T = \left[a_1,\ a_{2,}\ a_3, \ldots\ a_{na},\ b_0, b_1, b_2, \ldots\ b_{nb},\ d_0,\ c_1,\ c_2, \ldots\ c_{nc} \right] \tag{3}$$

$$x^T = \begin{bmatrix} y(t-1), y(t-2), \ldots y(t-na), u(t-1), \\ u(t-2), \ldots u(t-nb-1), 1, e(t-1), \ldots e(t-nc) \end{bmatrix} \tag{4}$$

The PID control algorithm's discrete version can be turned into a self-tuning equivale. The following is the control equation:

$$U(t) = \frac{S}{R}\left[r(t) - y(t) \right] \tag{5}$$

Here $r(t)$ represents the set point, and:

$$S = s_0 + s_1 z^{-1} + s_2 z^{-2} \tag{6}$$

$$s_0 = K_c\left(1 + \frac{\Delta t}{2\tau_1} + \frac{\tau_D}{\Delta t}\right) \tag{7}$$

$$s_1 = K_c\left(-1 + \frac{\Delta t}{2\tau_1} - \frac{2\tau_D}{\Delta t}\right) \tag{8}$$

$$s_2 = K_c\left(\frac{\tau_D}{\Delta t}\right) \text{ and } R = \left(1 - z^{-1}\right) \tag{9}$$

Here Δt is the sampling interval. The PID constants can be found from the values of s_0, s_1 and s_2. Substituting the control equation into CARMA, process model yields the following closed-loop response equation:

$$y(t) = \frac{z^{-1}BS}{AR + z^{-1}BS}\ r(t) + \frac{RC}{AR + z^{-1}BS}\ e(t) \tag{10}$$

The characteristic equation is called as Tailoring polynomial T and it is given by:

$$T\left(z^{-1}\right) = A\left(z^{-1}\right)R + z^{-k}B\left(z^{-1}\right)S\left(z^{-1}\right) \tag{11}$$

The features of this closed-loop can be changed by moving the poles of the characteristic equation to the unit-circle in the z plane. The Bierman UDU^T algorithm (Bierman, 1975) is used to estimate the coefficients of the A and B polynomials, whereas the coefficients of the T-polynomial are defined by the user. The characteristic Eq (11) can be used to calculate s0, s1, and s2.

In the characteristic equation, the degrees of the polynomials are:

$$n_a + n_r = n_b + n_s + 1 = n_t \tag{12}$$

Because of the polynomial representation of velocity form of the PID algorithm, ns is the degree of the s polynomials and its value must be 1, and nr is the degree of the r polynomials and its value must be 1. This suggests that $n_a = n_b + 2$ and $n_t = n_b + 3 = n_a + 1$. A unique set of PID controller coefficients may be produced from the design if a second order A polynomial (n

= 2, n_b = 0 and n_t = 3) is chosen. If the order of the A polynomial is three, i.e. n = 3, n_b = 1, and n_t = 4, all the coefficients of the T polynomial should be user defined in order to simply put the poles of the characteristic equation. The system transfer function used in this example is a third order T polynomial (n = 2, n_b = 1) with the following form:

$$y(t) = \frac{b_0 z^{-1}}{1 + a_1 z^{-1} + a_2 z^{-2}} u(t) \tag{13}$$

Combining the system model equation (Eq. (13)) and the controller equation (Eq. (5)) yields the closed loop connection.

$$y(t) = \frac{b_0 z^{-1} S}{R\left(1 + a_1 z^{-1} + a_2 z^{-2}\right) + b_0 z^{-1} S} r(t) \tag{14}$$

The equivalent chosen closed loop T polynomial is of the form:

$$T = 1 + t_1 z^{-1} + t_2 z^{-2} + t_3 z^{-3} \tag{15}$$

The discrete form of the necessary incremental PID control low may be written in terms of the change in the control signal as

$$\Delta \mathrm{U} = s_0 \varepsilon(t) + s_1 \varepsilon(t-1) + s_2 \varepsilon(t-2) \tag{16}$$

STPID control algorithm may be summarized as follows:

1. The coefficients of polynomials are calculated from the following equations according to the tuning parameters as

$$s_0 = \frac{t_1 - a_1 + 1}{b_0} \tag{17}$$

$$s_1 = \frac{t_2 - a_2 + 1}{b_0} \tag{18}$$

$$s_2 = \frac{t_3 + a_2}{b_0} \tag{19}$$

2. The STPID control parameters are found from the values of s_0, s_1 and s_2 as

$$K_c = \frac{s_0 - s_1 - 3s_2}{2} \tag{20}$$

$$\tau_1 = \frac{K_c}{K_1} = \frac{(s_0 - s_1 - 3s_2)/2}{(s_0 + s_1 + s_2)/\Delta T} \tag{21}$$

$$\tau_d = \frac{K_D}{K_c} = \frac{s_2 \Delta T}{(s_0 - s_1 - 3s_2)/2} \tag{22}$$

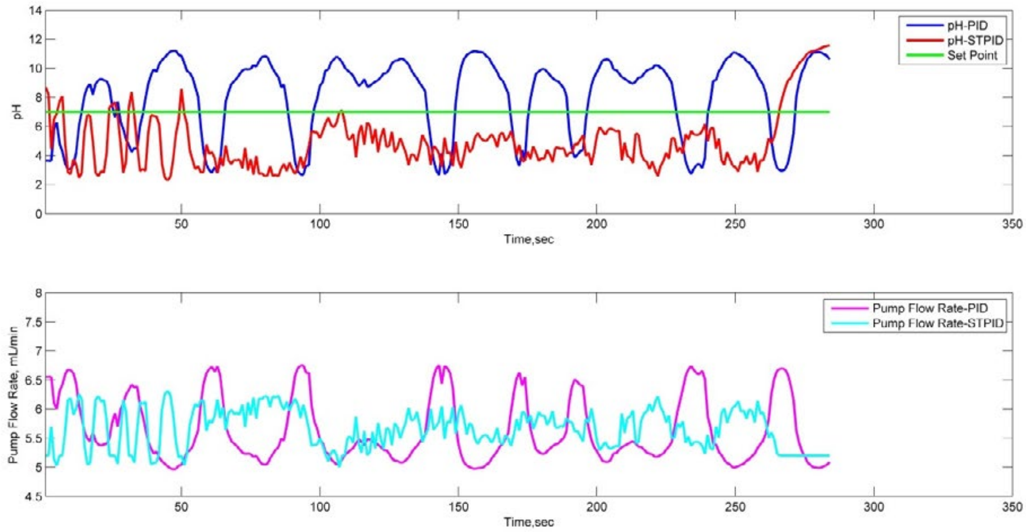

Fig. 5. Comparison between PID and STPID control of pH value for coagulation process (pH = 7) a) time change with pH, b) time change of adjustable variable

3. The incremental control signal Δu_n is calculated from the following equation

$$\Delta u_n = K_c \left(1 + \frac{\Delta T}{2\tau_1} + \frac{\tau_d}{\Delta T}\right) e_n + K_c \left(\frac{\Delta T}{2\tau_1} - 1 - \frac{2\tau_d}{\Delta T}\right) e_{n-1} + K_c \frac{\tau_d}{\Delta T} e_{n-2} \quad (23)$$

4. The calculated output value is compared with the set point and thus an error is found.
5. It is returned to step 3.

The form of the model of the system to be controlled was preserved in this study to ensure that only one set of PID controller coefficients was produced from the design, and the integral action in the PID controller provides steady-state following even if the system or controller parameter values change.

RESULTS AND DISCUSSION

This work includes both theoretical and experimental research. The STPID algorithm has been implemented using a series of computer programs. The experimental experiments make use of the VisiDAQ application, which was created for data acquisition and control.

In Figure 5, while the HCl solution is sent at a constant flow rate of 20% for pH=7, 10% NaOH solution is used as the adjustable variable. Since self-adjusting PID control experiments and PID control experiments are very difficult to control at set value pH=7, a very effective control could not be made.

In Figure 6, while the HCl solution is sent at a constant flow rate of 20% for pH=9, 10% NaOH solution is used as the adjustable variable. When STPID control experiments and PID control experiments are performed at set value pH=9, it is seen that the self-adjusting PID controller controls nonlinear systems more effectively.

In Figure 7., while a 20% constant flow rate HCl solution is sent for pH = 11, 10% NaOH solution is used as an adjustable variable. When self-adjusting PID control experiments and PID control experiments were performed at set value pH=11, PID control could not be performed effectively.

For brine samples, samples at set values of 7, 9 and 11 were taken and the settling percentages

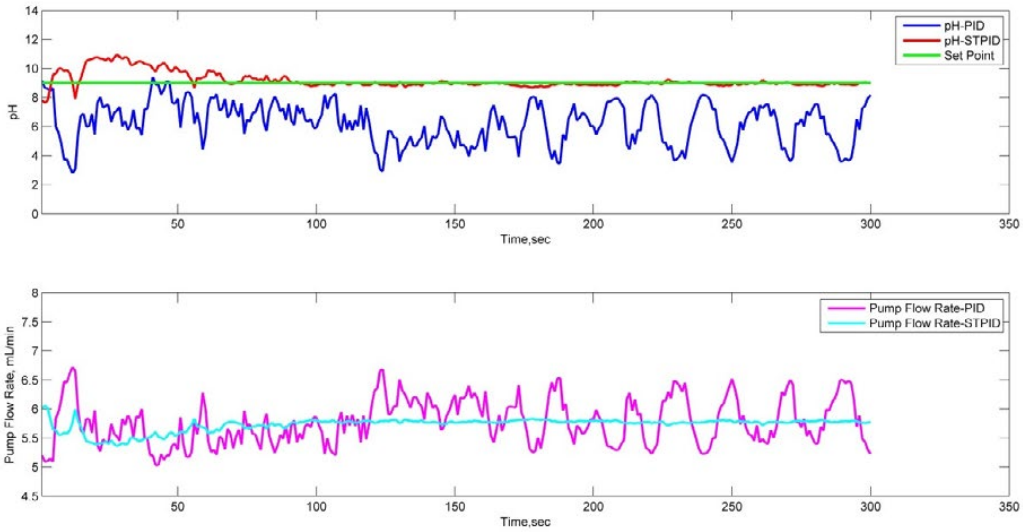

Fig. 6. Comparison between PID and STPID control of pH value for coagulation process (pH= 9) a) time change with pH, b) time change of adjustable variable

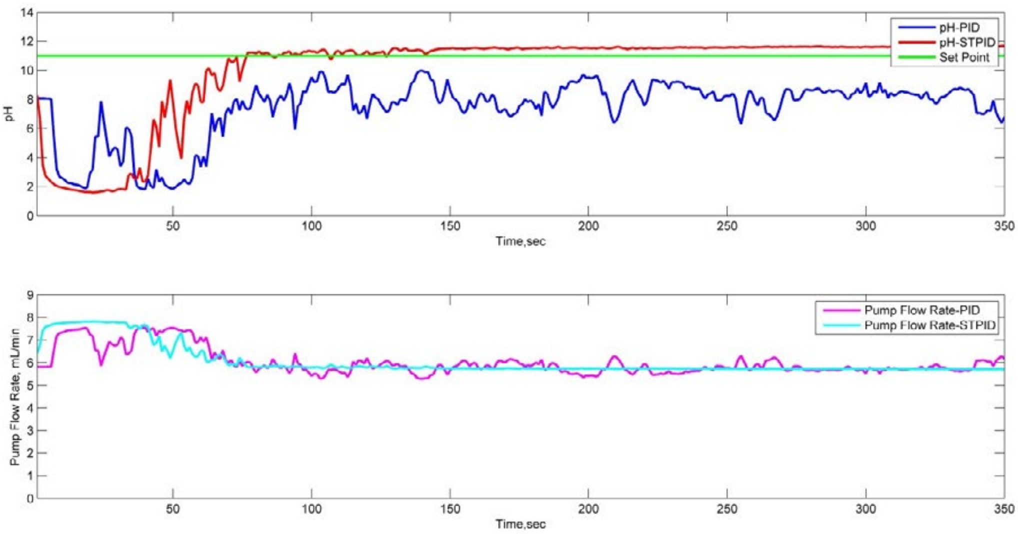

Fig. 7. Comparison between PID and STPID control of pH value for coagulation process (pH= 11) a) time change with pH, b) time change of adjustable variable

obtained as a result of STPID-controlled precipitation and PID-controlled analysis of these samples are given in Table 2. Settlement percentage has been calculated as 90-95%. According to the obtained data, PID-controlled settling was insufficient compared to STPID-controlled settling. While there are offsets and noises in the settling process with PID control, the settling process with STPID control is free from offset and noise.

As a result of the literature research, as a result of the mathematical operations made by using the solubility product of magnesium hydroxide, it was calculated that the best operating condition for the precipitation of $Mg(OH)_2$ as a result of the reaction of magnesium with NaOH was pH=10.52. The adjusted pH was found to be at 11 and, as can be seen, the same result was reached with the literature.

NOMENCLATURE

A monic polynomial in the z-domain representing the poles of the discrete-time system
B polynomial in the z-domain representing the zeros of the discrete-time system
C monic polynomial in the z-domain representing the zeros of the process noise
e(t) white noise
K_c steady-state gain for three term controller
r(t) set point
u(t) input variable at time t
x data vector
y(t) output variable at time t
z, z^{-1} forward and backward shift operators
t_1 the first coefficient of the real denominator T of the closed loop system model
T the real denominator of the closed loop system model with STPID, which is of the form: $T = 1+t_1z^{-1}+t_2z^{-2}+ t_3z^{-3}$.

GREEK LETTERS

ε(t) difference between the measured variable and set point at time t
τ_D derivative constant coefficient
τ_I integral constant coefficient
θ the parameter vector, defined as the collection of coefficients in the A, B, and C polynomials.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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