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OPTIMIZATION OF COAL FLOCCULATION WITH AN ANIONIC FLOCCULANT USING A BOX-WILSON STATISTICAL DESIGN METHOD

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Abstract: In this study, the Box-Wilson statistical experimental design method was employed to evaluate suspension pH, salt ($CaCl_2{\cdot}2H_2O$) concentration and anionic flocculant (A-150) amount in flocculation of coal. Response function coefficients were determined by the regression analysis of experimental data and the predictions were found to be in good agreement with the experimental results. The optimum pH, salt ($CaCl_2{\cdot}2H_2O$) concentration and anionic flocculant (A-150) amount were determined as 9.8, 0.0009 M and 791 g/Mg respectively, when minimum turbidity and maximum settling rate are considered.

Keywords: *coal, flocculation, anionic flocculant,* $CaCl_2{\cdot}2H_2O$

Introduction

Both mechanized coal mining methods and cleaning processes continuously increase the fine coal particle concentration (Hogg, 1980; Pawlak et al., 1985; Kim et al., 1991; Cebeci, 1996; Cebeci et al., 2002) creating problems in dewatering, drying, handling, transportation and storage. Significant quantities of fine coal lost in coal preparation plants result in energy loss and environmental problems (Hogg, 1980; Kim et al., 1991; Cebeci, 1996). Conventional coal beneficiation techniques such as dense-media separation, shaking tables, water-only cyclones are quite inefficient in fine coal processing. Due to the limited success of coal cleaning process, studies have shifted increasingly towards the use of froth flotation, flocculation and oil agglomeration as alternative fine particle processing methods (Kim et al., 1991; Somasundaran 1980; Mehrotra et al., 1983; Hamza et al., 1988).

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Flocculation of fine or ultra fine particles using a polymeric flocculant is frequently employed for dewatering or solid-liquid separation process (Somasundaran, 1980; Attia, 1992; Somasundaran and Das 1998; Hogg, 2000). The electrokinetic behavior of the particles affects the recovery and the selectivity in the concentration processes, which depend on the surface properties such as froth flotation, flocculation and oil agglomeration (Cebeci and Sonmez, 2006).

The settling rate and turbidity (or water clarity), which are improved by flocculation, depend heavily on the proper control of both chemical variables (pH, flocculant type, flocculant molecular weight, flocculant amount, charge density, presence of metal ions, ionic strength, zeta potential etc.) and physical factors (mixing conditions, solid concentration, particle surface area, particle size, pulp temperature etc.) (Hogg, 2000; Angle et al., 1997; Ateşok et al., 1988; Clark et al., 1990; Hogg et al., 1993; Su et al., 1998; Besra et al., 2000; Mpofu et al., 2003; Sabah and Cengiz, 2004; Hulston et al., 2004).

In this study, a Box-Wilson statistical experimental design method was used to determine the major operating parameters effects on settling rate, turbidity and zeta potential. This experimental design is a type of response surface methodology, an empirical modeling technique, devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. This optimization process involves three major steps: performing the statistical design experiments, estimating the coefficients in a mathematical model, and predicting the response and checking the adequacy of the model. It could be beneficial to know whether the Box-Wilson statistical experimental design procedure is applicable to the prediction of important variables such as the settling rate, turbidity and zeta potential in the flocculation of fine coal particles. In order to test the hypothesis, flocculation experiments were carried out using coal waste samples from the Alpagut-Dodurga Coal basin in Corum (Turkey). Regarding the flocculation, pH, $CaCl_2 \cdot 2H_2O$ concentration and anionic flocculant (A-150) were selected as the most relevant independent variables. Settling rate, turbidity, and zeta potential were measured to determine the effects of these independent variables in the experimental design.

Materials and methods

Material

The coal waste sample was obtained from the Alpagut-Dodurga Coal basin in Corum-Turkey. The total ash value was 39.80%. The coal sample was dry-ground to a nominal top size of –53 μm in a rod mill for flocculation tests. The ground coal has 86% passing at 20 μm based on the wet screening results.

The mineral composition was determined by X-ray diffraction (XRD) using a RIGAKU DMAX-III C diffractometer. According to the XRD results of the original coal sample, quartz, calcite, smectite, chlorite and kaolinite were the main mineral matter minerals.

Chemicals

An anionic (A-150) Superfloc synthetic flocculant was obtained from Cyanamid Company. The A-150 polymer used as the flocculant consisted mainly of polyacrylamide and its derivative monomers. The molecular weight was in the range of 5-15x10^6 g·mol^{-1} (American Cyanamid Company, 1989). A 0.05 M stock solution of $CaCl_2·2H_2O$ (147.02 g·mol^{-1}) (Merck) salt was prepared and added into the suspension at the required amount in order to obtain the final desired concentration and investigate the effect on flocculation process. Solutions of HCl (Merck) and NaOH (Carlo Erba) were used to adjust pH. All chemicals used were at least analytical grade.

Flocculation studies

The experiments were carried out in a 400 ml beaker having 4 baffles at the border to create homogeneous slurry during mixing. Mixing was carried out using a Heidolph RZR 2021 model mechanical stirrer. The agitation was provided by a centrally located flat blade turbine impeller (consisting of four blades) at a fixed distance from the bottom of the vessel. Mono-distilled water (pH ~ 6.5) was used in the experiments. The solid concentration was kept constant at 5.0 wt% (w·w^{-1}) for each test and the weight of suspension was subjected to 200 g (10 g coal sample + 190 g water). The mixture was conditioned for 3 minutes before and after adding the salt solution. After adding the A-150 flocculant, the suspension was conditioned for 2 minutes under constant stirring. The A-150 amount was based on the mass ratio of coal on dry basis. After 2 minutes, the stirring speed was reduced to the half of stirring speed for 1 minute to allow floc growth. Then, the suspension was transferred into a 500 cm^3 measuring cylinder (272 mm height), and the cylinder was inverted end-over-end for 20 times. In order to evaluate the experimental results, the settling rate and turbidity values were determined. The settling rate (mm·min^{-1}) was calculated based on the changing slurry-supernatant interface height in time. After a settling time of 5 min, 15 cm^3 supernatants were drawn from a depth of 7.0 cm below the air-liquid interface for turbidity measurements. The turbidity of the supernatant was measured in Nephelo Turbidity Units (NTU) using an Orbeco-Hellige 966 turbidimeter. Additionally, the zeta potentials of the coal samples were measured at the experimental conditions of axial points, factorial points and centre point using a zeta potential analyzer (Malvern Instruments, Zetasizer Nano Z model).

Box-Wilson experimental design

The Box-Wilson statistical experimental design method includes three types of combinations, the axial (*A*), factorial (*F*), and center (*C*) points. The independent variables are at five specified levels depending on the number of variables in the experiment and their range. In order to maintain convenience, the following codes were used for the operating levels of the variables. For this purpose, a factor k =

range/2 is defined for each variable where k is approximately equal to $\sqrt{p}$ (p = number of variables), and with three variables k = 1.73. The axial points included each variable at its extreme levels were coded as $-k$ and $+k$ with the others at their center point level. The factorial points, with two levels of each of the factors coded as –1 and +1, included all combinations of intermediate levels. A center point coded as 0 is a single test at the average level of each variable. The details of the method can be found elsewhere (Davies, 1956; Crozier, 1992).

Three operating parameters i.e., pH, salt concentration ($CaCl_2 \cdot 2H_2O$) and the amount of anionic flocculant (A-150) were chosen as the most important independent variables. The pH (X_1) was changed between 3 and 11, the salt concentration (X_2) between 0 and 0.001 M and A-150 amount (X_3) between 0 and 800 $g \cdot t^{-1}$. The experimental design consisted of six axial (A), eight factorial (F) and three centre (C) points. The center point was repeated three times for estimating experimental error. The experimental conditions as coded values and real values used for the Box-Wilson statistical design are presented in Table 1.

Table 1. Experimental conditions according to the Box-Wilson statistical design

	Coded Values			Real Values		
No.	X_1	X_2	X_3	pH	SC (M)	AF ($g \cdot t^{-1}$)
*A*1	1.73	0	0	11	0.000500	400
*A*2	–1.73	0	0	3	0.000500	400
*A*3	0	1.73	0	7	0.001000	400
*A*4	0	–1.73	0	7	0.000000	400
*A*5	0	0	1.73	7	0.000500	800
*A*6	0	0	–1.73	7	0.000500	0
*F*1	1	1	1	9.31	0.000789	631.21
*F*2	1	1	–1	9.31	0.000789	168.79
*F*3	1	–1	1	9.31	0.000211	631.21
*F*4	1	–1	–1	9.31	0.000211	168.79
*F*5	–1	1	1	4.69	0.000789	631.21
*F*6	–1	1	–1	4.69	0.000789	168.79
*F*7	–1	–1	1	4.69	0.000211	631.21
*F*8	–1	–1	–1	4.69	0.000211	168.79
C1	0	0	0	7	0.000500	400
C2	0	0	0	7	0.000500	400
C3	0	0	0	7	0.000500	400
C(Ave)	0	0	0	7	0.000500	400

SC: salt concentration; AF: amount of flocculant

The settling rate, turbidity and zeta potential (Y) were correlated with the other independent parameters (X_1, X_2, X_3) using Eq. (1). A Design Expert 8.0 program was used for determination of the coefficients of Eq. (1) by regression analysis of the experimental data.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \tag{1}$$

where Y – the predicted response function (settling rate, turbidity or zeta potential)
b_0 – constant
b_1, b_2, b_3 – linear coefficients
b_{12}, b_{13}, b_{23} – cross product coefficients
b_{11}, b_{22}, b_{33} – quadratic coefficients.

Results and discussions

A comparison of the experimental and predicted values for the settling rates, turbidities and zeta potentials are summarized in Table 2. The observed settling rates varied between 1.050 and 500.740 mm·s^{-1}, turbidities varied between 9.2 and 195.8 NTU, while the observed zeta potentials varied between –35.80 and -7.25 mV.

Table 2. Observed and predicted settling rates, turbidities and zeta potentials

Experiment No.	Settling Rate (mm·min^{-1})		Turbidity (NTU)		Zeta Potential (mV)	
	Observed	Predicted	Observed	Predicted	Observed	Predicted
*A*1	292.540	311.736	70.2	67.7	–35.80	–34.45
*A*2	1.050	–1.631	195.8	201.8	–7.25	–11.13
*A*3	183.426	208.403	71.0	78.0	–21.80	–23.33
*A*4	149.970	141.508	119.6	116.1	–24.90	–25.89
*A*5	434.226	377.279	9.2	50.9	–19.90	–20.30
*A*6	1.902	75.363	159.9	121.7	–18.10	–20.22
*F*1	500.740	463.554	19.2	14.7	–22.30	–23.11
*F*2	173.502	174.304	75.3	76.3	–29.00	–28.33
*F*3	226.305	298.200	118.6	89.6	–34.80	–35.11
*F*4	246.788	167.249	54.1	88.9	–30.30	–30.61
*F*5	132.444	199.460	140.8	103.4	–17.90	–15.70
*F*6	66.060	–18.619	159.4	186.0	–22.30	–20.12
*F*7	142.740	129.184	138.4	134.9	–17.60	–16.39
*F*8	44.508	69.404	153.2	155.1	–13.80	–11.08
C1	225.300	255.544	72.2	59.9	–20.90	–22.10
C2	281.106	255.544	36.4	59.9	–23.10	–22.10
C3	260.226	255.544	71.1	59.9	–22.30	–22.10

Experimental results were modeled using a Design Expert 8.0 Trial program to determine the coefficients of the response function (Eq. (3)). The calculated coefficients were used in calculating predicted values of flocculation recoveries and zeta potentials and are listed in Table 3. The determination coefficients (R^2 values) between the observed and predicted values were 0.8779, 0.8259 and 0.9426 for settling rate, turbidity and zeta potential, respectively, indicating a good agreement between the observed and predicted values.

Table 3. Coefficients of the response function

Coefficient	b_0	b_1	b_2	b_3	B_{12}	b_{13}
Settling Rate	–284.276696	95.973172	–96889.4670	–0.005819	35604.9375	0.033314
Turbidity	448.370069	–78.057864	20508.22816	–0.172501	–16275.0	0.009797
Zeta Potential	17.440958	–4.5828133	–31599.13	–0.0301012	4237.5	0.000375
Coefficient	b_{23}	b_{11}	b_{22}	b_{33}	R^2	
Settling Rate	592.261875	–6.280734	–322354952.38	–0.0001826421	0.8779	
Turbidity	–233.25	4.679167	148666666.67	0.0001651042	0.8259	
Zeta Potential	36.375	–0.042932	–10047619.05	0.0000114881	0.9426	

The effect of pH and A-150 amount

It is known that flocculation recovery or the extent of flocculation (floc size) depends on the surface properties of particles, suspension pH, and the nature of the flocculants (Somasundaran and Das, 1998; Foshee et al., 1982; Yu and Somasundaran, 1996; Rattanakawin and Hogg, 2001). The H^+ and OH^- ions are the potential determining ions for many mineral particles including coal, clay minerals, and quartz (Leja, 1982; Laskowski, 2001). Both the electrokinetic properties of the particles and charge characteristics and the conformation (structure) of polymer flocculant are subjected to change by the suspension pH, and thus may affect the flocculating power of the polymer (Foshee, 1982; Reuter and Hartan, 1986). Therefore, controlling the pH of the aqueous medium is important.

The flocculation strategy may depend on the process goals. For example, low turbidity would be critical for producing high water clarity while the high settling rate may be desired in other cases. In either case, the ideal flocculant should settle the largest amount of desired fine particles with the lowest flocculant concentration in the shortest time resulting in the highest clarity.

The variations of the settling rate, turbidity and zeta potential as functions of the pH and A-150 amount at a constant $CaCl_2 \cdot 2H_2O$ concentration of 0.0005 M are given in Fig. 1, Fig. 2 and Fig. 3, respectively.

Figure 1 shows that the settling rate increased with both rising pH and A-150 amount at a 0.0005 M $CaCl_2 \cdot 2H_2O$ concentration. Conversely, Fig. 2 indicates that the turbidity decreased by increasing pH value up to pH 9, and it increased partially

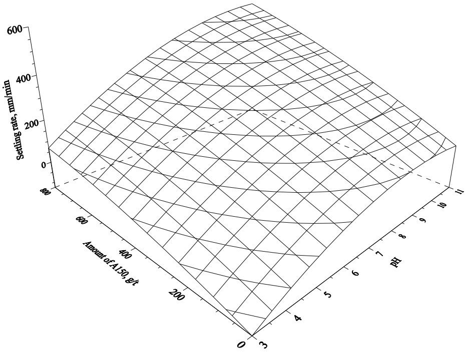

Fig. 1. Effect of pH and A-150 amount on settling rate ($CaCl_2 \cdot 2H_2O$: 0.0005 M)

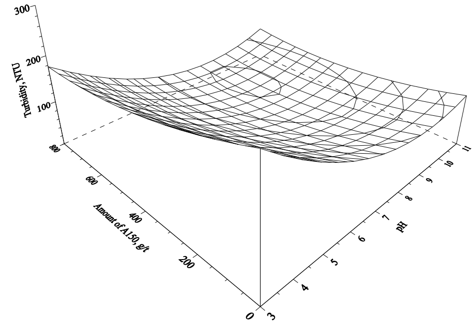

Fig. 2. Effect of pH and A-150 amount on turbidity ($CaCl_2 \cdot 2H_2O$: 0.0005 M)

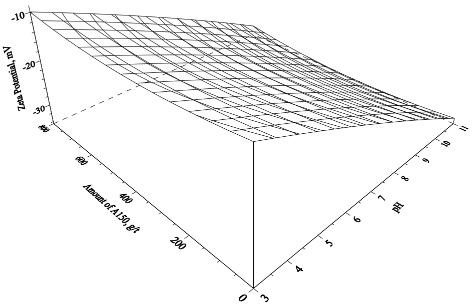

Fig. 3. Effect of pH and A-150 amount on zeta potential ($CaCl_2 \cdot 2H_2O$: 0.0005 M)

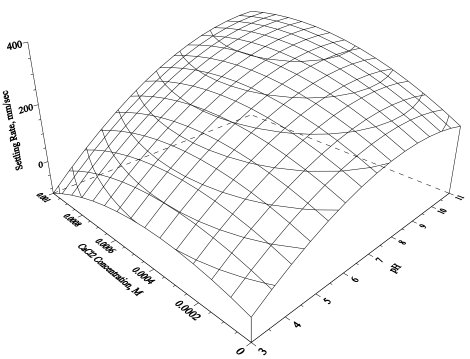

Fig. 4. Effect of pH and $CaCl_2 \cdot 2H_2O$ concentration on settling rate (A-150: 400 $g \cdot t^{-1}$)

afterward. Moreover, the turbidity partially decreased with increasing the A-150 amount. According to the effect of anionic flocculant dosage and pH values, Fig. 1 and Fig. 2 display a clear reverse relationship between the settling rate and the turbidity.

After dissociation of $CaCl_2$, Ca^{+2} ions may undergo association with hydroxyl ions yielding $Ca(OH)^+$ and $Ca(OH)_2$ species especially at alkaline pH values (Sillen and Martell, 1971). The positively charged Ca^{+2} ions alkaline salt products were specifically adsorbed onto the ash-forming mineral matter and coal particle surfaces (James and Healy, 1972a, 1972b, 1972c). As the specific adsorption of Ca^{+2} ions hydrolysis products increases, an attraction should take place between the anionic A-150 polymer chains and newly formed cationic surfaces, which facilitates polymer adsorption (Mpofu, 2005). Accordingly, we obtained a distinct increase in the settling rate at high pH values (maximum at pH 11), whereas the lowest settling rate was recorded at pH 3.

Low settling rates obtained at low pH values may be due to the weak electrostatic interaction of the negative particle surfaces. It can also be attributed to the covalent bond and/or electrostatic bond formation between the (=C–O$^-$) groups of anionic polymers and metal cations on the external surface of mineral particles may be inhibited (Sabah and Cengiz, 2004). Furthermore, at low pH values (pH = 4 and below), except for electrostatic attraction forces, the low settling rate may indicate that the other forces such as hydrogen bonding would be more effective between the polar groups of flocculant and the particle surfaces (Sarioglu et al., 2002).

It is commonly known that high molecular weight polymers generate large size but less compact flocs (Hogg, 2000; Gregory, 1989; Tao et al., 2000). Similar to our observation, Sabah and Erkan (2005) reported that anionic flocculants with a high molecular weight produced large flocs sufficient for settling. At low flocculant amounts, low settling rates reflected an inadequate level of flocculant or insufficient flocculant bridging among the particles. In this case, the floc size was very small due to inadequate amount of polymer adsorption on particle surfaces. As the amount of adsorbed polymer increased, greater amounts of suspended particles were incorporated into the floc leading to enlargement of the floc size and increased settling rate.

As shown in Fig. 3, the zeta potential of the coal sample was negative at all pH values and without a zero point of charge. Moreover, the zeta potential decreased with increasing pH at all studied anionic flocculant amounts. This can be attributed to the increment of OH^- and/or Cl^- anions adsorption over the ash-forming mineral matter and coal particles. However, the zeta potential scarcely changed, depending on A-150 amount at all pH values. This situation may reflect the adsorbed A-150 amount on the particle surfaces.

The effect of pH and $CaCl_2 \cdot 2H_2O$ concentration

The settling rate, turbidity and zeta potential as a function of pH and $CaCl_2 \cdot 2H_2O$ concentration at a constant A-150 amount of 400 g/Mg are presented in Fig. 4, Fig. 5, and Fig. 6, respectively.

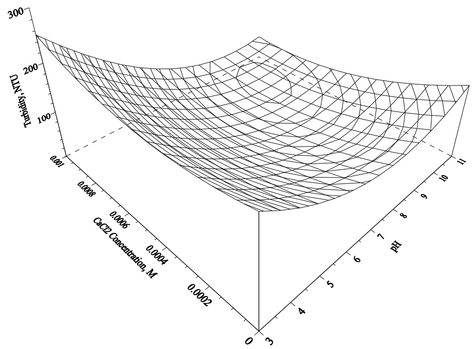

Fig. 5. Effect of pH and $CaCl_2 \cdot 2H_2O$ concentration on turbidity (A-150: 400 g/Mg)

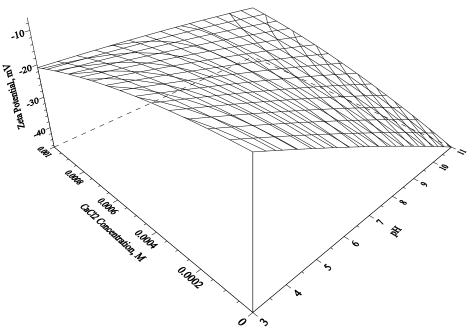

Fig. 6. Effect of pH and $CaCl_2 \cdot 2H_2O$ concentration on zeta potential (A-150: 400 g/Mg)

Because of the increment of A-150 adsorption after specific adsorption of Ca^{+2} ions hydrolysis products on particles surfaces, while the settling rate was increased, the turbidity was decreased with the increasing salt concentration up to 0.0007 M and it reversed partially afterward at all studied pH values. Furthermore, the settling rate was increased whereas the turbidity was decreased with increasing pH value, as can be seen in both Fig. 4 and Fig. 5, indicating a reverse relationship between settling rate and turbidity.

Figure 6 depicts the variation in the zeta potential as a function of pH and $CaCl_2{\cdot}2H_2O$ concentration at a constant A-150 amount of 400 g/Mg. The zeta potential was decreased slightly by increasing the $CaCl_2{\cdot}2H_2O$ concentration at low pH values while it was increased at high pH values. The increasing of the negative zeta potential value with boosting the $CaCl_2{\cdot}2H_2O$ concentration at low pH values can be attributed to the adsorption/precipitation of Cl^- anions onto the ash-forming mineral matter and coal particles surfaces. At high pH, the decreasing of the negative zeta potential value with increasing the $CaCl_2{\cdot}2H_2O$ concentration could be due to A-150 adsorption after specific adsorption of Ca^{+2} ions hydrolysis products on particles surfaces instead of OH^- and/or Cl^- anions adsorption.

The effect of $CaCl_2{\cdot}2H_2O$ concentration and A-150 amount

The variation of settling rate, turbidity and zeta potential with both A-150 amount and $CaCl_2{\cdot}2H_2O$ concentration at pH 7 are presented in Fig. 7, Fig. 8, and Fig. 9, respectively.

As seen from Fig. 7 and Fig. 8, there is a reverse relationship between settling rate and turbidity at pH 7. The settling rate increased with both A-150 amount and $CaCl_2{\cdot}2H_2O$ concentration at pH 7 (Fig. 7). The settling rate was greater at higher $CaCl_2{\cdot}2H_2O$ concentration, which can be attributed to the A-150 adsorption on particle surfaces. Correspondingly, the turbidity decreased as shown in Fig. 8 with increasing A-150 amounts at high $CaCl_2{\cdot}2H_2O$ concentration.

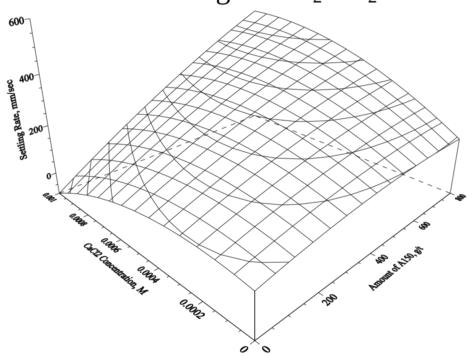

Fig. 7. Effect of A-150 amount and $CaCl_2{\cdot}2H_2O$ concentration on settling rate (pH 7)

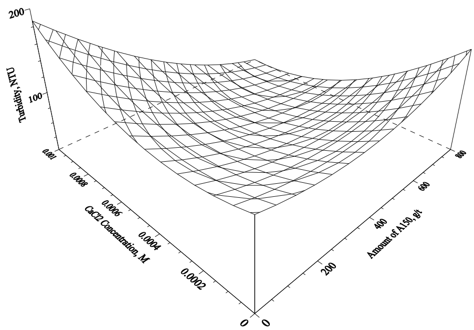

Fig. 8. Effect of A-150 amount and $CaCl_2{\cdot}2H_2O$ concentration on turbidity (pH 7)

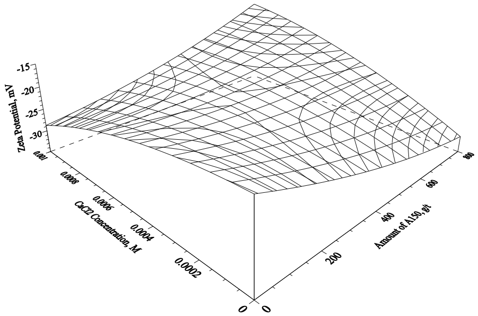

Fig. 9. Effect of A-150 amount and $CaCl_2 \cdot 2H_2O$ concentration
on zeta potential (pH 7)

Figure 9 indicates the variation in the zeta potential at pH 7 as a function of A-150 amount and $CaCl_2 \cdot 2H_2O$ concentration. As can be seen in Fig. 9, the negative zeta potential value boosted with increasing the $CaCl_2 \cdot 2H_2O$ concentration at low A-150 amounts, while it decreased at high A-150 amounts. This could indicate that the A-150 adsorption depends on both Ca^{+2} ions hydrolysis product amounts and pH value.

Conclusions

The Box-Wilson statistical experimental design procedure was found to be applicable to modeling the effects of important variables on the settling rate, turbidity and zeta potential in flocculation of coal. Response function predictions determined by regression analysis were in a good agreement with the experimental results. In general, there was a reverse relationship between settling rate and turbidity. The settling rate was increased with an increment in suspension pH, anionic flocculant (A-150) amount and salt ($CaCl_2 \cdot 2H_2O$) concentration. The turbidity decreased with A-150 amount and $CaCl_2 \cdot 2H_2O$ concentration and increasing pH up to 9. The zeta potential value decreased with increasing pH values depending on both A-150 amount and $CaCl_2 \cdot 2H_2O$ concentration, contrary to the flocculation expectation.

Considering the minimum turbidity and maximum settling rate, flocculation of fine coal particles can be optimized at pH 9.8, salt ($CaCl_2 \cdot 2H_2O$) concentration of 0.0009 M and anionic flocculant (A-150) amount of 791 g·Mg as predicted by the model.

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