

Factors involved in Coal Slurry Flocculation Process

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Contributor: Atousa Khazaie, Mahmoud Mazarji, Bijan Samali, David Osborne, Tatiana Minkina, Svetlana Sushkova, Saglara S. Mandzhieva, Alexander Soldatov

Coal slurry is a mixture of finely grained coal and other minerals suspended and/or sediment in the water, generated during the coal preparation processes, accounting for more than half of mining operating cost. Dewatering technology is simultaneously confronted with obstacles and possibilities, and it may yet be improved as the crucial step for reducing the ultimate processing cost. Coagulation/flocculation is a process in which solid and liquid parts of a solution are separated using different types of coagulants and flocculants.

Keywords: polymeric flocculants ; flocculation process ; coal slurry ; coal tailings

1. Coagulation

A combination of coagulation and sedimentation of suspended particles has been widely used for wastewater treatment purposes for many years. Inorganic salts of multivalent metals such as ferric chloride, ferrous sulfate, magnesium chloride, and alum are commonly used as coagulants ^{[1][2]}. It is generally accepted that inorganic salts are subjected to hydrolysis into the corresponding cations and anions when they are added into the aqueous environment. Under this circumstance, they form a wide variety of monomeric and polymeric products, depending on the temperature, solution pH, type, and dosage of ions ^[3]. Therefore, the primary mechanism in the coagulation of coal tailings slurry is the adsorption of metal ions on the coal surface and the neutralization of the electrical double layer (EDL) charges ^[4]. In this context, a small amount of positively charged metal ions could neutralize the negatively charged suspended coal particles and reduce the repulsion force between them; therefore, particles will form floc together due to the domination of Van der Waals forces. However, an excessive amount of coagulants reverses the charge of particles from negative to positive, which results in the dispersion of the non-coagulated particles ^[4].

The low-cost market price is the key factor for choosing coagulants, as given in **Table 1**. According to the literature, electrolytes cannot coagulate suspended particles larger than 75 µm in size in coal slurry; as a result, small particles form in the coagulation process of coal slurry using electrolytes flocs, and the coarser materials are entrapped in them ^[5].

Table 1. The market price for bulk sales of coagulants ^{[6][7]}.

Chemical Material	Coagulants				
	FeCl ₃	Lime	Alum	PACL	Fe ₂ (SO ₄) ₃
Price, €/tonne	250–450	130	175–200	250–400	250–350

2. Role of Different Factors in Coal Slurry Flocculation Process Using Polymeric Flocculants

Flocculation characteristics, including floc size and structure, cake resistance, and moisture content in CPPs, are influenced by different factors such as coal slurry composition, charge density and molecular weight of flocculants, polymer structure, polymer dosage, the hardness of water, suspension pH, etc. ^[8]. The characteristics of flocs produced in the flocculation process are very important because they can affect subsequent operations such as dewatering and filtration in CPPs. Filtration cake with high moisture content can cause many problems such as lower fuel heat value and higher transportation costs ^[9]. The experimental results showed that anionic flocculants produced large and strong flocs with less porosity; hence, they increased the filtration rate. On the other hand, cationic flocculants small and tight flocs that decrease the filtration rate due to the poor permeability of the filter cake ^{[10][8][11][12]}.

2.1. Composition of Coal Tailings

Coal tailing slurries can contain variable amounts of coal depending on the applied beneficiation approach. Metallurgical coals of higher market value are normally treated in fines treatment processes, including gravity and flotation methods. Thermal coals are often only treated to 0.25–0.50 mm with the ultrafine passing into the tailing stream. According to the literature, the composition of coal tailing slurry significantly affected the flocculation process [10]. Chemical analysis results of CPP tailings indicated that they usually contain organic matter (coal), quartz, metal oxides, sulfides and carbonates, mica, predominantly muscovite, and different clay minerals such as kaolinite, illite, montmorillonite, etc. [10][13][14][15][16]. Generally, in run-of-mine coal, clay particles can occur as 60–80% impurities [17]. Therefore, it is necessary to understand how clay particles can influence coagulation, flocculation and sedimentation, and filtration of coal tailings solids. In clay particles, the face charges and irregular edges significantly impact flocculation mechanisms and efficiency [10].

Regarding a coal-kaolinite suspension, it is reported that the repulsive electrostatic force between the suspended particles can be decreased by adding Ca^{2+} ions. This makes the Van der Waals attractive force the dominant interaction force that results in the aggregation of particles [18][19]. Several experimental results have shown that anionic polymers with high molecular weight are generally desirable for flocculation and dewatering of negatively charged kaolinite and smectite clay particles [20][21][22][23][24]. On the other hand, some experiment results indicated that repulsive electrostatic forces between anionic groups of polymers and negatively charged kaolinite particles limit the polymer adsorption. Furthermore, variations in pH and ionic strength can change the stability of these long-chain polymers [20][25][26][27]. In another study, montmorillonite suspensions formed clay platelet networks and captured coal particles [28]. Scanning electron microscopy (SEM) for clay minerals results reveal that the house-of-cards structures formed by permanent contact of clay platelets with surrounding particles have high porosity and low settling rate, attributed to the attractive forces keeping the platelets together [29]. The house-of-cards structure comprised edge-to-edge (EE) and edge-to-face (EF) contacts. Edge-to-face attraction results from attractive double-layer forces between negatively charged faces and positively charged platelet edges [30]. On the other hand, EE contact results from the coalescence of nanobubbles attached to platelet edges [29].

2.2. Effects of pH on the Performance of Polymeric Flocculants

Lignite coal and rock particles may carry a negative charge in an aqueous medium resulting from hydrogen ions dissociating from the alumina-silicic acid surface depending on the pH of the solution [4][5]. Consequently, applying any change in the pH of the medium or the concentration of electrolytes can alter the properties of the EDL, the stability of the suspension, and subsequently the settling rate in the flocculation process with or without flocculant [31][32]. The influence of pH change on the zeta potential of coal particles can be associated with the presence of pH-dependent ionizable functional groups on the surface of particles. The protonation of basic nitrogen-containing functional groups created a positive surface charge on coal particles. In contrast, the negative surface charge is attributed to the dissociation of acidic surface functional groups such as carboxylic [33]. Sabah and Erkan (2006) showed that decreasing the acidic pH value decreased the zeta potential by increasing the H^+ ion concentration; as a result, coagulation occurs due to the van der Waals force domination [32]. Some researchers suggest that in pH value above the natural pH of plant water, inorganic ions such as Ca^{2+} and Mg^{2+} stemmed from water hardness or pH adjustment become active and act as a bridge between negatively charged particles and increase the settling rate [17][32].

Moreover, pH can influence the structure of flocs and change the polymer adsorption and conformation because for most mineral particles, i.e., coal, quartz, and clay, OH^- and H^+ ions are the potential determining ions (PDI) [15]. For example, face-face and edge-face interactions form different structures at different pH values in a kaolinite suspension. Kaolinite particles at low pH carry a positive charge on their edge and a negative charge on their basal surfaces due to proton loss/gain face-edge. Therefore, edge-face electrostatic interaction between clay particles form flocs in the three-dimension house-of-cards structure [27][32][34][35]. On the other hand, both the basal and surfaces of kaolinite particles become negatively charged at high pH values and form a Bandermodel arrangement [27]. The pH also contributes to the conformation of polymers, which changes the final strength of flocs. For instance, anionic polyacrylamides have a coil shape conformation in low pH while they are extended at high pH due to electrostatic repulsion between the charged groups [27][36][37]. Another researcher investigated the effect of pH on the adsorption of polymeric flocculants and indicated that the increasing the pH value increased the negative charge of kaolinite particles. This would improve the flocculation using CPAM and deteriorate the process using anionic polyacrylamide due to the increase and decrease of electrostatic attraction force between negatively charged particles and ionic groups of polymers [27][38]. However, this explanation contradicts the experimental results using anionic polymers undertaken by Ciftci and Isik [39]. According to their flocculation experiments, the anionic groups of polymers become ionized in acidic pH, weakening the bridge formation and flocculation efficiency [39].

The acquired electrical charge by particles, or adsorbed films on their surface, causes aggregation resistance in the fine-particle suspensions. The electrical charge of particles can be controlled through the solution pH. At some pH (isoelectric point), particles have no electrical charge. They are unstable enough for the coagulation process to occur; however, this method could be impractical if the isoelectric point occurs in an unconventional pH range. Moreover, these ions can reverse the zeta potential in which the system is destabilized, according to Hogg (2000) [23]. This destabilization close to this range may be attributed to charge reversal and destabilization of colloidal particles [40]. Polymeric substances are very effective for this purpose since their molecules absorb on the oppositely charged surface (charge-patch mechanism) and aggregation occurs subsequently through the interaction of patches with regions of bare surface on other particles. High molecular weight polymers are most frequently used for floc development, while low molecular weight is used for destabilization purposes [41].

2.3. Water Hardness

Since the water in a tailing slurry is generally recycled and reused in CPPs, the concentration of suspended particles should be at the lowest level. Otherwise, they would harm the efficiency of coal washery processes [17][42]. Water hardness in coal tailings can be characterized approximately with the concentration of multivalent cations, including Ca^{2+} and Mg^{2+} , which are brought to coal tailings through the clean water and leaching from minerals [43]. The results of the research study showed that the mineralogical composition of run-of-mine coal directly affected the water hardness of recycled water. Zhang et al. (2017) has asserted that carbonate minerals, especially gypsum, increase the water hardness because they can release ions including Ca^{2+} and Mg^{2+} ions, while the clay minerals can adsorb these ions and decrease the water hardness on the contrary [43].

2.4. Properties of Polymers

For desirable flocculation results, characteristics of the polymer flocculant such as molecular weight, charge density, and structure have crucial roles [23][44]. For a specific type of polymeric flocculant, the increase in the molecular weight achieved by increasing the length of the molecular backbone would speed up the sedimentation rate due to improving the bridge-binding of small particles [45][46]. Although increasing the charge density enhances the settling velocity, an excess increase in charge density adversely affects the flocculation process in floc size and floc density [47]. A research experiment investigating the effect of polyacrylamide polymers on floc characteristics showed that increasing the charge density from 10 to 35% increased the adsorption rate by increasing the electrostatic attraction force between the negatively charged kaolinite particles and the positively charged polymer chains. Increasing the adsorption rate resulted in decreased floc size by reducing the available sites for bridging [48]. This experiment also exhibited that both the adsorption rate and bridging decreased by increasing the charge density in the case of the anionic polymers. This occurs by increasing the electrostatic repulsion force between the negatively charged surface of the particles and anionic polyacrylamides (PAM) chains.

Polymer conformation is another factor that contributes to the adsorption of polymeric flocculants onto the suspended particles. It depends on different factors such as the solvent nature, the structure of the polymer itself, the position and number of active groups, and the number of available sites on the surface of solid particles.

2.5. Mixing Condition

The optimum mixing time of suspended particles in the flocculation process can be defined as the time needed to coat the half-surface particles by flocculants. The required time must be adjusted to create flocs through the adsorption of flocculants onto the particle surfaces. Long mixing times can hinder flocculation due to the steric effect resulting from overcoating the surface of particles. In contrast, a short mixing time can increase floc touchiness by decreasing the possibility of connecting particles and flocculant molecules and increasing floc breakage rate [49]. Hogg (2000) has asserted that mixing and agitation are the most important affecting factors that contribute to the flocculation process [23]. Moreover, mixing speed is important in breaking or shearing the produced flocs [49].

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