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Application of low-field NMR in the study of flocculant-aided filtration process of coal tailings

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Abstract: Preconditioning of coal tailings with flocculants is a useful technology to improve filtration performance. In this study, anionic and cationic polyacrylamides were used for the pretreatment coal tailings before filtration. Nondestructive and rapid measurement of the filter cakes of coal tailings at different filtration stages was conducted using a nuclear magnetic resonance (NMR). The transverse relaxation time (T_2) results of NMR provided the information concerned the state of water in filter cake, showing that free water entrapped in larger pores was removed mainly during coal tailings filtration, and the pressure in this study cannot remove the inherent moisture of filter cake of coal tailings. The significant increase in the amplitude of T_2 value between 0.1 and 1.0 ms revealed that the flocs collapsed into smaller ones with water entrapped in them during filtration. Comparing the NMR results with different flocculants shows that anionic polyacrylamide of 800 g/Mg produced a larger structure in the initial stage of filter cake formation. The final filter cake entrapped more water. The NMR results well validated the filtration experiments.

Keywords: filtration, coal tailings, NMR, flocculation, inherent moisture

1. Introduction

Filtration is a solid-liquid separation technology widely used in various fields such as papermaking, industrial water recycling, and sewage sludge treatment (Jean-Paul, 1993; Gong et al., 2010; Dash et al., 2011; Qi et al., 2011). The filtration process is also essential for dewatering the coal tailings due to the practical, economic and environmental advantages (Attia and Yu, 1991; Tao et al., 2000). The presence of clay minerals with small particle size results in the low filtration efficiency of coal tailings. In this case, flocculant-aided filtration could be a powerful technique to improve the filtration performance of coal tailings (Sabah et al., 2004; Fan et al., 2020). Polymeric flocculant, which allows the formation and growth of flocs, has been used as a dewatering reagent of coal tailings. Alam et al. (2011) studied the effect of preconditioning of coal tailings with flocculants on filtration performance and established the optimal dosage required for anionic and cationic flocculants. Tao et al. (2003) investigated the kinetics of ultrafine coal filtration using cationic and anionic flocculants. They found that the addition of flocculant reduced the resistance of both filter cake and filter medium.

The properties of floc and filter cake are usually analysed to explore the mechanism of flocculant-aided filtration. The floc property mainly includes floc size and compactness, which can be investigated by combining the light scattering or image technique with fractal theory (Gungoren et al., 2020). The filter cake property can be characterized by observation techniques such as scanning electron microscope (SEM) and X-ray microtomographic techniques (Thapa et al., 2009; Lin and Miller, 2000; Raspati et al., 2013). However, contradictory conclusions are obtained regarding the effects of floc properties on filtration performance (Fitria et al., 2013; Cao et al., 2016), because both floc size and compactness significantly affect the filtration process, and it is difficult to predict which one is

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dominant. More precisely, the determining factors of filtration are the structure and the formation process of filter cake, which intrinsically account for the filtration performance (Wei et al., 2018). Nevertheless, insufficiently advanced technologies and sophisticated analytical instruments are significant difficulties in filter cake analysis. The limitations and shortcomings of existing technologies include the damage to the filter cake structure during sampling and the lack of a quantitative analysis method of highly complicated cake structures (Wei et al., 2018).

Low-field Nuclear magnetic resonance (NMR) provides an available tool for characterizing water in porous media, and the migration of water can be analysed qualitatively and quantitatively by comparing the differences of relaxation time (T_2) distribution at various stages (Hu et al., 2020). Yao et al. (2015) assessed the permeability and moisture migration of anthracite and bituminous coal samples using NMR relaxation spectrometry. Qian et al. (2017) used NMR to characterize the water imbibition in sandstone. The application of NMR in measuring water distribution can also be found in meat batters (Shao et al., 2016). Therefore, NMR may be applicable to characterize the distribution of water in filter cake. The advantages of the NMR technique are that it is efficient and non-destructive, so the cake structural changes and water evaporation can be avoided.

The present work aims to achieve better understanding of the flocculant-aided filtration process of coal tailings by the low-field NMR measurement of the filter cake formed at different filtration stages. The filtration experiments were conducted with the addition of anionic and cationic flocculants at different dosages. The NMR was used to determine the water distribution of filter cakes. The effect of flocculants on filtration performance of coal tailings was assessed according to the NMR results coupled with the filtration results. The NMR technique can provide detailed information about water distribution, which is vital for understanding the flocculant effects on floc formation and filter cake structure in the filtration process.

2. Materials and methods

2.1. Materials

The coal tailings slurry used in this study was obtained from the filter press feed stream in Huainan coal preparation plant in Anhui province, China. The solid percentage in the slurry is approximately 500 g/dm^3. The particle size distribution of the coal tailings slurry was analysed by a wet sieving analysis. The sieving results and the corresponding ash content are shown in Table 1. The results indicated that the slurry contained many high ash fine particles (-45 μm), which is considered to have a detrimental effect on filtration (Sabah et al., 2004).

The anionic and cationic polyacrylamides with a molecular weight of 10 Mg/mol and a charge density of 30% were purchased from Sinopharm Co., Ltd. Both polyacrylamides were prepared as 0.3 g/ 100 dm^3 of deionized water with a resistivity 18.2 MΩ·cm (Canrex Analytic Instrument Ltd., China).

2.2. Filtration experiments

Filtration experiments were carried out using a filtration device shown in Fig. 1. It is composed of Buchner funnel, vacuum flask, measuring cylinder, and vacuum pump. First, the coal tailings slurry of 80 dm^3 in a beaker of 200 dm^3 was mixed with the specified amount of polyacrylamide and agitated for 2 min using a stirrer at 300 rpm. Then, the slurry was poured into the Buchner funnel to filtrate at a vacuum pressure of 0.1 MPa. During filtration, the volume of the filtrate was recorded over time.

2.3. NMR measurement

The NMR evokes the hydrogen protons to rotate and create a dipole moment in the sample's hydrogenous fluid by an external magnetic field. The amplitude of the dipole moment is proportional to the number of hydrogen atoms. The transverse relaxation time (T_2) spectra are the transverse magnetization decay time of aligned protons when the external magnetic field is removed. The T_2 distribution is closely related to the water distribution in the porous medium.

In the present study, a low-field NMR instrument (NMRC12-010V, Niumag, China) was used to explore the water distribution in filter cake during the flocculant-aided filtration process coal tailings. A resonance frequency of 12.5 MHz and a constant magnetic field strength of 0.3±0.05 T were used. The

Table 1. The particle size distribution of the coal tailings slurry

Size /micron	Wt /%	Ash /%
+125	8.61	55.44
125-75	4.06	52.75
75-45	6.03	42.11
-45	81.30	59.17
Total	100.00	57.56

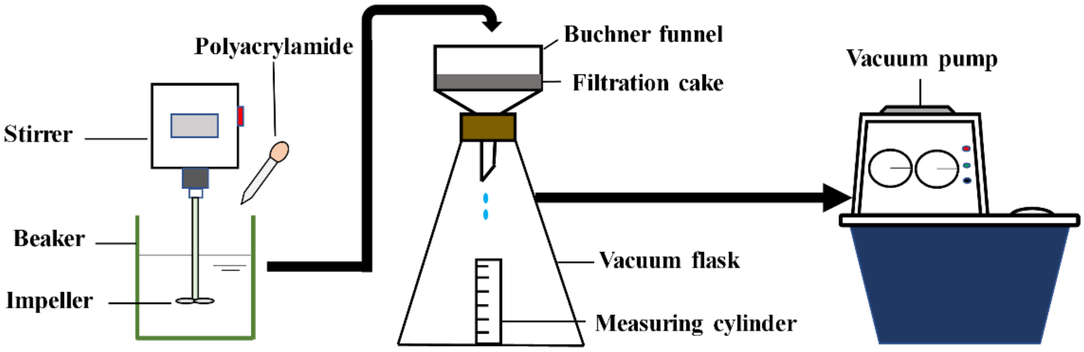

Fig. 1. The schematic of the filtration experimental system

temperature of a permanent magnet was fixed to 32 °C. The T_2 spectra were acquired using a Carr–Purcell–Meiboom–Gill (CPMG) echo sequence with an echo time of 0.3 ms, a repeat sampling wait time of 6000 ms and a total number of echoes (NECH) of 18000.

The filtration was stopped at different stages (i.e., the filtrate volume reached the predetermined values). Then, a cylindrical sample with a diameter of 2.0 cm was cut from the filter cake centre by a sharp knife to avoid the destruction of the filter cake structure. Subsequently, the sample was placed into the NMR tube, which was sealed to prevent water loss during the experiment.

3. Results and discussion

3.1. Results of filtration experiments

Fig. 2 shows filtrate volume as a function of filtration time at cationic and anionic polyacrylamide dosages of 0, 400 and 800 g/Mg. The filtration rate can be represented by the curve slope, i.e., the larger slope means the faster filtration rate. It can be found that the filtration rate increased with the increase of flocculant dosage from 0 to 800 g/Mg. Compared to the cationic polyacrylamide, the anionic polyacrylamide observed a higher filtration rate at 800 g/Mg. According to the literature, the formation of interparticle bridge is the main flocculation mechanism of anionic flocculants, making the negatively charged particles form large flocs (Sabah and Erkan, 2006). The formation of negatively charged particles by cationic flocculants is caused by the charge patch mechanism, which is reported to produce relatively small flocs (Chandra et al., 1997; Sabah et al., 2004; Nasser and James, 2006).

The filtration results of anionic and cationic polyacrylamides were similar at the dosage of 400 g/Mg. It should be noticed that different types and dosages of flocculants affect not only the filtration rate but also the ultimate filtrate volume. The ultimate filtrate volume decreased steadily with the increase of flocculant dosage. In other words, the addition of flocculant could accelerate the filtration rate, but it also increased the ultimate moisture content in filter cake. The ultimate filtrate volume decreased from 59.5 dm^3 to 55.0 dm^3 as the anionic polyacrylamide increased from 0 to 800 g/Mg. It suggested that the flocs that facilitated the filtration rate are easily to entrap water within the floc structure and result in the higher ultimate moisture content of filter cake. The results are consistent with the previous studies. Bourgeois and Barton (1998) proposed that there is no cake microstructure that can provide both a high filtration rate and a low filter cake moisture. Tao et al. (2003) reported that the anionic flocculant with high molecular weight could form larger flocs than the cationic flocculant, resulting in a faster filtration rate. However, the larger flocs lead to higher cake moisture because the looser structure entraps more

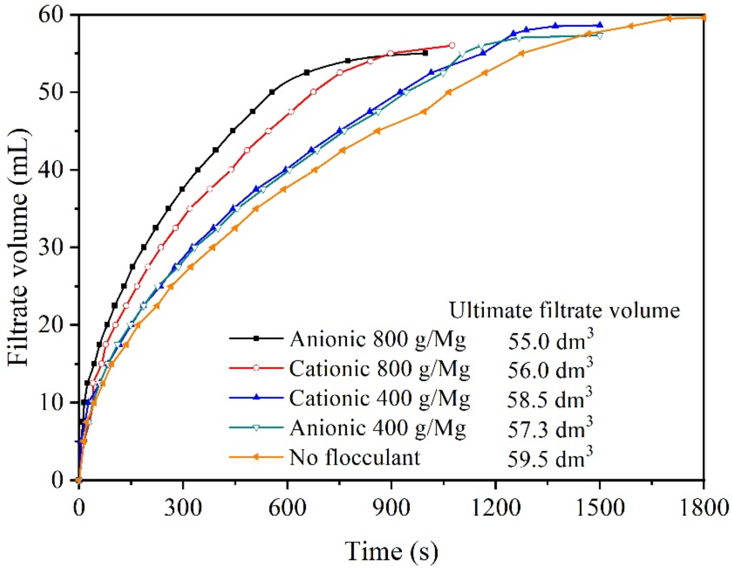

Fig. 2. Filtrate volume as a function of filtration time at anionic and cationic polyacrylamide dosages of 0, 400 and 800 g/Mg.

moisture. In the following section, the flocculant mechanism on filter cake structure was verified by the NMR results.

3.2. NMR relaxation time distributions of filter cakes

The NMR measurements were used to analyze the water distribution in filter cake at different filtration stage. The method is based on the principle that the corresponding relaxation times of water in the large pores are longer than that in the small pores. Thus, the T_2 values arranged from small to large correspond to the inherent moisture, capillary water, and free water in the filter cake (Yao et al., 2010; Hong et al., 2016).

As shown in Fig. 3, NMR measurements at different filtrate volumes were performed for filter cakes with anionic polyacrylamide of 800 g/Mg. It was found that the maximum T_2 value of the filter cakes decreased from 11.0 ms to 7.0 ms with the filtrate volume increased, and there was an apparent decrease in the amplitude of the T_2 value greater than 1.0 ms. This indicates that the water in large pores, which is termed as free water, was removed. This is consistent with the results in literature showing that free water is potentially removable by mechanical techniques (Parekh, 2009). It should be noted that the amplitude has a significant increase in the amplitude of T_2 value between 0.1 and 1.0 ms. This suggested that the floc structure collapsed into smaller ones, and water was entrapped more closely within the structure. The comparison of each filtration stage's NMR results shows that the amplitude of T2 value less than 0.1 ms is essentially the same, which may correspond to inherent moisture, which may correspond to inherent moisture, including interior adsorption water and surface adsorption water. This finding is consistent with previous studies reporting that the inherent moisture cannot be removed by applied pressure (Parekh, 2009; Alam et al., 2011). The photographs of the filter cakes show that the water observed on the surface of the filter cake decreased with the increase of filtrate volume. It is also observed that as the filter progressed, the filter cake became thinner and denser. These observations are consistent with the NMR results.

Fig. 4 shows the T_2 amplitude distributions of filter cakes at different filtration volumes with varying dosages of flocculant. In the initial stage of filter cake formation, i.e., the filtrate volume was 47.5 dm^3, the maximum T_2 value with anionic flocculant of 800 g/Mg was the largest at almost 20 ms. This is a significant increase from around 10 ms with no flocculant. Because the cake was saturated with water, the T_2 value was positively correlated with the structure size in the filter cake. It indicated that 800 g/Mg of anionic polyacrylamide produced a larger structure in the initial stage of filter cake formation as indicated by the higher T_2 value. The comparison of the NMR results of different flocculants also shows that the amplitude of T_2 value between 0.1 and 1.0 ms increased most dramatically with anionic poly-

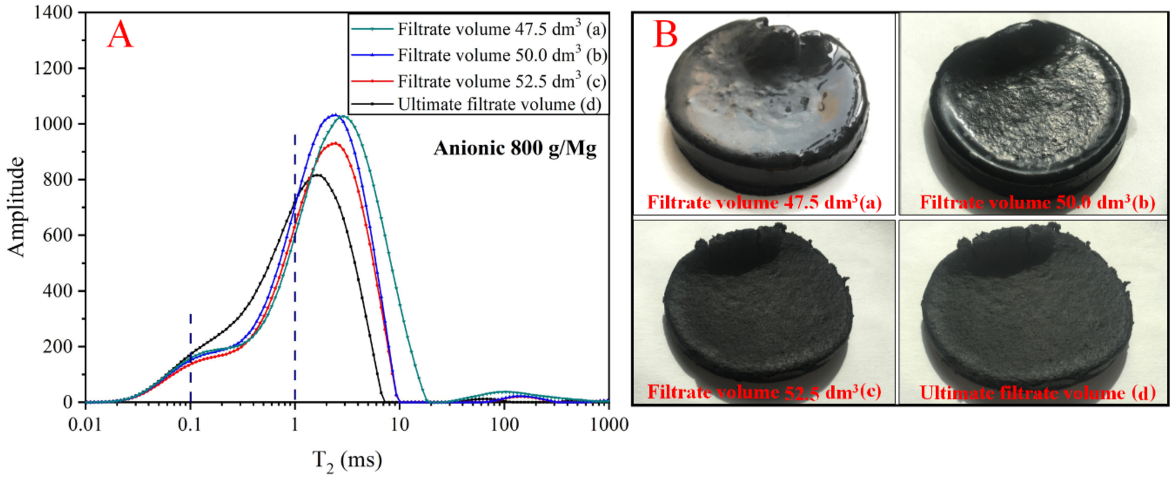

Fig. 3. (A) The T_2 amplitude distributions of filter cake at different filtrate volumes. (B) The photographs of the filter cakes at different filtrate volumes

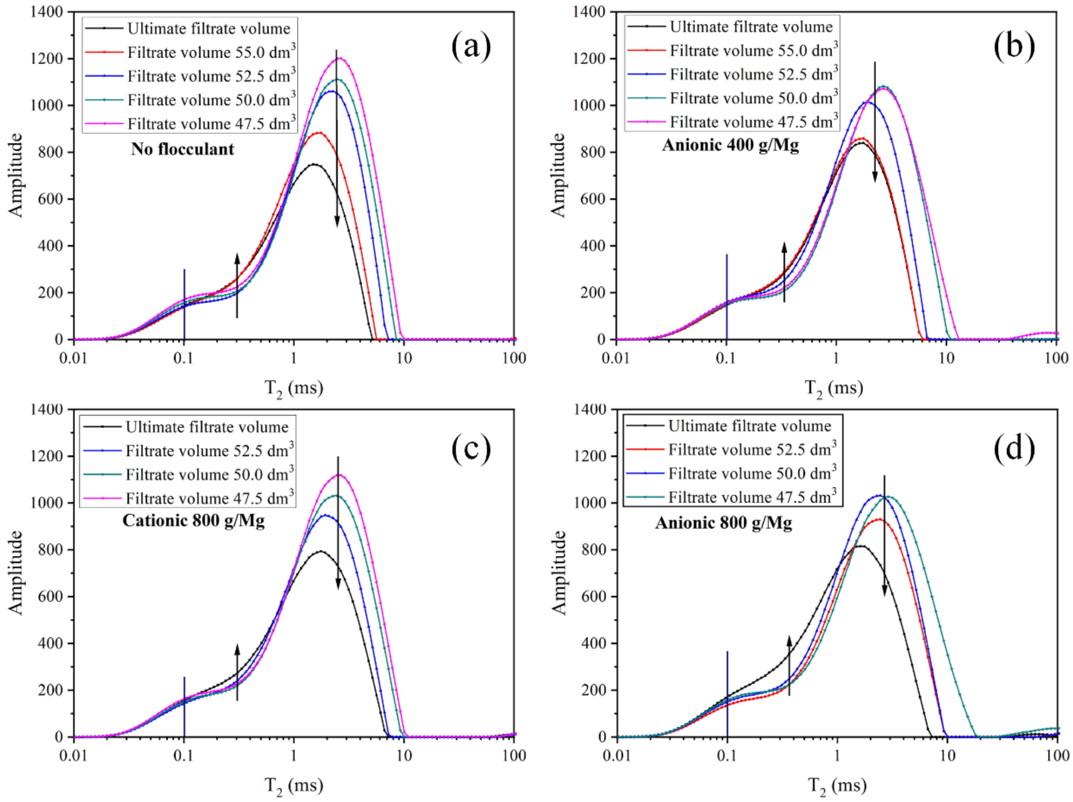

Fig. 4. The T_2 amplitude distributions of filter cakes at different filtration volume for no flocculant, anionic 400 g/Mg, cationic 800 g/Mg and anionic 800 g/Mg

acrylamide of 800 g/Mg, suggesting that more water was entrapped in the small structures of filter cake.

The intensity of NMR signal is proportional to the number of hydration (Zhao et al., 2017). Thus, the cumulative amplitude is proportional to the total volume of water in the filter cake. Fig. 5 shows the T_2 cumulative amplitudes of the ultimate filter cakes with flocculants of different types and dosages. The cumulative amplitude of anionic 800 g/Mg is the largest, followed by cationic 800 g/Mg, anionic 400 g/Mg, cationic 400 g/Mg and no flocculant. The cumulative amplitude was inversely proportional to the ultimate filtrate volume, which is consistent with the residual moisture in the filter cakes.

The industrial application of polymer flocculant as a filtration aid in coal tailings filtration is less than that of coagulant. This may be because although the flocculant significantly increases the filtration

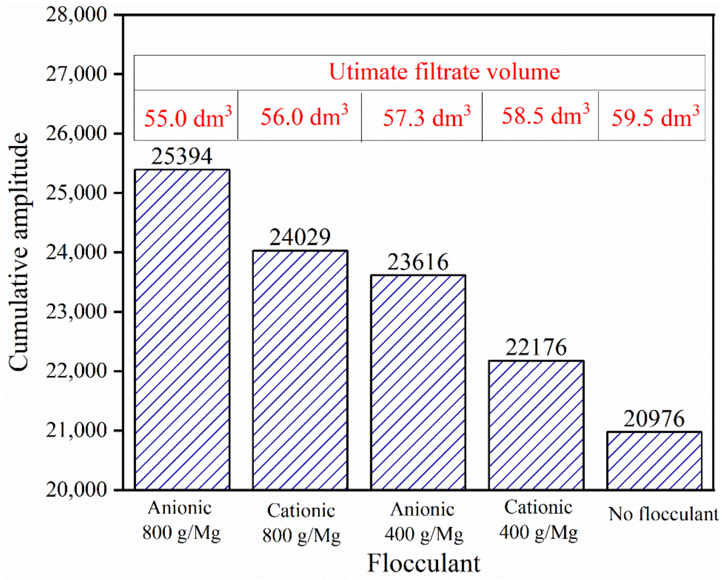

Fig. 5. The T_2 cumulative amplitudes of ultimate filter cakes

speed, the residual water entrapped in the filter cake is more severe (Alam et al., 2011). Thus, it is of great significance to get the information of the water entrapped in filter cake at different filtration stages and study the flocculant-aided filtration mechanism to select and evaluate other flocculants. According to previous studies, it is quite difficult to get the water information within the filter cake (Vaxelaire and Cézac, 2004). This study shows that low-field NMR measurements can provide a clear picture of the distribution of water entrapped in filter cake during the flocculant-aided filtration process. In general, the NMR measurements at various filtration stages provide both qualitative and quantitative information of the migration of water. The effects of flocculants on filtration can be understood by comparing the T_2 spectrums.

4. Conclusions

The NMR measurement was used to characterize the water distribution in the filter cake of coal tailings at different filtration stages. The NMR results revealed that the water in larger pores was largely removed, and the inherent moisture cannot be removed by the pressure in this study. The process of floc structure collapsed into a smaller structure, and entrapped water was presented. By comparing the NMR results of different flocculants, it can be found that the large flocs produced by flocculant pretreatment are easily to entrap water in the flocs structure and result in the higher ultimate moisture content of filter cake. This accepted inference was validated directly by the NMR measurement. This study shows that NMR measurement is a feasible method of characterizing water in filter cake and enables a better understanding of the flocculant-aided filtration process for coal tailings.

Acknowledgements

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