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Effect of dispersants on coal slime classification in a novel classification apparatus

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Abstract: The effects of the dispersants NaOH and Na₂CO₃ on the classification of coal slimes was studied in a novel classification apparatus. A dispersion effect was characterized through slurry pH and transmittance measurements as well as zeta potential determinations of the slimes. The pH increased and the zeta potential became more negative, while the transmittance decreased with the increase in the NaOH and Na₂CO₃ addition. The miscellany rates in the overflow decreased by 15.18% and 11.22% with NaOH and Na₂CO₃, respectively, while that in the underflow was 31.81% and 27.08%, respectively. An ash-removal efficiency from the coal slurries increased by 20.03% and 10.50% with NaOH and Na₂CO₃, respectively. It was found that the largest difference in classification efficiency between these dispersants in the overflow was 26.05% and underflow was 14.86%. At the high classification efficiency, the transmittance of the slurry decreased, indicating that better dispersion effect led to the higher classification efficiency of the coal slurry. NaOH showed to be a better dispersant for coal slimes classification than Na₂CO₃ in the novel classification apparatus.

Keywords: classification; dispersant; coal slime; transmittance; miscellany rate

1. Introduction

Clays are fine particles of less than 45 μm size in coal concentrates (Min et al., 2015; Xing et al., 2017; Zhu et al., 2018). These clays are responsible for an increase in ash content of coal concentrates, an increase in chemical reagent consumption and a decrease in the flotation concentrate yield (Ayhan et al., 2005; Jena et al., 2008; Ozkan, 2017). On the other hand, particle size of 0.25 mm to 0.075 mm is deemed as the optimum flotation size (Koca et al., 2003; Li et al., 2013; Zhu et al., 2015; Ni et al., 2016), thus it is essential to pre-classify the particles and separately process the classified products.

Desliming pond is considered as a representative application of hindered settling in gravitational field for classifying coal slimes (Zhu et al., 2013). This system is based on the difference of the hindered settling velocities between particles of different sizes. Coarse particles have a relatively high settling velocity and settle fast to the bottom of the pond as the underflow, while fine particles are discharged from the overflow due to the slow settling velocity (Takács et al., 1991; Kim and Klima, 2004; Sarkar et al., 2008; Tripathy et al., 2015). However, the operation efficiency of the desliming ponds is limited due to defects in structural design and dispersion of coal slimes (Maleksaeedi et al., 2010; Lee et al., 2015).

Many studies have been conducted for enhancing the dispersion of coal slimes. With NaOH and Na₂CO₃ hydroxyl ions are produced in the coal slurry and adsorbed on the particle surfaces making the negative zeta potential of the particles more negative (Wang et al., 2016). Zou et al. (2006) determined the zeta potential of fourteen different coals with various dispersants and found that the zeta potential of high-rank coal was low. In general, higher zeta potential values lead to better dispersion of coal slimes. Zhang et al. (2008) reported that water hardness affected dispersion of coal slurries, where coal slimes and kaolinite particles dispersed well in hard water with up to 1×10⁻³ M Ca²⁺. Feng et al. (2010)

evaluated the effect of particle size, zeta potential and water hardness on the sedimentation characteristics of coal slimes. They reported that clay was easily degraded resulting in difficult sedimentation. Moreover, the particles readily settled down when their zeta potential was low, while low water hardness led to good dispersion of coal slimes. However, not much work has been carried out combining the effect of dispersion of coal slime dispersants and pond structure.

The overall aim of this study was to provide a better understanding of the effects of the dispersants Na_2CO_3 and NaOH on coal particle classification. The effects of Na_2CO_3 and NaOH on slurry pH, zeta potential of coal slimes, transmittance of supernatant, miscellany rate, ash-removal efficiency and classification efficiency were investigated. In addition, the relationship between the dispersion and the classification efficiency of a novel apparatus was assessed.

2. Experimental

2.1. Materials

In this study, NaOH and Na_2CO_3 from Langfang Longxing Chemical Co., Ltd, China were used as dispersants (Zhang et al., 2001; Shie et al., 2003; Zhang and Hu, 2014). The water solubility of NaOH is 1.09 g/cm^3 , and that of Na_2CO_3 is 0.22 g/cm^3 at 20°C . Coal slime slurries with 24.26 % ash content from Dingji coal preparation plant in Anhui, China was used for the classification experiments. The mineralogical composition of the coal was determined using a XRD-6000 type X-ray diffractometer. The result of XRD analysis of the sample is given in Fig. 1.

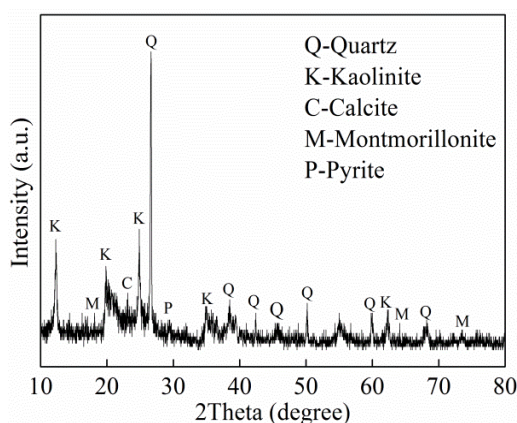


Fig. 1. X-ray diffractogram of coal slime sample

From Fig. 1, the major minerals in the coal slimes were quartz, kaolinite, calcite, montmorillonite and pyrite. Kaolinite and montmorillonite easily exfoliate into ultrafine particles smaller than $5 \mu\text{m}$ in water due to their layered structure (Milne and Earley, 1958; Gui et al., 2016; Xing et al., 2016). The clay particles present anisotropic surfaces with both a negative and positive electric charge which causes attachment between these fine particles and coarse particles, and this situation makes the classification difficult (Vijayalakshmi and Raichur, 2003; Sabah and Cengiz, 2004; Alam et al., 2011). Table 1 shows the particle size distribution and ash content in each size fraction in the coal slime. As noted, the mass fraction of fine slimes ($<0.045 \text{ mm}$) was high, 32.14 %, as well as the ash content in the slimes, which was 44.2 %. This leads to difficult classification.

Table 1. Ash content and particle size distribution in coal slurry

Size/mm	Mass fraction/%	Ash/%	Cumulative yield/%	Cumulative ash/%
0.500~0.250	9.56	10.96	9.56	10.96
0.250~0.125	30.96	12.53	40.51	12.16
0.125~0.075	15.78	15.68	56.29	13.15
0.075~0.045	11.57	22.92	67.86	14.81
<0.045	32.14	44.20	100.00	24.26
Total	100.00	24.26		

2.2. Classification system

Based on the hydraulic classification principle, a novel structural classification apparatus different from hydro-cyclone and desliming pond was designed. Fig. 2 depicts the main components of the classification apparatus system used in this work: (1) a stirrer fixed in a feed tank for mixing dispersants and slurry, (2) a feed groove, (3) a pump for pumping the slurry to the feed groove, (4) a baffle for dividing the apparatus into an upflow area and a downflow area, (5) many rectifying bundles with the form of a cuboid of 50×50×170 mm (width×depth×height) for bestrewing the transverse upflow area, (6) an underflow pipe for discharging the large particles and (7) an overflow groove fix at the top of the upflow area for collecting the fine particles. The area of the cross section of the apparatus is 350 mm depth×150 mm width, while that of the upflow area is 150 mm depth×150 mm width. A gradient wall, which is fixed at the bottom of the downflow area, is designed to guide the large particles to the underflow pipe, and its horizontal angle is 39.71°. The base of the rectifying bundles is 100 mm away from the apparatus bottom and the height of the baffle is 225 mm.

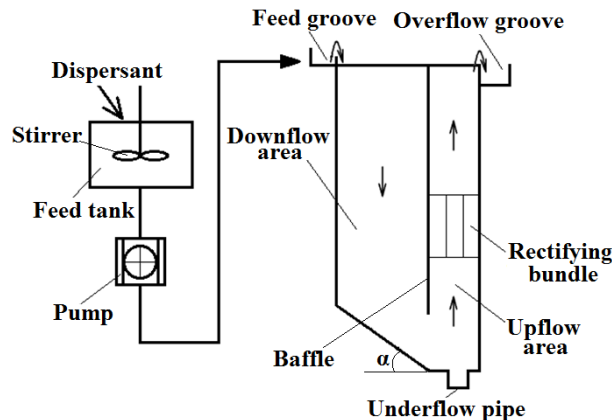


Fig. 2. Schematic diagram of the classification apparatus system

The slurry flows to the downflow area from the feeder (feed groove), which is fixed at the top of the apparatus, then around the baffle where the slurry moves upward. The particles with hindered settling velocities smaller than the upward flow velocity pass to the overflow groove installed at the upper part of the apparatus. The particles with settling velocities higher than the upward flow velocity fall to the bottom of the apparatus towards the underflow. A valve connected in the underflow pipe was used to control the underflow flux, through which the overflow flux, upward flow velocity and classify size could be indirectly controlled at an expected value while a constant feed flux was held. In this study, the classifying size was set at 0.045 mm, and the upward flow velocity, which was equal to the hindered settling velocity of the 0.045 mm coal slime, was calculated using the Stokes formula, v_g (Sjöberg, 2003):

$$v_g = 54.5\chi d^2 \frac{\delta - \rho}{\mu(1-\lambda)^n} \quad (1)$$

where χ is the shape index of the coal slimes (0.7), d is the particle diameter ($d=0.045$ mm), δ is the particle density of the coal slimes (1.81 g/cm³), ρ is the water density (1.00 g/cm³), μ is the dynamic viscosity of water at 20 °C (1.005×10^{-3} Kg m⁻¹ s⁻¹), n is the concentration interference index (5-0.7 Re), and λ is the volume ratio of solids and liquid (Gahlot et al., 1992), given by

$$\lambda = \frac{q}{1000\delta} \quad (2)$$

where q is the ratio of the mass of the solids to volume of the slurry (80 g/dm³). The value of λ and v_g were found to be 0.044 and 0.076 cm/s, respectively. Calculations on the volume flux indicate that the overflow flux is 0.616 m³/h.

2.3. Measurements

In this study, tap water of pH 8.60 and zeta potential -27.94 mV was used to prepare the coal slurries and all experiments were conducted at 20±1 °C. A solid concentration close to the optimal flotation

concentration of 80 g/dm³ was applied for the coal slurry in this study. Slurries were prepared in the absence and presence of the dispersant with various additions at 0.04, 0.08, 0.12 and 0.16 g/dm³.

Slurries were prepared with 40 g coal slimes added in seven measuring cylinders of 500 cm³ pre-filled with the tap water, after stirring 2 minutes the dispersant was added at a given addition. Then 50 cm³ supernatant was successively extracted from the cylinders at different times (0.0, 0.5, 1.0, 2.0, 4.0, 8.0, 12.0 h) for transmittance measurements, which were carried out using an UV-5500PC spectrophotometer at a wavelength of 650 nm (Shanghai Metash Instruments Co. Ltd, China). Each measurement was threefold repeated for reporting the average value as the final data.

10 dm³ coal slurry and 800 g coal slimes were added into the feed tank for classification experiments, after stirring 2 minutes and cycling 2 minutes the overflow and underflow were respectively sampled of the same volume for the analysis of solid content and size composition. To macroscopically quantify the effect of dispersant addition on zeta potential and pH, coal slurry samples of 250 cm³ from the feed tank with different dispersant additions were prepared for pH and zeta potential measurements, which were performed using a Zeta probe analyzer (Colloidal Dynamics Pty, Ltd. USA). Each sample was directly used for the measurement, and three repetitive tests of each measurement were performed for obtaining an average value as the final data.

Three parameters were used for evaluating the classification. The miscellany rate (m) was calculated as follows (Zhu et al., 2013):

$$m = \frac{m_m}{m_f} \times 100\% \quad (3)$$

where m_m is the mass fraction of the misplaced particles, and m_f is the mass fraction of the feed.

The classification efficiency (η) was calculated as Eq.(4) (Honaker et al., 2001).

$$\eta = \left| \frac{m_o - m_n}{m_{max} - m_{min}} \right| \times 100\% \quad (4)$$

where m_o is the miscellany rate of overflow (underflow) without dispersant, m_n is the miscellany rate of overflow/underflow in the presence of dispersant addition of n , m_{max} is the maximum miscellany rate of overflow/underflow, and m_{min} is the minimum miscellany rate of overflow/underflow.

The ash-removal efficiency (r_d) was evaluated as Eq.(5) (Zhu et al., 2015).

$$r_d = \frac{A_{do} - A_{df}}{A_{df}} \times 100\% \quad (5)$$

where A_{do} is the ash content in the overflow, and A_{df} is the ash content in the feed.

3. Results and discussion

3.1. Effects of NaOH and Na₂CO₃ on pH and zeta potential

Fig. 3 presents the pH value as a function of dispersant addition. The pH value increased with increasing the dispersant addition, being the pH higher with NaOH than with Na₂CO₃. Furthermore, with the increase in dispersant addition, the difference in the pH between NaOH and Na₂CO₃ increased due to more production of hydroxyl ions by the NaOH (Henrist et al., 2003). As noted, the natural pH value of the slurry without dispersant was 8.6, which illustrated the coal slimes were slightly alkaline.

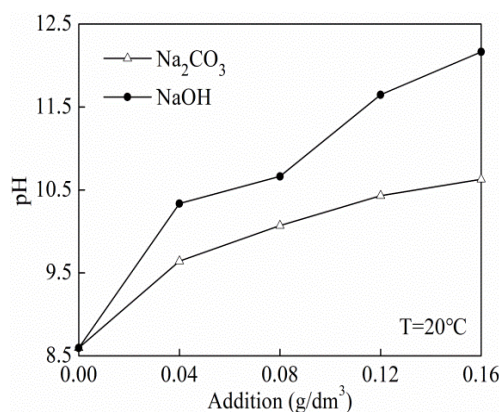


Fig. 3. pH value as a function of dispersant addition

Fig. 4 shows the zeta potential as a function of NaOH and Na₂CO₃ addition. Without dispersant the zeta potential was -27.94 mV, indicating that the electric charge of the surfaces of the coal slimes were predominantly negative. Increasing the dispersant addition significantly increased the zeta potential negatively more with NaOH than with Na₂CO₃. This is mainly owing to the more generation in hydroxyl ions of NaOH.

The relationship between zeta potential and pH is given in Fig. 5. It was clear that the zeta potential depends on the pH rather than the dispersant type. The zeta potential of the clay slimes increased with pH indicated that hydroxyl ions were potential determining ions for the coal slime surfaces.

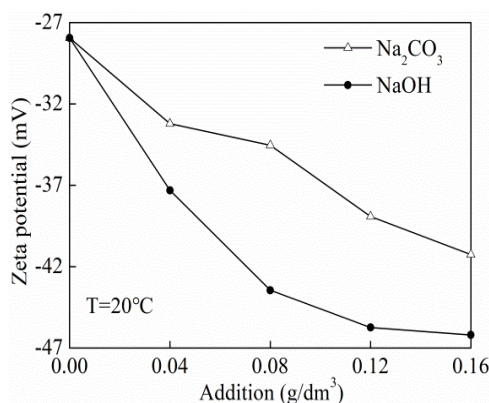


Fig. 4. Zeta potential of coal slimes as a function of dispersant addition

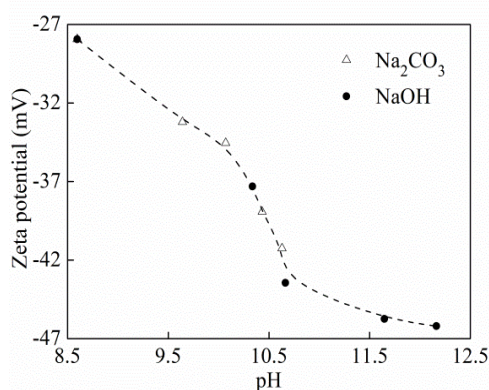


Fig. 5. Relationship between zeta potential and pH

3.2. Effects of NaOH and Na₂CO₃ on transmittance

Fig. 6 shows the slurry transmittance as a function of time in the absence and presence of various NaOH and Na₂CO₃ additions. In general, the transmittance increased as the time increased especially during the first 2 hours, indicating that the sedimentation of the coarse coal slime roughly completed in the first 2 hours while that of the fine coal slime almost continued throughout the studied time. The transmittance of Na₂CO₃ was found to be larger than that of NaOH through the comparison between Figs.6 (a) and (b), which agreed well with the higher negative charge in zeta potential by NaOH. In this study, the time for the liquid flowing from the pond inlet to the overflow groove was calculated to be approximately 0.5 hour, indicating that the time for particles flowing through the route would be longer than 0.5 hour. Hence a comparison on the transmittance at the standing time of 0.5 hour is shown in Fig. 7.

As noted, the transmittance of the liquid with NaOH was lower than that with Na₂CO₃ at every dispersant addition, which agreed well with the above results. A significant difference in the transmittance between NaOH and Na₂CO₃ was observed at the dispersant additions of 0.12 g/dm³ (6.4 %) and 0.08 g/dm³ (6.2 %). After that, the difference in transmittance decreased and was very low with the dispersant addition indicating that full dispersion of the particles was reached. Overall, the dispersion of coal slimes is actually enhanced by the dispersants, and coal slimes disperse better with NaOH.

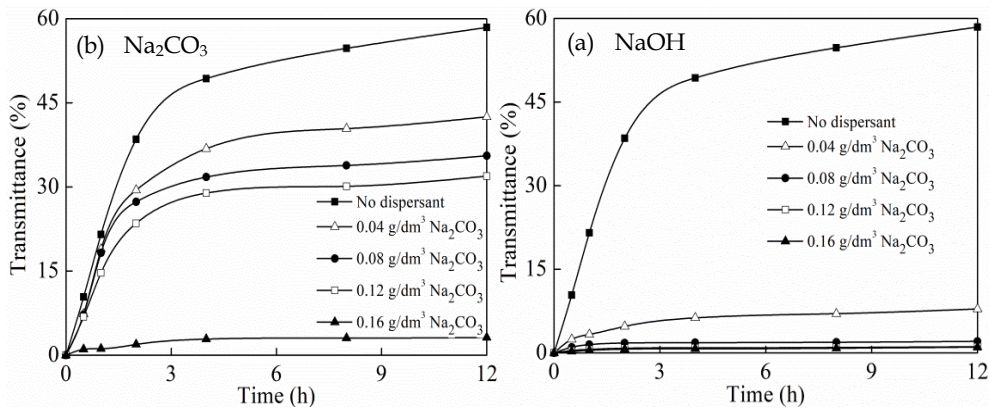


Fig. 6. Transmittance as a function of time for NaOH and Na₂CO₃

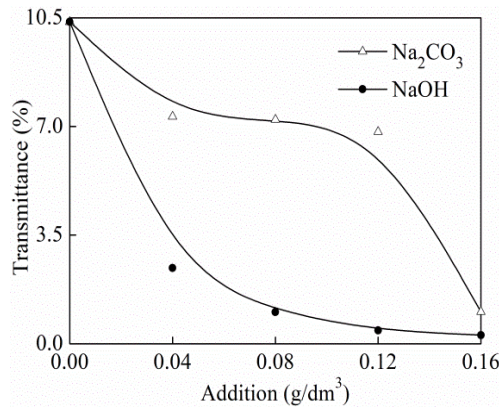


Fig. 7. Transmittance as a function of dispersant addition at the standing time of 0.5 h

3.3. Effects of NaOH and Na₂CO₃ on miscellany rate, ash-removal efficiency and classification efficiency

Tables 2 and 3 show the classification results from the experiments in the classification apparatus in the absence and presence of various NaOH and Na₂CO₃ additions, respectively.

The term yield in Tables 2 and 3 represents the ratio of the mass of a certain size fraction divided by the mass of the solid in the overflow or underflow. The >0.045 mm fraction in overflow and <0.045 mm fraction in underflow were all considered as the misplaced materials, thus the miscellany rates of overflows and underflows for NaOH and Na₂CO₃ were calculated and shown in Fig. 8.

Table 2. Results of classification experiments with Na₂CO₃

Addition (g·dm ⁻³)	Overflow					Underflow				
	>0.045mm		<0.045mm		Ash/ %	>0.045mm		<0.045mm		Ash/ %
	Yield/ %	Ash/ %	Yield/ %	Ash/ %		Yield/ %	Ash/ %	Yield/ %	Ash/ %	
0	18.51	9.13	81.49	46.11	39.27	34.86	8.04	65.14	45.33	32.33
0.04	11.82	8.85	88.18	45.32	41.01	37.23	8.70	62.77	43.28	30.41
0.08	10.82	7.81	89.18	45.20	41.15	53.37	8.91	46.63	45.07	25.77
0.12	10.53	8.67	89.47	45.35	41.49	59.75	8.81	40.25	45.09	23.41
0.16	7.29	8.51	92.71	44.43	41.81	61.94	8.77	38.06	44.14	22.23

As shown in Figs.8 (a) and (b), the miscellany rates of overflows and underflows decreased with the increase in dispersant addition, and the differences in miscellany rates increased as the dispersant addition increased. And also, Na₂CO₃ performed larger miscellany rates than NaOH. The miscellany

rates of NaOH and Na₂CO₃ in overflow respectively decreased by 15.18 % and 11.22 %, whereas in the underflow the decrease was by 31.81 % and 27.08 %. Even though the dispersant addition was as high as 0.16 g/dm³, the miscellany rates in the underflows were as high as 33.33 % (NaOH) and 38.06 % (Na₂CO₃), illustrating that a high amount of ultrafine particles was misplaced in underflow. However, the miscellany rates in the overflows at dispersant addition 0.16 g/dm³ were 3.33 % (NaOH) and 7.29 % (Na₂CO₃), demonstrating that a low amount of coarse particles was misplaced in overflow. Overall, fine particles are more easily affected by dispersant addition than coarse particles, and NaOH presents a more significant effect on decreasing miscellany rate than Na₂CO₃.

Table 3. Results of classification experiments with NaOH

Addition (g·dm ⁻³)	Overflow					Underflow				
	>0.045mm		<0.045mm		Ash/ %	>0.045mm		<0.045mm		Ash/ %
	Yield/ %	Ash/ %	Yield/ %	Ash/ %		Yield/ %	Ash/ %	Yield/ %	Ash/ %	
0	18.51	9.13	81.49	46.11	39.27	34.86	8.04	65.14	45.33	32.33
0.04	10.31	9.01	89.69	45.15	41.42	38.89	8.68	61.11	41.14	28.52
0.08	9.27	8.06	90.73	45.86	42.36	55.73	8.12	44.27	41.25	22.79
0.12	6.79	7.98	93.21	44.93	42.42	61.73	9.09	38.27	43.44	22.24
0.16	3.33	8.01	96.67	45.37	44.12	66.67	8.94	33.33	43.84	20.57

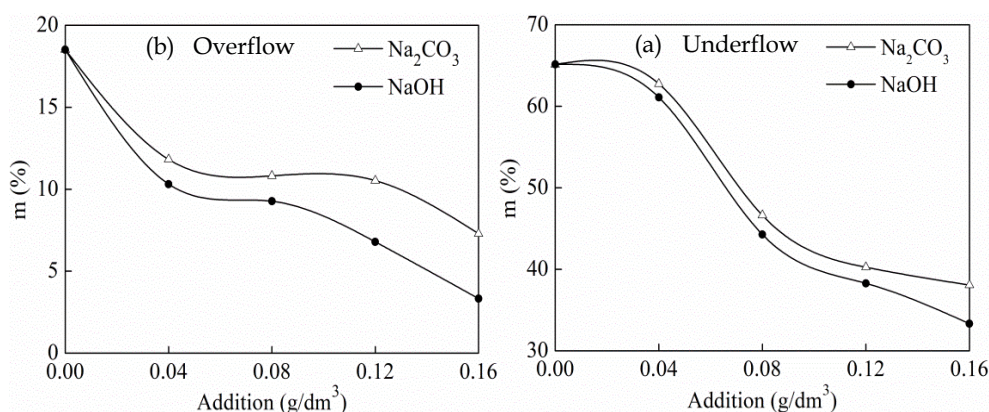
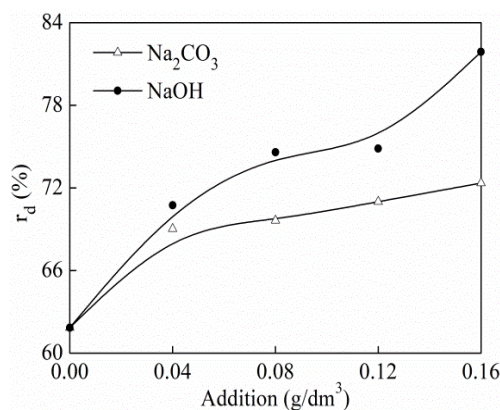
Fig. 8. Miscellany rate as a function of dispersant addition in overflows and underflows for NaOH and Na₂CO₃Fig. 9. Ash-removal efficiency as a function of dispersant addition for NaOH and Na₂CO₃

Fig. 9 presents the ash-removal efficiency as a function of dispersant addition for NaOH and Na₂CO₃. The ash-removal efficiency was found to increase as the dispersant addition increased due to the decrease in miscellany rate in the underflow as shown in Fig. 8. The difference in ash-removal efficiency

between NaOH and Na₂CO₃ was observed to increase with increasing the dispersant addition, being the ash-removal efficiency of Na₂CO₃ smaller than that of NaOH under every dispersant addition. In addition, the ash-removal efficiencies of NaOH and Na₂CO₃ increased by 20.03 % and 10.50 %, respectively. Overall, the addition of Na₂CO₃ and NaOH effectively increases the amount of ash removed, in which NaOH presents a better performance than Na₂CO₃. It is beneficial for the flotation processing the underflow as contains a lower amount of fine particles and ash.

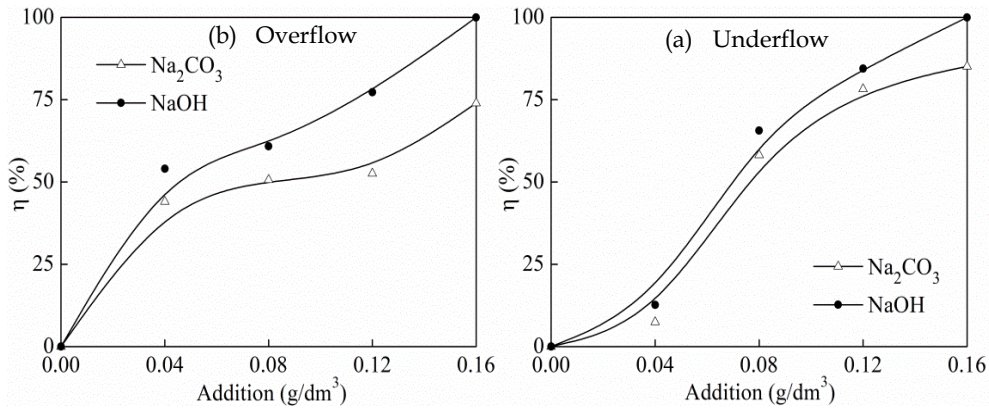


Fig. 10. Classification efficiency as a function of dispersant addition in overflows and underflows for NaOH and Na₂CO₃

Further analysis on classification efficiency as a function of dispersant addition in overflows and underflows for NaOH and Na₂CO₃ is shown in Fig. 10. The classification efficiency gradually increased as the dispersant addition increased, and the difference in classification efficiency between NaOH and Na₂CO₃ likewise increased with the increase in dispersant addition in overflow and underflow. It was noteworthy that the classification efficiencies of underflow were higher than those of overflow under an identical dispersant addition during the region of 0.04 g/dm³ to 0.16 g/dm³, illustrating that the motion of fine slimes was less influenced by coarse slimes and less fine slimes were discharged from the underflow. The largest difference in classification efficiency of overflow and underflow were 26.05 % and 14.86 %, respectively. Overall, NaOH performed a better enhancement on the classification efficiencies of overflow and underflow than Na₂CO₃.

3.4. Relation between transmittance and classification efficiency

Fig. 11 presents the relation between transmittance and classification efficiency for NaOH and Na₂CO₃ in overflow and underflow.

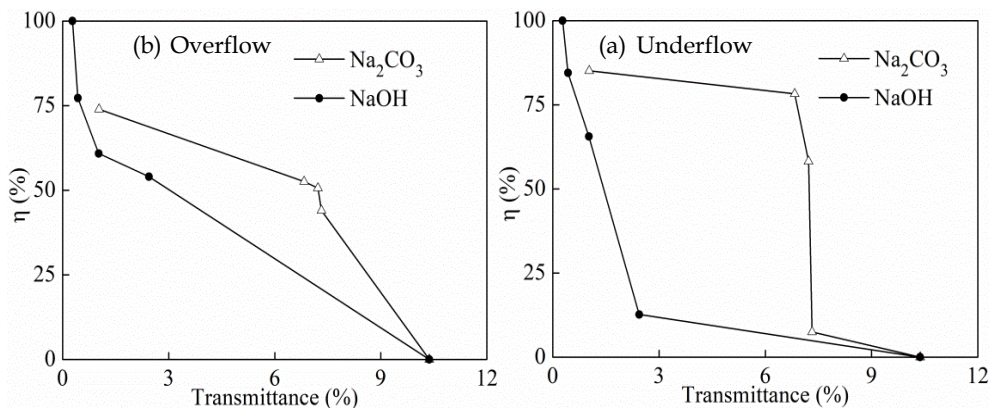


Fig. 11. Relation between transmittance and classification efficiency for NaOH and Na₂CO₃ in overflow and underflow

The classification efficiency decreased with the increase in transmittance, indicating that better dispersion resulted in higher classification efficiency. The classification efficiencies of Na₂CO₃ in

overflow and underflow were larger than those of NaOH at the same transmittance, and in this case larger Na₂CO₃ addition was required for obtaining the same transmittance with NaOH. As shown in Fig. 11 (a), the highest decline rate of NaOH in overflow located in the transmittance region of 0.28 to 1.02 %, while that of Na₂CO₃ located in the region of 7.22 to 7.32 %. Almost the same trend was observed in Fig. 11 (b), the highest decline rate of NaOH in underflow located in the transmittance region of 0.28 to 2.44 %, and that of Na₂CO₃ located in the region of 6.83 to 7.32 %. The transmittance region, where the highest decline rate located, of overflow agreed with that of underflow, and the region of NaOH was smaller than that of Na₂CO₃. Overall, higher classification efficiency can be achieved by NaOH at an identical addition with Na₂CO₃ according to lower transmittance but better dispersion of NaOH.

4. Conclusions

Both dispersion and classification efficiencies of the coal slurry were assessed using NaOH and Na₂CO₃ in a novel classification apparatus. Some conclusions can be drawn as follows:

(1) Both NaOH and Na₂CO₃ performed improvement on the dispersion of coal slimes like the increase in slurry pH, decrease in negative zeta potential of coal slimes and decrease in supernatant transmittance, wherein the improvement from NaOH is better. The transmittance was also found to increase with increasing standing time of the coal slurry but decrease with increasing dispersant addition.

(2) NaOH was also proved to present a better enhancement on the classification of coal slimes in the novel classification apparatus like lower miscellany rate, higher ash-removal efficiency and higher classification efficiency than Na₂CO₃.

(3) Compared to Na₂CO₃, NaOH performed lower slurry transmittance which gave rise to higher classification efficiency in both the overflow and underflow, indicating that NaOH is better for coal slimes classification than Na₂CO₃.

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