Which is Preferable for Coal Cleaning by Flotation: Pine Oil or $MgCl_2$?

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Abstract

Coal flotation using inorganic salts receives special attention. It utilizes coal hydrophobicity to float coal without adding collectors. Although different salts were tested, chloride salts are the most promising ones. However, the stabilization of froth layer using the salts only is dubious. Therefore, in this study, the flotation of coal was tested using either magnesium chloride or pine oil as a frother to see if there is a difference in coal flotation between these reagents in terms of ash removal and coal recovery in the float fraction. Additionally, both magnesium salt and pine oil were added together to clarify their interactive effect using statistical design. The results proved that the presence of either reagent (i.e., pine oil or $MgCl_2$) is significant in reducing the ash content and increasing coal recovery. Using the $MgCl_2$ only reduced the ash to less than 4.3% with a coal recovery up to 28% while adding 1.0 kg/t pine oil along with 4 kg/t $MgCl_2$ enhanced the reduction of ash to less than 3% with a coal recovery of up to 80% at pH 2.

Keywords: *magnesium chloride, pine oil, frother, coal, flotation*

1. INTRODUCTION

Removal of ash forming minerals from coal is environmentally mandated. The flotation of coal is a promising process to remove or even minimize the ash content. Recently, the flotation of coal in salt solutions attracts the researchers' attention worldwide, where the coal can be floated without collector or frother, but with the addition of inorganic salts [1-3]. The flotation of coal, although it is a hydrophobic material, in electrolyte solutions has numerous advantages. For instance, adding salts to water reduces the occurrence of cavitation as the amount of dissolved air is minimized [4]. Salt flotation is a physicochemical process, therefore the presence of electrolytes enhances the effect of electrostatic interaction, affects the electrical double-layer (EDL) between bubbles and particles, and reduces their zeta potentials [5]. Using salts not only reduces bubble coalescence but also the bubble size [6-7]. At high electrolyte concentrations, a strong attraction between the particles occurs due to the specific adsorption of cations that leads to significant changes in the surface charge of the particles [8].

Several papers have studied the collector-less flotation of coal using different salts. Most of these studies referred to chloride salts and especially to $MgCl_2$ as the most promising salt for removing ash with relatively suitable recovery [2-3; 9-10].

This paper studies the effect of either magnesium chloride or pine oil as a frother on ash removal from coal by flotation using the statistical design. The individual and interactive effects of using reagents were revealed and their interactive effect. The flotation using $MgCl_2$ in the presence and absence of pine oil was compared to show the importance of pine oil in stabilizing bubbles in the froth layer in terms of ash removal and coal recovery in the float fraction.

2. EXPERIMENTAL

2.1 Materials

The coal sample was provided from El-Maghara region, Sinai, Egypt. The sample was subjected to several steps of crushing and grinding to get the suitable particle size for subsequent processes of characterization and flotation.

2.2 Methods

2.2.1. Proximate and ultimate analyses

The coal sample was characterized by proximate, ultimate, and calorific values analyses. Standard analysis procedures were followed according to ASTM Standards [11-13].

2.2.2. Flotation tests

Denver flotation cell (D-12) with a cell capacity of 1.5 L was used for flotation tests. The coal sample, of −0.5+0.075 mm particle size, was added to the flotation cell and pulped in 300 ml of distilled water through which the sodium hydroxide was added to adjust the pH at pH 9. The predetermined $MgCl_2$ salt dosage was added and left for 5 min as a conditioning time then the 10% solids was achieved by adding water. The frother (pine oil) was added before the air was introduced at impeller speed of 1200 rpm, and the concentrate was collected for 3 min.

2.2.2.1. Statistical design

23 factorial design with three mid-points was used fo coal flotation by $MgCl_2$ in the absence or presence of pine oil, at different pH values taking ash content or coal recovery in the float fraction as responses. The Design-Expert software, Stat-Ease, Inc., Minneapolis, USA was used for statistical analysis and to estimate the statistical parameters using analysis of variance (ANOVA) within 95% confidence interval.

Tab. 1. Proximate and ultimate analysis of El-Maghara coal (As received, a.r; dry base, d.b; dry-mineral-matter-free, dmmf basis; moist-mineral-matter-free mmmf basis)

Tab. 1. Analiza zbliżeniowa i końcowa węgla El-Maghara (w stanie otrzymanym, ar; sucha baza, db; sucha-bez substancji mineralnych, dmmf; baza wilgotno-mineralna-wolna mmmf)

Sample No.	As-received basis, %				Dry basis, %								MM (Parr Formula)	Dmmf, %		GCV (mmmf)	Ro %
	M	Ash	V.M	F. C	Ash	V.M	F.C	C	H	N	S	O		F.C%	V.M%		
1	2.78	5.4	49.95	41.87	3.18	54.82	42	73.38	5.79	1.32	3.95	12.38	5.61	46.8	53.2	30.64	**0.47**
2	2.48	6.5	48.75	42.27	6.67	49.99	43.3	71.6	5.07	1.01	2.63	13.02	8.65	48.3	51.7	30.05	**0.46**
3	0.9	3.15	54.33	41.62	5.55	51.38	43.1	69.79	5.36	0.98	2.44	15.88	7.34	44.3	55.7	32.16	**0.43**
4	1.19	6.24	52.44	40.13	2.49	54.84	42.7	73.34	6.22	1.12	3.47	13.36	4.60	44.5	55.5	28.9	**0.44**
5	2.06	4.48	53.56	39.9	4.57	54.69	40.7	67.31	5.85	0.97	3.62	17.68	6.93	44.2	55.8	31.45	**0.43**
6	1.24	2.46	54.16	42.14	6.49	52.89	40.6	67.73	6.06	0.98	2.78	15.96	8.54	44.8	55.2	31.34	**0.41**
7	2.58	5.13	52.56	39.73	3.55	54	42.4	76.14	5.52	1.1	3.3	10.39	5.65	44.8	55.2	29.93	**0.45**
8	1.08	2.31	52.58	44.03	2.34	53.15	44.5	69.91	5.52	1	3.3	17.93	4.34	46.5	53.5	32.1	**0.44**
9	2.61	3.46	52.59	41.34	5.27	53.95	40.8	42.74	4.89	1.24	2.9	42.96	7.29	45.7	54.3	30.94	**0.44**
10	2.03	13.8	49.83	34.38	14.05	50.86	35.1	73.28	5.51	1.21	7.2	3.75	9.65	43.37	56.63	28.46	**0.41**
Average	1.9	5.3	52.1	40.5	5.3	53.1	41.6	68.1	5.6	1.1	3.6	16.3	6.86	45.33	54.67	30.6	**0.44**

Tab. 2. Ash% in float and coal recovery according to factorial design runs

Tab. 2. % popiołu w spławikach i odzysku węgla według czynnikowych przebiegów projektowych

Std	Factors			Responses	
	A:pH	B:$MgCl_2$, kg/t	C:Pine oil, kg/t	Ash in float %	Coal Rec. % in float
1	2	0	0	4.9	5.3
2	10	0	0	4.3	46.8
3	2	4	0	4.3	27.2
4	10	4	0	4.8	69.3
5	2	0	1	3	25.6
6	10	0	1	3.9	63.8
7	2	4	1	3	81.9
8	10	4	1	4.7	51.7
9	6	2	0.5	3.3	35.5
10	6	2	0.5	4.2	22.0
11	6	2	0.5	3.9	30.0

3. RESULTS AND DISCUSSION

3.1 Coal sample characterisation

3.1.1 The proximate and ultimate analyses

Proximate and ultimate analyses, as received or on a dry basis, are given in Table 1. The sample indicates a low to medium ash content of 5.32% with remarkably high sulfur of 3.6%, Table 1. The gross calorific value was determined to be 30.83 MJ/Kg and is considered in rank determination [14]. Accordingly, the coal sample was classified as medium rank and high volatile bituminous coal (ASTM Standard) [15-16].

3.1.2 Petrography

The photomicrographs of El-Maghara coal sample are shown in Fig. 1. All photomicrographs were taken in white light in oil immersion. Fig 1a Shows Framboidal pyrite mineral (py) within the dark groundmass of liptodetrinite maceral. Fig 1b shows Pyrite mineral (py) filling the coal cracks of collotelinite maceral. Fig 1c shows disseminated pyrite mineral (py) (framboids) within collotelinite maceral. Fig 1d shows Irregular lath shape of carbominerite (ca) of mostly siderite mineral. Fig 1e shows Association of dark liptodetrinite and clay minerals (cly) occupies disseminated gray detrovetrinite macerals. Fig 1f shows High relief quartz grain mineral (qz) with collodetrinite maceral. In addition, Figure 2 shows the volumetric distribution of associated minerals in 10 coal samples.

3.2. Flotation results

The flotation results according to statistical design runs are listed in Table 2. The lowest ash (as low as 3%) in the float fraction was achieved at the highest levels of $MgCl_2$ salt dosage and pine oil dosage and at the lowest level of pH. The analysis of variance (ANOVA) analyses indicated that the pine oil dose is the most significant factor in the ash % in the float fraction, while the pH is the most significant for coal recovery. The standard deviation and R-squared for the fitted factorial model are 0.35 and 0.8893 for ash% and 5.57 and 0.9802 for coal recovery %, respectively. The responses (Ash % and coal recovery in the float fraction) were correlated with the studied factors by the following equations:

Ash in float % = 4.11 + 0.31*A - 0.46*C + 0.24*A*B + 0.34 *A*C + 0.11* B*C

Float Rec. % = 46.45+11.45*A+11.06*B+9.31* C-8.48*A*B - 9.45*A*C - 8.65*A*B* C

Where

A: pH of the pulp

B: MgCl2 dosage, kg/t

C: pine oil dosage, kg/t

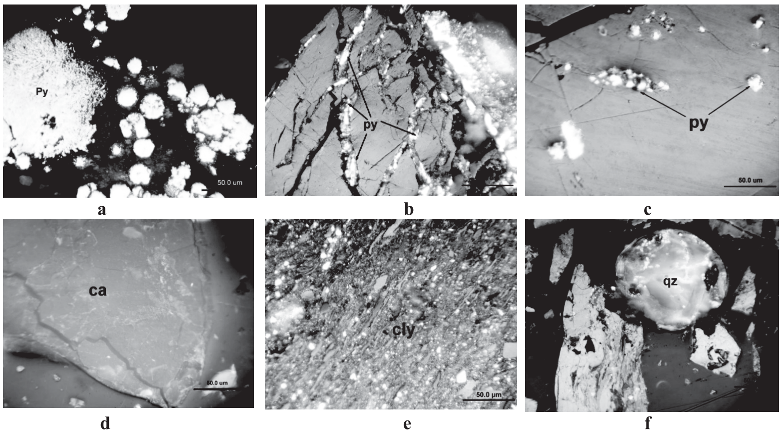


Fig. 1. Typical different minerals of the El-Maghara coal
Rys. 1. Typowe różne minerały węgla El-Maghara

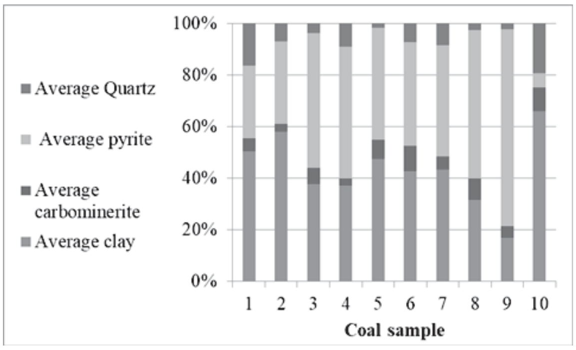


Fig. 2. Volumetric percentages of coal associated minerals
Rys. 2. Procenty objętościowe minerałów związanych z węglem

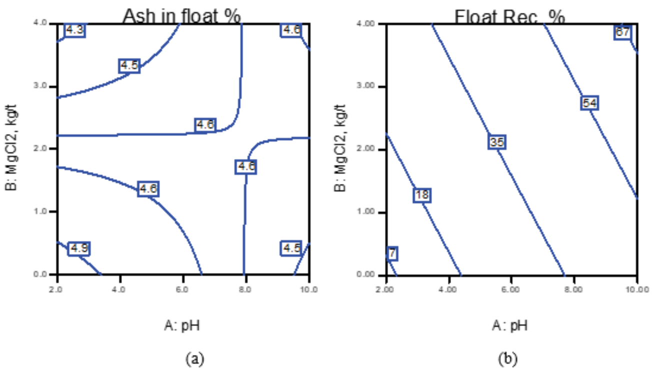


Fig. 3. Effect of $MgCl_2$ on a) ash % and b) coal recovery in the float fraction as a function of pH
Rys. 3. Wpływ $MgCl_2$ na a) procent popiołu i b) odzysk węgla we frakcji flotacyjnej w funkcji pH

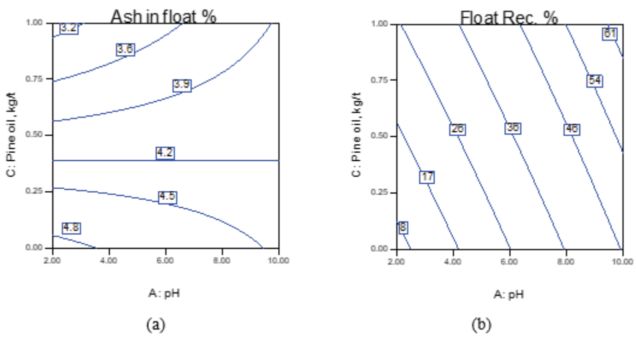


Fig. 4. Effect of pine oil on (a) ash % and (b) coal recovery in the float fraction as a function of pH
Rys. 4. Wpływ oleju sosnowego na (a) % popiołu i (b) odzysk węgla we frakcji flotacyjnej w funkcji pH

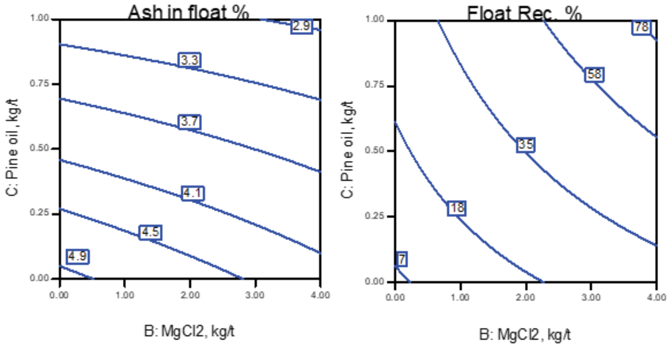
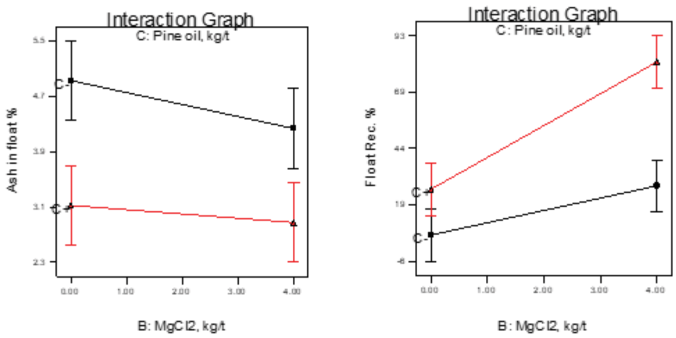


Fig. 5. Effect of pine oil and $MgCl_2$ on ash % and coal recovery in the float fraction at pH 2

Rys. 5. Wpływ oleju sosnowego i $MgCl_2$ na % popiołu i odzysk węgla we frakcji flotacyjnej przy pH 2



(a) (b)

Fig. 6. Effect of $MgCl_2$ and pine oil on (a) ash % and (b) coal recovery in the float fraction at pH 2 (C+: high pine oil dosage level, 0 kg/t and C- : low pine oil dosage level, 1 kg/t)

Rys. 6. Wpływ $MgCl_2$ i oleju sosnowego na (a) % popiołu i (b) odzysk węgla we frakcji flotacyjnej przy pH 2 (C+: wysoka dawka oleju sosnowego, 0 kg/t oraz C-: niska dawka oleju sosnowego poziom, 1 kg/t)

3.2.1. Effect of $MgCl_2$ dosage

Figure 3 shows the ash removal at various pH values in the presence of $MgCl_2$ only. It shows that the lower the $MgCl_2$ dose is the lower the ash removal even at high pH values. The ash content decreases by increasing the $MgCl_2$ to 4 kg/t where the ash content reaches 4.2%, at pH 2, with coal recovery of 28% compared to 5.3% ash in the feed. The effective reduction in ash in the presence of magnesium salt at acidic pH can be referred to the higher ionic concentration of Mg^{2+}, which helps in repelling the hydrophobic coal particles to the froth layer where they were aggregated [17]. The existence of these hydrophobic particles in the froth layer works on stabilizing the bubbles of this layer for a longer time [4, 18]. In addition, the ionic species in the solution significantly affect the bubbles size and stability due to increasing the bubble surface charge that consequently prevents coalescence [4, 9].

3.2.2 Effect of pine oil

Figure 4 depicts the effect of pine oil at different pH values on ash % and coal recovery% in the floated fraction in the absence of $MgCl_2$. The higher the pine oil dosage is the lower the ash in the concentrate where the ash decreases from more than 4.9 % to less than 3.2% at coal recovery of 28% using 1.0 kg/t of pine oil at pH 2, Fig.4. The lower ash content is attributed to the effect of the pine oil on lowering the interfacial tension that leads to produce small bubbles as well as the stabilization of bubbles in the froth layer, which assists in collecting the coal particles as hydrophobic particles with low ash content [19-20]. Notably, the pine oil reduces the ash to about 4% and increases the coal recovery, where it reaches 60% at 1 kg/t pine oil and pH 10, Fig.4.

3.2.3. Effect of MgCl2 – pine oil mixture

The effect of adding both pine oil and $MgCl_2$ on ash % and coal recovery % in the floated fraction at pH 2 is shown in Figure 5. The higher the pine oil and $MgCl_2$ dosage is the lower the ash in the concentrate. The ash content decreases from more than 4.5% to less than 2.9% at 1.0 kg/t of pine oil and 4 kg/t $MgCl_2$, Fig.5a. The lower ash is attributed to the effect of the pine oil on lowering the interfacial tension that leads to produce small bubbles as well as the stabilization of bubbles in the froth layer, which assists in collecting the coal particles as hydrophobic particles with low ash content [19-20]. Interestingly, the combination of pine oil and $MgCl_2$ enhances both the ash removal and coal recovery. The ash content as low as 2.8% at coal recovery of 80% at 4 kg/t $MgCl_2$ and 1 kg/t pine oil was achieved, Fig.5b.

Figure 6 shows the interaction between the magnesium salt and the pine oil. It indicates that the combination of pine oil and salt is better than each one alone. For example, comparing the ash % in the feed and after adding 4.0 kg/t $MgCl_2$, the ash reduction is gradually decreased from 5.3% in the feed to 4.2% without adding pine oil. Adding pine oil, along with $MgCl_2$, reduces the ash % to lower than 3%. Likewise, the addition of pine oil along with $MgCl_2$ significantly improves coal recovery. Thus, the pine oil is more effective in reducing the ash content by stabilizing the froth layer while the salt is more effective in increasing coal recovery by providing the repelling environment to hydrophobic coal particles in the pulp leading to their aggregation at the water-air interface (froth layer).

4. CONCLUSIONS

The low-rank high-bituminous coal was subjected to flotation using magnesium chloride salt in the presence or absence of pine oil. The lowest ash concentrate was achieved at acidic pH. In addition, although the use of either the magnesium salt or the pine oil individually effectively reduces the ash content at almost the same recoveries, the pine oil is better in achieving a lower ash content. Adding the pine oil along with $MgCl_2$ not only reduces the ash content to less than 3% out of 5.3% in the feed but also increases the coal recovery to about 80% in the float fraction at acidic pH. The effectiveness of $MgCl_2$ – pine oil mixture over each one alone is attributed to the role of magnesium salt in assisting the formation of small bubbles by preventing the bubbles coalescence as well as providing the ionic environment that leads to aggregation of the coal particles while the pine oil reduces the bubble size and maintains their stability at the water-air interface in the froth layer. In addition, the effect of $MgCl_2$ is pH-dependent due to the gradual conversion of Mg^{2+} at acidic pH to hydroxide forms at alkaline pH values.

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Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Preferowany sposób czyszczenia węgla metodą flotacji: olej sosnowy czy $MgCl_2$?

Szczególną uwagę poświęca się flotacji węgla przy użyciu soli nieorganicznych. Wykorzystuje hydrofobowość węgla do flotacji węgla bez dodawania kolektorów. Chociaż testowano różne sole, najbardziej obiecujące są sole chlorkowe. Jednak stabilizacja warstwy piany wyłącznie za pomocą soli jest wątpliwa. Dlatego w tym badaniu flotacja węgla była testowana przy użyciu chlorku magnezu lub oleju sosnowego jako spieniacza, aby sprawdzić, czy istnieje różnica we flotacji węgla między tymi odczynnikami pod względem usuwania popiołu i odzysku węgla we frakcji flotacyjnej. Dodatkowo dodano razem zarówno sól magnezową, jak i olejek sosnowy, aby wyjaśnić ich interaktywny efekt przy użyciu projektu statystycznego. Wyniki dowiodły, że obecność każdego z odczynników (tj. oleju sosnowego lub $MgCl_2$) ma znaczący wpływ na zmniejszenie zawartości popiołu i zwiększenie odzysku węgla. Zastosowanie $MgCl_2$ tylko zmniejszyło popiół do mniej niż 4,3% z odzyskiem węgla do 28%, podczas gdy dodanie 1,0 kg/t oleju sosnowego wraz z 4 kg/t $MgCl_2$ zwiększyło redukcję popiołu do mniej niż 3% przy odzysku węgla do 80% przy pH 2.

Słowa kluczowe: *chlorek magnezu, olejek sosnowy, spieniacz, węgiel, flotacja*