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Simultaneous ash and sulfur removal from bitumen: Experiments and neural network modeling

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ABSTRACT

Flotation and leaching methods were used to remove ash and sulfur from bitumen by sulfuric acid. The bitumen samples had sulfur content of 9.6% (6.74% in the pyrite sulfur form) and 30% ash. All the experiments were done under aeration rate of 4 L/min using pine oil and gasoline as frother and collector agents, respectively. The factors studied were including the amounts of collector and frother agents, pH, solid weight percentage in the pulp, stirrer speed, and particle size. The bitumen samples with dimensions less than 0.5 mm were crushed. The flotation experiments were performed in a 3-L Denver laboratory flotation cell to ease the ash and sulfur removal. The optimum condition for plant operation were; foaming (50 gr/t), collector (1 kg/t), impeller speed of 1200 rpm, pH = 7, pulp containing 5% of solid, particle size of 100 mesh, and flotation time of 3 min. In these circumstances, 52.9% of pyrite sulfur (e.g.; 36.45% of total sulfur) and 43% of ash were removed. With the approach of leaching using sulfuric acid, the organic and pyrite sulfur removal were 7% and 13%, respectively. Combination of these two methods (in optimal conditions), removed up to 47% of the total sulfur and 61% of ash through bitumen sample. In the next step of study Artificial Neural Networks (ANN) was employed to model the ash and sulfur removals data obtained by flotation method. A network consisting of two layers of six and nine neurons in the hidden layer were considered. Meanwhile learning algorithm Levenberg–Marquardt (LM) was used. In neural network models "Tansig" and "Purelin", transfer functions for hidden and output layers were applied, respectively. Very low error in the network estimation confirmed validity of the obtained networks for further analysis and optimization. Moreover, process optimization were carried out by using ANN to predict the best operating conditions, which resulted in the maximum percentage of ash and pyrite sulfur removal from bitumen. The maximum percentage of ash was estimated by ANN to be 42.39% under the following operational conditions; foaming amount of 50.5gr/t, the collector amount of 1.12 kg/t, impeller speed of 1200 rpm, pH = 7.5, pulp equal to 5% of solid, particle size of 110 mesh, and flotation time of 3 min. The maximum percentage of pyrite sulfur removal was estimated by ANN to be 52.15% under the following operational conditions; foaming amount of 50gr/t, the collector amount of 1.4 kg/t, impeller speed of 1200 rpm, pH = 7, pulp equal to 5% of solid, particle size of 100 mesh, and flotation time of 3 min.

1. Introduction

Fossil fuels are mainly consists of oil, natural gas and coal. Oil production is more costly compared to last decade causing increase in oil price. On the other hand, noting abundant coal resources in the world make it a proper substitution for oil. Therefore, the coal production is expected to grow in the future. Coal is known as a material with widespread industrial applications, but the production and the consumption of coal has more environmental issues than other fuels. Many researches are on going to develop the new and innovative techniques to use the coal with less environmental side effects [1]. In our recent work underground coal gasification was reviewed as one of these techniques [2].

Bitumen is a glossy black substance consisting of different hydrocarbons with high molecular weight. Bitumen is produced by the oxidation of petroleum. Bitumen is a heterogeneous mixture of chemical compounds including about 90% of hydrocarbons, between 1% and 6% sulfur, less than 1.5% of oxygen and nitrogen molecules and a few ppm of metal components such as vanadium, nickel and iron [3]. This substance can be categorized based on various colors, hardness, density, volatile materials.

Sulfur has the most impact to limit the bitumen application as a clean fuel compared to all other elements in bitumen [4]. Different forms of sulfur are organic, pyrite and sulfate. Generally, more than

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half of the sulfur in bitumen is in the pyrite format [1]. Bitumen also contains inorganic minerals which are so-called ash. The main minerals in coal are silicates or shale (kaolinite type), quartz and sandstone, pyrite and siderite carbonates and anchorite. International standards limit the ash value in the coal to be less than 7% [5].

Akdemir and Sonmez investigated the effect of aeration on the efficiency of flotation and recovery of bitumen. They investigated the effects of particle size, impeller speed, pulp solid percentage and aeration rate on the flotation. All the experiments were performed at pH = 7. The results showed that the particle size was the most important parameter affecting recovery and aeration and pulp percentage and impeller speed were the ones with the less effect than particle size effect [6].

Srivastava studied recovery of sulfur from a kind of coal with a high content of ash and sulfur pyrite by ferric sulphate. They reported a completely removal of sulfur pyrite and sulphate. Samples were in contact for 4 to 5 times with ferric sulfate and total reaction time lasted for 23 h. Reaction temperature was changed from 90 to 130°c as at this temperature pyrite can react with ferric sulphate. Although different particle sizes were tested (e.g.;10 to 100 mesh), the best removal efficiency, which was 90 to 95, obtained at 100 mesh [6]. Karaca et al. studied pyrite sulfur removal from coal with nitric acid. They examined the effect of parameters such as reaction time, reaction temperature, particle size, acid concentration and impeller speed. The results showed that increasing the impeller speed has little effect at low temperatures. Increasing in acid concentration, reaction time and impeller speed and reducing particle size, leads to enhance the removal of the pyrite content. Under the optimal conditions (reaction time 2 h, 25 wt% acids and boiling acid, temperature equal to 103 °C) they could achieve to removal of 30% of the pyrite content [7]. Makherjee and Borthakur used hydrochloric acid and sodium hydroxide and tried to eliminate ash and sulfur from Indian coal. They found out that the increasing in the concentration of sodium hydroxide improves the sulfur and ash removal. They succeed to remove 10% of the organic sulfur, all inorganic sulfur and 45% to 50% of ashes [8]. The effect of leaching with hydrochloric acid and potassium hydroxide was investigated separately on the ash and sulfur removal. The temperatures were 95 °C and 150 °C. By combination of both solvents, 28–45% of ash was removed at 95 °C. The yield was 39–68% at 150 °C, and at this temperature 53% of the total sulfur was removed [9]. Kelebek and his colleagues investigated the effect of collector and pH on Turkish coal floating. All tests were performed in a 2-L Denver device for the pH of equal to 4.9. They examined three parameters at two levels. These conditions were applied: 7.5% pulp, impeller speed of 1250 rpm, temperature was set at 20 °C and methyl iso butyl carbonyl and kerosene were used as collector and foam maker, respectively. The optimum particle size was to be less than 10 mm. The experiment results showed that the effect of particle size is more than other parameters such as different chemical reagents. The maximum recovery at this experiment was 88% [10].

The effect of flotation variables on the recovery of different particle size fractions in froth and pulp was studied by Rahman. He investigated the effect of some parameters on the behaviour of collection and froth zone with respect to particle size. In this case the influence of collector concentration, air flow rate, froth depth, and the ratio of fine to coarse particles in the feed were considered. The results showed that the overall fine particle recovery is much higher than for coarser particles. The significance of the froth barrier to coarse particle flotation was also established. The important finding of this study is that in the presence of fine particles can enhance the collection of coarse particles both in the collection and froth zones [11]. Piñeres investigated effect of pH, air velocity and frother concentration on combustible recovery, ash and sulfur rejection by column flotation. High combustible recovery was obtained at air velocity in the range of 0.7 to 1.4 cm/s. The results showed that for low air flows, small bubbles are generated which increases the combustible recovery due to the increase in surface area of bubbles [12].

Abkhoshk studied the effect of particle size on coal flotation kinetics using fuzzy logic. The relationship between flotation kinetics constant and theoretical flotation recovery with particle size was estimated using nonlinear equations. Analysis of variance showed that varying of particle size is statistically significant on kinetics constant with approximately 96.5% confidence level; however it is not significant on the maximum theoretical flotation recovery (RI) in 95% confidence level [13]. Angadi investigated the experimental analysis of solids and water flow into the coal flotation froths. He studied the role of different variables on solids and water flow into the flotation froths. The experiments carried out in conventional (batch) and column cells using coking coal fines. The mass ratio of solids to water was higher in conventional cell compared with the flotation column. [14]. In Table 1 a summary of some recent studies on the removal of ash and sulfur from bitumen are presented.

Iran has a large volume of bitumen mines which is sold with a very low price of natural bitumen to the developed countries. This material is sold back to Iran after a series of processing and separating with a significant higher price compared to the original price. Thus, reducing the sulfur and ash with a new and improved method is a very important topic. The samples used in this study were obtained from mines located in Kermanshah (in Iran). In this study the effect of some of the important parameters on the percentage of ash and sulfur removal from bitumen have been investigated. Also artificial neural network (ANN) was used for modeling the ash removal and desulfurization data. To our knowledge the application of ANN in this type of modeling is novel.

2. Materials and experimental procedures

2.1. Materials and analytical tests

The bitumen samples were supplied by mines, in Kermanshah/Iran. Pine oil as frother was supplied by Boyakhsaz Company/Iran in liquid

Table 1
Various reagents used to remove ash and sulfur from coal.

Author	Reagent	Time	Sulfur and or ash removal
Chandra et al. [15]	AtmospHeric oxidation	106 days	44% sulfur removed (36% organic sulfur removal)
Steinberg et al. [16]	O_3 and O_2	1 h	Using a flow rate of 200 ml/min, 1% O_3 at 25 °C, 20% sulfur removed
Chaung et al. [17]	Combination of dissolved oxygen and alkalis $NaHCO_3$, Na_2CO_3 and Li2CO$_3$	1 h	0.2 M alkali solution with 3.4 atm O_2 partial pressure at 150 °C — Na_2CO_3: 72% of sulfur removed, Li_2CO_3: 73.1% of sulfur removed. At 0.4 M $NaHCO_3$: 77% of sulfur removed
Liu et al. [18]	Aeration + NaOH, HCl	5 h	Using 0.25 M NaOH at 90 °C with aeration rate of 0.136 m^3/hr and 0.1 N HCl solution: 73% organic sulfur removed; 83% sulfide sulfur removed; and 84% pyritic sulfur removed.
Zaidi [19]	NaOH	3 h	Using 0.2 N NaOH at 70 °C, 36.2% sulfur removed
Aarya et al. [20]	NaOH	8 h	Using 100 g/dm^3 NaOH at 80 °C, 30% sulfur removed and 29% ash removed
Rodriguez et al. [21]	HNO_3	2 h	Using 20% HNO_3 at 90 °C, 90% inorganic and 15% organic sulfur removed
Prasassarakich and Thaweesri [22]	Sodium benzoxide	90 min	Using 600 ml sodium benzoxide at 205 °C, 45.9% sulfur removed. 83.7% sulpHate, 68.6% pyritic, 33.3% organic sulfur removed).
Yang et al. [23]	NaOH	60 min	Using 10 wt% NaOH at 250 °C: 55% sulfur removed (95% pyritic and 33% organic sulfur removed)
Kara and Ceylan [24]	Molten NaOH at different temperatures	30 min	Using 20 wt% NaOH at 450 °C: 83.5% sulfur removed and 91% ash removed from Dadagi Lignite
Baruah et al. [25]	Water	120 h	77.59% pyritic sulfur removed with aqueous leaching at 45 °C