Leaching of coal by trioxoboric acid for coal cleaning

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Abstract: Trioxoboric acid (H_3BO_3) is a white weakly soluble acid produced from boron minerals. This acid type was used for the first time in this study for ash and sulfur removal from coal. Ash and sulfur are the most important impurities in the content of coal and have significant effects on environmental pollution. It is possible to remove ash and sulfur by H_3BO_3 leaching. However, there have not been enough studies in this area and the performance of trioxoboric acid has not been fully demonstrated. In this study, leaching performance of trioxoboric acid and other strong acids (hydrofluoric, hydrochloric and sulfuric acids) has been demonstrated. Trioxoboric acid removed ash and sulfur from coal by 41.18% and 32.16%, respectively. This acid can compete especially with hydrochloric and sulfuric acid in sulfur removal. However, hydrofluoric acid provided the best results in ash and sulfur removal.

Keywords: trioxoboric acid, coal beneficiation, leaching, work index

1. Introduction

The quality of coal depends on the content of ash and sulfur. The calorific value of coal decreases with increasing ash content. Sulfur(S) in the atmosphere cause acid rain. In addition, the amount of mineral substances present in coal also causes slag formation in combustion units and the release of large amounts of particles. The large amounts of mineral matter, ash, and sulfur present in coal cause the use of coal in limited areas (Mukherjee and Borthakur 2003; Dash et al. 2013; Behera et al. 2018a). Moreover, the mineral matter in coal generates some problems in methods such as gasification, coking and liquefaction (Kumar and Gupta, 2007; Rubiera et al., 2003; Hacifazlioglu, 2016; Whab et al., 2015). In this respect, the removal of ash content and sulfur content from coal sample at maximum levels is important both economically and to prevent environmental pollution.

Turkey is a poor country compared to other countries in the world in terms of coal reserves. Moreover, Turkish coals have low-calorie, high moisture, and ash content. About 73% of boron reserves in the world are located in Turkey, and the demand for boron from Turkey is approximately 50%. Boron products obtained from colemanite, tincal, and ulexite, which are boron minerals, are exported abroad. Among the most important boron products are trioxoboric acid, borax pentahydrate, borax decahydrate and sodium perborate. Trioxoboric acid is formed by the reaction of colemanite (boron mineral) with sulfuric acid (Hacifazlioglu et al., 2016).

It has been stated by many scientists that it is difficult to clean Turkish coal using physical and physicochemical methods (jig, shaking table, spiral, flotation, etc.), that is, to remove the ash and sulfur value at the desired rate (Yagmur et al., 2005; Ayhan et al.,2011; Ceylan and Kucuk, 2004). Acid leaching techniques are used as an alternative to the conventional cleaning processes of coals (Behera et al., 2018a; Sriramoju et al. 2017; Sriramoju et al. 2020). There are many studies on reducing coal ash using acid leaching methods for example with caustic acids (Chriswell et al. 1989; Sharma and Gihar 1991; Hacifazlioğlu, H., Uçkan, D., 2014; Dash et al., 2013; 2014; 2015a; 2015b). In a study by Lingam et al., (2016), clean coal with 19% ash was obtained by applying the caustic-acid leaching method.

Chemical leaching is the most effective enrichment method for Turkish coals. In a study conducted by Karaca and Ceylan (1997), hydrogen peroxide was used to reduce the ash and sulfur contents of Turkish coal by up to 70% with 95% efficiency. Demirbaş (2002) had removed 37.2% of the whole sulfur from a Turkish lignite by using the leaching method with biomass ash. In another study, the ash of lignite coal from Nallıhan was reduced from 17.12% to 6.98% by leaching with hydrofluoric acid Gülen et al., (2013). In a study conducted by Karaca and Onal (2003), the ash value of Kutahya coal, when 10% hydrochloric acid and 30% NaOH was applied, was also reduced to 3.3%. Hacifazlioglu (2016) produced ultra-clean coal (ash, 0.82%) with hydrofluoric acid. Dikici and Hacıfazlıoğlu (2019) produced super-clean coal (ash, 2.92%) by leaching only with organic reagents (citric and formic acid).

In the study by Behera et. al. 2018b; three independent variables, such as hydrofluoric acid (HF) concentration (10-20% by volume), temperature (60-100°C) and time (90-180 minutes) were investigated for the effect of coal on ash reduction. The study finally, it is revealed that using HF is an effective method for ash reduction.

Chemical enrichment by leaching of low-grade coals is a suitable method to reduce both organic and inorganic mineral components. Chemical leaching is the most effective method for removing undesirable impurities in coal in order to obtain ultra-clean coal products with an ash value of less than 1% (Behera et. al. 2018c).

In the research conducted by Behara et al. 2018d; efficient demineralization is achieved at the concentration of 30% NaOH and 30% H_2SO_4 in 180 μm particle size coal samples. Alkaline leaching resulted in 46% and 42% demineralization, while acid treatment resulted in 34% and 32% demineralization.

According to the study by Behara et al. 2017, caustic (NaOH) leaching followed by acid (H_2SO_4) treatment was applied to the coal. The maximum demineralization obtained in the investigation was 26% ash level with 27.5% NaOH(100g/L) leaching and 48% efficiency was obtained with the chemical cleaning method (100 g/L NaOH followed by 20% H_2SO_4).

Numerous studies aimed at calculating the optimum operating parameters for coal ash cleaning, exist in the literature (Mohanta et. al., 2010; Mohanta et. al., 2011a; Mohanta et. al., 2011b; Mohanta et. al., 2012). In this study, the performance of trioxoboric acid in the removal of ash and sulfur from coal was investigated. In addition, the performance (optimum) results obtained were compared with the performance of strong acids (hydrocluoric acid, hydrofluoric acid, sulfuric acid).

2.   Materials and methods

2.1. Coal sample

Lignite coal sample, located in the Black Sea region of Turkey is taken from a mine. The coal taken was first crushed in a rotary crusher. The coal, which was then reduced in a ball mill, was reduced to -106 μm for use in leaching experiments. Parameters in experimental studies overlap with various scientific studies. Leaching is generally applied to particles below 150 microns. Solid ratio and acid dosage are also in line with most scientific studies. In addition, the optimum values (60°C, 80°C, 120min and 500kg/t) were determined by preliminary tests. The selected parameters were not chosen arbitrarily, and the optimum value was determined for optimum ash and sulfur removal on a scientific basis. The size of ash liberation was not determined in the experiments. The selected particle size was determined according to the literature data. According to this; in coal leaching enrichment processes, grinding the coal particle size below 150 microns is generally applied. In this study, leaching enrichment experiments were carried out with a particle size of less than 150μm. The results of the proximate analysis on the dry matter basis of the raw coal sample according to ASTM standards were determined as 14.62% ash, 8.77% sulfur, 6200 kcal/kg calorific value, 36.85% volatile matter, and 48.53% fixed carbon.

2.2. Method

Acid leaching experiments were carried out at different mixing speeds at 20ºC, 40ºC, 60ºC, and 80ºC temperatures. The coal sample was completed to 100 ml with the addition of pure water (distilled) and reagent solution, with a solid pulp ratio of 20%, and placed in a plastic-coated Erlenmeyer flask inside the device. Reagents of analytical purity: trioxoboric acid, hydrofluoric acid, hydrochloric acid, and

sulfuric acid were used. Separate experiments were carried out with varied reagent amounts of 125 kg/t, 250 kg/t, 500 kg/t and 750 kg/t (60°C and 120min.), with different acid types. The concentrations of acid reagents in the prepared leach solution were determined as 2.45%, 4.76%, 9.09%, and 13.04%. Experiments were investigated at different temperatures (20°C, 40°C, 60°C, 80°C) with different reagents (trioxoboric acid, hydrofluoric acid, hydrochloric acid, and sulfuric acid) and times (60min, 120min, 240min, 360min). After the leaching experiment was completed, the solid-liquid mixture was washed by filtering through filter paper. Then, the concentrated coal sample was subjected to ash and sulfur analysis. The equations used in the removal of ash and sulfur were given below.

$$\text{Ash removal, \%} = \frac{(\text{Feed ash,\%} - \text{Product ash,\%})}{(\text{Feed ash,\%})} . 100 \tag{1}$$

$$\text{Sulfur removal, \%} = \frac{(\text{Feed sulfur,\%} - \text{Product sulfur,\%})}{(\text{Feed sulfur,\%})} . 100 \tag{2}$$

In order to effectively remove the mineral matter from the coal, it is required to grind the coal to a micronized size prior to chemical leaching. The grinding process is a significant cost. Therefore, the grindability of coal must be determined. Based on this grindability value, the total process cost can be estimated. Hardgrove Grindability Index (HGI) is a measure of the grindability of coal. Smaller HGI value means more difficult to grind. The HGI value of the coal determined by the Hardgrove mill (ASTM D409/D409M-12) was 52.20. As the HGI value was between 50 and 70, the sample coal is one that can be hardly ground. The formula [3] *developed* by Bond (1954), showing the transformation of HGI into the Wi (work index) is given below. The grinding work index (Wi, kWh/ton) represents the energy required to reduce a material of theoretically infinite size below 100 microns. In this formula, the Wi (work index) value calculated for the coal was calculated as 12.18 kWh/t (energy required for grinding 1 ton of coal).

$$W_i = \frac{88}{HGI^{0.5}} \tag{3}$$

In addition, the chemical reagents used in this study were disposed of after neutralization. However, they can be used in an industrial application by re-generating. So it can be adjusted and used over and over again. In order for the process to be economical, chemicals must be adjusted and used repeatedly. In this study; reagent consumption is quite high and the process is not economical in its current form.

3.   Results and discussion

3.1. Leaching test results for ash content reduction

The dependence of ash content reduction on acid dosage (60 °C; 120 min) is shown in Fig. 1. When the results are examined; as the reagent amounts increase, the ash removal rate increases. However, after 500kg/t, there is a decrease in ash removal. This ratio becomes negative when adding 750 kg/t trioxoboric acid. The reason for this is that trioxoboric acid is not fully soluble in water at a temperature of 60°C and 750 kg/t, and remains in the solid phase (c.a. 15 g of boron compounds remain of filter paper). For this reason, reagent amounts were not evaluated above 500 kg/t in subsequent experiments.
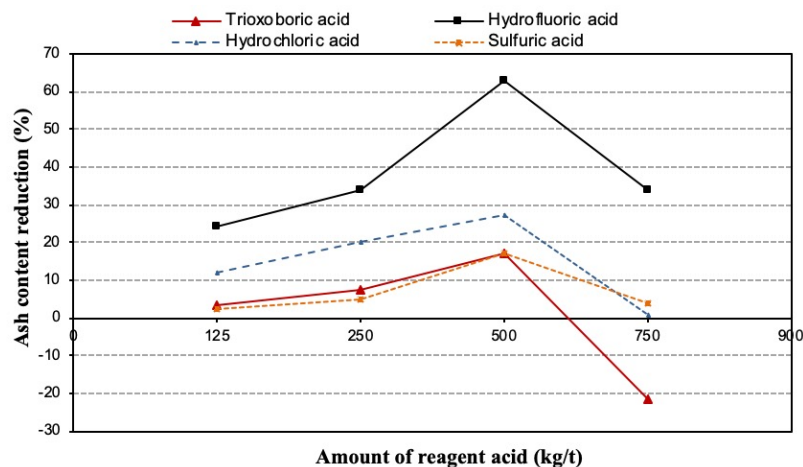

Fig. 1. The dependence of ash content reduction on acid dosage (60 °C; 120 min)

Fig. 2 shows the dependence of ash content reduction to pulp temperature (500kg/t; 120min.). When the temperature is increased to remove the ash from the coal with trioxoboric acid, the ash rate at 80°C was determined as 25.31%. According to this, 500kg/t of trioxoboric acid (10 g of H_3BO_3 in 100 ml of pure water) was used at 20°C and 40°C temperatures, there was no success in removing the ash due to insufficient dissolution.
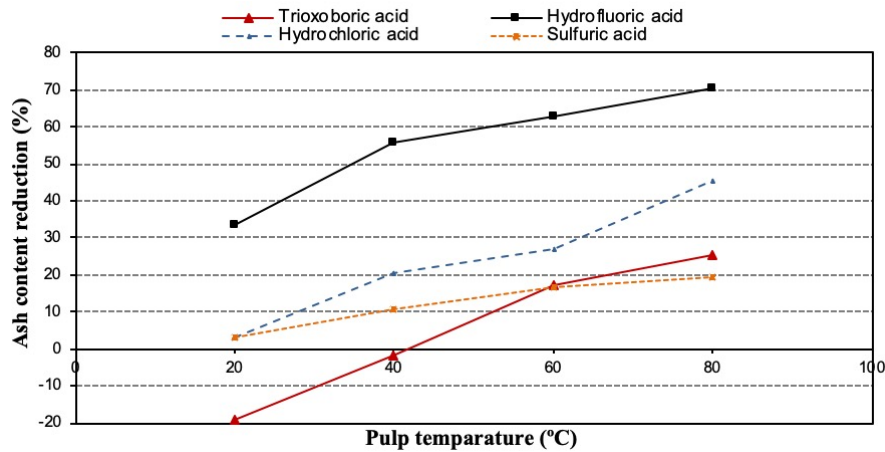

Fig. 2. The dependence of ash content reduction to pulp temperature (500kg/t; 120min)

In Fig. 3, pH changes depending on temperature are given according to trioxoboric acid dosage. The highest ash removal and lowest pH value were at 80°C temperature and 500kg/t trioxoboric acid dosage.

In Fig. 4 is shown the dependence of ash content reduction on leaching time (500 kg/t; 80 °C). It is seen that as the leaching times increase, the removal of ash increases for each reagent type. It was determined that 41.18% of the coal ash was removed with trioxoboric acid especially in the enrichment with leaching applied in 360 minutes. But, the course of the leaching curve indicates that the ash reduction is not complete after 6h. Here, the optimum leaching time is 120 min. considering the cost. Moreover, the removal of coal ash content with hydrofluoric, hydrochloric, and sulfuric acid is 79.34%; these are 51.30% and 43.09%, respectively.
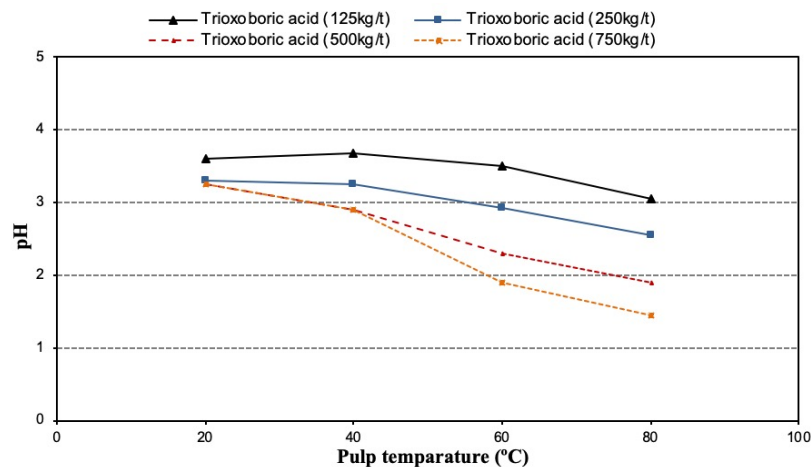

Fig. 3. The dependence of pulp pH on temperature for dosage of trioxoboric acid

3.2. Leaching test results for sulfur content reduction

The dependence of sulfur content reduction on acid dosage (60 °C; 120min.) is given in Fig. 5. A sulfur removal reaching 30% was ensured with 500 kg/t trioxoboric acid. Hydrofluoric acid, which provided the best result, ensured sulfur removal of over 40%.

In Fig. 6 is shown the dependence of sulfur content reduction on pulp temperature (500kg/t; 120min.) The efficiency of sulphur removal increases with the increase of temperature. For instance, only 6.16% of sulfur in coal could be removed with trioxoboric acid at 20 °C. Sulfur content reduction corresponding to leaching time (500 kg/t; 80 °C) is shown in Fig. 7. By increasing the leaching time, the removal of sulfur content from coal sample increased for each acid type. But after a specific leaching time (2 hours) the curve of sulfur content removal approaches linear and doesn't change much. The
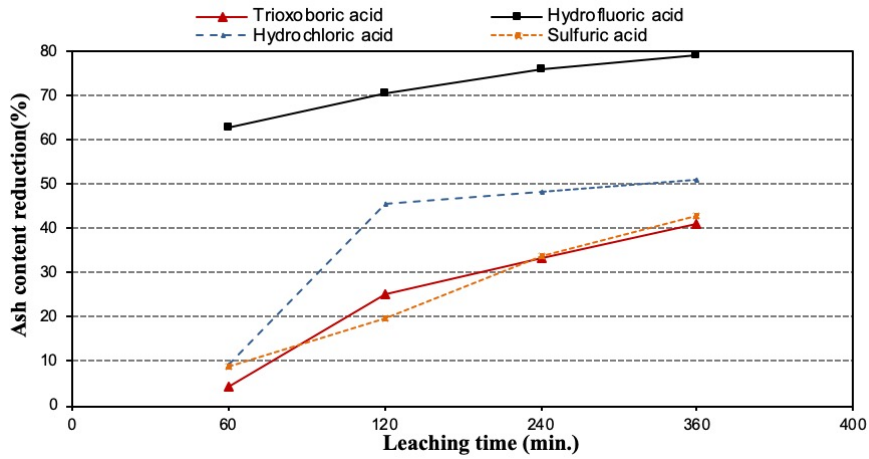

Fig. 4. The dependence of ash content reduction on leaching time (500 kg/t; 80 °C)
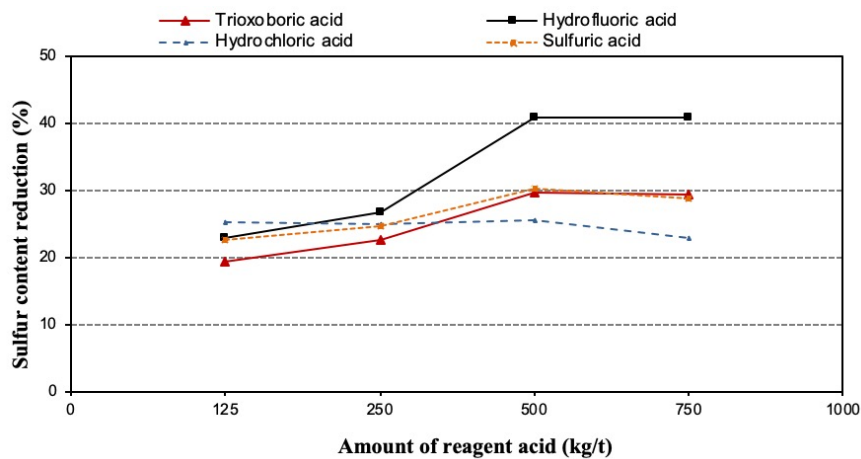

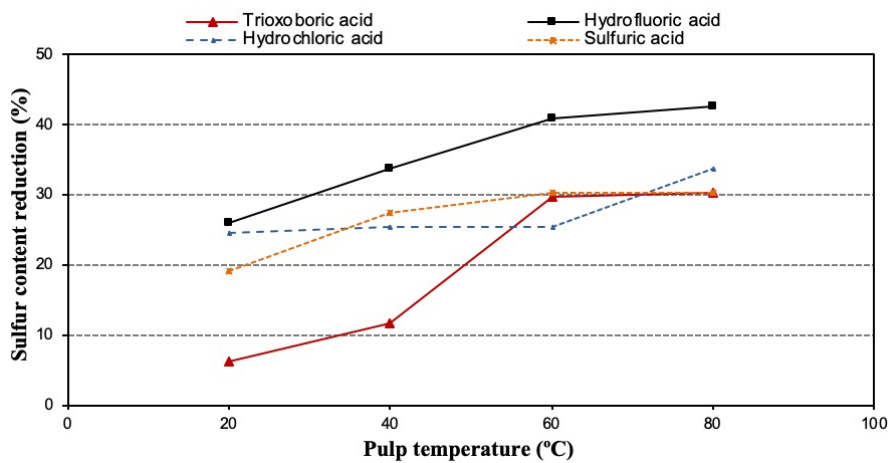Fig. 5. The dependence of sulfur content reduction on acid dosage (60 °C; 120min)

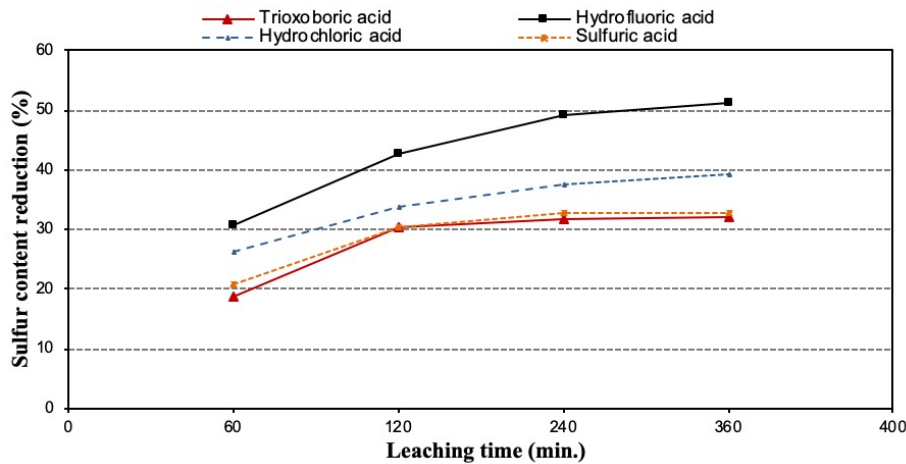Fig. 6. The dependence of sulfur content reduction on pulp temperature (500kg/t; 120min)

Fig. 7. The dependence of sulfur content reduction on leaching time (500 kg/t; 80 ℃)

leaching time was determined by considering the cost. In 6 hours(360min), the sulfur removal of trioxoboric acid is 32.36%. In the same period, the sulfur removal of hydrofluoric was found as 51.31%. And the sulfur content removal rates using hydrochloric acid and sulfuric acid were found as 39.11% and 32.73%, respectively.

Trioxoboric acid had provided similar results with sulfuric acid with respect to sulfur removal. Lignite coal before and after leaching is shown in Fig. 8. As can be seen from this photo, trioxoboric acid has removed inorganic materials (SiO_2, Al_2O_3, CaO, MgO, S etc.) from the coal. Lignite coal turned from brown to black after leaching.

Fig. 8. Photograph of lignite coal before and after leaching with trioxoboric acid

4. Conclusions

This study proved that trioxoboric acid can be used as leaching reagent in removing ash and sulfur from coal. Comparing its performance with other strong acids, it gives similar results with sulfuric acid. Ash and sulfur removal were achieved with lower efficiency compared to hydrofluoric and hydrochloric acids. In trioxoboric acid leaching experiments, 41.18% ash removal and 32.16% desulfurization were achieved from coal. In other words, the ash value of the coal sample has decreased from 14.62% to 8.6%, and the sulfur value from 8.77% to 5.95% at a temperature of 80°C for 360 min. and 500 kg/t acid dosage. In trioxoboric acid leaching experiments, the most important parameter to be considered is pulp temperature. When the pulp temperature drops below 60 °C, trioxoboric acid does not dissolve in water sufficiently. This situation both creates ash (sediment) and prevents the removal of ash and sulfur. Also, the pH of the pulp does not drop sufficiently at low temperatures. The pH remaining at 3-4 levels causes the ash and sulfur forming compounds in the coal to dissolve more difficultly. Therefore, the effective

temperature value for trioxoboric acid leaching is above 60 °C. Trioxoboric acid is an acid that dissolves in hot (>60 degrees Celsius) water. Trioxoboric acid is particularly effective in sulfur removal. Reactive hydrofluoric acid gives the best results in ash and sulfur removal.

Acknowledgements

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