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Short Communication

Ultrasonic coal washing to leach alkali elements from coals

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ABSTRACT

Deposition of fly ash particles onto heat-transfer surfaces is often one of the reasons for unscheduled shut-downs of coal-fired boilers. Fouling deposits encountered in convective sections of a boiler are characterized by arrival of ash particles in solidified (solid) state. Fouling is most frequently caused by condensation and chemical reaction of alkali vapors with the deposited ash particles creating a wet surface conducive to collect impacting ash particles. Hence, the amount of alkali elements present in coals, which, in turn, is available in the flue gas as condensable vapors, determines the formation and growth of fouling deposits. In this context, removal of alkali elements becomes vital when inferior coals having high-ash content are utilized for power generation. With the concept of reducing alkali elements present in a coal entering the combustor, whereby the fouling deposits can either be minimized or be weakened due to absence of alkali gluing effect, the ultrasonic leaching of alkali elements from coals is investigated in this study. Ultrasonic water-washing and chemical-washing, in comparison with agitation, are studied in order to estimate the intensification of the alkali removal process by sonication.

1. Introduction

Fossil fuels satisfy almost 67% of the total energy consumption in India, with coal accounting for 57% of the primary commercial energy need (as compared to 29% world over) [1,2]. Considering the scant availability of resources of crude oils and natural gas, the regulations in expanding and operating hydel power plants, and geo-political apprehensions over nuclear energy and research, coal will continue to dominate the Indian power sectors. India is the third largest producer of coals, having reserves of 293.5 billion tones; coal thus offers a unique fuel source readily and indigenously available for Indian domestic energy markets. Hence, coal will be dominating Indian power sector for at least 3–4 decades [3].

Though coal is available in abundance, almost 87% of available coals are of inferior quality having inorganic noncombustible content, ash, from 40% to 45% by weight [1]. During coal combustion, these inorganic constituents undergo various physical and chemical transformations and are converted into fly ash and bottom ash. Owing to the fineness, fly ash particles will be carried away by the flue gas and deposited on the heat-transfer surfaces. Deposition of fly ash particles on to heat-transfer surfaces – termed as fouling and slagging – results in reduced heat transfer, interferes with the aerodynamic flow of flue gas, reduces the flow area, and causes corrosion and erosion of boiler tubes, thereby affecting the normal functioning of a boiler [4–8]. Studies have demonstrated that the condensable alkali elements in flue gas act as ‘glue’ in holding together impacting ash particles [4,7–11]. Hence, presence of alkali elements in coals which, in turn, are transported along with the flue gas as vapors, leads to formation and growth of fouling deposits. Reducing the amount of alkalis present in a coal before entering the combustor could eventually reduce the severity of fouling deposits in convective sections of a boiler.

Conventionally, coal washing had been investigated as a method to primarily remove ash and sulfur present in coals. A few studies have focused on removal of alkali elements – particularly sodium – by water washing and chemical washing. Sodium in a coal maybe present in three forms: (1) water-soluble sodium, (2) ion-exchangeable sodium, and (3) fixed sodium. The amount of ion-exchangeable sodium in a coal varies from 30% to 80% of the total sodium with the balance sodium distributed between water-soluble and fixed sodium [12].

Smit et al. [13] investigated the chemical leaching of coal with the objective of removing ash, alkali, and vanadium. The steps followed in their studies are: pressure-leaching the coal with aqueous alkali chloride solution – sodium or potassium chloride- and pressure-leaching the alkali residue with hydrochloric acid. The combined pressure-leaching schemes removed alkali metals, chlorine, vanadium, and other soluble components. The following conditions were used during the process: alkali leaching – 25% NaOH solution, 30% coal sample, 2 h at 230 °C; acid leaching – 10% HCl

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solution, 30% solids, 2 h at 80 °C. The ash contents before and after leaching were 3.15% and 0.36%, respectively. Blytas and Trogus [12] studied sodium leaching of coal with a weak acid. With the aim of upgrading coals, they concentrated on removing ion-exchangeable sodium. They followed a two-step process: washing with ion-free water to remove water-soluble sodium, and exposing the residue to sodium-free weak acid – carbonic acid or acetic acid. All studies were carried out for a total time of 4 days. They concluded that any weak acid capable of maintaining a pH of about 3–6 may be used.

Vuthularu et al. [14] investigated various mitigation strategies: additive techniques, coal washing, and alternative bed materials. They observed that pre-treating the coal with aluminum and water-washing reduced the propensity for agglomeration and defluidization. Water-washing leads to a reduction in sodium content as proven by SEM images. Quast [15] estimated the number of stages required to achieve equilibrium in leaching sodium from coal in a counter-current ion exchange set-up. A coal-to-water ratio of 1:2, and a pH of 2 were maintained by sulfuric acid which acted as an ion-exchanger, and leaching was carried out for 30 min in each stage. The author measured the reduction in sodium content in a three-stage process to be 15% of the initial sodium content. Finkelman et al. [16] studied various leachable elements present in coals and the different conditions to be maintained. Among the various elements investigated, leachability of alkali elements – Na, K – was also studied. Agitating the coal samples (10 gm – in 50 ml of 1 N ammonium acetate for a period of 16–24 h) resulted in removal of up to 95% of sodium and 32% of potassium.

All the studies listed above substantiate the removal of alkali elements by normal agitation and its enhancement by adding ion-exchangers. Most of the investigations exposed the sample for long periods of time or maintained an elevated temperature or pressure to achieve desirable results. The novel technique of ultrasonic coal-wash has been shown to drastically reduce the processing time by intensifying the process. Such an effect was reported by Ambedkar et al. [17] in desulphurizing coal by ultrasonic wash. This motivated us to investigate the application of an ultrasonic field to leach alkali elements of coal. The combined effect of cavitation and streaming, required to perform size reduction and leaching, respectively, is ideal to remove alkali elements from coals. In this study, leaching of alkali elements – sodium and potassium – present in coals was investigated. The coal suspensions were subjected to stirring and ultrasonic washing, and the effect of each on leaching the alkali elements was studied. In order to remove the bound alkali elements, coal solutions were treated with an ion-exchange solution with stirring and ultrasonic waves to study their effect on leachability of alkali elements of coals. This study is a preliminary investigation into intensification of leaching of alkali elements by sonication, with two frequencies and three time levels, with and without added chemical reagents being examined.

2. Ultrasonic mechanism

Ultrasound is a sound wave with a frequency greater than the upper limit of human hearing. Typically, sound waves with frequencies greater than 20 kHz are termed as ultrasound. Studies have confirmed the intensifying effect in many processes due to ultrasonic irradiation, e.g., in coal desulphurization and deashing [18], degradation of methyl violet dye [19], dyeing of leather [19], and surface cleaning in microelectronic manufacturing [20].

When a medium is exposed to ultrasound, the physical phenomena involved in producing changes reflected in the medium are of two types: acoustic cavitation and acoustic streaming. During ultrasonic irradiation, the medium gets exposed to alternate compression and rarefaction cycles, which results in the cavitation phenomenon. A bubble cavity is formed during the rarefaction stage of the cycle, when the acoustic stress exceeds the tensile stress of the fluid. This leads to the inception of cavitation with a drop in local pressure below the vapor pressure of the liquid. Cavitation bubbles created in this manner expand and contract due to continuous oscillations. During expansion and contraction, the gas from the liquid diffuses into the bubble and leaves the bubble, respectively. Surface tension holds the bubble intact; however, once a critical size is reached, the bubble tends to collapse violently, creating a shock wave. Temperatures of up to 5000 K and pressures of 1000 atm may be developed during the violent collapse [21]. For an in-depth discussion on the cavitation phenomenon, readers are directed to Suslick et al. [21]. Cavitation is predominant in the frequency range between 20 and 40 kHz.

On the other hand, acoustic streaming occurs in higher frequency ultrasonic (>400 kHz) and megasonic (>1 MHz) systems. While cavitation is omni-directional in terms of dissipation of energy, a strongly one-directional motion in the medium characterizes streaming. Hence, streaming refers to unidirectional flow currents formed in a liquid on passing of sound waves. It causes of several important effects: (1) bulk motion of the liquid medium, (2) micro-streaming, and (3) streaming inside the boundary layer. The paramount effect of acoustic streaming is the bulk motion of the fluid creating shear stress. Micro-streaming – the second effect of acoustic streaming – occurs at the substrate surface, and outside the boundary layer. Hence, micro-streaming aids in dislodging particles and contributes to surface cleaning. Both the bulk motion of the liquid and micro-streaming occur outside the boundary layer. The third effect, however, occurs inside the boundary layer with very high local velocity and vortex motion due to cavitation collapse. Acoustic streaming is a contributory phenomenon in high-frequency acoustic surface cleaning and in intensifying chemical reactions [21].

In a detailed experimental investigation into ultrasonic coal wash for de-sulphurization, Ambedkar et al. [18] arrived at the following conclusions:

1. The cavitation-dominated low-frequency – 20 and 25 kHz – ultrasonic coal washing produces fine coal particles. Finer particles increase the contact area with the oxidizing agents produced by the ultrasonic system, leading to efficient coal desulphurization.
2. The streaming-dominated high-frequency ultrasonic coal washing – 430 kHz – causes sulfur removal from coal by leaching effect. Because of streaming, the radicals produced by the ultrasound penetrate the pores of coals particles.
3. Sonication accelerates the solvent-based reactions involved in the increased removal of sulfur.
4. Individual frequencies – 25 kHz and 430 kHz – showed a low removal propensity for organic sulfur of ∼14% and 9%, respectively.

From the above study, it had been confirmed that both phenomena – cavitation and acoustic streaming – are necessary to enhance and intensify the leaching of alkali elements. Since the objective of the present work is to remove organically-bound alkali elements, a dual-frequency system with a sequential irradiation of low-frequency and high-frequency of ultrasound waves is employed in this study.

3. Materials and methods

A schematic representation of the coal washing procedure adopted in this study is presented in Fig. 1. Two coals of Indian origin, obtained with the help of BHEL, Thiruchy, were investigated. The as-received coal lumps were crushed in a jaw crusher and in