Effect of cavitation on removal of alkali elements from coal

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Abstract. The main impurities in coal are sulphur, ash and alkali. On combustion, the volatile forms of these impurities are either condensed on the boilers, or emitted in the form of potentially hazardous gases. The alkali elements present in coal help the fly ash particles adhere to boiler surfaces by providing a wet surface on which collection of these particles can take place. Use of ultrasonic techniques in cleaning of coal has stirred interest among researchers in recent times. Extraction of alkali elements by cavitation effect using low-frequency ultrasound, in the presence of reagents (HNO₃ and H₂O₂) is reported in this paper. Powdered coal was dissolved with the reagent and exposed to ultrasonic fields of various frequencies at different time intervals. The treated solution is filtered and tested for alkali levels.

1. Introduction
Coal accounts for around 40% of the world’s source of power. Although harnessing clean, green sources of energy has been gathering momentum in recent years, nearly 66% of power in India still comes from coal [1]. Coal is projected to dominate the world’s power sector in the decades to come considering the abundant reserves available, and the high costs involved in using alternate forms of energy. Most coals contain ash and sulphur as impurities. On combustion, ash particles get deposited on heat transfer surfaces and reduce efficiencies, while sulphur is hazardous to the eco-system on the whole. The third form of impurities which affect heat transfer surfaces indirectly are alkali elements. Sodium and potassium are known to enhance fouling tendencies in heat transfer equipment. These elements in their volatile form act as ‘glue’, stick to the ash particles that impact the surface of heat transfer equipment, and hold them together [2, 3]. The high adhesion forces provided by the molten alkali salts make it increasingly difficult for the deposits to leave the surface. It is therefore important to remove these alkali elements from coal.

Ultrasound is an oscillating pressure wave with frequency higher than the human hearing range. Ultrasonic technology has found tremendous applications in medicine, imaging, non-destructive testing, etc. This technology can be used to remove sulphur and ash from coal prior to combustion. Though Indian coals have a high ash content of 35-45% [1], ultrasonic coal washing is not commonplace in India yet. Application of ultrasound on liquids has two main effects- acoustic cavitation and acoustic streaming. At higher frequencies, acoustic streaming is prominent. Acoustic streaming refers to the unidirectional flow that is induced in the liquid when a high-frequency ultrasound is coupled to it.

Cavitation is the implosion of bubbles resulting in a shock wave. This phenomenon is observed at lower frequencies. If the ambient pressure is sufficiently reduced, a liquid boils without heating. This technique is put to use on a small scale in ultrasonication by reducing the pressure at a local level. When the
pressure is reduced, small bubbles of vapor form. They subsequently implode, releasing energy as a shock wave in the compression cycle [5]. Thus, cavitation effects are stronger at lower frequencies.

![Figure 1. Formation of cavitation bubble and implosion close to the surface](image)

Ambedkar et al. [5] used HNO₃ and H₂O₂ as reagents to carry out experiments on de-sulphurisation of coal. They concluded that at low frequencies, the cavitation phenomenon, being dominant, leads to breakage of coal particles and results in better contact with the oxidising agents, resulting in higher removal of sulphur. Balakrishnan et al. [4] used two ultrasonic frequencies, viz. 25 kHz and 430 kHz, in sequence to remove alkali elements from coal.

From a brief review of literature, it is apparent that some experiments have been conducted based on ultrasonic technology that are aimed at removing ash and sulphur from coal. However, very little data are available for removal of alkali from coal using ultrasonic methods. In this paper, the effects of low-frequency ultrasound and two reagents, hydrogen peroxide and nitric acid - on alkali removal from coal are studied.

2. Procedure

2.1 Preparation of coal sample
Grade-G Coal from Orissa coal mines was used in as-received condition for this study. Lumps of coal were ground in a roll mill and the size was reduced. Next, the coal was placed in hard-metal tungsten carbide grinding bowls of 250ml capacity, and powdered in a planetary mill of FRITSCH make and model Pulverisette 5 for 30 minutes at 100 rpm with stainless steel balls, and with a sample-to-ball ratio of 1:7 [2]. The powdered coal was sieved, and coal particles of size less than 210µm were used for the experiments after drying in an oven at 110°C to remove excess moisture and dissolving the dried coal in acid. The initial sodium and potassium levels, estimated using the standard method (ASTM D6349-09), were found to be 31.7 mg/l and 47.2 mg/l, respectively.

2.2 Ultrasonic method
The reagents used were 2N HNO₃ and 3 volume percent H₂O₂, both of analytical grades. 10g of the coal sample was added to 100ml of the reagent, and the resulting liquid was placed in the ultrasonic tank. Tanks of four different frequencies were used: 25 kHz, 40 kHz, 58 kHz and 68 kHz. The sample was removed after 10 minutes and filtered. The clear liquid was collected and tested for sodium and potassium levels using Inductively Coupled Plasma (ICP) spectrometer of Perkin Elmer make and model Optima 5300DV [4]. This experiment was repeated at intervals of 10 minutes for one hour and for different frequencies and reagents. An aluminium foil test was performed to check the efficiency of the ultrasonic tanks.
3. Results and discussion

3.1. Effect of time
From Figure 2 and Figure 3, it may be inferred that the initial leaching of both potassium and sodium remains low, and increases only when the sample is exposed to ultrasound for a longer period of time. Sodium shows a sudden jump in leaching tendency, while the amount of potassium leached with time shows a more gradual increase. This indicates that sodium is bonded to the coal differently from potassium, as corroborated later by the study on effect of solvent used.

Figure 2. Sodium leached at 68 kHz using HNO₃

Figure 3. Potassium leached at 68 kHz using H₂O₂

3.2 Effect of frequency
The result of effect of frequencies on extraction of sodium is reported in Figure 4 and Figure 5. 58 kHz appears to be the most effective frequency for removal of both the alkali metals. This is likely to be due to the fact that the 58 kHz displays the highest cavitation intensity among the systems employed. Although cavitation should scale inversely with frequency, this trend can be influenced by the design and operating conditions of the specific system.

The results of the aluminium foil test (exposure, followed by mass loss measurement) to measure cavitation intensity were analysed quantitatively. 25 kHz appears to be most eroded, while extent of erosion decreases progressively as the frequency increases. However, leaching behaviour is strongest at 58 kHz. This may be due to an optimum combination of cavitation and streaming effects being simultaneously present at 58 kHz, making it ideal for removal of alkali.

Figure 4. Sodium leached for various frequencies- 20 mins using H₂O₂ as solvent

Figure 5. Potassium leached for various frequencies-30 mins using HNO₃ as solvent
3.3 Effect of solvent

When a comparison is made of the solvents used, nitric acid appears to be only slightly better compared to hydrogen peroxide as far as removal of sodium is concerned. However, for potassium removal, nitric acid seems to be far better than hydrogen peroxide as a reagent (Refer Figure 6 and Figure 7). This may be due to the fact that potassium is in the form of silicates and aluminates in coal, and requires a stronger solvent such as nitric acid to achieve significant leaching behaviour.

![Figure 6. Sodium leached at 40kHz for HNO₃ and H₂O₂ as solvents](image)

![Figure 7. Potassium leached at 25kHz for HNO₃ and H₂O₂ as solvents](image)

4. Conclusions

Exposure of coal to low-frequency ultrasound leads to the following interesting results:

- The effects of frequency, time and solvents on the removal of sodium and potassium from coal were studied. It is notable that percent extraction is consistently low, indicating that the samples need to be exposed additionally to high-frequency ultrasound in order to optimize the leaching effect.
- Further analysis needs to be done on effectiveness of the solvents used in leaching of sulphur from coal. A comprehensive process optimisation study is required to identify the ideal sonication time, best frequency to be used, and the best reagent to leach sodium, sulphur and ash from coal. These results will be presented at the Conference.
- It has been observed that reagents such as nitric acid, when used at a high concentration, can break the potassium-silica bonds [5] and lead to significant removal of potassium.

5. References

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