

Sono-Processing of Coal for Removal of Ash and Other Impurities

Dr. R Nagarajan¹, Dr. B. Ambedkar² and Dr. H. Srivalli³

1: Department of Chemical Engineering, IIT Madras, Chennai 600036, India

2: Department of Chemical Engineering, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam 603110, India

3: Saint Gobain Research India, IIT Madras Research Park, Chennai 600036, India

Keywords

Sono-processing, desulfurization, de-ashing, fouling, slagging, erosion, corrosion, coal wash, alkalis in coal and ash, process intensification

ABSTRACT

Although the global thrust is shifting towards alternative sources of energy, it will not be feasible to entirely eliminate the use of coal in the near future. It is, therefore, important to minimize the harmful effects associated with its use. While environmental impact is certainly to be addressed, fouling and slagging, and consequent erosion and corrosion--phenomena associated with fly ash deposits that can severely damage process equipment-- are also of concern. These can lead to a reduction in heat-transfer efficiency in power plants, and to sudden power outages. While fly ash transport and deposition are significant contributors to fouling and slagging, other impurities play a role as well. Sodium and potassium in the ash are directly linked to deposition of fly ash, as they form a molten salt film which aids in sticking of ash particles to heat transfer surfaces. Sulfur in ash also contributes to molten alkali sulfate formation, and, in addition, promotes corrosion of process equipment.

Hence, removal of these impurities—ash, sulfur, alkalis—prior to coal burning would be highly beneficial to power plant operations. In this paper, ultrasonic and megasonic systems are investigated with respect to the enhancement they provide for impurity removal, and the associated “Process Intensification Factors” are quantified. These are

quite significant, but the associated “Cost Impact Factors” also need to be evaluated in parallel so that the commercial viability of these processes in high-volume power production may be assessed. This paper deals with these aspects and summarizes data and findings.

INTRODUCTION

Impurities in coal and their downstream effects

Coal is the largest source of fuel for generation of electricity throughout the world. The full utilization of coal is limited by the presence of high levels of ash and sulfur in it. During coal combustion, the mineral matter transforms into ash. Fly-ash is the finely divided mineral residue resulting from the combustion of ground or powdered coal in an electricity-generating plant. It consists of inorganic matter present in the coal that has been fused during coal combustion.

Mineral matter in coal causes several disadvantages, including: unnecessary cost for transportation, handling difficulties during coal processing, leaching of toxic elements during ash disposal, sulfur emission from pyrite-like minerals giving rise to an environmental issue, and ash deposition leading to the deterioration of boilers and accessories (thereby diminishing operating efficiency). During coal combustion, fly-ash particles entrained in the flue gas from boiler furnaces in coal-fired power plants can cause serious erosive wear on steel surfaces along the flow path, thereby reducing the operational life of the mild-steel heat transfer plates that are used in the rotary regenerative heat exchangers. Moreover, in technical practice, erosion is often accompanied by a chemical attack.

In coal-fired power stations, nearly 20% of the ash in the coal is deposited on boiler walls, economizers, air-heaters and super-heater tubes, and is eventually taken out as bottom ash. The deposited ash is subsequently discharged as slag and clinker during the soot-blowing process. The rest of the ash is entrained in the stream of flue gas leaving the boiler. The ash-laden flue gas passes through the narrow passages between the corrugated steel plates that constitute the air heater elements. The ash

particles collide with the surfaces of the steel air heater elements, and material is eroded from the surfaces. In an advanced stage of erosion, the plates become perforated. The air heater elements fail once they are unable to maintain their structural integrity.

SO_x as a pollutant are a real threat to both the ecosystem and to human health. Sulfur is found in two forms in coal: 1. Inorganic sulfur, and 2. Organic sulfur. The inorganic sulfur again classified into two classes: i. sulfate sulfur, and ii. pyritic sulfur. Sulfate-sulfur occurs in combination with Ca, Mg, Ba, Fe, etc. Pyritic sulfur in coal occurs as pyrite (FeS₂), dimorphic marcasite (FeS₂), sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS₂), pyrhotite (Fe_{1-x}S), arsenopyrite (FeAsS) and others. The chemical structures of organic sulfur components of coal are generally part of the macro-molecular structure of the coal itself. Organic-sulfur is chemically bonded and very difficult to remove by physical cleaning methods.

Methods to control SO₂ emissions may be classified as:

1. De-sulfurization (Physical, Chemical, Microbial) of coal prior to combustion,
2. Removal of sulfur oxides during combustion,
3. Removal of sulfur oxides after combustion, and
4. Conversion of coal to a clean fuel by gasification and liquefaction.

However, these are ineffective in the sense that time and energy consumption are high, and many chemicals are involved, introducing difficulties in handling of by-products during the process. Nowadays, online flue gas de-sulfurization is being attempted to remove sulfur from coal post-combustion. The biggest disadvantage associated with this method is formation of by-products [Flue Gas Desulfurization (FGD) gypsum is one]. According to the American Coal Ash Association's annual Coal Combustion Product Production and Use Survey, total production of FGD gypsum in 2006 was approximately 12 million tons. Close to 9 million tons of FGD gypsum were put to beneficial use, while the remainder was land-filled. There is, at present, no way for full usage of all FGD gypsum generated as by-product (www.epa.gov/osw).

There are also concerns about environmental effects when FGD gypsum is used for soil amendment, and there are some reports on how chemical properties of soils, plants and animals are affected following FGD gypsum application (Environmental Protection Agency, USA). When concentrations of elements in soil, soil water, plant tissue and earthworms were measured, results indicate that Ca and S increased in plant tissue, soil, and soil water, and the concentrations of Al and Fe decreased in plant tissue. This will lead to acute and chronic effects to humans as well as plants. Over the next ten years, annual production of FGD gypsum may double as more coal-fired power plants come online, and as scrubbers are added to existing power plants to meet the environmental clean-air standards. In the worst case, where sulfur in coal is 10% or higher, releasable sulfur amount can become very high. This would lead to unnecessary transport and storage before, as well as after, combustion in terms of FGD gypsum. There is thus clearly a need for removing ash and sulfur from coal prior to combustion (Ambedkar et al., 2011).

Alkalis such as sodium and potassium in coal are directly linked to deposition of fly ash, as they form a molten salt film, which aids in sticking of fly ash particles to the heat transfer surfaces. Thus, removal of alkalis from coal prior to combustion is an imperative as well (Srivalli et al., 2019). Sono-intensification of impurity removal from coal is the focus of this paper.

When an acoustic field is coupled to a liquid and transient cavitation is induced, it can significantly intensify ongoing processes, making them run faster, cheaper, and better. Cavitation enhancement of mass transfer phenomena such as diffusion, dissolution and leaching has been quantified in literature. Cavitation and acoustic streaming—phenomena prevalent in acoustic fields coupled to liquids-- have been evaluated here as a mechanism to remove ash, sulfur and alkalis from coal prior to combustion, thereby greatly mitigating the downstream propensity for slagging, fouling, corrosion and erosion. Their effectiveness in impurity removal- quantified via the Process Intensification Factor (PIIF)-- is assessed simultaneously with the associated impact to

process cost, and conclusions are drawn in this paper regarding the economic viability of introducing ultrasonic/ megasonic processes in high-volume power plant operations.

Ultrasound-Assisted Process Intensification

When ultrasound is applied to a medium such as water, the basic physical phenomena involved in producing changes observed (physical and chemical effects) in the medium are of two types— acoustic cavitation and streaming. Cavitation is the dominant mechanism in ultrasonic fields in the <100 kHz frequency range. Two types of acoustic cavitation are identified, namely stable cavitation and transient cavitation. In stable cavitation, bubbles continue to oscillate near their resonance size without collapsing; in transient cavitation, encountered in the present system, bubbles grow and collapse, as observed visually and via measurements of cavitation intensity. Cavitation collapse results in extreme conditions producing light emission, shock waves, and localized high temperatures (up to approx. 5000 K) and pressures (up to 100 atm). These shock waves are responsible for the rupturing of neighboring solids (which may be vessel walls or immersed solids), leading to the generation of shear forces and eddies which, in turn, lead to an increase in turbulent energy dissipation. The number of these shock waves is related to the frequency of the waves [Suslick (1988) and Lorimer et al. (1991)]. Typical acoustic cavitation that occurs in a low-frequency ultrasonic tank is shown in Figure 1.

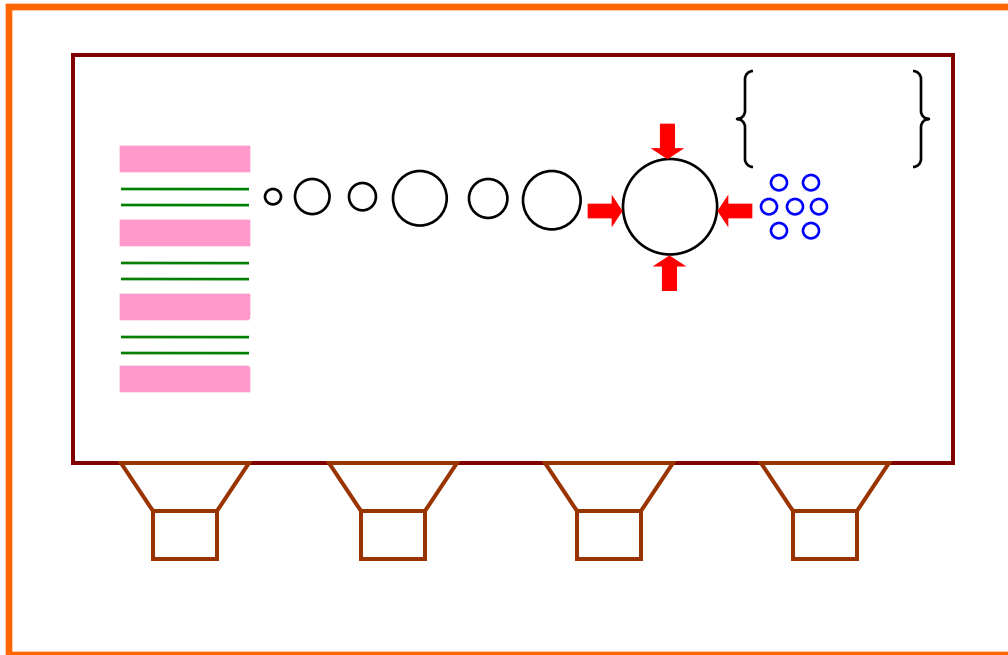


Figure 1: Acoustic cavitation in ultrasonic tank (Ambedkar, 2011)

Acoustic streaming refers to unidirectional flow currents in a fluid formed due to the presence of sound waves. Typical acoustic streaming that occurs in high-frequency ultrasonic and megasonic tanks is shown in Figure 2. The formation of acoustic fountains is observed at the center of the transducer locations. Acoustic streaming comprises several important effects: (i) bulk motion of the liquid (Rayleigh streaming), (ii) micro-streaming (Eckert streaming), and (iii) streaming inside the boundary layer (Schlichting streaming). The primary effect of acoustic streaming is steady bulk motion of the liquid which generates a shear force. A second effect of acoustic streaming is micro-streaming. Micro-streaming occurs at the substrate surface, outside the boundary layer, due to the action of bubbles as acoustic lenses that focus sound power in the immediate vicinity of the bubble. Micro-streaming aids in dislodging particles and contributes to megasonic cleaning. Most of the flow induced by acoustic streaming occurs in the bulk liquid outside the boundary layer. However, there is a third effect of acoustic streaming – Schlichting streaming – which is associated with cavitation collapse. Schlichting streaming occurs inside the boundary layer, and is characterized by very high local velocity and vortex (rotational) motion. Acoustic streaming, both inside and outside the boundary layer, enhances cleaning and other chemical reactions.

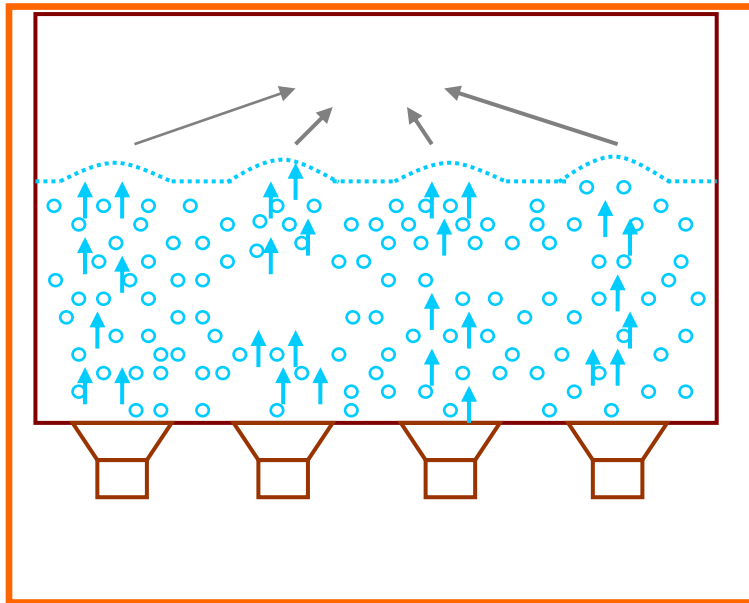


Figure 2: Acoustic streaming in ultrasonic tank (Ambedkar, 2011)

Two basic mechanisms for acoustically enhanced coal washing have been suggested by Mason et al. (2004): (a) an increase in the abrasion of suspended coal in slurries leading to the removal of dust material from the surface of coal, and (b) an enhanced leaching of contaminants (mineral matter) from the interior of coal particles. Under the influence of ultrasound, normal leaching occurs, but several additional factors contribute towards improvements in the efficiency. These include:

- i. Asymmetric cavitation bubble collapse in the vicinity of the solid surface leads to the formation of high-speed micro jets targeted at the solid surface. The micro jets can enhance transport rates and also increase surface area through surface pitting.
- ii. Particle fragmentation through collisions will increase surface area.
- iii. Cavitation collapse will generate shock waves which can cause particle cracking, and propagation of cracks through which the leaching agent can enter the interior of particle by capillary action.
- iv. Acoustic streaming leads to the disturbance of the diffusion layer on the surface.

- v. Diffusion through pores to the reaction zone will be enhanced by the ultrasonic capillary effect.

The objective of the present study is to investigate the effectiveness of ultrasound-assisted washing for high-ash, high-sulfur coals, with simultaneous removal of alkalis present, while at the same time accounting for the associated cost impact.

EXPERIMENTAL PROCEDURE

Determination of Ash Content (Ambedkar, 2011)

The air-dried coal sample was thoroughly mixed and ground to pass through a 212-micron IS sieve. A clean dry empty dish was weighed. Into this dish, 0.5 grams of coal sample were taken and weighed accurately. Then, the material was distributed uniformly so that the spread does not exceed 0.15 g per cm². The uncovered dish was kept inside a muffle furnace at room temperature. The temperature was then raised to 500°C in 30 minutes and to 815 ± 10°C in a further 60 minutes, and was maintained at this temperature until the delta change in mass of the ash was less than 0.001 g. The dish was then removed from the furnace, covered with its lid, allowed to cool and weighed. The ash was brushed out and the empty dish reweighed. Ash percent by mass, was calculated as $100 \times [(M3 - M4) / (M2 - M1)]$ where

M1 = mass in gm of dish,

M2 = mass in gm of dish and sample,

M3 = mass in gm of dish and ash, and

M4 = mass in gm of dish after brushing out the ash and on reweighing.

Determination of total sulfur content (Ambedkar, 2011)

The sample of coal was heated in intimate contact with Eschka's mixture (mixture of two parts of MgO and one part of Na₂CO₃) in an oxidizing atmosphere to remove combustible matter and to convert the sulfur to sulphate. This was then extracted and precipitated gravimetrically with barium chloride as barium sulfate.

The bottom of the 50 ml crucible was uniformly covered with 0.5 g of Eschka's mixture. The appropriate quantity of the material, crushed to pass 212-micron IS sieve, was weighed accurately and mixed intimately with 2.5 g of Eschka's mixture in an evaporating basin or other suitable vessel, and is brushed into the crucible. The content was leveled by tapping gently on the bench and covered uniformly with one gram of Eschka mixture. The charged crucible was placed into the cold muffle furnace. The temperature was raised to $800 \pm 25^{\circ}\text{C}$ in about one hour and then heated for a further 90 minutes. The plate was withdrawn with its crucible and cooled. The ignited mixture was transferred as completely as possible from the crucible to a beaker containing 25 to 30 ml of water. The crucible was thoroughly washed out with about 50 ml of hot distilled water and the washings added to the contents of the beaker.

A cover-glass was placed on the beaker, and sufficient amount of concentrated hydrochloric acid (analytical grade) added to dissolve the solid matter, with the contents of the beaker being kept at warm condition to effect solution. Then, the solution was boiled for 5 minutes to expel carbon dioxide and filtered through a filter pad or medium-textured double acid-washed filter paper, the filtrate being collected in a 400-ml conical beaker. The residue on the filter pad or filter paper was washed with four 20-ml portions of hot distilled water. To the combined filtrate and washings, 2 to 3 drops of methyl red indicator were added; then, ammonium hydroxide solution was added cautiously until the color of the indicator changed and a trace of precipitate was formed. Sufficient amount of concentrated hydrochloric acid was added to re-dissolve the precipitate; subsequently, one milliliter was added in excess.

The volume of the solution was made-up to approximately 300 ml with water. The beaker was covered and heated until the solution boiled; then, the heating was slightly reduced until ebullition ceases. 10 ml of barium chloride solution was added within approximately 20 seconds from a pipette held such that the barium chloride fell into the middle of the hot solution which was being agitated. The solution was kept for 30 minutes just below boiling point.

The barium sulfate was recovered by gravity, through an ash-less fine-textured double acid-washed filter paper in a long-stemmed 60° funnel (Whatman No. 42 filter paper is suitable for this purpose). Then, it was dried and weighed. Sulfur, percent by weight, was calculated as $[13.74 \times (A - B + 0.008) / W]$ where

A = weight in grams of barium sulfate found in the determination,

B = weight in grams of barium sulfate found in the blank determination, and

W = weight in grams of the material taken for the test.

Determination of alkali content (Srivalli, 2019)

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 (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. The powdered coal was sieved, and coal particles of size less than 210 μ m were used for the experiments after drying in an oven at 383 K to remove excess moisture and dissolving the dried coal in acid. The sodium and potassium levels were estimated using ASTM D6349-09 Standard method. 0.25 gm of coal was mixed with 2 ml of concentrated hydrofluoric acid and 5 ml of aqua regia (mixture of HCl and HNO₃ in the ratio 1:3). The sample was poured into a digestion vessel, sealed and heated to 473 K for 2 hours in a microwave. The digestion vessel was then removed and allowed to cool. 25ml of H₃BO₃ was added to the sample to prevent the formation of sparingly-soluble species in the sample. The digested liquid was filtered to remove coal particles, made up to 100ml using ultrapure water and tested for sodium and potassium using ICP-OES (Inductively coupled plasma, followed by optical emission spectroscopy- Perkin Optima 5300DV).

Ultrasonic System

The ultrasonic system (Figure 3) has three components, namely, an ultrasonic generator, an ultrasonic transducer and a tank with liquid. The ultrasonic tank is a bright-annealed stainless steel tank that has piezo-electric transducers mounted at the bottom. The ultrasonic generator transforms the line voltage to a frequency

corresponding to the operating frequency of the transducer. The transducer transforms these electric oscillations to mechanical sound waves.

Figure 4 shows schematic view of probe-type ultrasonic system. In the probe-type, the horn tip vibrates and generates ultrasonic waves in liquid present in a vessel. During propagation of wave, cavitation in the liquid and bulk fluid motion due to streaming are formed. Photographic view of probe-type ultrasonics is shown in Figure 5.

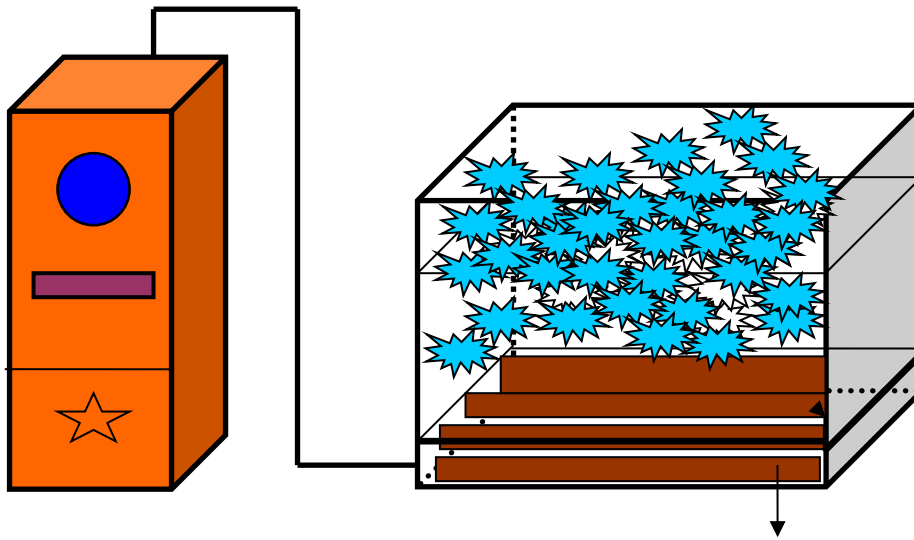


Figure 3: Schematic of tank-type ultrasonic system (Ambedkar, 2011)

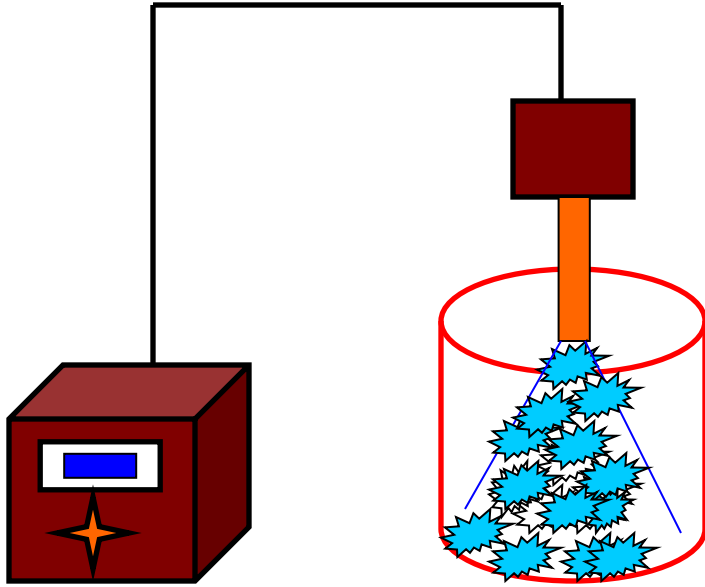


Figure 4: Schematic of probe-type ultrasonic system (Ambedkar, 2011)



Figure 5: Photographic view of probe-type ultrasonic system (Ambedkar, 2011)

Figure 6 shows fluid behavior at various ultrasonic frequencies. At 25 kHz, the liquid medium appears stagnant, but is experiencing very high intensity cavitation in the tank. The liquid behavior in the dual-frequency (58/192) tank is somewhat different (Figure 7),

resembling a slithering movement. In the 430 kHz tank (Figure 8), acoustic streaming is the dominant phenomenon. This is confirmed by “fountain” effect seen in the center of the tank.

Energy dissipated as heat in an ultrasonic irradiation is calculated using calorimetric study (Mason et al. (1992) and Toma et al. (2011)) and is shown in Table 1 (Ambedkar, 2011). The energy dissipation is minimum in the case of tank-type ultrasonic system.



Figure 6: Appearance of the water surface in the 25 kHz ultrasonic tank; 500W (Ambedkar, 2011)



Figure 7: Appearance of the water surface in the (58/192 kHz) ultrasonic tank; 500W (Ambedkar, 2011)



Figure 8: Appearance of the water surface in the 430 kHz ultrasonic tank; 500W (Ambedkar, 2011)

Table 1: Power dissipated as heat (by calorimetric study)

Frequency (kHz)	Power input (W)	Slope (°C / s)	Power dissipated as heat (W)
25	500	0.0056	11.72
58/192	500	0.0052	10.88
430	500	0.0086	18.00
20kHz_Probe	500	0.0261	54.63

The coal samples were taken in a beaker with water (or solvent), and subjected to various ultrasonic conditions. The results obtained for impurity removal constitute the remainder of this paper.

RESULTS & DISCUSSION

Ash Removal

Aqueous-based coal beneficiation using ultrasound is attributable to two basic mechanisms: i. Coal particle breakage, and ii. Leaching. Ultrasound-assisted particle breakage is entirely different from conventional particle breakage. The interaction mechanism between suspended coal particle and ultrasound, and mechanism of coal particle breakage and ash removal, are quite unique.

In low-frequency ultrasound (<100 kHz), cavitation phenomena are predominant, and particle breakage is extensive. In high-frequency ultrasound (>100 kHz), streaming phenomena are dominant, and leaching effect prevails. Cavitation is due to implosion of bubbles in the acoustic field, and to the resulting transmission of a shock wave. Millions of bubbles will form, grow and collapse within a nano-second. The effect of cavitation is several hundred times greater in heterogeneous than in homogeneous systems (Luche, 1994). Unlike cavitation bubble collapse in homogeneous systems (liquid-liquid interface), collapse of a cavitation bubble in heterogeneous systems (e.g., liquid – solid)

on or near to a surface is non-symmetrical in nature since the surface provides resistance to liquid flow. The result is an in-rush of liquid predominantly from the opposite side of the bubble, resulting in a powerful liquid jet being formed and targeted at the surface. It is also important to note that the rapid collapse of the cavitation bubbles generates significant shear forces in the bulk liquid immediately surrounding the bubbles and, as a result, produces a strong stirring mechanical effect. These effects can significantly increase mass transfer to the surface (Ratoarinoro et al., 1995).

Cavitation is also important in case of heterogeneous systems in that most of the cavitation bubbles are generated close to the surface of the substrate, thus providing an important additional benefit of the “opening up” of the surface of solid substrates as a result of mechanical impacts produced by powerful “jets” of collapsing cavitation bubbles.

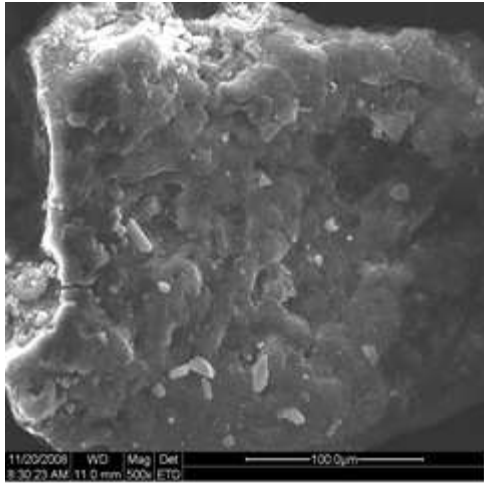
This will cause particle breakage in different ways: pitting of coal particle surface to produce fines, and forming cracks on the surface, which are widened and deepened due to prolonged exposure, finally causing breakage. Coal particle breakage mechanism is illustrated here using lignite I coal sample sonicated for 5 minutes by 25 kHz frequency of ultrasound, 500 W input powers. SEM images of virgin and sonicated coal samples are shown in Figures 9a to 9e.

Four stages for ultrasound assisted coal particle breakage can be observed here. These are: (Ambedkar, 2011)

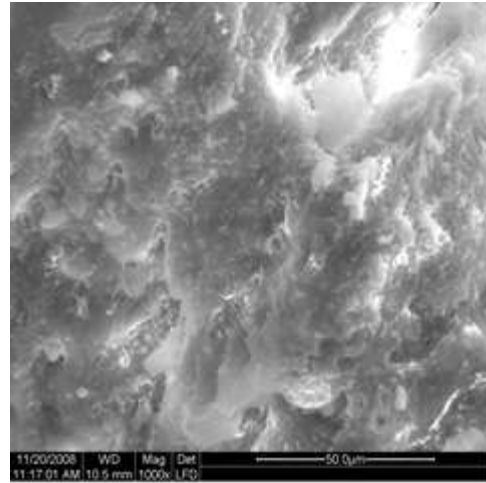
- i. Pitting of the coal surfaces (Figure 9b)
- ii. Formation of cracks on the coal surface (Figure 9c)
- iii. Widening and deepening of coal surface cracks (Figure 9d) and,
- iv. Breakage of coal particles (Figure 9e).

Table 2 shows ash analysis of virgin and treated coal samples. The sonicated sample was separated into three levels by decantation. Top level was expected to be rich in

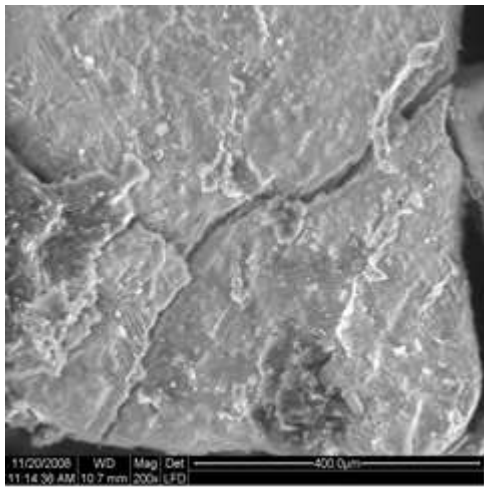
lighter impurities, middle level was expected to be mostly clean coal; and bottom level was expected to be ash-rich coal (heavier impurities).



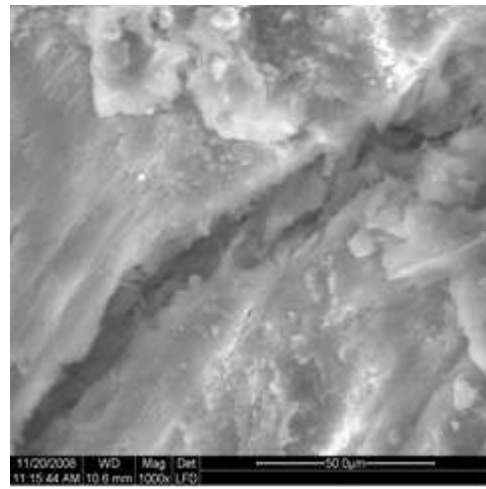
a



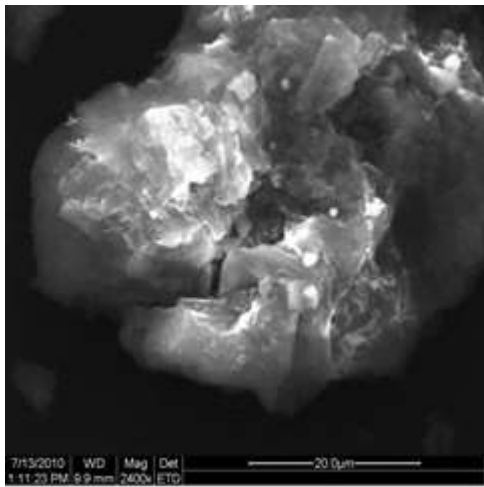
b



c



d



e

Figure 9: SEM images of sonicated coal: (a) Virgin coal sample; (b) Pitting of surfaces; (c) Crack formation; (d) Widened cracks; and (e) Breakage of particle ((Ambedkar, 2011))

Table 2: Ash Analysis of Virgin and Treated Coal Samples

	Virgin, %	Top, %	Middle, %	Bottom, %
Ball milling	18.9	18.61	19.12	22.35
20 kHz Probe	18.9	6.73	14.66	21.82
25 kHz Tank	18.9	9.80	13.36	21.07
58/192 kHz Tank	18.9	8.13	15.34	20.61
430 kHz Tank	18.9	15.26	17.78	21.02

To confirm these trends, a semi-quantitative ash analysis was done on three levels of coal samples by selecting coal samples from the three levels for ash analysis (Ambedkar, 2011). From Table 2, it can be confirmed that the ash content of the top and middle level is lower than that of the bottom level and virgin coal. Sono-fragmentation of coal leads to the detachment of ash impurities from coal and separation by decantation process using density difference as a driving force. In these experiments, 35 to 40% of coal samples are recovered from top and middle level, remaining are settled in the bottom at a given settling time. The bottom level coal sample requires further sonication for de-ashing. This process of sonication followed by decantation clearly lends itself to recasting as a continuous operation, which would greatly enhance the processing throughput, possibly up to several tons a day.

De-sulfurization

Sulfur is found in two forms in coal: 1. Inorganic sulfur, and 2. Organic sulfur. The inorganic sulfur again classified into two classes: i. sulfate sulfur, and ii. pyritic sulfur. Analysis has been performed on ultrasonically-treated samples to see how the forms of sulfur are distributed after ultrasonic treatment. From Figure 10, it is apparent that almost all the cases show 90% and above sulfate sulfur removal. However, the pyritic and organic sulfur show high resistance to ultrasonic treatment in water. 20 kHz probe systems remove almost 20% of pyritic + organic sulfur due to high energy transferred to the sample mixture. The 25 kHz ultrasonic tank system removes 14% of pyritic + organic sulfur, whereas the 430 kHz system removes only about 9% due to a single

relatively-mild mechanism being in effect. Dual system removes about 36% of pyritic + organic sulfur removal due to coupled mechanisms (cavitation + streaming). In general, ultrasonic method is a time-dependent process. To intensify the ultrasonic treatment method, some insight into its kinetics is needed. Suitable reagents are to be used in order to minimize the treatment time and reagent consumption, and to maximize sulfur removal.

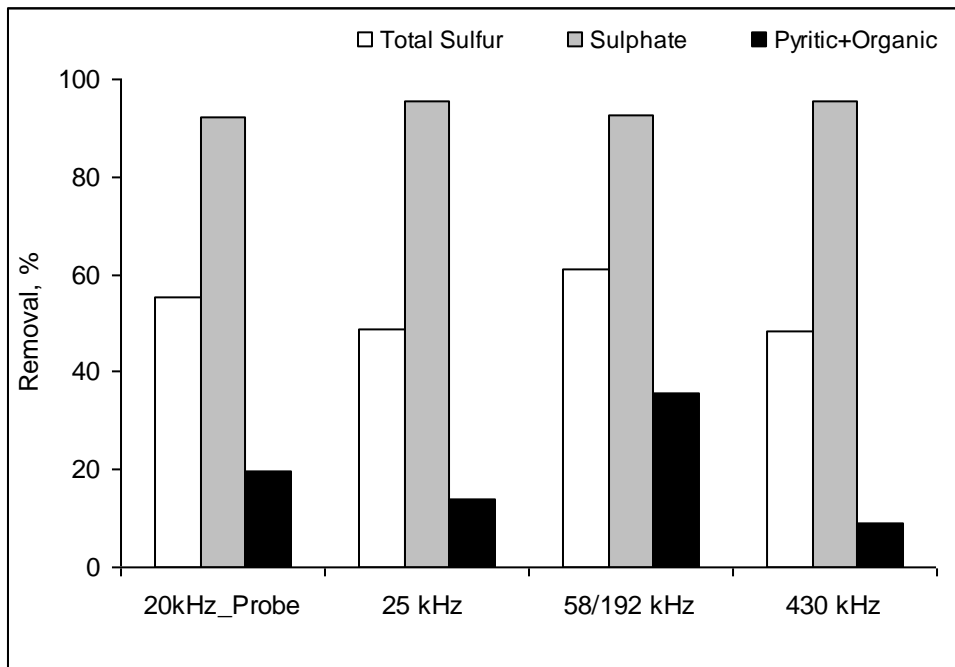


Figure 10: Effect of frequency on removal of different forms of sulfur ((Ambedkar, 2011)

In order to achieve minimum treatment time and maximum removal, reagent-based ultrasonic desulfurization was investigated. To intensify the ultrasonic treatment method, 2N nitric acid and 3-volume percentage of hydrogen peroxide were used as reagents. The reasons for choosing the above mentioned reagent concentrations are that as per IS1350 (forms of sulfur determination) procedure, 2N of nitric acid is used to extract entire inorganic sulfur from coal by 30 minutes of boiling, and higher volume percent of H₂O₂ resulted in foaming and uncontrolled reactions.

To assess the enhancement effect of the ultrasonic method, conventional methods of desulfurization were compared. 2N of HNO_3 and 3-volume % of H_2O_2 were used as reagents. 10 grams of 212 μm sieve pass-through high-sulfur lignite coal I and 100 ml of reagents were taken in a 250 ml beaker. The same coal-to-reagent ratio was maintained for reagent-based soaking, stirring and sonication.

Figure 11 shows a comparison between conventional and ultrasonic methods of coal de-sulfurization (Ambedkar, 2011). 120 hours soaking of high-sulfur coal I in reagents leads to about 46% removal by HNO_3 and 35% removal by H_2O_2 , due mainly to chemical reaction. The majority of sulfur removal occurs only by surface reaction. The reaction moves gradually towards the core of the particle as time progresses, thereby extending the process. Stirring was conducted for about 1 hour at 1000 rpm. It is apparent that using nitric acid at 1000 rpm, 29% removal is possible; in the case of H_2O_2 , 27% removal was observed. In order to assess the effect of ultrasound on reagent-based coal desulfurization, 20 kHz probe is used at 500 watts input power. 30 minutes of sonication leads to 74% of TSR by H_2O_2 and 23 minutes of sonication leads to 87% of TSR by HNO_3 .

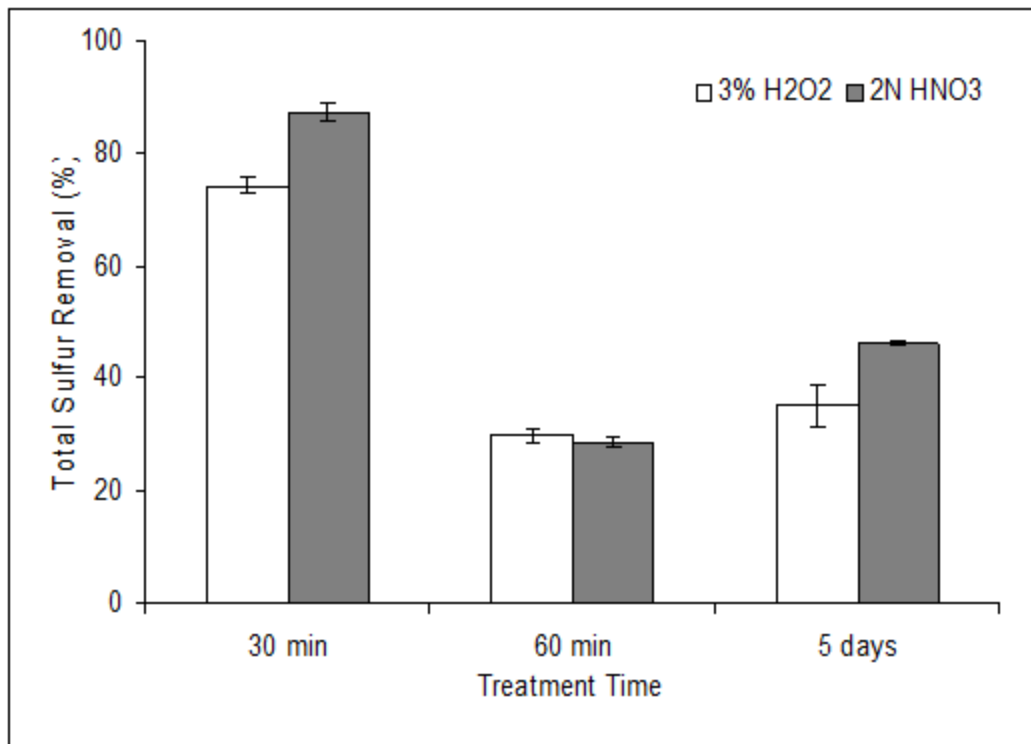


Figure 11: Comparison between conventional and ultrasonic methods of sulfur removal (Ambedkar, 2011)

The reaction mixture was sonicated at intervals of 10, 20 and 30 minutes and the corresponding temperature rise of the reaction mixture was monitored using a data-logger. The prime reason for measuring mixture temperature is to track the rate at which the reaction proceeds during ultrasound irradiation. In Figure 12, for 3-volume percentage of H₂O₂, the percentage removal of sulfur is seen to increase with increasing sonication time. Interestingly, even the low reagent concentration (3 volume %) and the short period of sonication (10 min) lead to more than 63% removal. The reason is that the directional probe creates an intense ultrasonic field near the top which leads to rapid breakage of the coal particles, thereby accelerating the reaction between H₂O₂ and sulfur. For both the reagents, the kinetics are very rapid; when using 3% H₂O₂, 30 minutes sonication leads to 74% of total sulfur removal, and for 2N HNO₃, 23 minutes of sonication leads to 87% removal. The slope of the curve at 3% hydrogen peroxide condition is steeper than 2N nitric acid condition.

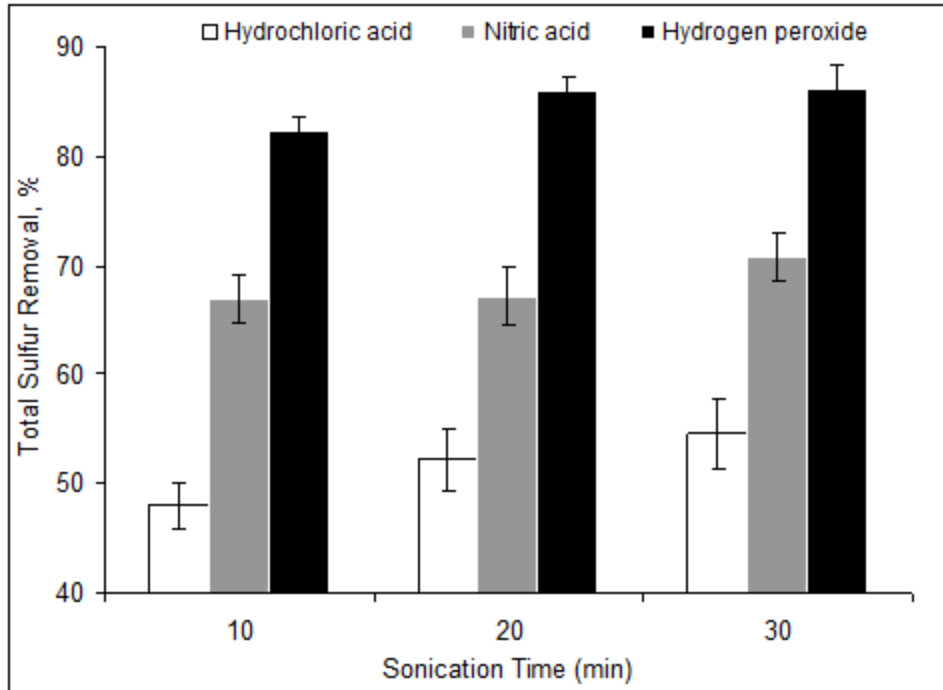


Figure 12: Effect of reagent-based ultrasonic methods on total sulfur removal (Ambedkar, 2011)

Reagent-based ultrasonic desulfurization is much faster than aqueous-based or conventional methods of desulfurization. Hydrogen peroxide seems to be a more suitable reagent for removing sulfur from coal than HNO_3 because it is less harmful to the environment, and appears to be effective even with 3% by volume concentration, whereas typical application of H_2O_2 as an oxidizing agent requires up to 6% concentration.

An optimum set of process parameters for reagent-based ultrasonic coal desulfurization was determined on the basis of highest TSR (total sulfur removal), and are shown in Table 3.

Table 3: Optimum value of process parameters based on maximum TSR

	Ultrasonic Frequency, kHz	Reagent Concentration	Sonication Time, min	Coal Particle Size, μm	Reagent Volume, ml
HCl	Dual	5 N	30	-600+212	100
HNO₃	Dual	2 N	30	-600+212	60
H₂O₂	Dual	6 volume %	30	-600+212	100

To validate the above optimum conditions, two different types of high-sulfur lignite coals were chosen and tested. The first is the one already used for this investigation, and the second one has slightly higher sulfur and ash than the first. The % removal of total sulfur and ash under optimum conditions for high sulfur lignite coals I and II is shown in Table 4. An impressive amount of simultaneous removal of sulfur and ash was obtained using the optimum set of process parameters for lignite I. For lignite II, sulfur removal of 85% and ash removal of 66% were obtained with H₂O₂ as the reagent. Therefore, the method looks very promising for coal beneficiation.

Table 4: Percent Removal of Total Sulfur and Ash under Optimum Conditions for High Sulfur Lignite I and II

		Total Sulfur Removal, %	Ash Removal, %
Lignite I	HNO₃	82.5	44.3
	H₂O₂	94.8	63.5
Lignite II	HNO₃	74.5	38.0
	H₂O₂	85.5	66.2

Scale-Up Strategy

The main objective of scaling up of ultrasonic method for coal-wash is to achieve better sulfur removal with minimum reagent usage and high throughput of coal processing.

Figure 13 shows effect of sonication time on total sulfur removal with different volumes

of coal-reagent mixture. Three different volumes (10 g in 100 ml, 50 g in 500 ml and 150 g in 1500 ml) were taken for this investigation. From Figure 13, it may be observed that the rate of sulfur removal for first 10 minutes of sonication is high. It is very close to 80 % for 100 ml case and 62 – 70 % for 500 and 1500 ml cases. Then, the next 20 minutes of sonication yields a further 20 to 25 % of total sulfur removal. Further 30 minutes of sonication yields 5 to 7 % of sulfur removal. In almost all the cases, the first 30 minutes of sonication yields > 85 % of total sulfur removal. These results show that the sulfur removal results can be scaled up.

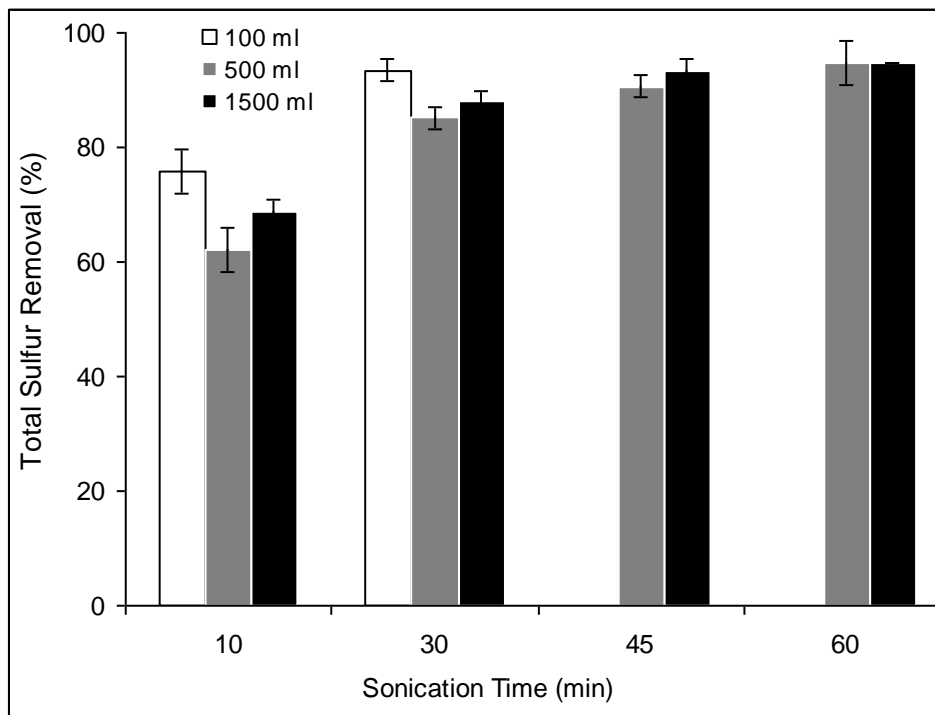


Figure 13: Effect of sonication on total sulfur removal with various process volumes (Ambedkar, 2011)

An assessment can be made of the amount of coal that can be processed assuming that the experimental results can be extended to continuous mode of operation. These estimates are summarized in Table 5. The size of the lab-scale ultrasonic tank is (45*30*30 in cm) 40 liters. A liquid level corresponding to 28.35 liters is maintained for all experiments. Hence, the corresponding quantity of coal to be processed is 2.835 Kg (1:10). As per the previous investigation, reagent-based ultrasonic methods remove

more than 90% of maximum total sulfur even at the lowest coal-to-reagent (1: 3) volumes included in this investigation. Hence, 9.45 kg of coal can be processed using 28.35 liters of 3 volume % of H₂O₂ during 30 minutes of treatment time. From Table 5, it may be observed that the coal processed per day using lab-scale ultrasonic tank is equivalent to approximately 0.5 ton/day. The reagent consumed for processing the 0.5 ton of coal is 1360 liters of 3 volume % H₂O₂.

Table 5: Amount of coal that can be processed per day using Lab-Scale Ultrasonic Tank

Coal-reagent Ratio (g/cc)	Mass of Coal (g)	Volume of reagent (ml)	Size of Container (Liter)	Treatment Time	TSR, %
1:10	10	100	0.25	30 min	93.4
1:10	50	500	1		85.21
1:10	150	1500	3		87.94
1:10	2835	28350	40		-
1:03	9450	28350			
	18900	56700			
	453600	1360800	[(45*30*30) in cm]	1 hr	
				1 day	
Kg Per Day	453.60	1360.8 liter	40	1 day	

The present investigation shows that reagent-based ultrasonic coal wash is a promising technique to remove sulfur and ash from coal. Results indicated that more than 90% removal was achieved within the bounds of low concentration, low treatment time and low reagent volume consumption. This has a positive implication for scaling up reagent-based ultrasonic coal wash to larger coal quantities. The different types of coal tested using optimum conditions derived from the investigation have yielded good results, increasing the level of confidence in scale-up efforts for ultrasonic reagent-based coal wash. This method has the potential to replace conventional methods in terms of less treatment time, less reagent volume, low reagent concentration and commercially-available ultrasonic coal-wash equipment.

Alkali Removal

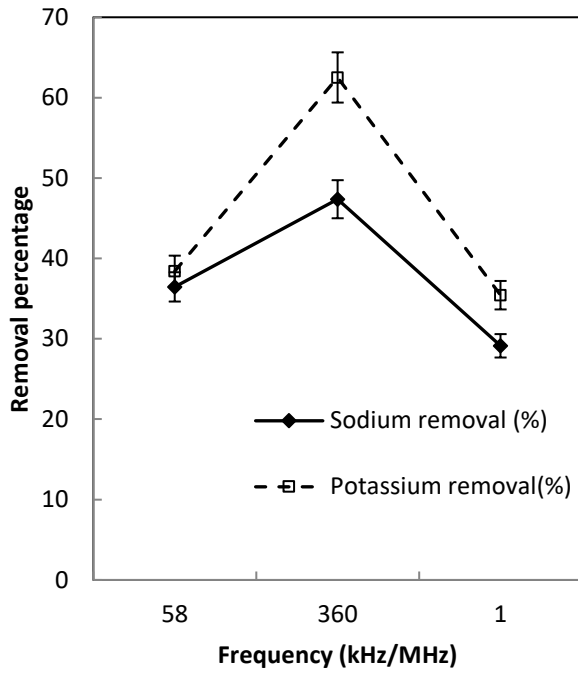
To carry out a study to find the most optimum conditions for leaching of sodium and potassium from coal, a Taguchi orthogonal array was chosen (Srivalli, 2019). Five parameters and three levels were identified. These are frequency (58 kHz, 360 kHz, 1 MHz), temperature (303K (30°C), 318K (45°C), 333K (60°C)), liquid/solid ratio (10, 15, 20), pulsing cycle (2s, 5s, 7s) and solvent concentration of (0.5N, 1N, 2N). The lower and upper limits of these parameters were fixed on a trial-and-error basis, with the requirement of no significant change in leaching rate when the lower and upper values were increased or decreased beyond the limits selected. These values were also chosen after considering various factors such as effectiveness of lower and higher limits on the leaching efficiency, process costs involved, optimum leaching rates achieved, etc. The parameters and levels are shown in Table 6. Since this is a five-parameter, three-level design, the L-27 array was chosen. All the experiments were replicated thrice and results were compared for repeatability and reproducibility. Alkali removal was quantified as follows:

$$\% \text{ of alkali leached} = \frac{\text{Amount of } \frac{\text{sodium}}{\text{potassium}} \text{ present in the filtrate}}{\text{Amount of } \frac{\text{sodium}}{\text{potassium}} \text{ present initially}} \times 100$$

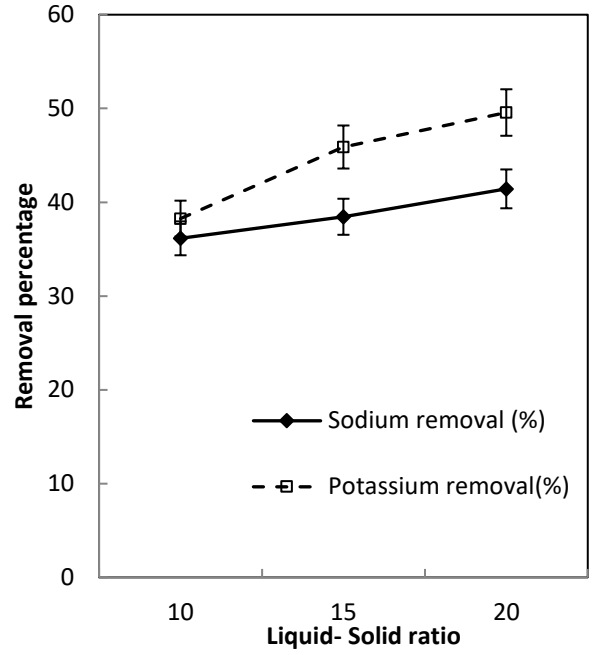
Table 6: Experimental factors and levels used

S.No.	Parameter	Level 1	Level 2	Level 3
1	Frequency (kHz/MHz)	58 kHz	360 kHz	1 MHz
2	Temperature (K)	303	318	333
3	Liquid/Solid ratio	10	15	20
4	Pulsing cycle (seconds)	2	5	7
5	Solvent concentration (N)	0.5	1	2

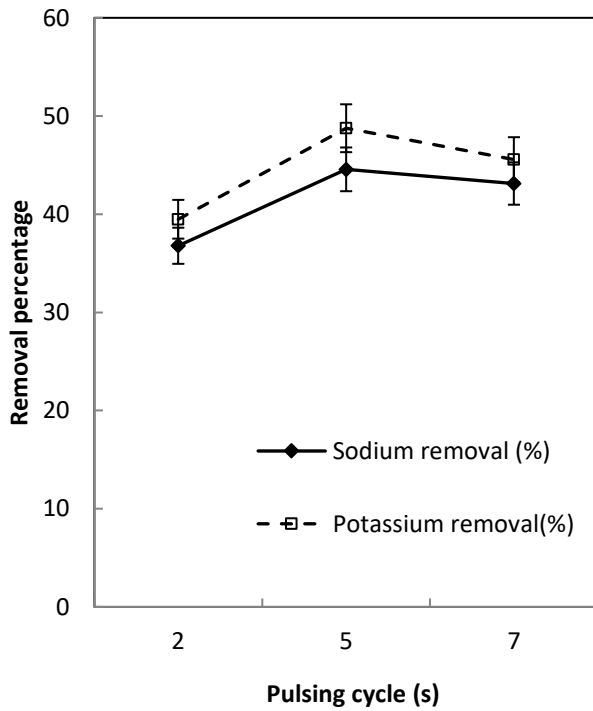
Figure 14 shows a comparison between pulsed and continuous modes of operation for removal of sodium and potassium from coal. Experiments were conducted with a low frequency (58 kHz), intermediate frequency (360 kHz) and high frequency (1 MHz). It is apparent from the plots that though potassium removal has increased by a small percentage in the pulsed mode, sodium removal is greatly enhanced compared to continuous mode of operation. When the ultrasonic tank is operated in pulsed mode, the system is subject to sudden on- and off-cycles. When the transducer is suddenly switched on, it creates localized hot spots where the size of cavitation bubbles is large, and hence when the bubble collapses, the localized temperatures and pressures are very high. This was studied by Vetrinurugan and Nagarajan (2008). The on-off cycle also ensures that temperature rise due to continuous operation of the sonication system is negligible even when a thermostatic water bath is not used. Pulsed mode of operation can be the preferred mode for alkali removal from coal as it affects leaching of both sodium and potassium favorably.



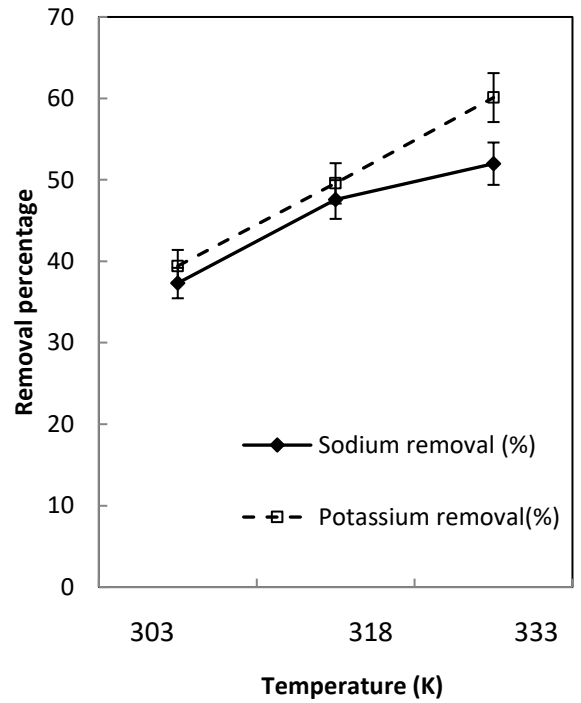
a



b



c



d

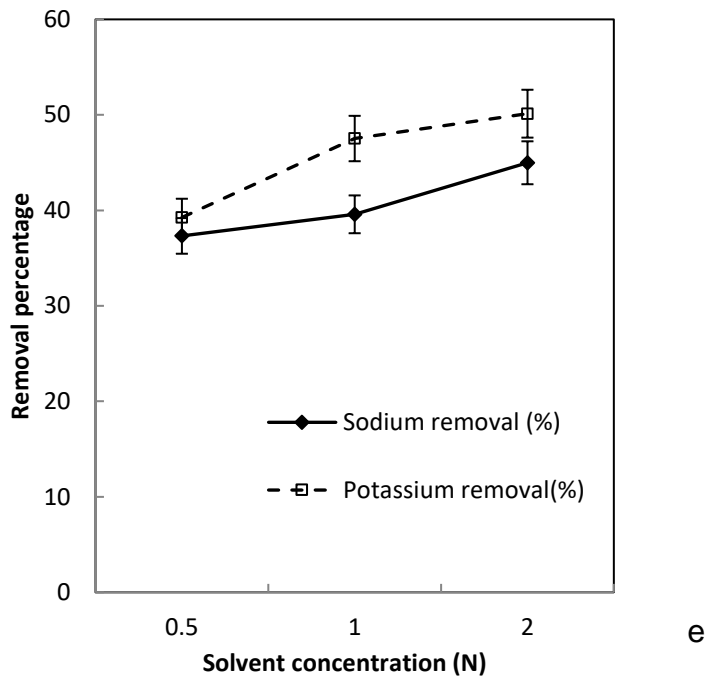


Figure 14. Effect of a) Frequency b) Liquid/solid ratio c) Pulsing cycle d) Temperature e) Nitric acid concentration on Sodium and Potassium removal (%) (Srivalli, 2019)

A key benefit of pulsing is that the “hot spots” are continuously relocated, thus rendering the effect more uniform. Each time the field is switched off and then on, “hot spots” form at locations that are not necessarily the same as in the previous off-on cycle. Over time, the net result is that the average ultrasonic field intensity at any point in the liquid is the same. This addresses a significant limitation of ultrasonic processing—viz., effects are not reproducible.

Figure 14 (a) shows the effect of frequency on ultrasound-assisted solvent leaching of sodium and potassium, respectively, from coal. Sonication has been done with three frequencies- a low frequency of 58 kHz, an intermediate frequency of 360 kHz and a high frequency of 1 MHz. Leaching of sodium and potassium from coal occurs due to a combination of two main factors – cavitation and acoustic streaming. At 58 kHz, the

system is predominantly exposed to the phenomenon called cavitation. While the pressures and temperatures reached during bubble implosion may be affected by suspended particulates, "hot spots" would still be present and serve as process intensifiers. In low-frequency systems, cavitation also causes fragmentation of solid particles, thereby increasing the available surface area, which in turn favors higher liquid-solid reaction rates.

A higher frequency system, such as the 1MHz megasonic system, is dominated by acoustic streaming. Acoustic streaming is the flow generated in a liquid due to viscous attenuation. The viscous dissipation that occurs is imparted to the liquid as steady momentum, as shown by Castro and Hoyos (2016). To obtain high leaching efficiency, the right mix of cavitation and acoustic streaming is essential as cavitation contributes to particle breakage, and streaming contributes to the reaction in the presence of a solvent. This is seen in Figure 14 (a) where the highest leaching efficiency is seen in the 360 kHz ultrasonic tank.

Figure 14 (d) gives the effect of temperature on the removal of sodium and potassium from coal. Leaching of alkali elements with ultrasound and nitric acid as solvent was carried out at three different temperatures - (303K (30°C), 318K (45°C) and 333K (60°C)). From the Figure, it is clear that temperature has a significant effect on leaching of alkali elements. When the temperature is increased, the viscosity decreases, and the solvent diffuses better into the pores of the coal particles aiding higher leaching rates. Therefore, maximum leaching of sodium and potassium is observed at 333K for all liquid/solid ratios and concentrations of nitric acid. Considering economic factors, energy savings obtained and ideal cavitation intensities, the upper bound for temperature was capped at 333K.

Figure 14 (b) describes the effect of liquid-to-solid ratio on sodium and potassium removal from coal. The three liquid-to-solid ratios chosen for this study are 10, 15 and 20. From the plots, it can be seen that the removal efficiency is higher for higher liquid-to-solid ratios. At lower liquid/solid ratios, the nitric acid present may not be sufficient

for the completion of the reaction, and this may have resulted in an acid-deficient condition. As the ratio increases, the viscosity of the mixture decreases and there is reduced diffusion resistance, leading to better mixing and higher removal efficiency.

Figure 14 (c) shows the effect of pulsing cycle on alkali removal. Three different pulsing cycles were tried as part of this study: 2 seconds, 5 seconds and 7 seconds. During cavitation, alternate compression and rarefaction cycles lead to the formation of bubbles which grow and collapse violently, leading to physicochemical changes in the structure of a substance. During pulsing, high shear energy and turbulence cause breakage of the bond between the molecules and enhance the reaction. While a pulsing cycle of 2 seconds is too short to cause significant removal, a pulsing cycle of 7 seconds proves to be too long and all the cavitation effects wear off. At a pulsing cycle of 5 seconds, highest removal efficiency is obtained, as seen in the results.

Figure 14 (e) describes the effect of solvent concentration on the removal of sodium and potassium from coal. The concentration of nitric acid used for the leaching process was varied over three levels: 0.5N, 1N and 2N. The process of leaching alkali elements from coal is surface-diffusion controlled. When the nitric acid concentration is low, the solvent is not strong enough to penetrate to the core of the coal particles and hence the removal efficiency is low. When the concentration of nitric acid is increased, the reaction rate increases, the levels of oxides and hydroxides of sodium and potassium also increase, and better removal is achieved. Increasing the concentration of nitric acid beyond 2N does not lead to significant increase in leaching percentage as seen in preliminary studies. The higher limit of concentration was therefore kept at 2N for nitric acid solution.

Scale-Up Strategy

Scaling-up of an ultrasound-assisted leaching system aims to achieve maximum removal of alkali from industrial-use volumes of coal in the minimum time possible, so that it does not represent the rate determining step in the process. The reagent used also needs to be optimal for the process to be feasible, while alleviating environmental

concerns. Ultrasound technology would also be beneficial in removal of sulfur and ash using the same solvents that are used for alkali. It would therefore enable a complete clean-up of coal and hence, better energy efficiency and increased Gross Calorific Values. Though economic factors play a major role in scaling-up, viability and feasibility also need to be ensured.

Sonication of coal also contributes to various combustion process improvements besides direct benefits such as de-ashing, de-sulfurization and de-alkalization. Sonication increases the surface area by promoting particle breakage, and fine particle separation using froth-flotation technique is also enhanced. Vujnovic (1996) developed a sono-technology designed to be retrofitted into an existing system and did not require any modifications in the existing flow scheme of the power plant. To apply this technology to power plants, he conducted six tests across three different coal cleaning plants. It is noteworthy that the clean coal yield increased considerably, and that the ash and sulfur content of coal decreased in all the tests conducted. The quality of residue also improved, hence making disposal easier. In the method prescribed in the patent, coal is passed through a conduit vertically and ultrasound is applied to it. This process contains three parts: combining coal with water to form a slurry, passing the slurry through the conduit, applying ultrasound to separate ash and sulfur, and separating the clean coal from sulfur and ash using equipment such as cyclone separators or vibratory screens. The same method can be used for alkali removal as well after making slight modifications to the process, so that leaching of alkali also takes place along with sulfur and ash.

The experiments conducted at laboratory-scale made use of coal ground to ~210 microns size and this matches with industrial coal as well. The coal is then mixed with the chosen solvent and made up to 100ml. This solution is placed in an ultrasonic bath type system and operated at various frequencies and varying periods of time to check their effectiveness. Between a probe-type and a bath-type ultrasonic system, the probe-type is slightly disadvantageous compared to the latter because the energy transferred

to the system is not very uniform. Hence, the tank-type ultrasonic system is chosen for this study.

It was also observed in laboratory scale experiments that pulsed mode of operation provided better results in leaching of coal as against continuous mode due to the high shear energy and turbulence caused during each pulsing cycle, as well as the periodic relocation of “hot spots”. Therefore, a pulsing cycle of 5s was chosen for the scale-up experiments as well. 360 kHz frequency was chosen for this study owing to the fact that the highest leaching percentage was achieved at this frequency in laboratory tests. The experimental matrix employed for the scale-up study (Phase I) using different volumes of the reagent and coal is given in Table 7. The specifications of various ultrasonic tanks utilized in the lab-scale trial are shown in Table 8.

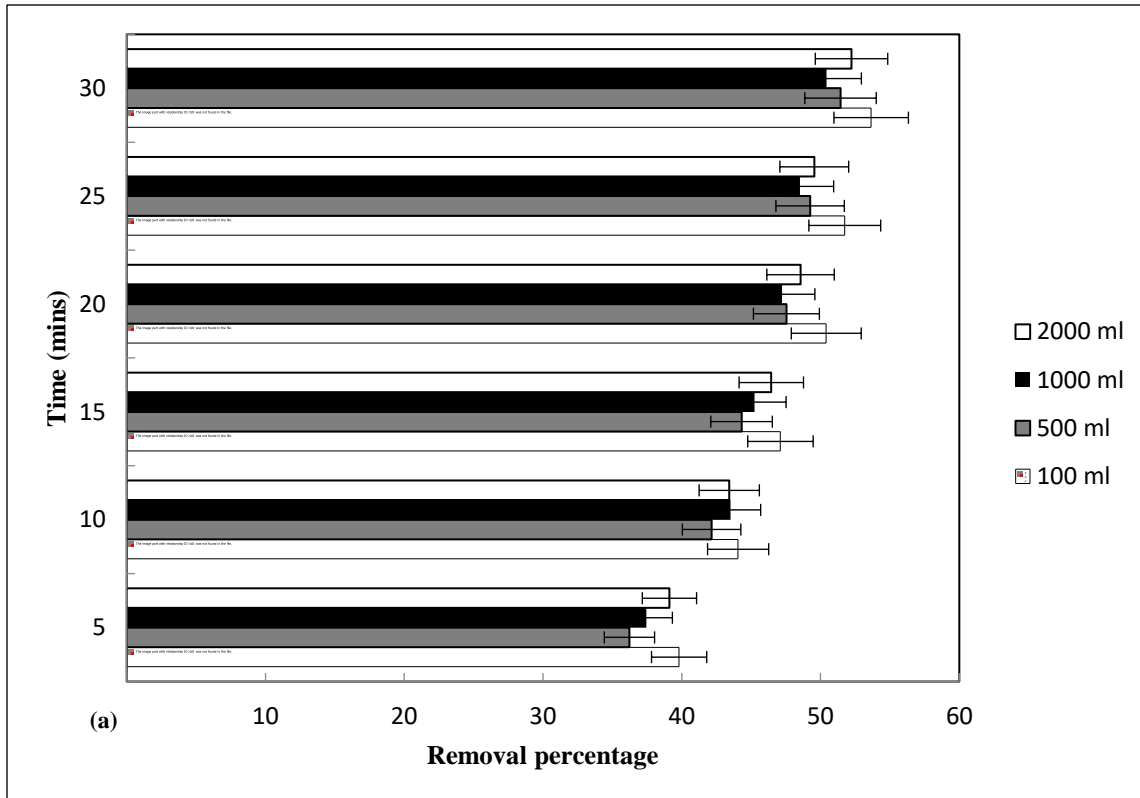
Four different coal quantities were chosen for this study: 10g, 50g, 100g, 200g. Coal-to-reagent volume was maintained in the ratio 1:10. The results are shown in Figures 15 and 16. It can be seen from the results that for 10 g of coal, the sodium leaching percentage stood at 39.8% at 5 minutes of exposure, and it increased to 53.6% at 30 minutes of exposure to ultrasound. For 100 g and 1000 ml of solution, sodium and potassium leaching stood at 50.4% and 61.1%, respectively. Comparable results were obtained for 200g of coal where the sodium leaching was found to be 39.1% and 52.2% at 5 minutes and 30 minutes of exposure, respectively. This shows that ultrasound-assisted leaching of coal can be scaled-up.

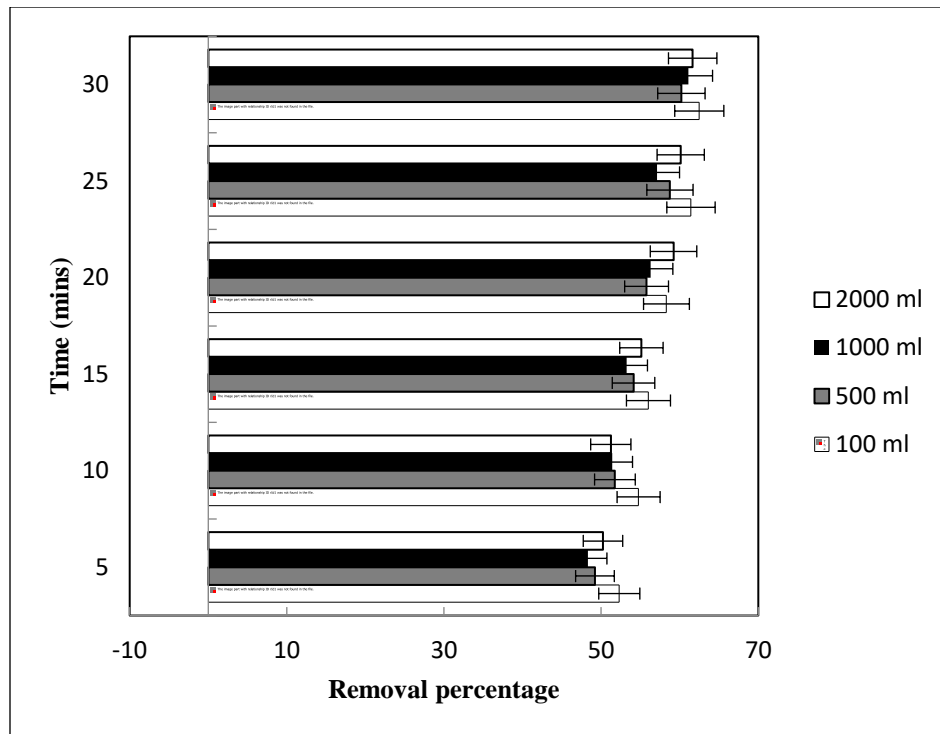
Table 7: Coal quantities and reagent volumes used in Phase I

S.No.	Coal quantity (g)	Total reagent volume (ml)
1	10	100
2	50	500
3	100	1000
4	200	2000

Table 8: Specifications of ultrasonic tanks used

Frequency	(in. x in. x in.)	Generator required(W)
25 kHz	10x14x10	500
40 kHz	10x14x10	750
58/192 kHz dual	11x12x8.5	600
360 kHz	12x18x12	600
1 MHz	10x8x8.5	600





(b)

Figure 15: Scaling-up of ultrasonic leaching of coal for various reagent volumes showing (a) Sodium leaching percentage (b) Potassium leaching percentage.

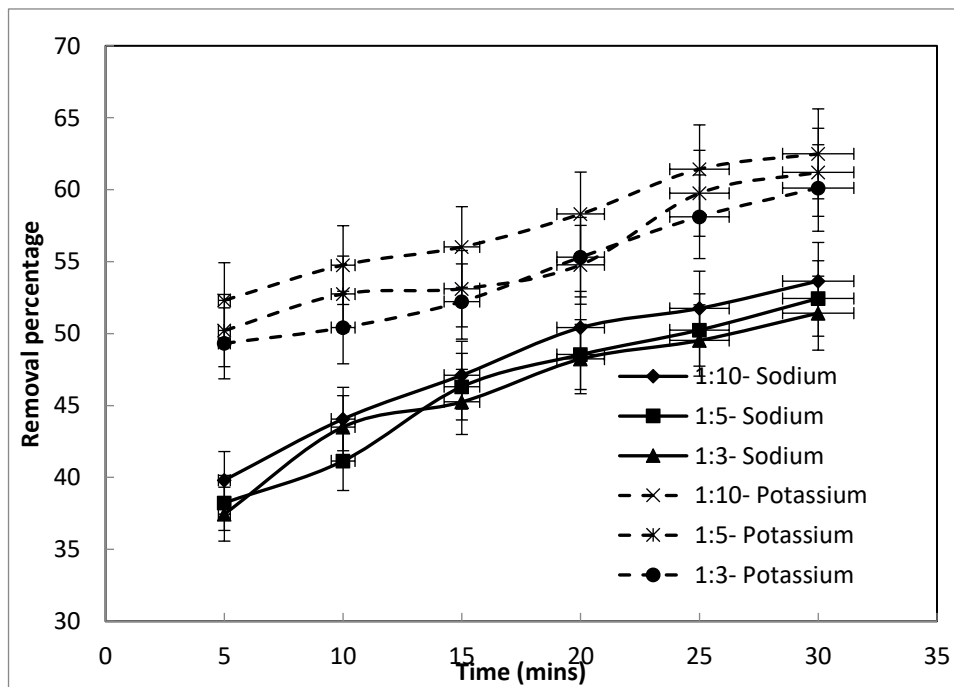


Figure 16: Leaching percentage of Sodium and Potassium for various solid liquid ratios.

The 360 kHz tank used for scale-up studies has a capacity of 42.5 l. An ultrasonic tank can be filled up to three-fourth its capacity to function efficiently. Therefore, 31.875 l of liquid can be filled in the 360 kHz tank for the present purpose. For a solid-liquid ratio of 1:10, 3.187 kg of coal can be processed for 30 minutes of operation. The next objective as part of scale-up, Phase II, was to increase the solid-liquid ratio so that a larger amount of coal can be sonicated in the same time. Three ratios were chosen: 1:3, 1:5 and 1:10. The coal quantity and reagent volume are tabulated in Table 9.

Table 9: Coal quantity and reagent volume used.in Phase II

S.No.	Coal quantity (g)	Total reagent volume (ml)
1	10.0	100
2	20.0	100
3	33.3	100

The results are presented in Figure 17. The continuous lines indicate sodium removal percentages and dotted lines indicate potassium removal percentages. Leaching efficiency is measured at an interval of every five minutes, and removal percentage for three different solid-liquid ratios are plotted against time for a maximum exposure of 30 minutes. The experiments were performed thrice to check for repeatability. It can be seen from the graph that although the highest removal percentage of both sodium and potassium is recorded for a solid-liquid ratio of 1:10, a solid-liquid ratio of 1:3 gives comparable and satisfactory results as well.

For a solid-liquid ratio of 1:3, the minimum leaching efficiency of sodium was found to be 37.4% and maximum was observed at 51.4%, compared to a solid-liquid ratio of 1:10 where the minimum and maximum efficiency was 39.8% and 53.6%, respectively. For potassium, the minimum and maximum leaching percentage for a S/L ratio of 1:10 was found to be 52.3% and 62.5% and for a S/L ratio of 1:3, it was 49.3% and 60.1%, respectively. The lowest leaching efficiency in all the cases was observed at 5 minutes of exposure to ultrasound, and the highest leaching efficiency at 30 minutes of

exposure. A solid-liquid ratio of 1:3 would therefore be adequate to obtain satisfactory results while scaling-up. For a solid-liquid ratio of 1:3, and for a liquid hold-up of 31.875l, the amount of coal that can be cleaned would amount to 10.625 kg in 30 minutes.

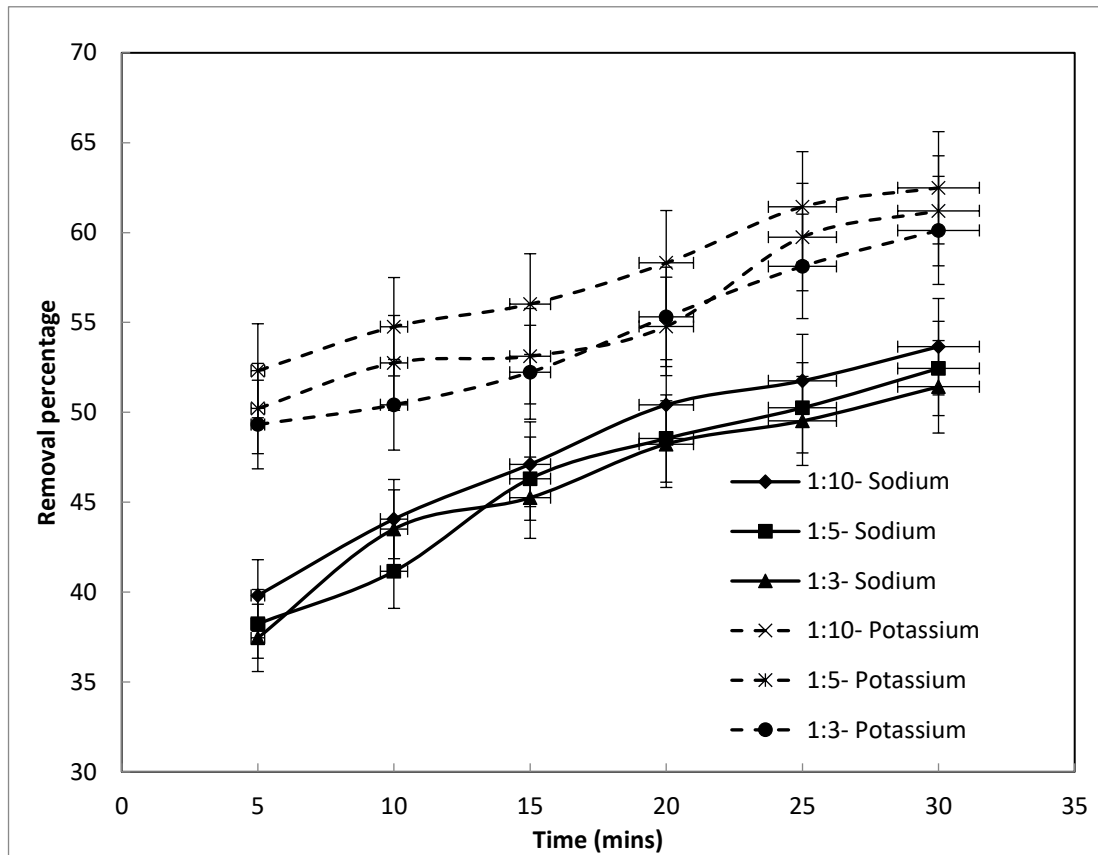


Figure 17: Leaching percentage of Sodium and Potassium for

The transducer and generator in the ultrasonic tank are sensitive to heat, and any overheating of the electronic components may lead to damage of the equipment itself. It is therefore advisable to allow a small cooling off time between experiments/ runs to prevent any irreversible damages to the tank and its parts. Considering a cooling time of 15 minutes between runs, the calculations have been done in Table 10. It is evident that around 340 kg of coal can be processed in a day considering a cooling time of 15 minutes between each cycle. If the temperature of the transducer and generator are strictly controlled, up to 510 kg of coal can be processed in a day by doing away with

the equipment cooling time. If many such tanks can be installed and run simultaneously on an industrial scale, that would correspondingly increase the amount of coal that can be processed. It is possible, therefore, to envisage tons per day of processing capacity with sonication applied.

Scale-up of ultrasound-assisted alkali leaching of coal is thus feasible and should be pursued further. Compared to conventional leaching methods where the samples are exposed to reagents for prolonged periods of time, ultrasound provides a good solution for removal of alkali from coal in the minimum time possible with minimum utilization of solvents. The results are encouraging, and call for large scale trials with either bigger ultrasonic tanks or multiple small tanks where large amounts of coal can be processed at a time. These would go a long way in effective removal of ash, sulfur and alkali from coal, providing an increase in its gross calorific value and minimizing fouling, erosion and corrosion problems downstream.

Table 10: Amount of coal that can be processed in a day

Volume of the ultrasonic tank	42.5 l
Liquid hold-up (3/4 th the volume of tank)	31.875 l
Amount of coal processed in 30 mins (1:10 S/L ratio)	3.187 kg
Amount of coal processed in 30 mins (1:3 S/L ratio)	10.625 kg
Cooling time between cycles	15 mins
No. of cycles per day	32
Amount of coal that can be processed in a day	340 kg

PROCESS INTENSIFICATION & COST IMPACT FACTORS

The general definitions of Process Intensification Factor (PIF) and Cost Impact Factor (CIF) are as follows:

PIF = Enhanced value of process parameter (e.g., ash content in sono-processed coal)/ Baseline Value (e.g., ash content in normally-processed coal)

CIF = Cost Associated with Intensified Process/ Baseline Cost

PIF/CIF = Intensification per unit delta cost

The ratio (PIF/CIF) is a key parameter in the business decision of whether to intensify the process or not. For the cases of ash, sulfur and alkali removal coal through sonication, these parameters may be estimated as given in Table 11.

Table 11: PIF, CI and their ratios for Ash, Sulfur and Alkali removal from coal via sonication

Process	PIF	CIF	Ratio
Ash removal	$48/8 = 6$	1.2	5
Total Sulfur Removal	$80/10 = 8$	1.6	5
Alkali Removal	$60/6 = 10$	2.0	5

Interestingly, to a rough approximation, the eco-viability of ultrasonic enhancement to coal wash is the same whether the impurity of concern is ash, sulfur or alkalis—or indeed all of them. In order to do a fair comparison of PIF and CIF, however, both must be evaluated in equivalent—i.e., financial—terms. The improvement in profits for an operating power plant due to a 6X reduction in ash, 8X reduction in total sulfur, or 10X reduction in alkali is a little more nebulous. It certainly does not lend itself to generalization. The methodology is made clear here, and must be rigorously applied in

every case where process intensification, via ultrasound or other means, is being contemplated.

ACKNOWLEDGMENTS

The contribution of ultrasonic systems utilized in this study by Crest Ultrasonic Corporation (Trenton, New Jersey, USA) is gratefully acknowledged. The coal samples employed were provided by Bharat Heavy Electricals Ltd. (BHEL), Trichy, India, and Central Power Research Institute (CPRI), Bangalore, India.

BIBLIOGRAPHY

1. Ambedkar, B., "Ultrasonic Coal-Wash for De-Ashing and De-Sulfurization: Experimental Investigation and Mechanistic Modeling", Ph.D. Thesis, Indian Institute of Technology Madras, 2011
2. Castro, M. and A. Hoyos, "Study of the onset of the acoustic streaming in parallel plate resonators with pulse ultrasound.," *Ultrasonics*, Vol. 66, 2016, pp. 166-171
3. Lorimer, J.P., Mason, T.J., and Fiddy, K., "Enhancement of chemical reactivity by power ultrasound: an alternative interpretation of the hot spot", *Ultrasonics*, 29, (1991), pp. 338-343
4. Luche, J.L., "Effect of ultrasound on heterogeneous system", *Ultrasonics Sonochemistry*, 1, (1994), pp. 111 – 118
5. Mason, T.J., Lorimer, J.P., and Bates, D.M., "Quantifying sonochemistry: Casting some light on a black art", *Ultrasonics*, 30, (1992), pp. 40 – 42
6. Ratoarinoro, N., Contamine, F., Wilhelm, A. M., Berlan, J. and Delmas, H., "Activation of a solid-liquid chemical reaction by ultrasound", *Chemical Engineering Science*, 50, (1995), pp. 554-558
7. Srivalli, H., "Mechanistic Study of Leaching of Sodium and Potassium from an Indian Coal Using Ultrasonic and Additive Methods", Ph.D. Thesis, Indian Institute of Technology Madras, 2019
8. Srivalli, H. and Nagarajan, R. (2019). Mechanistic study of ultrasound-assisted solvent leaching of sodium and potassium from an Indian coal using continuous

and pulsed modes of operation. *Chemical Engineering Communications*, 206(2):207–226. doi: 10.1080/00986445.2018.1481833

9. Suslick, K.S., “Ultrasound: Its chemical, physical and biological effects”, VCH: New York, (1988)
10. Vetri Murugan, R. and R. Nagarajan, “Pulsed ultrasonic mixing: An experimental study,” *Chem. Eng. Res. Des.*, Vol. 86, No. 5, 2008, pp. 454–460
11. Vujnovic, J.B., “Apparatus and method for the beneficiation of ore and coal with the aid of ultrasound”, U.S. Patent 5,577,669, November 26, 1996