



## Ultrasonic coal-wash for de-sulfurization

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### ARTICLE INFO

#### Article history:

Received 3 February 2010

Received in revised form 1 September 2010

Accepted 9 September 2010

Available online 17 September 2010

#### Keywords:

Power Ultrasound

Cavitation

Streaming

De-desulfurization

### ABSTRACT

Coal is the one of the world's most abundant fossil fuel resources. It is not a clean fuel, as it contains ash and sulfur. SO<sub>x</sub> as a pollutant are a real threat to both the ecosystem and to human health. There are numerous de-sulfurization methods to control SO<sub>2</sub> emissions. Nowadays, online flue gas de-sulfurization is being used as one such method to remove sulfur from coal during combustion. The biggest disadvantage associated with this method is formation of by-products (FGD gypsum). A way for effective usage of FGD gypsum has not yet been found. This will lead to acute and chronic effects to humans as well as plants. Power ultrasound can be used for the beneficiation of coal by the removal of sulfur from coal prior to coal combustion. The main effects of ultrasound in liquid medium are acoustic cavitation and acoustic streaming. The process of formation, growth and implosion of bubbles is called cavitation. Bulk fluid motion due to sound energy absorption is known as acoustic streaming. In addition, coupling of an acoustic field to water produces OH radicals, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, ozone and HO<sub>2</sub> that are strong oxidizing agents. Oxidation that occurs due to ultrasound is called Advanced Oxidation Process (AOP). It converts sulfur from coal to water-soluble sulphates. Conventional chemical-based soaking and stirring methods are compared here to ultrasonic methods of de-sulfurization. The main advantages of ultrasonic de-sulfurization over conventional methods, the mechanism involved in ultrasonic de-sulfurization and the difference between aqueous-based and solvent-based (2 N HNO<sub>3</sub>, 3-volume percentage H<sub>2</sub>O<sub>2</sub>) de-sulfurization are investigated experimentally.

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### 1. Introduction

Coal is the one of the world's most abundant fossil fuel resources. It is not a clean fuel, as it contains ash and sulfur. SO<sub>x</sub> 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. Sulphate-sulfur occurs in combination with either Ca or Fe. The hydrated calcium sulphate remains in the ash during combustion and does not contribute to SO<sub>x</sub> pollution. Iron sulphate is water-soluble and is readily removed during coal cleaning. The amount of sulphate-sulfur increases with weathering. Pyritic-sulfur refers to iron disulfide (FeS<sub>2</sub>) as pyrite, marcasite and melnikovite-pyrite. Organic-sulfur is chemically bonded and very difficult to remove by physical cleaning methods.

Methods to control SO<sub>2</sub> emissions may be classified as:

1. De-sulfurization of coal prior to combustion (Physical, Chemical, Microbial).
2. The removal of sulfur oxides during combustion.
3. The removal of sulfur oxides after combustion.

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 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 De-sulfurization (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 effective usage of all FGD gypsum generated as by-product.

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 [1]. Concentrations of elements in soil, soil water, plant tissue and earthworms were measured. Results indicate that concentrations of Ca and S increased in plant tissue, soil, and soil water and the concentrations of Al and Fe decreased in plant tissue by both gypsums. This will lead to acute

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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.

### 1.1. Ultrasonic methods

Power ultrasound can be used for the beneficiation of coal by the removal of sulfur from coal prior to coal combustion. In overseas power plants, ultrasonic method of coal wash is in practice. However, in India, such advancement in coal washeries is not present, even though India has high ash and sulfur coal. Ultrasonic coal wash method removes ash as well as sulfur from coal. This will reduce the unnecessary cost for transportation, as well as for storage, of coal prior to combustion. The main effects of ultrasonic vibration in liquids are acoustic cavitation and acoustic streaming. Cavitation is due to implosion of bubbles in the acoustic field, and resulting transmission of a shock wave. Whenever ambient pressure is reduced, the boiling point of a liquid is also lowered. If the pressure is reduced far enough, the liquid will begin to boil without needing to be heated (as the boiling point is reduced to below room temperature). When this happens on a small scale, due to localized pressure reduction, small bubbles of vapor are formed. The subsequent collapse of these bubbles during the compression cycle is called cavitation. Acoustic streaming is caused by unidirectional flow currents in a fluid caused by the presence of sound waves. There are two mechanisms in effect when ultrasound is coupled to the coal slurry: (1) physical breakage, which breaks the physical bonds between sulfur and coal; and (2) leaching, which removes some of the impurities by a mass transfer mechanism. In conventional coal de-sulfurization, the main focus is on surface cleaning, with little penetration to the interior part of the coal matrix. Ultrasonic coal de-sulfurization is a prime technique for removal of sulfur from surface and interior part of the coal matrix.

## 2. Literature review

This review addresses work on ultrasound-assisted coal de-sulfurization already initiated by other researchers. The second part of the review includes the mechanism of ultrasound in aqueous medium and its contribution towards high-sulfur coal de-sulfurization. Finally, the existing conventional chemical-based de-sulfurization methods and their demerits relative to ultrasonic methods are reviewed.

### 2.1. Ultrasonically enhanced de-sulfurization

Very few researchers have focused on ultrasonic coal de-sulfurization. Existing literature failed to explain the mechanisms involved in ultrasound-assisted coal de-sulfurization. Conclusions drawn by researchers are very general in nature. The ultrasonic de-sulfurization methods studied are either aqueous or chemical based. The biggest advantage of ultrasonic method is simultaneous removal of ash and sulfur. Zaidi [2] investigated ultrasound-promoted de-sulfurization of low-rank coals with dilute solutions of sodium hydroxide (0.025–0.2 M) at 30 and 70 °C. The sulfur removal was higher for samples sonicated at a lower temperature. The shear forces produced by the ultrasound energy are responsible for exposing the finely disseminated sulfur sites in coal to alkali attack. However, the mechanism involved in the interaction between sonication and dilute sodium hydroxide is not explained.

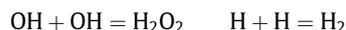
Ze et al. [3] investigated the enhancement of de-sulfurization and de-ashing of coal. One hundred grams of Zibo coal and 300 ml of water mixture were sonicated for 10 min using 20 kHz frequency and 200 W power. Then, the sample was wet screened. The same procedure was followed without sonication. Yield, sulfur and ash analysis were performed, and results revealed that ultrasonic conditioning can drive physical separation of pyrite and refuse from coal. On the other hand, ultrasonic conditioning can change the surface of the coal and pyrite particles, and increase the hydrophobicity of slime and the hydrophilicity of pyrite and refuse. For a 1.3 kg/t flotation agent-to-coal ratio, the perfect index of flotation, the perfect index of de-sulfurization and the percentage of de-sulfurization after ultrasonic processing increased by 22.51%, 25.36% and 2.49%, respectively. It may be concluded that ultrasonic conditioning can, in general, enhance the performance of coal flotation methods used for de-sulfurization and de-ashing.

### 2.2. Ultrasound in aqueous medium

Ultrasound is cyclic sound pressure with a frequency greater than the upper limit of human hearing. It starts from the frequency of 20 kHz. Ultrasound behaves differently in liquid and liquid–solid media compared to gas medium. Ultrasound in aqueous medium produces highly reactive species such as OH radicals, H<sub>2</sub>O<sub>2</sub> and ozone that are strong oxidizing agents of high oxidation potential (2.8, 1.8 and 2.1 V, respectively). These radicals are capable of initiating and enhancing oxidation and reduction reactions. Oxidation occurring due to ultrasound is called “Advanced Oxidation Process” (AOP). Sonication enhances mass transfer and chemical reaction, and is expected to reduce or eliminate chemical usage, resulting in minimum disposal problems. Lindstorm et al. (1951) first suggested the mechanism for this reaction, followed by many researchers who proved it in different manners by experiments. Webster (1963) [4] explained the cavitation mechanism as follows: two classes of chemical effect are induced by ultrasonic cavitation. The first is the acceleration of reactions, and the second class of effect is the initiation of reactions that would not otherwise occur; this takes place predominantly in an aqueous medium. Under the action of cavitation, water decomposes into free radicals.



The predominant back reactions attendant on this process are



The products of these reactions are then responsible for secondary reactions involving dissolved substances. The reacting ions or molecules will be selectively subjected to reduction or oxidation according to their properties and structure. The oxidation of dissolved substances is detectable in the absence of dissolved oxygen. In its presence, the rate of formation of hydrogen peroxide is increased, with a consequent increase in the rate of oxidation; this effect has been attributed to the occurrence of the reaction



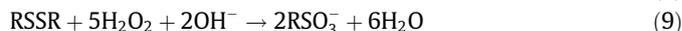
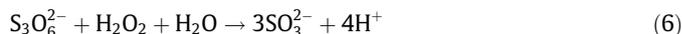
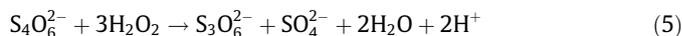
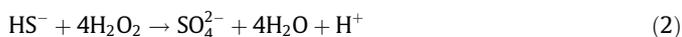
Makino et al. (1982) [5] reported that intense ultrasound causes chemical damage through the phenomenon called cavitation. Cavitation produces high local instantaneous temperatures, pressures, and sonoluminescence. In sonolysis studies of aqueous solutions, it is proposed that hydroxyl radicals (OH<sup>•</sup>) and hydrogen atoms (H) are produced by ultrasound. Riesz et al. (1985) [6] were able to observe by spin traps the highly reactive radicals produced during cavitation. Christman et al. (1987) [7] found experimental evidence for free radicals produced in aqueous solutions by using electron spin resonance method (ESR). In 1994, Misik et al. [8] conducted spin trap and electron spin resonance studies to investigate free radical formation and sono-chemical reactions in organic liquids

using 50 kHz frequency of ultrasound. Margulis [9] proposed that the fundamental problem in sonochemistry and cavitation is that hot-spot theory is not sufficient to elucidate the mechanism involved. A new electrical theory has been proposed and validated with experiments, with the electric field developed during cavitation mechanism being identified as a contributor for enhancing the sono-chemical reaction. Entezari et al. [10] conducted an experiment to explain the effect of frequency on sono-chemical reactions. The effect of sonication on iodide oxidation in presence of an air and argon atmosphere using two extreme frequencies (20 and 900 kHz) was investigated. The rate of sonochemical oxidation in an aqueous solution is about three times faster in an air atmosphere compared to argon environment. The  $H^+$ ,  $OH^-$  and  $H_2O_2$  produced by the ultrasound in an aqueous solution are responsible for the oxidation reaction. Luche et al. [11] investigated sono-chemical reactions occurring in a heterogeneous system. Jana et al. [12] made an estimation of hydroxyl free radicals produced by ultrasound in Fricke solution using Fricke dosimeter. The dose–response relation was found to be linear for different intensities of ultrasound. 20 kHz frequency ultrasound produces 14 times more hydroxyl radicals than those produced by 3.5 MHz. Henglein et al. [13] stated that the free radicals produced by the cavitation effect are responsible for reaction. The OH radicals produced by the ultrasound are strong oxidation agents and lead to  $H_2O_2$  formation.

Hoffmann et al. [14] investigated sonochemical degradation of organic compounds present in water. Three distinct pathways of sonochemical degradation of organic compounds by acoustic cavitation have been proposed. (i) Oxidation by hydroxyl radicals, (ii) pyrolytic decomposition and (iii) supercritical water oxidation. Gogate et al. [15] analyzed and mapped sono-chemical reactors by experimental verification. Generalized correlations were developed for effective design and scale-up of sono-chemical reactors. Decomposition of potassium iodide was taken as a model reaction; iodine liberation from the reaction is only by cavitation effect, and not by shear temperature and pressures. This is because free  $OH^-$  radicals are formed in the solution only under cavitating conditions. Controlling reduced sulfur compounds by using hydrogen peroxide has been investigated and reported [16]. Hydrogen peroxide combines advantages not obtainable with any other single form of chemical control. It is cost effective and specific, forming no toxic byproducts. It is safe to work with when handled properly, and produces soluble sulphates, thus avoiding the sludge problem. Hydrogen peroxide has been used for industrial purposes for a long time because of its physical and chemical nature, i.e., low freezing point, unlimited solubility in water, and reactivity.

### 2.2.1. Possible reactions between sulfur compound and hydrogen peroxide

Eqs. (1)–(3) show reactions between sulfide and hydrogen peroxide at various pH conditions. Eq. (1) represents the reaction occurring at acid pH, Eq. (2) at neutral pH and Eq. (3) at alkaline pH. Since hydrogen peroxide is a strong oxidizing agent, it converts all sulfides into soluble sulphates. The oxidation of thio-sulphates by hydrogen peroxide proceeds through a series of reactions (Eqs. (4)–(7)), forming tetrathionates, then trithionates, then sulphites, and finally sulphates. Regardless of pH, sulphites (Eq. (7)) react with hydrogen peroxide to form sulphates.



This reaction between sulphites and hydrogen peroxide is fast, requires no catalyst, and uses relatively little peroxide. Mercaptans and disulfides (Eq. (8) and (9), respectively) are the sulfur analogs of alcohols, containing the  $-SH$  (sulfohydryl) group. They react with hydrogen peroxide in alkaline conditions to form disulfides. Disulfides generally form an insoluble oil layer that is easy to separate. Disulfides also react with hydrogen peroxide to form sulfonic acid.

Given the wealth of data available in literature pertaining to formation of free radicals in water irradiated with ultrasonics, no specific attempt was made as part of this study to confirm or quantify the presence of such species. Instead, this study focuses on the physical aspects of ultrasonic de-sulfurization, namely cavitation, streaming and their combined effects. Since the ultrasonic systems used in this study are state-of-the-art with respect to energy transmission and uniformity characteristics, it was felt that the emphasis in the study should be placed on ultrasonic field parameters such as frequency and amplitude.

### 2.3. Conventional chemical-based coal de-sulfurization

From Table 1, it is apparent that researchers are still looking for ways to maximize coal sulfur removal, and to optimize the operating conditions by choosing suitable solvents. Using chemical-based coal de-sulfurization methods, one could achieve considerable amount of sulfur removal at the expense of more solvent usage and treatment time. At the end of treatment process, more difficulties in neutralizing the chemically-doped coal sample are encountered. These factors have motivated researchers to find alternatives to conventional chemical-based de-sulfurization. Ultrasound-based de-sulfurization is one such technique to achieve maximum removal with minimal solvent use and minimum treatment time. In addition, it is easy to scale-up as a continuous process.

## 3. Experimental details

### 3.1. Experimental setup

The ultrasonic system (Fig. 1) has three components. (i) Ultrasonic generator, (ii) ultrasonic transducer and (iii) tank with liquid. 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 operative frequency of the transducer. The transducer transforms these electric oscillations to mechanical sound waves.

Sectrex Laser Particle Counter (Fig. 2) is used to measure the particle size. Utilizing the principle of “near angle light scatter”, a revolving laser beam passes through the walls of a glass container of a flow-through cell. When it is directed through a central “sensitive zone” the PC-2200 not only counts the particles in suspension, but tabulates their size as well. The analog signals generated by the light pulses are routed to a computer and digitized.

### 3.2. Experimental procedure

As-received coal was ground to  $-212 \mu m$  size and air-dried. The proximate analysis of the coal samples was performed using IS 1350 procedure. De-sulfurization experiments were carried out by conventional soaking, agitation and ultrasonic methods. Sieve

**Table 1**  
Literature on conventional chemical-based coal de-sulfurization.

Author	Title	Reagent used	Treatment condition	% Removal
Moran et al. [17]	Bio-de-sulfurization of coal	Thiobacillus	51 days	30% of total sulfur
Mukherjee et al. [18]	Chemical demineralization/de-sulfurization of high-sulfur coal using sodium hydroxide and acid solutions	Sodium hydroxide & Sodium hydroxide followed by HCl	More than 8 h at 90–95 °C	Entire inorganic sulfur and 10% of organic sulfur
Balaz et al. [19]	Chemical treatment of coal by grinding and aqueous caustic leaching	10% NaOH	2 h at 90 °C	50% of total sulfur
Ahnonkitpanit et al. [20]	Coal de-sulfurization in aqueous hydrogen peroxide	aqueous hydrogen peroxide/ sulphuric acid solution	2.30 h	Complete removal of organic and pyritic sulfur
Riley et al. [21]	Comparison of sulfur in HNO <sub>3</sub> -extracted and physically-cleaned coal	2 M HNO <sub>3</sub>	30 min at boiling condition with constant stirring	25–78.5% of total sulfur
Sain et al. [22]	De-sulfurization of Assam coal by chlorinolysis and hydrothermal techniques	CCl <sub>4</sub> & water with continuous exposure of chlorine gas	4 h at 80 °C	56.5% of total sulfur
Schuetz et al. [23]	Fine coal de-sulfurization by leaching with bromine containing hydrobromic acid	Bromine in hydrobromic solution (0.5–2.5 M)	10–30 min at 100–120°C	67% of total sulfur
Prem et al. [24]	Radiolytic desulphurization of high-sulfur coals	Gamma rays irradiation	58 × 10 <sup>4</sup> , 175 × 10 <sup>4</sup> & 250 × 10 <sup>4</sup> Gy	47.3% of total sulfur
Sinha et al. [25]	Removal of sulfur from coal by air oxidation at 350–450 °C	Air oxidation	10–60 min, at 350–450 °C	90% of Pyritic sulfur
Kara et al. [26]	Removal of sulfur from four Central anatolian lignites by NaOH	Molten caustic	15–60 min at 300–450 °C	47–83% of Total sulfur & 77–91% of ash
Lee et al. [27]	Selective pre-combustion de-sulfurization of Ohio coals using supercritical fluids	Methanol–water mixture	70 ml/hr	37–44% of Total sulfur
Kusakabe et al. [28]	Simultaneous de-sulfurization and demineralization of coal	Molten NaOH and KOH	1 h at 623 K	90% of Total sulfur and ash
Nicholas et al. [29]	Solvent effects in coal de-sulfurization chlorinolysis near ambient temperature	Chlorinated water, CCl <sub>4</sub> /Methanol mixture	0.3 g/min, 2–3 h at various temperatures	70% of Inorganic sulfur and 44% of organic sulfur
Liu et al. [30]	De-sulfurization of coal via low temperature atmospheric alkaline oxidation	0.25 M NaOH & aeration at 0.136 m <sup>3</sup> /hr	4 h at 90 °C	73% Organic, 83% sulphate, 84% pyritic
Ratanakandilok et al. [31]	Coal de-sulfurization with methanol/water and methanol/KOH	Methanol–water & Methanol–KOH	15–90 min & 120–180 °C	36–74% Pyritic, 20–42% organic & 33–62% of total sulfur



**Fig. 1.** Ultrasonic tank.

(212 μm) passing-through high-sulfur lignite coal was taken for de-sulfurization experiments. Water, 2 N HNO<sub>3</sub> and 3-volume percentage H<sub>2</sub>O<sub>2</sub> were used as a solvent. The reagents used were of analytical grade. The mixture was subjected to soaking/stirring/sonication. Then, the treated sample mixture was filtered, washed with water and dried for about 5 h in an oven at 100 °C. The treated



**Fig. 2.** Laser Particle Counter.

coal sample was analyzed for sulfur content according to the procedure given in IS 1350.

### 3.3. Basic composition of coal

The proximate and sulfur analysis of coal is shown in Tables 2 and 3.

**Table 2**  
Proximate Analysis of as-received lignite coal (wt.%).

Moisture	Volatile matter	Fixed carbon	Ash
17.86	26.77	36.47	18.9

**Table 3**  
Different forms of Sulfur (wt.%).

Total sulfur	Sulphate sulfur	Pyritic + organic sulfur
5.034	2.448	2.586

## 4. Results and discussion

### 4.1. Ultrasonic aqueous de-sulfurization

The experiments were conducted for 20 g of 212  $\mu\text{m}$  sieve pass-through high-sulfur lignite in 500 ml of water using probe-type and tank-type sonicator. Probe-type of 20 kHz frequency and tank-type of 25, 58/192 (dual), 132, 430 kHz frequencies was used. Experiments were conducted for about 60 min and 500 W power (excluding the dual system, where low and high frequency-coupled ultrasonics are used. Each frequency operates at 500 W power, and drives an alternating diagonal set of transducers).

In low-frequency ultrasound, cavitation phenomena are predominant, and particle breakage is extensive. In high-frequency ultrasound, 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 fraction of a millisecond. The collective effect due to bubble implosion will be enormous. This produces millions of micro jets that are impinging on the surface of the coal particle. This will cause particle breakage in two different ways. (i) Pitting of coal particle surface to produce fines, and (ii) forming cracks on the surface, which are widened due to prolonged exposure, finally causing breakage.

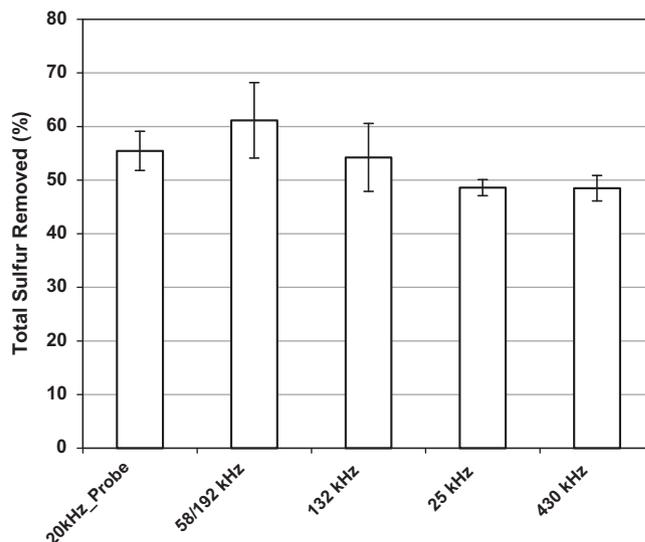
Effect of cavitation is several hundred times greater in heterogeneous than in homogeneous systems. Ultrasonic fields are transmitted much more effectively in homogeneous liquid media, as the presence of solids causes effects such as energy absorption and attenuation. While at lower frequencies, solids can (to some extent) promote cavitation by providing nucleation sites, at higher frequencies (in the >200 kHz range) where “acoustic streaming” is predominant, solids provide a significant blockage to flow, causing energy dissipation. Unlike cavitation bubble collapse in homogeneous systems (liquid–liquid interface), collapse of a cavitation bubbles 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. Cavitation is also important in case of heterogeneous systems in that most of 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.

The formation of  $\text{H}^+$  and  $\text{OH}^-$  is attributed to the thermal dissociation of water vapor present in the cavities during the compression phase. Sonolysis of water also produces  $\text{H}_2\text{O}_2$  and hydrogen

gas, via hydroxyl radicals and hydrogen atoms. The presence of oxygen improves sonochemical activities, but it is not essential for water sonolysis, and sonochemical oxidation and reduction can proceed in the presence of any gas. However, in the presence of oxygen acting as a scavenger of hydrogen atoms, the hydro-peroxy radical is additionally formed and acts as an oxidizing agent. This radical causes a number of other reactions to occur, resulting in the formation of  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{O}$ , and  $\text{H}_2$  as products. Thermal dissociation of oxygen molecule may also occur, leading to the generation of additional hydroxyl radicals. In the absence of OH scavengers, the main product of the sonolysis of water is  $\text{H}_2\text{O}_2$ .  $\text{H}_2\text{O}_2$  can also be produced in an “inert” atmosphere but only at the expense of OH radicals.

When a liquid is irradiated by ultrasound, cavitation will appear when the pressure amplitude of the applied ultrasound reaches a certain minimum. If it happens on the surface of the liquid, it consumes atmospheric air due to low pressure in an ultrasonic field. Atmospheric air consists of  $\text{O}_2$ ,  $\text{N}_2$ , and some trace gases. The nitrogen tends to undergo advanced oxidation process and form  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{HNO}_3$ . This has significant effect when the experiments conducted in a large scale, the reason being that the surface available for absorbing  $\text{N}_2$  from atmosphere is large. But, for experiments conducted in a laboratory scale, surface available for absorbing atmospheric  $\text{N}_2$  is small; hence,  $\text{HNO}_3$  formation and consequent enhancement of de-sulfurization of coal has insignificant effect.

Fig. 3 shows effect of ultrasonic frequency on total sulfur removal. The sulfur removed using 25 kHz ultrasonic system is mainly because of acoustic cavitation, which produces high surface area of particle leading to intimate contact with the oxidizing agent (OH radicals,  $\text{H}_2\text{O}_2$ , ozone) produced in the ultrasonic fields. Size distribution analysis was performed using Spectrex Laser Particle Counter (1–100  $\mu\text{m}$  size range) to see the effect of sonication on coal particle breakage with varying frequency of ultrasound. Figs. 4 and 5 show the size distribution of virgin and sonicated coal samples with two different ultrasonic frequencies – 25 kHz ultrasonic tank, and 20 kHz probe. Breakage was more predominant at low-frequency ultrasound field [32–34]. It produces very fine particle within short period (2 and 5 min) of sonication, thereby increasing surface area of coal particle, causing it to have an intimate contact with the strong oxidizing agents produced by the ultrasound in an aqueous medium. The sphericity of the particle also increases with sonication time, due to the associated micro-polishing mechanism



**Fig. 3.** Effect of ultrasonic frequency on total sulphur removal.

[33,34]. Fig. 6 shows effect of ultrasonic frequency on coal particle breakage. Low-frequency ultrasound leads to more particle breakage due to cavitation mechanism, whereas high-frequency ultrasound causes minimum particle breakage due to the gentle streaming that prevails. The 20 kHz field was emitted by a probe (nozzle), whereas 25 kHz was delivered by a tank (transducer) system. Uniformity of size reduction is much better in a tank system. This effect dominates over the slightly-higher power delivered by 20 kHz.

In the 430 kHz ultrasonic field, acoustic streaming phenomena are predominant. Acoustic streaming is caused by unidirectional flow currents in a fluid caused by the presence of sound waves, which leads to the bulk fluid motion due to sound energy absorption. This removes some of the impurities by leaching effect. The total sulfur removed in coal using 430 kHz ultrasonic system is mainly because of streaming effect. In 132 kHz ultrasonic frequency system, cavitation and streaming effect are both present, which results in a higher percentage removal for the same power input compared to the low and high-frequency systems mentioned earlier. While the dual-system has two separate 500 W generators providing input power, each generator only powers half the transducers (diagonally alternating set) in the tank. Hence, net power

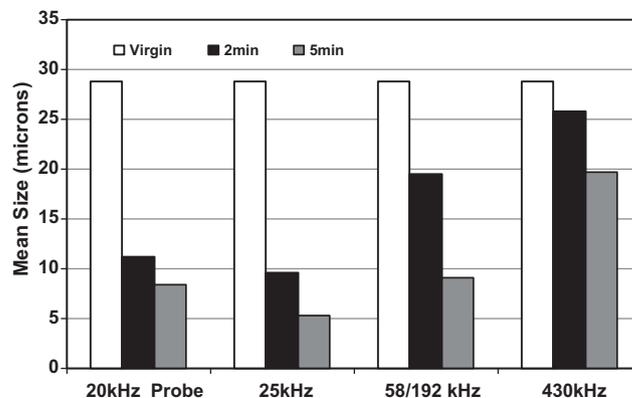


Fig. 6. Effect of ultrasonic frequency on coal particle breakage.

Table 4  
Power delivered to the reaction mixture by calorimetry.

Frequency (kHz)	Power input (W)	Slope (°C / s)	Power delivered (W)
25	500	0.0056	11.72
58/192	500	0.0052	10.88
132	500	0.0045	9.42
430	500	0.0086	18.00
20kHz_Probe	500	0.0261	54.63

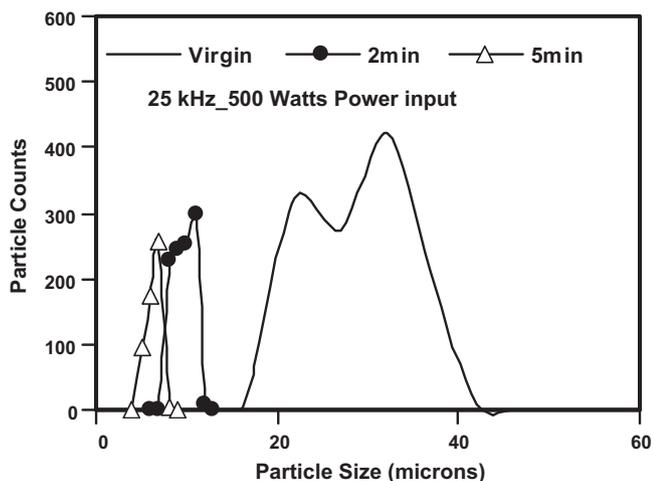


Fig. 4. Size distribution of virgin and sonicated coal sample (25 kHz tank).

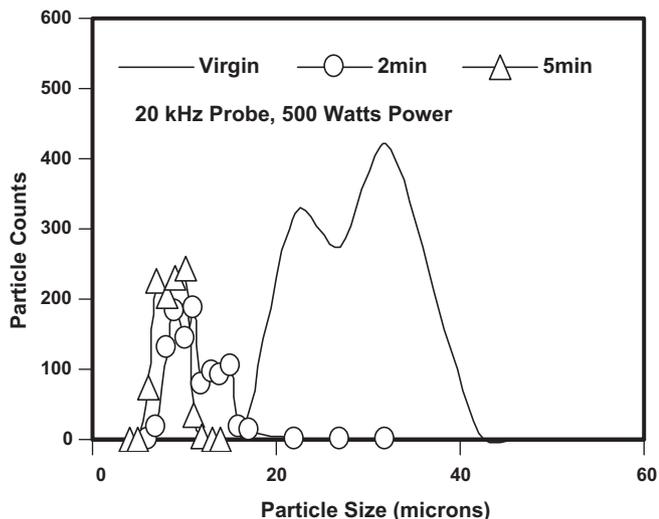


Fig. 5. Size distribution of virgin and sonicated coal sample (20 kHz probe).

input to tank remains the same in dual and single frequency systems, and is not a significant factor. In dual system, the cavitation present due to 58 kHz leads to particle breakage, while the streaming present associated with 192 kHz leaches out the contaminants. This dual mechanism effect results in highest removal of sulfur. In the 20 kHz probe-type sonicator, cavitation is dominant, and the probe is in direct contact with the sample mixture. Therefore, the energy transferred to the sample mixture is higher than in the other four cases (Table 4). It leads to higher sulfur removal compared to the other three ultrasonic tank systems with same power input.

In coal, sulfur exists in three different forms: (i) sulphate sulfur, (ii) pyritic sulfur and (iii) organic sulfur. Analysis has been performed on ultrasonically treated samples to see how the forms of sulfur are distributed after ultrasonic treatment. From Fig. 7, it is apparent that almost all the cases show 90% and above sulphate-sulfur removal. However, the pyretic and organic sulfur show high

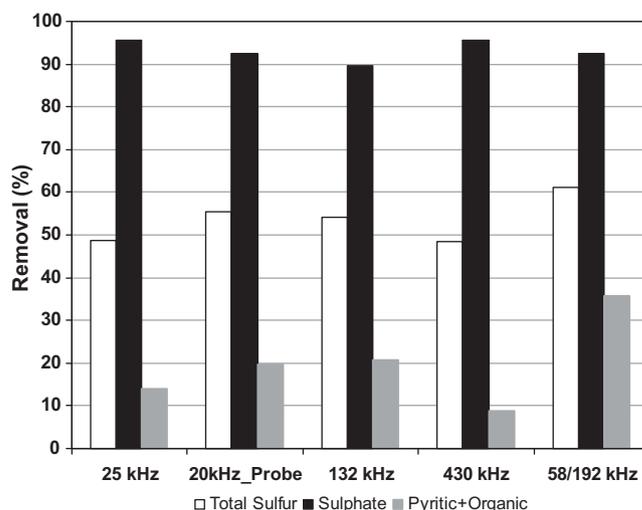


Fig. 7. Effect of frequency on different forms of sulfur removal.

resistance to ultrasonic treatment. Dual system removes about 36% of pyretic + organic sulfur removal due to coupled mechanisms (cavitation + streaming). 20 kHz probe and 132 kHz ultrasonic tank systems remove almost 20% of pyretic + organic sulfur. The former effect is due to high energy transferred to the sample mixture, whereas the latter is due to the combined effect of cavitation and streaming for the same 500 W power input. The 25 kHz ultrasonic tank system removes 14% of pyretic + organic sulfur, whereas the 430 kHz system removes only about 9% due to a single relatively-mild mechanism being in effect. In general, ultrasonic method is a time-dependant process. To intensify the ultrasonic treatment method, some insights into its kinetics is needed. Suitable solvents are to be used in order to minimize the treatment time and solvent consumption, and to maximize sulfur removal.

#### 4.2. Ultrasonically enhanced solvent de-sulfurization

In order to achieve minimum treatment time, less solvent consumption and maximum removal, solvent-based ultrasonic de-sulfurization was investigated. 2 N of nitric acid and 3-volume percentage of hydrogen peroxide were used as solvents. To assess the enhancement effect of the ultrasonic method, conventional methods of de-sulfurization were compared. The reasons for choosing the above mentioned solvent concentrations are that as per IS1350 (forms of sulfur determination) procedure, 2 N of nitric acid is used to extract entire inorganic sulfur from coal by 30 min of boiling, and higher volume percent of  $H_2O_2$  resulted in foaming and uncontrolled reactions.

##### 4.2.1. Soaking

Soaking experiments were conducted using 2 N  $HNO_3$  and 3-volume percentage  $H_2O_2$ . Ten grams of 212  $\mu m$  pass-through coal sample were soaked in 100 ml of 2 N  $HNO_3$  and 3-volume percentage of  $H_2O_2$  for about 5 h. Fig. 8 shows the effect of solvent soaking on coal de-sulfurization. The soaking of high-sulfur coal in solvents such as nitric acid and hydrogen peroxide 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 core of the particle as time progresses, thereby extending the process.

##### 4.2.2. Stirring

Ten grams of 212  $\mu m$  pass-through high sulfur lignite coal and 100 ml of 2 N  $HNO_3$  and 3-volume percentage of  $H_2O_2$  were taken for the conventional stirring process. Stirring was conducted for about 1 h at two different speeds (500 and 1000 rpm) of the stirrer. From Fig. 9, it is apparent that using nitric acid at 500 rpm, 25%

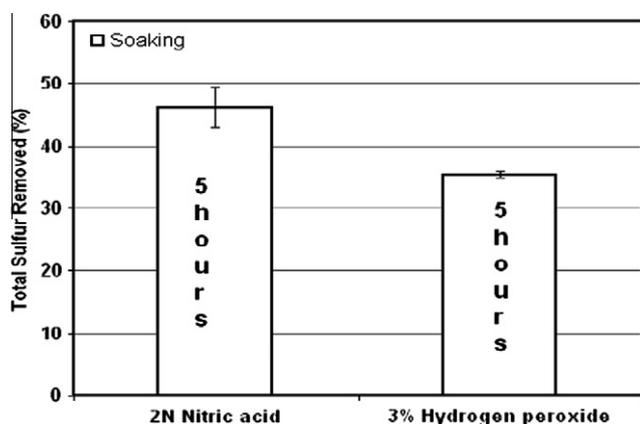


Fig. 8. Effect of solvent soaking on total sulfur removal.

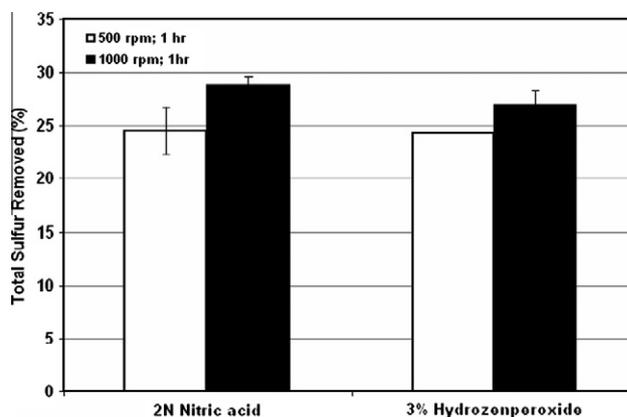


Fig. 9. Effect of solvent-based stirring on total sulfur removal.

removal and at 1000 rpm, 29% removal is possible. In the case of hydrogen peroxide, at 500 rpm level 24% and at 1000 rpm level, 27% removal was observed.

##### 4.2.3. Sonication

In order to see the effect of ultrasonics on solvent de-sulfurization, 20 kHz probe is used at 500 W power. Ten grams of 212  $\mu m$  sieve pass-through high sulfur lignite coal and 100 ml of solvents were taken in a 250 ml beaker. One end of the thermocouple was immersed into the coal-solvent mixture; the other end was connected to a data-logger to monitor the reaction temperature at regular intervals during sonication. The prime reason for measuring mixture temperature is to track the rate at which the reaction proceeds during ultrasound irradiation. The reaction mixture was sonicated at intervals of 10, 20 and 30 min. In Fig. 10, for 3-volume percentage of  $H_2O_2$ , the percentage removal of sulfur is seen to increase with increasing sonication time. Interestingly, low solvent concentration and short period of sonication (10 min) lead to more than 63% removal. The reason is that high energy is transferred to the sample mixture, thereby accelerating the reaction between  $H_2O_2$  and sulfur. The slope of the curve at 3% hydrogen peroxide condition is steeper than 2 N nitric acid condition.

From Fig. 11, it is clear that the reaction between hydrogen peroxide and sulfur is exothermic; this has been confirmed by a significant temperature rise in the reaction mixture within a short span of time. Once maximum temperature is reached, there is then a reduction due to further removal of total sulfur. Similarly, the temperature rise in an aqueous medium during sonication, solvent

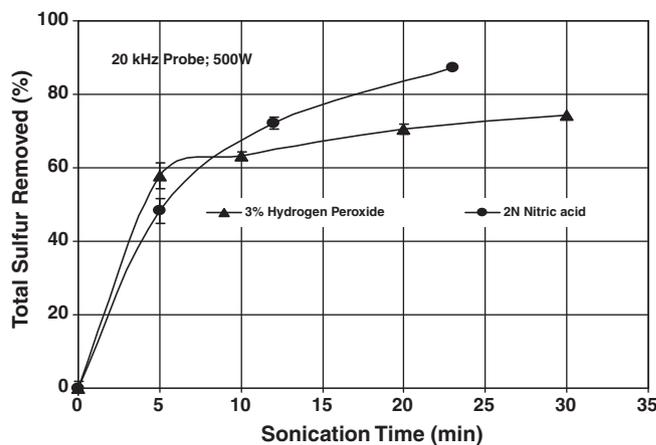


Fig. 10. Effect of solvent-based ultrasonic methods on total sulfur removal.

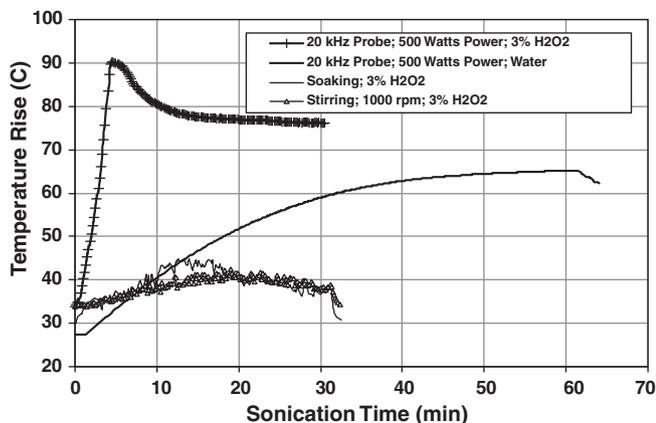


Fig. 11. Effect of sonication, soaking and stirring on solvent-coal mixture temperature.

Table 5

Fixed carbon content of sonicated coal sample.

Coal type	Virgin sample FC (%)	Sonicated sample FC (%)
Dipka ROM coal	33.02	39.56
Belphar ROM coal	27.79	28.95
Lignite	36.47	37.72

soaking and solvent-based stirring were also noted, but the temperature difference between solvent-based and other three cases (aqueous-based sonication, solvent soaking and solvent-based-stirring) even within a short span of time (4 min) is large. The temperature rise during 30 min of solvent soaking and stirring is 4–8 °C. Solvent-based ultrasonic de-sulfurization is much faster than aqueous-based, unlike in the case of conventional methods of solvent de-sulfurization. Sonication was stopped after 30 and 60 min, respectively. A temperature drop always accompanies the cessation of sonication.

Table 5 confirms that the significant temperature rise is partly due to sonication and remaining due to reaction between hydrogen peroxide and sulfur (and not between hydrogen peroxide and carbon or hydrogen). Table 5 shows the FC content of different coals before and after sonication with different solvents. “FC content” is the fixed carbon, i.e., organic matter remaining after volatile matter and moisture have been released. It is composed primarily of carbon, with minor amounts of hydrogen, nitrogen and sulfur. The first two represent sonication with water, and the third sonication with H<sub>2</sub>O<sub>2</sub>. There is no decrease in fixed carbon in coal; instead, an increase in FC content by ash removal is observed. This confirms that significant temperature rise only comes from the reaction between oxidizing agents and sulfur and not from the reaction between C/H and oxidizing agents. While oxidizing agents do react with the organic matter in coal as well, their extent and rate of reaction with inorganic impurities such as sulfur is much greater, happening in a much shorter time-scale.

#### 4.3. Effect of Sonication on Reaction Mixture Temperature

A similar trend was observed using 2 N of HNO<sub>3</sub>. From Fig. 12, it may be observed that the temperature rise in nitric acid and coal mixture is higher than in the H<sub>2</sub>O<sub>2</sub> case. The maximum temperature achieved during sonication was 98 °C within 12 min, and this relates to 72% sulfur removal. The percentage removal of sulfur increases with an increase in sonication time. In both cases, the kinetics are very rapid when using 3% H<sub>2</sub>O<sub>2</sub>, 30 min sonication leading to 74% of total sulfur removal, whereas 2 N HNO<sub>3</sub>, 23 min

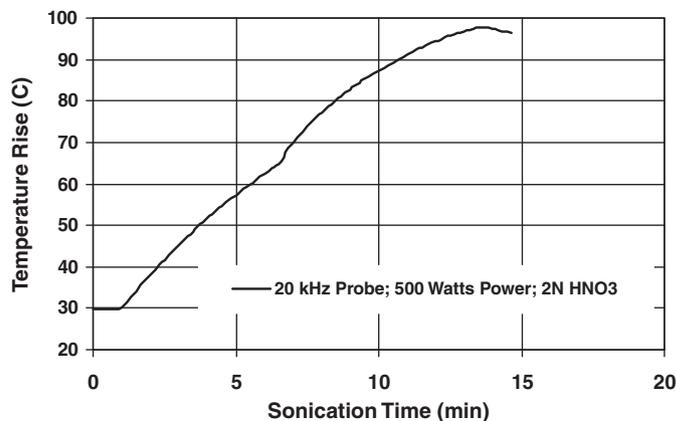


Fig. 12. Effect of sonication on HNO<sub>3</sub>-coal mixture temperature.

of sonication leads to 87% removal. Fig. 12, there is no temperature rise for first 1 min reason is sonication started after 1 min. Hydrogen peroxide seems to be a suitable solvent for removing sulfur from coal due to lower solvent concentration and lack of any harmful by-products.

## 5. Conclusions and recommendations

Ultrasound in aqueous medium produces OH, H<sub>2</sub>O<sub>2</sub>, HO<sub>2</sub>, O<sub>2</sub>, and ozone, which are strong oxidizing agents. The oxidation occurring in presence of ultrasound is called “Advanced Oxidation Process”, and this converts the sulfur present in the coal to water-soluble sulphates.

- The cavitation-dominant frequency characterizing the 20 kHz probe and 25 kHz tank systems produces fine coal particles, which enable intimate contact with the strong oxidizing agents produced by the ultrasonic system, leading to efficient coal de-sulfurization [32–34].
- The streaming-dominant frequency present in the 430 kHz tank system removes sulfur from coal only by leaching effect. The radicals produced by the ultrasound penetrate the pores of the coal particles due to streaming effect.
- Dual-frequency system is optimal for sulfur removal due to simultaneous presence of cavitation and streaming effects.
- In almost all cases, sulphate-sulfur removal is more than 90%, as observed in aqueous-based ultrasonic de-sulfurization.
- Solvent-based ultrasonic de-sulfurization results in highest removal within a short period of treatment time, at low solvent concentration and with less solvent consumption compared to conventional methods.
- Sonication accelerates the solvent-based reaction; this has been confirmed by increased removal of sulfur and significant temperature rise in the reaction mixture within a short span of time.
- In an ultrasonic field, the reaction between H<sub>2</sub>O<sub>2</sub> and sulfur is very fast, and the temperature rise in the reaction mixture within 4 min of treatment is 90 °C. Due to fast reaction and high sulfur removal, low solvent concentration and lack of by-products, hydrogen peroxide seems to be the most suitable solvent for ultrasonic de-sulfurization.

Based on laboratory experimental investigation, ultrasonic coal wash appears to be a promising technique to remove sulfur from coal. Ultrasonic aqueous-based de-sulfurization seems to be adequate for dealing with high-sulfur coal, which is composed mainly of sulphate sulfur. This method has the ability to replace

conventional methods in terms of less treatment time, less solvent volume, low solvent concentration and commercially available ultrasonic coal-wash equipment. At this stage, laboratory-scale results are promising enough that a larger-scale trial with high-sulfur coals is strongly recommended.

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