Chapter 2
Literature Review

2.1 General

This review addresses work on effect of burning high-ash and high-sulfur coal within the boiler equipment and environment. Within the boiler equipment, erosion of boiler accessories due to coal fly-ash impaction is reviewed, along with: ultrasound-assisted particle breakage; application of ultrasound in various fields; some of the patented ultrasonic coal-wash process for de-ashing; existing conventional chemical-based de-sulfurization methods and their demerits relative to ultrasonic methods; mechanism of ultrasound in aqueous medium and its contribution towards high-sulfur coal de-sulfurization; and, ultrasound-assisted high-sulfur coal and high-sulfur diesel fuel de-sulfurization already initiated by other researchers.

2.2 Effect of Burning High-Ash and High-Sulfur Coal

2.2.1 Boiler Equipment

The main disadvantages of burning high-ash and high-sulfur coal within the boiler are erosion and corrosion-accelerated erosion of boiler accessories. Erosion is defined as a process by which material is removed from the layers of a surface impacted by a stream of abrasive particles. Erosion can be broadly classified as solid particle erosion, slurry erosion and cavitation erosion. When the particles strike the substrate, part of their kinetic energy is spent on creating new particles, part on indentation of substrate, and a part on rebounding. In case of brittle materials, erosive wear is predominant in case of normal impact, whereas in case of metals, maximum erosive wear occurs at shallow angles. If the striking particle is much harder than the substrate and the effect of the force on particle is large, abrasion predominates.
Finnie [1] proposed the first analytical erosion-model. This model included a variety of parameters that influence the amount of material eroded from a target surface and the mechanism of erosion. It was observed that the wear of a surface due to solid particle erosion depends on the motion of the particles in the fluid, as well as the behavior of the surface when struck by the particles. These two parts of the problem are related in that a surface, roughened by erosion, may increase the fluid turbulence, and hence, accelerate the rate of material removal.

Hutchings and Winter [2] studied the mechanism of metal removal by impacting the metal targets at an oblique angle by metal balls at velocities up to 250 m/s. They suggested that the initial stage of metal removal is the formation of lip at the exit end of the crater, caused by shearing of the surface layers. Above a critical velocity, this lip is detached from the surface by the propagation of ruptures at the base of the lip.

Jennings et al. [3] derived mathematical models based on target melting and kinetic energy transfer for predicting ductile target erosion. Dimensional analysis was employed in the development of a mathematical model for predicting the erosion of ductile materials. The model identified an erosion mechanism (target melting) which was verified in an erosion testing program using three stainless steels, two aluminium alloys, a beryllium copper alloy and a titanium alloy; the erosive agents were three dusts with hard angular particles, and one dust with spherical particles.

By extending the relations of Hertz and Raleigh, Soo [4] studied ductile and brittle modes of erosion by dust and by granular materials suspended in a gas moving at moderate speeds with conditions including directional impact, random impact, and sliding-bed motion. Their experimental results show that the ductile mode, which is typical of metal targets, is characterized by maximum erosion occurring at some intermediate incidence angle between 0 and 90°.

Foley and Levy [5] investigated the erosion of heat-treated steels. The testing was conducted at room temperature using aluminium oxide particles with an average size of 140 µm in an air stream. An attempt was made to characterize the erosion behavior as it relates to the mechanical properties obtainable in these alloys by conventional heat treatments. It was found that the ductility of the steels had a significant effect on their erosion resistance which increased with increasing ductility, and that hardness, strength, fracture toughness and impact strength had little effect on erosion behavior.

Sundararajan and Shewmon [6] proposed a correlation between the erosion rate and the thermo-physical properties of the target, for the erosion of metals by particles at normal incidence. This model employs a criterion of critical plastic strain to determine when the material will be removed. It was concluded that their new erosion model (localized model), rather than the fatigue-type model, predicts very well the experimentally observed rates of erosion. The effect of hardness on erosion rate was also investigated. The volume erosion rate for pure metals is inversely related to the static hardness. Such behavior can be rationalized on the basis of the fact that the melting point of a pure metal is directly proportional to its static hardness value. In the case of high-temperature erosion, there may be
significant hardness effect on erosion, but in the case of room-temperature erosion, the influence is negligible.

Levy et al. [7] investigated elevated-temperature erosion of steels. The elevated-temperature erosion behavior of several commercial ferritic and austenitic steels was determined over a range of temperatures from room temperature to 900°C. Austenitic steels were determined to have lower erosion rates than ferritic steels, and their hardness had no correlation with their erosion rate.

Meng and Ludema [8] analyzed the origin, content and applicability of most wear models and equations in literature. Their work focuses on the need for new methods of wear modeling and offers recommendations on how to model the wearing process; the authors have found over 300 equations for wear and friction.

Wang [9] investigated the erosion-corrosion behavior of two steels and several thermal spray coatings due to impaction by fly-ash from a bio-mass fired boiler through laboratory tests using a nozzle-type, elevated-temperature erosion tester. They found that this bio-mass fired boiler fly ash had relatively high erosive effect due to its composition containing high concentrations of chemically-active compounds of alkali, sulfur, phosphorous and chlorine.

Xie and Walsh [10] measured the erosion of carbon steel by fly-ash and unburned char particles in the convection section of an industrial boiler firing micronized coal. Ash and char particles suspended in the flue gas entrained by the jet were accelerated towards the surface of the specimen under varying temperatures (450–650°C). Changes in the surface were measured using a surface profiler. They observed that erosion was slowest at the lowest metal temperature, regardless of the jet gas composition; and, under the nitrogen jet, erosion increased with increasing temperature. They have presented a model for simultaneous erosion and oxidation which is consistent with the temperature and oxygenation dependencies of the erosion rate.

Hubner and Leitel [11] carried out investigations on an erosion-corrosion apparatus to investigate time behavior of corrosion-resistant high-alloy iron-base materials containing hard phases, and optimized the materials for increased wear resistance under complex stress conditions.

Oka et al. [12] investigated the impact-angle dependence of erosion damage caused by solid particle impact. Erosion tests were conducted using a sand-blast type erosion test rig which included shallow impact angles. The dependence of erosion rates on impact angle was characterized by type of metallic (Al, Pb etc.), plastic and ceramic material. Impact velocity increased the erosion rate, but did not affect the dependence of erosion behavior on the impact angle for the metallic materials. Impact angle dependence was simulated by a basic equation involving a trigonometric function both of impact angle and of material hardness.

Hussainova et al. [13] investigated the surface damage and material removal process during particle–wall collision of solid particles with hard metal and cer-met targets. Targets were impacted with particles over a range of impact velocities (7–50 m/s) at impact angle of 67°. The experimentally-observed variations of the coefficient of velocity of restitution as a function of the test material properties, impact velocity and hardness ratio were adequately explained by a theoretical model presented by them.
With a FLUFIX computer code, Lyczkowski and Bouillard [14] analyzed the behavior of six representative erosion models (comprising both single-particle and fluidized bed models) selected from literature. Energy dissipation models are developed, and are shown to generalize to the so-called power dissipation model used to analyze slurry jet pump erosion. They have demonstrated, by explicitly introducing the force of the particle on the eroding material surface, that impaction and abrasive-erosive mechanisms are basically the same.

Using three different power-station ash types, Mbabazi et al. [15] investigated the effect of ash particle impact velocity and impact angle on the erosive wear of mild-steel surfaces through experiments. The experimental data were used to calibrate a fundamentally-derived model for the prediction of erosion rates. This model incorporates the properties and motion of the ash particles as well as target metal surface properties.

In their work, Marcus and Moumakwa [16] investigated the long-term solid particle erosion of a range of oxide and nitride-fired SiC-based ceramics and alumina with the aim of reducing wear damage in power plants. They carried out experiments using 125–180 μm silica sand at shallow and high impact angles, using an in-house built erosion testing machine simulating real industrial conditions.

Das et al. [17] investigated the effect of temperature on the basis of the observation that the erosion rate at acute impingement angle increases significantly with temperature, suggesting that steel tends to show behavior more typical of a ductile material at elevated temperatures. The yield stress and temperature functionality has been derived through a polynomial approximation for various grades of steel on the basis of the available tensile property data. Erosion behavior at elevated temperatures has been incorporated through the derived functionality of the tensile property (yield stress) with temperature, along with appropriate modification of yield strength.

Vicenzi et al. [18] investigated the effect of fly-ash erosion on three different thermal-sprayed coatings produced by high velocity oxygen fuel (HVOF) under high temperature conditions by means of an apparatus that simulated real conditions.

Wang and Yang [19] developed a finite element (FE) model of erosive wear of brittle and ductile materials. The FE model was used to simulate the effect of impact angle and velocity, and of particle penetration, on the targets. The predicted results were found to be in good agreement with the experimental and analytical erosion models.

Such erosion, together with the processes of blocking, fouling and corrosion, shortens the service life of the air heater elements. Once this happens, the power station unit has to be shut down in order to replace the damaged air heater elements. The resulting penalty is not only the cost of replacing the elements but also the cost of stoppage of power production. It is desirable, therefore, to be able to predict the rate of erosion of the air heater elements in order to plan systematically for their maintenance to avoid forced outages.
2.2.2 Environmental and Health Hazards of Coal Burning Power Plants

The two major environmental concerns today arising from the use of high-ash and high-sulfur coal are: increase in atmospheric carbon dioxide levels and acid rain. It is believed that combustion has partially contributed to the increase in atmospheric carbon dioxide levels. Increased atmospheric carbon dioxide levels may result in warmer climates due to the “greenhouse effect”. The increase in atmospheric carbon dioxide prevents heat from escaping from the earth, thus warming the atmosphere. The combustion of coal also appears to contribute to acid rain, although precise measures of the scope and seriousness of acid rain are not clear or well understood. Out of the entire US electric industry, coal-fired power plants contribute 96% of sulfur dioxide emissions (SO₂), 93% of nitrogen oxide emissions (NOₓ), 88% of carbon dioxide emissions (CO₂) and 99% of mercury emissions. [http://www.greenpeace.org/raw/content/seasia/en/press/reports/coal-plants-a-greenpeace-brie.pdf]

2.2.2.1 Global Warming Due to Coal Combustion

Carbon dioxide emissions are the essential outcome of coal combustion in power plants. Carbon dioxide has been identified as a heat trapping gas; it retains the infrared radiations returning from earth to sun, thus causing the global temperature to rise. These impacts include melting of polar ice, rise in sea-levels and the consequent flooding of coastal areas. In addition, it may increase erosion of coastal lands, subjecting coastal buildings and their residents to increased risks of violent storms. Coal emits 29% more carbon per unit of energy than oil, and 80% more than natural gas. CO₂ represents the major portion of greenhouse gases. Over the last 30 years, the concentration of greenhouse gases in the atmosphere has increased by 30%.

2.2.2.2 Acid Deposition Due to Coal Burning

Bituminous coal used in most power plants contains small amounts of sulfur and nitrogen. Combustion of coal in power plants converts them to sulfur and nitrogen oxides respectively. These oxides, upon reaction with water in the atmosphere, result in precipitation of acid, sometimes also called “acid rain”. Acid rain is often prevalent downwind from coal burning power plants, indicating the connection between acid formation and airborne emissions caused by coal-fired power plants. Acidification of lakes and streams results in decline of aquatic animal populations. In addition, crop damage, forest degradation, impaired visibility and chemical weathering of monuments are the major results of acid deposition. Furthermore, presence of acidic substances in air entails human health risks such as asthma and bronchitis. In 1997, pollution controls from power plants to reduce acid rain cost approximately $100 per ton.
2.2.2.3 Particulate Matter and Ground-Level Ozone

“Fine particles” are a mixture of a variety of different compounds and pollutants that originate primarily from combustion sources such as coal-fired power plants. Fine particles are of gravest concern because they are so tiny that they can be inhaled deeply, thus evading the human lung’s natural defences. Power plants also emit fine carbon soot particles directly from their smokestacks. In 1999, coal plants directly emitted nearly 300,000 tons of fine carbon soot particles. These suspended particulates are dangerous for human health and may cause respiratory illnesses. The airborne nitrogen oxide emissions associated with coal burning cause urban smog, which is a respiratory irritant. Moreover, increased ground level ozone due to nitrogen oxides reduces agricultural and commercial forest yields. 30,000 deaths each year are attributable to fine particle pollution from U.S. Power plants. It is further stated that hundreds of thousands of Americans suffer from asthma attacks, cardiac problems and upper and lower respiratory ailments associated with fine particles from power plants.

2.2.2.4 Mercury Emissions from Coal Burning

Most coal-fired power plants are major mercury emitters; mercury is present in coal in small traces and is released to the atmosphere during combustion. Although it is emitted in a non-hazardous elementary form, its accumulation in the environment can be hazardous for humans and wildlife. It is a neurotoxin, and if deposited in an aquatic environment in the form of methyl mercury, it can accumulate in invertebrates and fish and may affect their neural tissues. Coal-fired power plants are the single largest source of mercury pollution in the US. According to the US National Wildlife Federation (NWF), a single 100 MW coal-fired power plant emits approximately 25 pounds of mercury a year. According to the US Centre for Clean Air Policy, 50% of the mercury emitted from coal-fired power plants can travel up to 600 miles from the power plant. In 1994, mercury emissions by coal plants in the US reached 51 tons. According to NWF, as little as 0.002 pounds of mercury a year can contaminate a 25 acre lake to the point where fish are unsafe to eat.

These studies and data make clear that “clean coal technology” must be developed if coal continues to be used as a major source of energy. Removal of ash and sulfur from coal and coal combustion products is therefore a crucial component of clean coal technology.

2.3 Conventional Methods for De-Ashing and De-Sulfurization

Several methods are reported in literature for removal of mineral matter, total sulfur and different forms of sulfur from coal. The processes of sulfur removal from coal prior to combustion can be subdivided into physical and chemical
methods. Of these, physical methods can remove the soluble sulphates, as well as a considerable portion of the coarse pyrite (separable by a magnetic separator), but the fine pyrite (tightly bonded with coal matrix) and organic sulfur remain largely untouched. On the other hand, many of the chemical methods can remove almost all of the pyritic sulfur and at least a portion of the organic sulfur. A number of chemical methods have been presented in literature. Table 2.1 lists the reagents whose use has been reported in literature and their effects on coal desulfurization. From Table 2.1, it is apparent that researchers are still looking for ways to maximize coal ash and sulfur removal, and to optimize the operating conditions by choosing suitable reagents.

Yuda and Ayse [40] investigated the effect of supercritical ethyl alcohol/NaOH on the solubilization and de-sulfurization of Beypazari lignite. Supercritical experiments have been done in a 15 ml micro reactor at 245°C for 60 min, by changing the ethyl alcohol/coal ratio from 3 to 20 under a nitrogen atmosphere. Increase in ethyl alcohol/coal ratio increased the yield of solubilization and de-sulfurization. Higher yields of extraction in the case of ethyl alcohol/NaOH experiments may be due to the fact that alcohols can transfer hydrogen more easily in the presence of bases. As the ethyl alcohol/coal ratio was increased from 3 to 20, the sulfur content of the coal decreased to 0.75%.

Li and Guo [41] have studied de-sulfurization of a high-rank coal using alcohol/KOH and alcohol/water under supercritical conditions in a semi-continuous reactor and in a batch reactor. In the semi-continuous reactor mode, it was found that supercritical de-sulfurization is mainly taking place within about one hour at 400°C. Ethanol/KOH solution as supercritical solvent enhanced the de-sulfurization process in which inorganic sulfur was removed. The reaction between ethanol and KOH takes place in three steps: Ethanol reacts with KOH and forms potassium ethoxide and water. Then, these two combine to form potassium ethanolate and hydrogen. Part of potassium ethoxide gives ethylene and KOH. With increasing KOH concentration, a large amount of hydrogen is produced and is absorbed by the coal. The effect of hydrogenation makes the radical fragment more stable.

Mukherjee et al. [34] have investigated de-mineralization and de-sulfurization of high-sulfur coals from Assam (India) using aqueous NaOH followed by HCl treatment. They found that compared to alkali and acid alone, successive treatments with alkali and acid resulted in significant removal of mineral matter and sulfur from the coal.

Charatuwai et al. [42] have studied de-sulfurization of Mae Moh (Thailand) coal with supercritical ethanol/KOH in a semi-continuous reactor. A two-level factorial design was applied, and process variables investigated were reaction temperature, pressure, and reaction time and KOH concentration. The effects of process variables on coal yield, as well as on ash reduction and total sulfur reduction, have been analyzed using analysis of variance. Among the four variables, temperature and KOH concentration were found to be significant factors for removal of total sulfur.

Mukherjee and Borthakur [43] have investigated the effect of leaching on high-sulfur sub-bituminous Assam (India) coal using KOH and acid on removal of mineral
<table>
<thead>
<tr>
<th>Author</th>
<th>Reagents used</th>
<th>Time</th>
<th>Sulfur and or ash removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steinberg et al. [20]</td>
<td>O₃ and O₂</td>
<td>1 h</td>
<td>Using a flow rate of 200 ml/min, 1% O₃ at 25 °C, 20% sulfur removed</td>
</tr>
<tr>
<td>Aarya et al. [21]</td>
<td>NaOH</td>
<td>8 h</td>
<td>Using 100 g/dm³ NaOH at 80 °C, 30% sulfur removed 29% ash removed</td>
</tr>
<tr>
<td>Chandra et al. [22]</td>
<td>Atmospheric oxidation</td>
<td>106 days</td>
<td>44% sulfur removed (36% organic sulfur removal)</td>
</tr>
<tr>
<td>Krzymien [23]</td>
<td>Aqueous CuCl₂</td>
<td>48 h</td>
<td>Using 10 ml of 10% (vol) CuCl₂ at 200 °C, 100% sulfur removed</td>
</tr>
<tr>
<td>Chaug et al. [24]</td>
<td>Combination of dissolved oxygen and alcalis NaHCO₃, Na₂CO₃ and Li₂CO₃</td>
<td>1 h</td>
<td>0.2 M alkali solution with 3.4 atm O₂ partial pressure at 150 °C: Na₂CO₃: 72% of sulfur removed Li₂CO₃: 73.1% of sulfur removed At 0.4 M NaHCO₃: 77% of sulfur removed</td>
</tr>
<tr>
<td>Yang et al. [25]</td>
<td>NaOH</td>
<td>60 min</td>
<td>Using 10 wt% NaOH at 250 °C: 55% sulfur removed (95% pyritic and 33% organic sulfur removed)</td>
</tr>
<tr>
<td>Kara and Ceylan [26]</td>
<td>Molten NaOH at different temperatures</td>
<td>30 min</td>
<td>Using 20 wt% NaOH at 450 °C: 83.5% sulfur removed 91% ash removed from Dadagi lignite</td>
</tr>
<tr>
<td>Ahnonkitpanit and Prasassarakich [27]</td>
<td>Aqueous H₂O₂ and H₂SO₄</td>
<td>2 h</td>
<td>Using 15% H₂O₂ and 0.1 N H₂SO₄ at 40 °C: 48.7% total sulfur removed (97% pyritic, 89% sulphate and 7.1% organic sulfur removed) 72.2% ash removed</td>
</tr>
<tr>
<td>Ozdemmir et al. [28]</td>
<td>Chlorine in CCl₄ + H₂O</td>
<td>6 h</td>
<td>Using 0.033 l/min chlorine flow rate at ambient temperature and pressure: All pyritic and sulfate sulfur removed and 30% organic sulfur removed 15% ash reduced</td>
</tr>
<tr>
<td>Ali et al. [29]</td>
<td>H₂O₂, NH₄OH, K₂Cr₂O₇ and CH₃COOH</td>
<td>30 min</td>
<td>50–90% of sulfur removed, depending on concentration and solvent 50–55% of mineral matter removed, depending on concentration and solvent</td>
</tr>
<tr>
<td>Prasassarakich and Thaweesri [30]</td>
<td>Sodium benzoate</td>
<td>90 min</td>
<td>Using 600 ml sodium benzoate at 205 °C, 45.9% sulfur removed (83.7% sulphate, 68.6% pyritic, 33.3% organic sulfur removed)</td>
</tr>
</tbody>
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(continued)
matter and sulfur at temperatures of 90 and 150 °C. They reported that at 150 °C, successive treatments of coal with 18% KOH and 10% HCl leads to 52.7% desulfurization (all inorganic sulfur and 37% organic sulfur were removed from coal).

Mukherjee and Borthakur [44] have investigated the effect of mineral acids (HCl, HNO₃ and H₂SO₄) on de-mineralization of sub-bituminous high-sulfur Boragolai (Assam, India) coal at varying stirring speeds, and in the temperature range from ambient to 95 °C. They reported that HCl is less effective for de-mineralization compared to H₂SO₄ and HNO₃. They observed that

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>Rodriguez et al. [31]</td>
<td>HNO₃</td>
<td>2 h</td>
<td>Using 20% HNO₃ at 90 °C, 90% inorganic and 15% organic sulfur removed</td>
</tr>
<tr>
<td>Hamamci et al. [32]</td>
<td>Acidic Fe (NO₃)₃, 9H₂O</td>
<td>12 h</td>
<td>Using 50 ml of 1 M solvent at 70 °C, 72.2% sulfur removed (96.6% pyritic sulfur removed)</td>
</tr>
<tr>
<td>Aacharya et al. [33]</td>
<td>Thio-bacillas ferro-oxidants</td>
<td>30 days</td>
<td>91.81% sulfur removed from lignite 63.17% sulfur removed from polish bituminous coal 9.41% sulfur removed from Assam coal</td>
</tr>
<tr>
<td>Mukherjee and Borthakur [34]</td>
<td>H₂O₂ &amp; H₂SO₄</td>
<td>4 h</td>
<td>Using 15% (vol) H₂O₂ and 0.1 N H₂SO₄: 45% of total sulfur removed (complete removal of inorganic sulfur and 31% removal of organic sulfur) 45% ash removed</td>
</tr>
<tr>
<td>Ratanakandilok et al. [35]</td>
<td>Methanol/water and methanol/KOH</td>
<td>90 min</td>
<td>Using 2% methanol and 0.025 g KOH/g coal at 150 °C: 58% total sulfur removed (77% sulfate, 47% pyritic and 42% organic sulfur removed) 24% ash removed</td>
</tr>
<tr>
<td>Sonmez and Giray [36]</td>
<td>Peroxy acetic acid</td>
<td>72 h</td>
<td>45% sulfur removed from Gediz lignite 85% sulfur removed from Cayirhan lignite</td>
</tr>
<tr>
<td>Aacharya et al. [37]</td>
<td>Aspergillus</td>
<td>10 days</td>
<td>78% sulfur removed with 2% pulp density</td>
</tr>
<tr>
<td>Baruah et al. [38]</td>
<td>Water</td>
<td>120 h</td>
<td>77.59% pyritic sulfur removed with aqueous leaching at 45 °C</td>
</tr>
<tr>
<td>Liu et al. [39]</td>
<td>Aeration + NaOH, HCl</td>
<td>5 h</td>
<td>Using 0.25 M NaOH at 90 °C with aeration rate of 0.136 m³/hr and 0.1 N HCl solution 73% organic sulfur removed 83% sulfide sulfur removed 84% pyritic sulfur removed</td>
</tr>
</tbody>
</table>
de-sulfurization increases with increase in HCl concentration, and that increase of temperature to 95°C increases de-mineralization.

Alam et al. [45] have investigated the effect of process parameters on desulfurization of Mezino coal by HNO₃/HCl leaching. The parameters considered were reaction time, acid concentration, temperature and stirring speed. To optimize experimental parameters, Taguchi orthogonal experimental design was used with the chosen parameters. ANOVA indicated that acid concentration had the dominant effect on desulfurization.

The biggest disadvantage associated with conventional de-sulfurization is the processing time as well as increased reagent consumption. Also, at the end of the treatment, the coal is contaminated by byproducts that are produced during reaction. This may require neutralization of the treated coal. This indicates that there is a clear need for the new technology to overcome these issues.

2.4 Ultrasound-Assisted Coal Particle Breakage and Application of Ultrasound in Various Fields

This review comprises of four parts: particle breakage mechanism, application of ultrasound in various fields, some of the patented ultrasonic coal-wash process, and studies on free radical formation in an ultrasonic field.

2.4.1 Ultrasound-Assisted Coal Particle Breakage

Fridman [46] proposed a mechanism which explains the interaction of a cavitation bubble and a particle of the material medium, and also the effects of dispersion and coagulation in a cavitating liquid medium. It has been suggested that either cavitation or coagulation can be obtained by changing the physico-chemical and acoustic parameters of the medium. For more efficient dispersion, a combination of alternating cavitation and mechanical dispersion was recommended. The proposed mechanism was verified experimentally by slow-motion photography.

Kusters et al. [47] developed a model to describe the fragmentation of agglomerate powders by ultrasonication. An expression has been derived for the agglomerate fragmentation rate as a function of power input, suspension volume and agglomerate size. From the evolution of the mass mean diameter, it followed that the fragmentation rate varies linearly with agglomerate size, in agreement with experimental data. Fragmentation by erosion results in a bimodal fragment size distribution, requiring much finer section spacing in the sectional model than conventional fragmentation. In the case of an erosion-dominant type of fragmentation process, an additional term had to be included in the conventional breakage distribution expression to describe the production of fines. The amount of fines produced was found to be proportional to the surface area of the agglomerates. The fragmentation rate expression is evaluated by comparing simulated with
experimental size distributions. The required time and energy for particle size reduction is calculated as a function of ultrasonic power input.

Kusters et al. [48] have investigated the energy requirement for sono-fragmentation. Ultrasonic field is extensively used to disperse submicron agglomerated powders in liquid suspensions. Experiments were conducted to illuminate the effect of suspension volume on the ultrasonic fragmentation rate. The fragmentation or grinding rate is inversely proportional to suspension volume. The reduction ratio increases with time faster at the small than at the large suspension volume for equal power input. Lower power input for ultrasonication favors efficient energy use. For eroding powders (e.g., silica, zirconia), the energy expenditure per unit powder mass (specific energy) by ultrasonic grinding is lower than that of conventional grinding techniques. In contrast, it is slightly higher than ball milling for non-eroding powders (e.g., titania).

Gopi and Nagarajan [49] investigated fabrication of alumina nano particles by sono-fragmentation. Breakage was more predominant in a low-frequency (<60 kHz) ultrasound field. It produces very fine particles, thereby increasing total surface area. The sphericity of the particle also increases with sonication time, due to the associated micro-polishing mechanism.

Raman and Abbas [50] have investigated the effects of intensity of ultrasound on particle breakage in liquid medium and also the effect of sonication power, temperature and contact time on particle breakage. The experiments were conducted at three different input power levels of 150, 250 and 350 W (amplitude ratios of 0.3, 0.5 and 0.7 respectively). The particle size in the form of mean chord length ($l_m$) was monitored in-line while the sonication was performed. A decrease in $l_m$ was observed for all input power levels. Three different flow rates were studied: 1.0, 1.6 and 2.2 l/min. Breakage was more predominant at lower flow rates corresponding to larger values in residence time. As the residence time increases, the particles spend more time in contact with the breakage forces of the HIU (high intensity ultrasound) field.

Temperature has a significant effect on the cavitation phenomenon, which, in a liquid medium, is affected by its surface tension, viscosity and vapor pressure. Increasing temperature results in the liquids cavitating at lower intensities. This can be attributed to the increase in vapor pressure of the liquid, decrease in surface tension, and reduced viscosity of the liquid medium. The decrease in viscosity decreases the magnitude of the natural cohesive forces acting on the liquid, and thus, decreases the magnitude of the cavitation threshold. Lower cavitation thresholds translate into ease of cavity formation, thereby making higher temperatures more favorable for particle breakage. This is the reason for an increase in breakage of particles as temperature is varied from 10 to 25°C. As temperature is increased beyond 25°C, a decrease in particle breakage is observed. This is primarily caused by the cushioning effect of increased cavity internal vapor pressure at higher temperatures. Due to this cushioning effect, the intensity of the collapse, and subsequently the breakage, decreases above 25°C. There are, thus, two opposing factors that are at play during particle breakage; the first being the increase in the number of cavitation events with increase in temperature due to
which particle breakage increases, and the second being the cushioning effect of the cavity internal vapor pressure, which has a suppression effect on the cavitation intensity and subsequently on particle breakage.

### 2.4.2 Application of Ultrasonic Process

Newman et al. [51] suggest a methodology for the remediation of soils contaminated with inorganic pollutants. Copper oxide-doped granular pieces of brick were used as a model for contaminated soil. By passing water across the substrate on an ultrasonically-shaken tray, a 40% reduction in copper content was achieved, whereas in conventional washing, only 6% reduction is realized. The majority of the copper was removed as a result of the removal of surface materials which were more heavily contaminated with the copper oxide.

Kruger et al. [52] investigated the effect of ultrasound on degradation of highly-volatile chlorinated compounds present in groundwater. The main constituent of high volatility, chlorinated hydrocarbon 1, 2-dichloroethane (1, 2-DCA), was taken as a model pollutant, and it was experimentally observed that the destruction rate of 1, 2-DCA in deionized water depends on intensity of ultrasound, initial concentration and sample volume. The highly-volatile chlorinated hydrocarbons are completely destroyed in natural ground water within 60 min, but all minor halogenated components are destroyed within 30 min of sonication time. It was also observed that the destruction rate of 1, 2-DCA in deionized water is independent of temperature, and the pH value of the 1, 2-DCA solution in deionized water decreases with sonication time.

Farmer et al. [53] reviewed the application of power ultrasound to surface cleaning of silica and heavy mineral sands. They conducted experiments which revealed that reducing the iron contamination due to surface coating of the silica grains from 0.025 to 0.012% Fe$_2$O$_3$ would make this sand suitable for the production of tableware glass, and also investigated the effect of ultrasonic power level and concentration of reagents (sodium carbonate) on iron reduction. The optimum concentration of reagents which reduces exposure time required to reach the maximum iron reduction was evaluated.

Kim and Wang [54] investigated the effectiveness of ultrasound in enhancement of soil flushing method. The degree of enhancement varies with many factors, such as soil type, soil density, flow rate, temperature, wave frequency, energy level and others. The test soils were Ottawa sand, a fine aggregate, and a natural soil; the surrogate contaminant was Crisco Vegetable Oil. The percent contaminant removal increases with increasing sonication power to a maximum around 100 W, then decreases. The contaminant removal at 140 W is about equal to that around 75–85 W, corresponding to a loss factor of about 1.8. The drop in contaminant removal beyond about 100 W can be attributed to the effect of cavitation. When cavitation occurs, the sound pressure level at a distance drops, because cavitation takes power away from the field. Therefore, cavitation can reduce the effective sonication power in the soil.
The influence of hydraulic condition was investigated under 100 W sonication power using three levels of hydraulic gradient: 1.6, 5.5, and 13.0. Percent contaminant removal was studied as a function of hydraulic gradient for both with and without sonication conditions. It is seen that the percent contaminant removal decreases with increasing hydraulic gradient. Increasing hydraulic gradient will increase discharge velocity and flow rate, other factors being equal. The contaminant in a soil with a higher void ratio can be removed more easily than a soil with a lower void ratio; also, the effect of soil density on contaminant removal seems to be less significant for the case with sonication than without sonication. The effectiveness of sonication in contaminant removal is greater at lower discharge velocity. This can be attributed to the relatively longer time for interaction between sound wave and contaminant under slower flushing.

Mason et al. [55] have investigated sonic and ultrasonic removal of chemical contaminants from polluted soil in the pilot-scale and on the large scale. They analyzed three different industrial-site polluted solids, namely DDT, PCB, and PAH-doped soil, and concluded that % removal of chemical contaminants was 75, 75 and 85% during 5, 30, and 60 min of ultrasonic washing using 20 kHz ultrasound and 200 g contaminated soil in 200 g water. Cooke et al. [56] reported that “ultrasound (0.455–1.46 W/cm²) can extract at least 58% of mobile organic matter without rupturing any chemical bonds. The average molecular weight of the extract is 340–1,055”.

2.4.3 Patented Ultrasonic Coal-Wash Process for De-Ashing

In a patented process and apparatus for treatment of flowing slurries of particulate material mixed in liquid (US Patent # 4741839 [57]), a wide, elongated, downwardly-slanted metal tray with upturned edge flanges, is cable-suspended for unrestrained vibratory flexing and undulation. The tray is provided with a plurality of ultrasonic transducers mounted on its underside, and the flowing slurry is delivered to the upper tray end, flowing lengthwise down the tray in a shallow flowing sheet. Ultrasonic vibratory energy coupled through the tray to the flowing slurry has a “microscopic scrubbing” action on all particles and agglomerates, breaking the surface tension on the particle, cleaning particle surfaces, and separating different constituent particles and coatings of gels, slimes, algae, clay or mud. Mixtures of fine particles of coal or other valuable minerals with ash, clay, rock or sand particles are separated with unexpected efficiency by these techniques. Advanced Sonic Processing Systems (Oxford, CT, USA; [www.advancedsonics.com]) offers a “Vibrating Tray Equipment Series”, which is a high-volume ultrasonic trough effective in accelerating the surface dynamics of the fluidized particles. The ultrasonic cavitative energy scrubs each particle’s surface as it flows over the tray. The cleaning effect produced by water alone is very effective in removing surface
contaminates from the particulate pores. Chemical additives, added prior to the ultrasonic vibrating tray, become highly reactive in the acoustic field. This allows ore refining techniques to produce higher yields with lower consumable costs.

DOE, USA [www.rexresearch.com] reports on ultrasonic activation of several coal cleaning processes that in all cases “sonication demonstrated effects that would translate in production to processing efficiencies and/or capital equipment savings. Specifically, in the chlorinolysis process, pyritic S was removed 23 times faster with ultrasonic than without it. In NaOCl leaching, the total S extraction rate was three times faster with ultrasound. Two benefits were seen with oxy-desulfurization: ultrasonics doubled the reaction rate, and at slightly accelerated rates, allowed a pressure reduction from 960 to 500 psi”.

Another ultrasonic process for cleaning coal has been patented in Great Britain (British Patent # GB 2,139,245 [58]); in this, coal slurry (pH 6–9) is agitated with ultrasound and separated by centrifuging or froth flotation. A second treatment with ultrasound and ozone releases more contaminants. There is another US patent (US Patent # 4,156,593 [59]) on an ultrasonic coal cleaning process in which coal contaminants (e.g., pyrites, clay) are removed from coal slurry at relatively low temperature and pressure and at increased throughput rates by an ultrasonic source. Pyrites are reduced from ~30 to ~0.7%.

There are many such references in literature to the employment of ultrasonics in coal cleaning. However, none of them contains a systematic study of the effect of ultrasonic field parameters (amplitude, frequency), nor a delineation of the mechanisms involved. The study reported in this thesis focuses on these aspects.

2.4.4 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, H₂O₂ 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 and Lamm [60] first suggested the mechanism for this reaction, followed by many researchers who proved it in different manners by experiments. Webster [61] 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.

\[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \]
The predominant back reactions attendant on this process are

\[ \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2; \quad \text{H} + \text{H} \rightarrow \text{H}_2 \]

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

\[ \text{H} + \text{O}_2 \rightarrow \text{HO}_2 \text{ followed by } \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

Makino et al. [62] 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\(^-\)) and hydrogen atoms (H) are produced by ultrasound. Riesz et al. [63] were able to observe by spin traps the highly-reactive radicals produced during cavitation. Christman et al. [64] found experimental evidence for free radicals produced in aqueous solutions by using electron spin resonance method (ESR). Misik and Riesz [65, 66] conducted spin trap and electron spin resonance studies to investigate free-radical formation and sonochemical reactions in organic liquids using 50 kHz frequency of ultrasound. Margulis [67] 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 sonochemical reaction. Entezari and Krus [68] conducted an experiment to explain the effect of frequency on sonochemical 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 sonoochemical oxidation in an aqueous solution is about three times faster in an air atmosphere compared to argon environment. The H\(^+\), OH\(^-\) and H\(_2\)O\(_2\) produced by the ultrasound in an aqueous solution are responsible for the oxidation reaction. Luche [69] investigated sonochemical reactions occurring in a heterogeneous system. Jana and Chatterjee [70] 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 [71] 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\(_2\)O\(_2\) formation.

Hoffmann et al. [72] investigated sonochemical degradation of organic compounds present in water. Three distinct pathways of sonochemical degradation of organic compounds by acoustic cavitation have been proposed: (1) Oxidation by
hydroxyl radicals, (2) Pyrolytic decomposition, and (3) Supercritical water oxidation. Gogate et al. [73] analyzed and mapped sonochemical reactors by experimental verification. Generalized correlations were developed for effective design and scale-up of sonochemical 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. Hydrogen peroxide combines advantages not obtainable with any other single form of chemical control. It is cost-effective and specific, forming no toxic by-products. 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.

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 desulfurization, 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 investigating the effects of ultrasonic field parameters such as frequency and amplitude.

### 2.5 Ultrasonic Process for De-Ashing and De-Sulfurization

Very few researchers have focused on ultrasonic coal de-sulfurization. Existing literature fails to explain the mechanisms involved in ultrasound-assisted coal desulfurization. Conclusions drawn by researchers are very general in nature. The ultrasonic desulfurization methods studied are either aqueous or chemical based. The biggest advantage of ultrasonic method is simultaneous removal of ash and sulfur. Zaidi [74] investigated ultrasound-promoted de-sulfurization of low-rank coals with dilute solutions of sodium hydroxide (0.025 to 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. [75] investigated the enhancement of de-sulfurization and de-ashing of coal. 100 g 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
2.5 Ultrasonic Process for De-Ashing and De-Sulfurization

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 desulfurization and the percentage of desulfurization 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 desulfurization and de-ashing.

Grobas et al. [76] investigated hydrogenation of cyclohexene, biphenyl, and quinoline, and hydro-desulfurization of benzothiophene in the presence of formic acid (a hydrogen precursor), and a Pd/C catalyst; ultrasound irradiation was investigated as well. It was found that the use of formic acid in the presence of ultrasonic irradiation was effective in promoting hydrogenation and desulfurization at very mild conditions (i.e., ambient temperature and pressure).

Wang et al. [77] used several carbon-based sorbents for de-sulfurization of a model jet fuel. The results showed that the selective adsorption ability of PdCl₂ was higher than those of CuCl and metallic Pd. The results of desorption experiments showed that ultrasound-assisted regeneration was an effective method for the saturated PdCl₂/AC that was saturated with benzothiophene and substituted compounds. The amount of sulfur desorbed was higher with ultrasound, 65 wt% desorption vs. 45 wt% without ultrasound.

Mello et al. [78] investigated ultrasound-assisted oxidative process for sulfur removal from petroleum product feedstock. Dibenzothiophene is used as a model sulfur compound. The effect of sonication time, volume of oxidizing reagents, kind of solvent for the extraction step and kind of organic acid were investigated. Higher efficiency of sulfur removal was achieved using sonication in comparison to experiments performed without its application, under the same reaction conditions.

At present, Coal India Limited (CIL) operates 17 coal washeries, out of which 11 are for coking coal and the remaining are for non-coking coal, with a total capacity of 39.40 million tonnes per annum. CIL has been operating coking as well as non-coking coal washeries for a long period of time, but due to manpower constraints and operational cost, it has decided to outsource coal washery operation to private players. A number of private operators are already involved in coal washing in the country, and the power sector has started using washed coal for power generation, considering its economic and environmental benefits. Bilaspur Coal Washery produces 3 million tones per annum. Aryan Coal Washery produces nearly 22 million tones of coal per year. Tata Steel and SAIL’s joint-venture will set up a 1.8 million tonnes per annum (mtpa) coal washery at Bhelatand in Jharkhand, through an investment of Rs 200 crore. Twenty new washeries with an annual capacity of 111 million tonnes per annum are being taken up by Coal India (CIL) during the XI and XII Five-Year Plans.

There are several references in technical and trade literature regarding the employment of ultrasonics in coal cleaning and beneficiation; it is clearly a highly-scalable process that is in widespread use globally. Intuitively, there is no reason to
question the wisdom of its implementation for Indian coals, whose large ash content renders them very suitable for this purpose. This study attempts to validate ultrasonic wash for Indian coals on a laboratory scale, with the ultimate objective of defining a scalable process that can be implemented in production quantities.

2.6 Scope and Objectives for the Present Work

There are a number of methods available for remediation of ash related problems, but economically all have disadvantages. The utilization of ultrasound for the treatment of waste materials is a growing area of sonochemical research. Power ultrasound can be used for the beneficiation of coal by the removal of mineral matter (ash and sulfur) from coal. The following is a summary of key observations from a study of related literature:

- In conventional coal wash, the main focus is on surface cleaning, but there is little focus on interior part of the coal matrix.
- Ultrasonic coal wash method involves numerous influencing factors, and several complex, interdependent mechanisms have not been studied.
- Interaction mechanism between suspended coal particle and ultrasound has not been fully investigated.
- No attempt has been made to understand the mechanism of coal particle breakage and ash removal as a function of ultrasonic field parameters.
- So far, sono-fragmentation research has been primarily based on probe-type sonicator, not tank-type.

Ultrasonic coal-wash is thus widely used outside India, but not well understood by researchers. Hence, there is a necessity for experimental investigation and modeling to characterize the complex mechanisms and the effect of influencing parameters.

The specific objectives of present work are

1. Assessment of Fly–Ash Erosion Potential of Indian Coals
2. Experimental Studies on Ultrasonic Coal Beneficiation
   (a) Ultrasonic Aqueous-Based Coal Beneficiation
      i. De-Ashing
      ii. De-Sulfurization
   (b) Ultrasonic Reagent-Based Coal Beneficiation
      i. De-Ashing
      ii. De-Sulfurization
3. Experimental Optimization and Mechanistic Modeling of Ultrasound Assisted Reagent-Based Coal De-Sulfurization
4. Assessment of Benefits from Ultrasonic Coal-Wash (USCW)
References

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