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B. Ambedkar

Ultrasonic Coal-Wash for De-Ashing and De-Sulfurization

Experimental Investigation and Mechanistic Modeling

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Supervisor's Foreword

Dr. Ambedkar's thesis work has resulted in four papers, several conference presentations, and an "Outstanding Thesis" award. This comes as no surprise to me. Both in terms of the quantum of work and its quality, this dissertation is among the best in its breed. While "clean coal technology" is on everyone's wish-list, few have identified the relevant technologies. Removal of ash and sulfur from Indian coals prior to combustion using high-intensity acoustic fields is a novel concept with the promise of high throughput and cost efficiency. By means of well-designed experiments and sound analytical reasoning, Dr. Ambedkar has enunciated a path to follow. By focusing on Indian coals, this work becomes of immediate national relevance. While most Indian coals do have high ash content and low sulfur, there are exceptions; also, increasingly, foreign and Indian coals are being blended and used in power plants. Hence, simultaneous de-ashing and de-sulfurization become a critical need. Coal washeries being operated in India are unable to clean coal aggressively, being designed primarily to remove loosely-held dust, dirt and other debris. But more of these are being brought on-line regularly. This investigation paves the way for optimizing the design of coal washeries for maximum effectiveness with minimum cost and pollutant discharge. This is seminal work with potential for significant impact to the practice of coal washing in India.

Chennai, September 2011 R. Nagarajan

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Finally, I should thank my beloved parents Ms. Amsha and Mr. Balraj, for their constant support and encouragement throughout my studies so far. Without whose support I wouldn't have come this far as what I am today. I thank my brothers Mr. Alexander, Mr. Abraham and Mr. Kamesh for their support, unconditional love and affection on me. Last not least, my special thanks to my wife Ms. Puviarasi for her support in the form of love, affection and encouragement.

Nomenclature

Symbols

f	Frequency of ultrasound (kHz)
μ	Micrometer
Cs	Reagent concentration (mol/liter or gm/liter)
t	Sonication time (min)
A_{sp}	Total specific surface area (m^2/kg)
R_X	Rate of reaction with mass transfer (liter/mol*s)
d_{pi}	Initial coal particle size (μ)
d_{pf}	Final coal particle size (μ)
e_d	Energy dissipated/unit mass of liquid (W/kg)
To	Initial reaction mixture temperature (^oC)
T_f	Final reaction mixture temperature (^oC)
V_l	Reagent volume (m^3)
M_C	Mass of coal (Kg)
K_m	Mass transfer co-efficient (m/s)
D_{eff}	Effective diffusivity (m^2/s)
X_A	Fractional conversion of solid reactant
K	Model constant
a, b, c	Model parameters
E	Erosion loss (g)
d_p	Fly-ash particle size (μ)
Q_p	Fly-ash quantity (g)
V_F	Volumetric flow rate (m^3/min) [Area of Nozzle * Velocity]
Ro	Initial radius of particle (μ)
M_A	Molecular weight of sulfur

Abbreviations

AOP	Advanced Oxidation Process
ASTM	American Standard Testing Materials
DOE	Design of Experiments
EDAX	Energy Dispersive X-ray Analysis
FGD	Flue Gas De-Sulfurization
HCl	Hydrochloric Acid
HLA	High Level Analysis
HNO_3	Nitric Acid
H_2O_2	Hydrogen Peroxide
IS	Indian Standard
LPC	Laser Particle Counter
OH	Hydroxyl Radicals
ROM	Run of Mill
SEM	Scanning Electron Microscope
TSR	Total Sulfur Removal (%)
USCW	Ultrasonic Coal-Wash

Contents

Chapter 1
Introduction

1.1 Importance of Coal Washing

Coal is the largest source of fuel for generation of electricity throughout the world. The power sector will be the main driver of India's coal consumption. Currently, around 69% of the electricity consumed in India is generated from coal. Coal reserves in India are plentiful but of low quality. India has 10% of the world's coal reserves, at over 92 billion tons, third only to USA and China in total reserves [1]. The full utilization of coal is limited by the presence of high levels of ash and sulfur in it. During coal combustion, the mineral matter transforms into ash, and the amount of ash is so large that it is not easy to utilize ash effectively. Fly-ash is the finely divided mineral residue resulting from the combustion of ground or powdered coal in electricity generating plant. It consists of inorganic matter present in the coal that has been fused during coal combustion.

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

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

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particles collide with the surfaces of the steel air heater elements and material is eroded from the surfaces. In advanced stage of erosion, the plates become perforated. The air heater elements fail once they cannot maintain their structural integrity.

SOx as a pollutant are a real threat to both the ecosystem and to human health. Sulfur is found in two forms in coal: (1) Inorganic sulfur, and (2) Organic sulfur. The inorganic sulfur again classified into two class (a) sulphate sulfur and (b) pyritic sulfur. Sulphate sulfur occurs in combination with Ca, Mg, Ba, Fe, etc. Pyritic sulfur in coal are pyrite (FeS_2), dimorphic marcasite (FeS_2), sphalerite (ZnS), galena (PbS), chalcopyrite ($CuFeS_2$), pyrhhotite ($Fe_{1-x}S$), arsenopyrite (FeAsS) and others. The chemical structures of organic sulfur components of coal are generally part of the macro-molecular structure of the coal itself. Organic sulfur is chemically bonded and very difficult to remove by physical cleaning methods. The organic sulfur components can be broadly divided into aliphatic and aromatic or heterocyclic sulfur structures.

Methods to control SO_2 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, and
4. Conversion of coal to a clean fuel by gasification and liquefaction.

However, these are ineffective in the sense that time and energy consumption are high, and many chemicals are involved, introducing difficulties in handling of by-products during process. Nowadays, online flue gas de-sulfurization is being attempted to remove sulfur from coal post-combustion. The biggest disadvantage associated with this method is formation of by-products [Flue Gas Desulfurization (FGD) gypsum is one]. According to the American Coal Ash Association's annual Coal Combustion Product Production and Use Survey, total production of FGD gypsum in 2006 was approximately 12 million tons. Close to 9 million tons of FGD gypsum were put to beneficial use, while the remainder was land-filled. There is, at present, no way for effective usage of all FGD gypsum generated as by-product [2].

There are also concerns about environmental effects when FGD gypsum is used for soil amendment, and there are some reports on how chemical properties of soils, plants and animals are affected following FGD gypsum application (Environmental Protection Agency, USA). 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 gypsums. This will lead to acute and chronic effects to humans as well as plants. Over the next 10 years, annual production of FGD gypsum may double as more coal-fired power plants come online, and as scrubbers are added to existing power plants to meet the environmental clean-air standards. In the worst case, where sulfur in coal is 10% or higher, releasable sulfur amount can become very high. This would lead to unnecessary transport and storage before, as well as after, combustion in terms of FGD gypsum. There is clearly a need for removing ash and sulfur from coal prior to combustion. Ultrasonic coal-wash is one

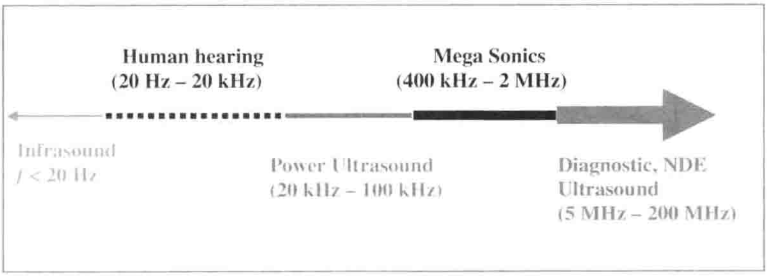

Fig. 1.1 Sound frequency range

such technique to effectively remove ash and sulfur from coal prior to combustion. In addition, it is easy to scale-up as a continuous process.

1.2 Ultrasound-Assisted Process Intensification

A wave is defined as a disturbance that propagates through space and time, usually with transference of energy. Waves travel and transfer energy from one point to another, often with no permanent displacement of the particles of the medium (that is, with little or no associated mass transport); they consist instead of oscillations or vibrations around almost fixed locations. A sound wave is a mechanical pressure wave that propagates or travels through a medium due to the restoring forces it produces upon deformation. Since a sound wave consists of a repeating pattern of high-pressure and low-pressure regions moving through a medium, it is sometimes referred to as a pressure wave.

Ultrasound is cyclic sound pressure with a frequency greater than the upper limit of human hearing. Although this limit varies from person to person, it is approximately 20 kHz (20,000 Hz) in healthy, young adults and thus, 20 kHz serves as a useful lower limit in describing ultrasound. The frequency ranges of sound are shown in Fig. 1.1. Sound wave of frequency less than 20 Hz is known as infrasound.

Ultrasound is a novel technology which is in widespread use in various scientific and medical fields [3, 4]—e.g., surface cleaning in microelectronics manufacturing, biomedical device cleaning, sono-chemical reactors designed to accelerate chemical reactions by several orders of magnitude, sono-intensification of mass-transfer and heat-transfer rates, sono-mixing and de-stratification in tall containers, nano-particle fabrication by sono-fragmentation, etc.

1.2.1 Basic Mechanism of Ultrasound

When ultrasound is applied to a medium such as water, the basic physical phenomena involved in producing changes observed (physical and chemical

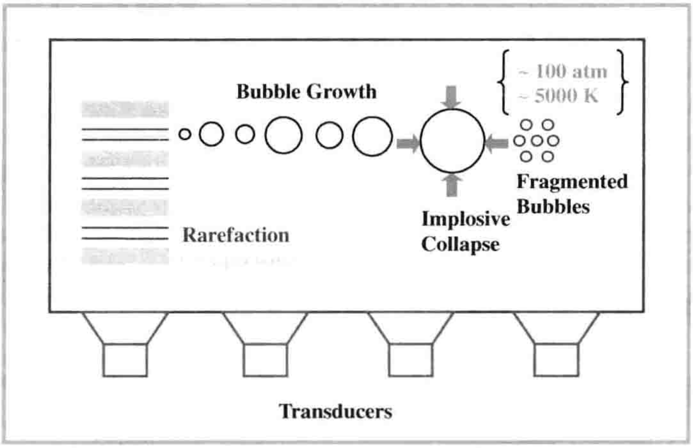

Fig. 1.2 Acoustic cavitation in ultrasonic tank

effects) in the medium are of two types—acoustic cavitation and streaming. Cavitation is the dominant mechanism in ultrasonic fields in the <100 kHz frequency. Two types of acoustic cavitations are identified, namely, stable cavitation and transient cavitation. In stable cavitation, bubbles continue to oscillate near their resonance size without collapsing; in transient cavitation, encountered in our system, bubbles grow and collapse, as observed visually and via measurements of cavitation intensity. Cavitational collapse results in extreme conditions producing light emission, shock waves, and localized high temperatures (up to approx. 5000 K) and pressures (up to 100 atm). These shock waves are responsible for the rupturing of neighboring solids (which may be vessel walls or immersed solids), leading to the generation of shear forces and eddies which, in turn, lead to an increase in turbulent energy dissipation. The number of these shock waves is related to the frequency of the waves [5, 6]. Typical acoustic cavitation that occurs in low-frequency ultrasonic tank is shown in Fig. 1.2.

Acoustic streaming refers to unidirectional flow currents in a fluid formed due to the presence of sound waves. Typical acoustic streaming that occurs in high-frequency ultrasonic and megasonic tanks is shown in Fig. 1.3. The formation of acoustic fountains is observed at the center of the transducer locations. Acoustic streaming comprises several important effects: (1) bulk motion of the liquid (Rayleigh streaming), (2) micro-streaming (Eckert streaming) and (3) streaming inside the boundary layer (Schlichting streaming). The primary effect of acoustic streaming is steady bulk motion of the liquid which generates shear force. A second effect of acoustic streaming is micro-streaming. Micro-streaming occurs at the substrate surface, outside the boundary layer, due to the action of bubbles as acoustic lenses that focus sound power in the immediate vicinity of the bubble. Micro-streaming aids in dislodging particles and contributes to megasonic

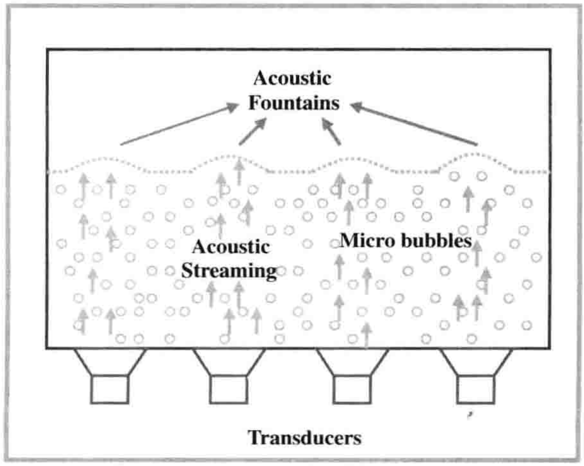

Fig. 1.3 Acoustic streaming in ultrasonic tank

cleaning. Most of the flow induced by acoustic streaming occurs in the bulk liquid outside the boundary layer. However, there is a third effect of acoustic streaming—Schlichting streaming—which is associated with cavitation collapse. Schlichting streaming occurs inside the boundary layer and is characterized by very high local velocity and vortex (rotational) motion. Acoustic streaming, both inside and outside the boundary layer, enhances cleaning and other chemical reactions.

Two basic mechanisms for acoustically enhanced coal washing have been suggested by Mason et al. [7]: (a) an increase in the abrasion of suspended coal in slurries leading to the removal of dust material from the surface of coal, and (b) an enhanced leaching of contaminants (mineral matter) from the interior of coal particles. Under the influence of ultrasound, normal leaching occurs, but several additional factors contribute towards improvements in the efficiency. These include:

1. Asymmetric cavitation bubble collapse in the vicinity of the solid surface, leading to the formation of high-speed micro jets targeted at the solid surface. The micro jets can enhance transport rates and also increase surface area through surface pitting.
2. Particle fragmentation through collisions will increase surface area.
3. Cavitation collapse will generate shock waves which can cause particle cracking through which the leaching agent can enter the interior of particle by capillary action.
4. Acoustic streaming leads to the disturbance of the diffusion layer on the surface.
5. Diffusion through pores to the reaction zone will be enhanced by the ultrasonic capillary effect.