Graphene's Application to Boiler's Fabrication and Design

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***ABSTRACT*— Problem Statement: Boilers have enormous applications and usefulness in power generation. It is to be reckoned as an all time employee in power generation sector and it is a device to create steam by applying heat energy to the water. It can also be used as steam generators. The pressure vessel of a boiler usually made of steel (or alloy steel), or historically of wrought iron is extremely exposed to the corrosion and embrittlement. This causes additional problems like boiler breakdown which can cost thousands of dollars in equipment repairs, as well as hundreds of thousands of dollars for additional property damage and business income losses. Despite numerous methods to minimize this problem the world hasn't come up with a concrete solution. Still today boiler accidents cause heavy economic and personal losses. Can we ever come up with a solution to almost nullify this problem with all the advancements in Material Sciences in recent years?**

Proposed Solution: We aim at coating the inner side of boiler with deposition of membrane of oxide of recently discovered super-material graphene. Researchers found that a multilayer of graphene dioxide when stacked up together act as perfect molecular sieves when immersed in water, blocking all molecules or ions with a hydrated size larger than 4.5 Å. Caustic Embritllement causing prime agent NaOH clearly is not contained within limits described in its molecular form. Also we found that except for water vapors it does not allow any other gas to bypass it hence we ideate that prime corrosion causing agents like dissolved O2 and C02 will not interact with boiler material and hence will significantly remove boiler corrosion.

Conclusion: Incorporating this hypotheses we tend to believe that prime boiler enemies will exert their least presence on boiler's functioning and its life. Its working life will be enhanced by several times. We believe that use of the latest advancement witha rather primitive subject of boilers will create a wave within boiler industries and help them to enhance boilers working and increase its life. Also it will eliminate the causticity of boiler water.

Keywords— Boilers, Graphene, Graphene Oxide, Applied Sciences Corrosion, Embrittlement, Material Science.

I. INTRODUCTION

A boiler is a closed vessel which is used to heat water or some other fluid. The fluid need not necessarily boil. The heated or/and vaporized fluid exits the boiler for use in various processes generally for heating applications which includes central heating, power generation, cooking. The pressure vessel of a boiler is usually made of steel, cast iron and alloy steel, is extremely exposed and prone to corrosion, embrittlement and other functioning complexities. Numerous researches and handful of papers along with abounding corrosion reduction techniques have been come up, still practically no efficient solution has been deduced yet to pave the way for minimizing the corrosion. The lack of minimizing techniques bears a testimony to the fact that nothing is perfect and therefore no near perfect let alone perfect solution is to be aimed at. The existing techniques and solutions to reduce ardent enemies of boiler functioning have been found to reduce the effect of corrosion by only 50%. This is nowhere near to what is desired and have indeed caused economic, functioning and personal losses. The US is losing more than $276 billion and India Rs 80,000 crore per annum on account of corrosion as in 2007. This is the measure of significance of corrosion reduction research in boiler driven industries. Personal loses severity include loss of life due to boiler breakdown. This paper tends to introduce a new dawn in corrosion reduction techniques in boilers by incorporating recently discovered and extensively researched super material "Graphene". Graphene is a crystalline allotrope of carbon with 2-dimensional properties. In graphene, carbon atoms are densely packed in a regular sp^2-bonded atomic-scale in hexagonal pattern. Graphene can be conveniently described as a one-atom thick layer of graphite. It is found to possess unnatural and excellent thermal, conducting, strength and mechanical properties. A perfect conductor of heat, its single layer have an exceptional tensile strength greater than 1teraPascal. It is the basic structural element of other allotropes, including graphite, charcoal, carbon and fullerenes.

The graphene dioxide used here is an oxide of graphene which have an exceptional membrane forming properties. The research focuses on applying multilayer of graphene dioxide on inner side of boiler by spray deposition along with highly adhesive epoxy resin nano-composites which we believe will provide a breakthrough in corrosion limiting techniques applied on boilers. Also having an exceptional potential in tackling other working problems of boilers like caustic embrittlement, tensile fatigue, dissolved oxygen corrosion, caustic attack, acidic attack and hydrogen attack , this idea and this method in general will serve as a versatile multipurpose one time solution to almost all boiler problems enhancing its working life, functioning and efficiency.

II. RELATED WORK

Graphene Oxide, currently, is prepared by using paper making techniques on oxidized, dispersed and chemically synthesized graphite in water. The resulting monolayer flakes form a single sheet and develop strong bonds. These sheets, called graphene oxide paper have a measured tensile modulus of 32 GPa. Graphene-based membranes are impermeable to all gases and liquids (vacuum-tight). However, astonishingly water evaporates through them as quickly as if the membrane was not present. It was found that membranes which are sub micrometer thick made from graphene oxide can be completely impermeable to liquids, vapors, and gases, including helium, but these membranes allow unimpeded passage of water (H_2O permeates through the membranes at least 10^{10} times faster than He)[1].This can be attributed to a low-friction flow of a monolayer of water through two-dimensional capillaries formed by closely spaced graphene sheets.

The capillaries between the individual graphene-oxide flakes appear to act like powerful little vacuum cleaners that suck up small ions. The Manchester researchers produced their membranes by putting together thousands of individual tiers of graphene oxide on top of each other using simple techniques such as vacuum filtration and spray-coating. The graphene-oxide sheets are separated from each other by about 6–7 Å when dry; but when the sheets are immersed in water, this separation increases to about 11–12 Å. Water layers formed inside this ultra-narrow graphene capillary can move very freely, something that helps ions and molecules which are smaller than the size of the capillary itself to pass through. Diffusion of other molecules is blocked by reversible narrowing of the capillaries in low humidity and/or by their clogging with water. These laminates of graphene oxide are vacuum-tight in the dry state but, if immersed in water, act as molecular sieves, blocking all solutes with hydrated radii larger than 4.5 angstroms. Smaller ions permeate through the membranes at rates thousand times faster than what is expected for simple diffusion.[2]

Graphene oxide is reported by many researchers to be aelectrically insulating material due to their disrupted sp2 bonding networks. Because electrical conductivity can be recovered by restoring the p-network, one of the most important reactions of graphene oxide is its reduction .Reduction is the only notable reaction found to exhibit by graphene oxide.The product is stable. Conditions of instability include simple factors like excess heat, and incompatible materials. It is reported as highly reactive with oxidizing agents. Polymerization will not occur under standard conditions.[3]

The reduction process is among the most important and significant reactions of graphene oxide, to date. For scientists and engineers aiming to use graphene in large scale applications, such as energy storage, chemical conversion of graphene oxide is the obvious and desirable route (at this time) to large quantities of graphene-like materials. These reduction methods can be achieved through chemical, thermal, or electrochemical reduction pathways.[3]

It has been reported that the fast, low-cost, simple fabrication of a large chemically-converted graphene (CCG) films by spray deposition of graphene oxide (GO)–hydrazine dispersions. This GO–hydrazine dispersion was prepared by the author of cited authors by mixing GO dispersion with excess amount of hydrazine monohydrate as written in their paper. By spray deposition on preheated substrate, the creation of the thin film and the reduction of GO to CCG were carried out simultaneously. Atomic force microscope images clearly showed continuous films resulting from the overlap of graphene sheets.[4]

Excellent Thermal Conductivity of Transparent Cellulose Nanofiber/Epoxy Resin Nanocomposites has been reported in researches.[5]

A paper was presented showing the results of attempts to perform pad welding of heat exchanger pipes with nickel alloys Inconel 625 and Inconel 686, and high-temperature resistance tests of the padded welds in an atmosphere of N_2 + 9% O_2 + 0.08% SO_2 + 0.15%HCl for 750 corrosion processes induce the formation of a Cr_2O_3 oxide film of 5–10 µm thickness on the Inconel padded welds, which constitutes a passivation layer, reducing the corrosion rate. The presence of iron on the padded weld surface is conducive to the formation of Fe_3O_4 oxide, which worsens the padded welds' resistance to corrosion and erosion.[6]

III. BASIC SYSTEM PARAMETERS

I. STEAM BOILER is a fired or unfired closed pressure vessel used to generate steam by application of heat.

A. Low Pressure Boiler is a boiler in which steam is generated at pressures not exceeding 15 PSI.

B. High Pressure or Power Boiler is a boiler in which steam or other vapor is generated at pressure exceeding 15 PSI.

C. Small Power Boiler is a boiler with pressure exceeding 15 PSI but not exceeding 100 PSI and having less than 350,000 BTU's per hour heat output.

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II. HOT WATER BOILER is a fired or unfired pressure vessel used to heat water.

A. Low Pressure Boiler is a boiler, which does not operate at water pressures exceeding 160 PSI or water temperatures exceeding 250ºF.

B. High Pressure or High Temperature Power Boiler is a boiler used to heat water or a liquid to temperatures above 212ºF at pressure exceeding 160 PSI or to a temperatures exceeding 250ºF regardless of pressure.

III. WATER HEATER is an appliance designed primarily to heat supply water and is equipped with automatic controls limiting water temperatures to a maximum of 210ºF.

IV. OTHER RELATED INFORMATION

C. Steam Boiler Horsepower is the term used to rate the generating capacity output of a steam boiler. A boiler horsepower is equivalent to the evaporation of 34.5 lbs. of water or 4.14 gallons per hour at a temperature of 212ºF into steam at the same temperature. Or, 1 boiler horsepower is the evaporation of 30 lbs. of water per hour into steam at 70

PSI gauge pressure from an initial water temperature of 100ºF. A boiler horsepower is equivalent to an output of 33,475 BTU's per hour.

V. PRESSURE VESSELS (UNFIRED) is defined as a closed vessel or tank having a nominal internal diameter exceeding 6" and a volume exceeding 1½ cu. ft., for liquids, gases or vapors subjected to pressure exceeding 15 PSI or steam under any pressure.

IV. PROBLEM STATEMENT

Feed water line corrosion:

High-velocity water and especially water-steam mixture often cause erosion problems which primarily occur at the hairpin bends in steaming economizers. Here, the mixture of steam and water thins the elbows, leaving a characteristic reverse horseshoe imprint.

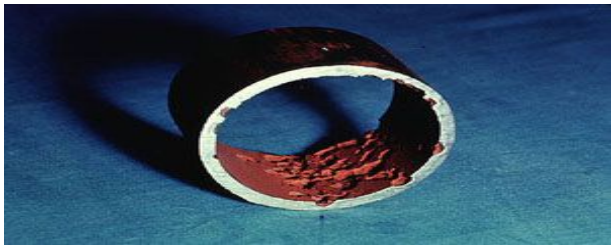


Fig.1. Economiser Tube Corrosion

Economizer tubesFaliures:

Water tube economizers are often subject to the serious and severe damages. The most severe of damages occurs at the economizer inlet valve and also at the tube weld seams of oxygen. Pitting is the most common form of water corrosion. This type of localized attack develops in an area of an economizer where steam generation is taking place beneath a deposit and free caustic soda is present in the feedwater. Other common causes of economizer failure include fatigue cracking at the rolled tube ends and fireside corrosion caused by the condensation of acid from the boiler flue gas.

Caustic embrittlement:

Caustic embrittlement is a specific form of stress corrosion, results in the developments of cracks in steel. This is basically intercrystalline cracking and results only when all of the following are present: specific conditions of stress, a mechanism for concentration such as leakage, and free NaOH in the boiler water. Therefore, boiler tubes usually fail from



caustic embrittlement at points where tubes are rolled into sheets, drums, or headers.

Fig.2. Caustic Embrittlement

Stress induced corrosion:

Certain portions of the boiler can be very susceptible to corrosion as a result of stress from mechanical forces applied



during the fabrication processes. Damage is visible in stressed components, such as rolled tube ends, threaded bolts, and cyclone separators.

Fig.3. Stress Induced Corrosion

Caustic attack:

Caustic attack (or caustic corrosion), is different from caustic embrittlement, is encountered in boilers with demineralized water. This often occurs in phosphate-treated boilers where tube deposits form, particularly at high heat input or poor circulation areas. Deposits of a porous nature allow boiler water to permeate the deposits, causing a continuous buildup of boiler water solids between the metal and the deposits. Because caustic soda does not crystallize under such circumstances, caustic concentration in the trapped liquid can reach 10,000 ppm or more. As long as the high caustic

concentrations remain, this destructive process causes a continuous loss of metal.

Hydrogen attack:

When atomic hydrogen permeates the metal structure, it reacts with the carbon content to form methane. Because the methane molecule is too large to diffuse through the steel, excessive pressure develops within the metal structure, causing the metal to rupture along the crystalline boundaries where methane has formed.[7]

These working and corrosion problems listed here are prime ardent enemies of boiler's life and efficiency, so will a single versatile solution be found out such that it tackles all of these problems?

V. SOLUTION AND ANALYSIS

We propose to introduce a multi layered graphene oxide sheet between metal and fluid media, pasted through epoxy resin.
Graphene oxide being chemically inert does not react with fluid and other salts and chemicals present in it.Also graphene oxide selectively allows only water and water vapors to permeate through it and is almost impermeable to every fluid and gas ,even helium, thus acting as perfect sieve. To be more specific it does allow molecules or atoms with hydration radii more than 4.5 Angstrom. Furthermore graphene oxide has a very appreciable tensile strength coupled with excellent thermal conductivity. Here we propose to deposit graphene oxide layer via spray deposition method. The fast, low-cost, simple fabrication of a large chemically-converted graphene (CCG) films by spray deposition of graphene oxide (GO)–hydrazine dispersions is to be used. By spray deposition on preheated substrate, the creation of the thin film is carried out. Here we epoxy resin as an adhesive over other adhesives on the grounds that besides being a strong adhesive it can be operated over a long range of temperature and also blocks the moisture to attack the metal surface. It is a very least reacting adhesive with almost negligible reactivity.
Economizer tubes problem can be resolved as graphene oxide membrane will block any acid to pass through it and enter the cracks at rolled tube ends of metal, thus eliminating the question of acid deposition. Also molecular cannot pass through graphene oxide membrane.
Feedwater line corrosion problem will be resolved as high velocity streams cannot break the graphene sheet because of its high tensile strength and furthermore it will allow water to permeate through it so water cannot erode the sheet.
Caustic embrittlement problem will be resolved as fluid will not be able to interact with any crack formed at the bends, due to the permeability of graphene oxide layer in between, thus eliminating the question of deposition of salts in cracks.
Stress induced corrosion problem will be resolved as fluid will no longer be able to interact with the metal ,furthermore the epoxy resin applied between metal and graphene oxide will also prevent metal surface against corrosion. The prime corrosion causing agent like carbon dioxide and oxygen will not permeate the limited size described for molecule permeation for a graphene oxide membrane.
Caustic attack problem will be resolved as stated many times by now non permeation characteristic of graphene oxide film.
Hydrogen attack problem will be resolved as no gas other than water vapors will be able to permeate through the graphene oxide sieve ,that clearly further implies that hydrogen will obviously not exert its influence.

VI. CONCLUSIONS

A versatile one stop multipurpose solution was proposed to tackle and overcome all working, practical and chemical disabilities of boilers. We used exceptional and unnatural properties of graphene and graphene oxide in specific to limit corrosion, attacks by chemicals and caustic embrittlement encountered in boilers functioning. Here using non permeability property of graphene oxide membranes we overcame almost all boiler related problems. Also it inertness helped us to carry out this research without chemical interruptions. Its excellent bonding with epoxy resin helped us to spray deposit graphene oxide (GO)–hydrazine dispersion layer on it thus making it highly adhesive to boiler's inner surface. Epoxy resin itself being highly anti-corrosive will prevent further interaction of water to boiler's surface as it will not let water or moisture pass through it. We believe that this method will be employed by industries driven by/on boilers to minimize boiler related problems and hence reduce their economic, efficiency and personal losses and simultaneously increase boiler's functioning, efficiency and working life to several times. This hypothesis will serve as a breakthrough research for industries which aim to achieve more over less in boiler's operating. Overheating problems leading to plastic flow cannot be handled through this hypothesis. Presence of lithium aluminum hydride LiAlH, can cause damage to graphene oxide membrane by reducing it into graphene.

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