

JUST

**JOURNAL OF UNDERGRADUATE
SCIENCE AND TECHNOLOGY**



IN THIS ISSUE:
ELECTRIC VEHICLE BATTERIES
CONCENTRATING SOLAR POWER
BIOMASS CO-FIRING



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ABOUT

The Journal of Undergraduate Science and Technology (JUST) aims to acknowledge and showcase undergraduate research being carried out within the College of Engineering, Mathematics and Physical Sciences (CEMPS) at the University of Exeter. The Journal, as well as providing undergraduate students with an opportunity to develop their writing and presentation skills, also enables them to engage with the wider ‘STEM’ communities within the University and beyond, and to exchange ideas and share intellectual activity.

All undergraduates within CEMPS are eligible to submit to the Journal for print and online publication and the editorial team welcome contributions from students at any stage of their academic programme.



FOREWORDS

At this year's British Conference of Undergraduate Research, a keynote speaker asked, 'When your students hand in a piece of work, do they feel a sense of achievement or relief?' Providing undergraduates with opportunities to publish and present their work moves beyond awarding a grade, to recognition that the work undertaken is of interest to a wider community. The Journal of Undergraduate Science and Technology and Annual Conference provide opportunities for undergraduates within the College of Engineering, Mathematics and Physical Sciences to showcase their research. This provides valuable formative experience for postgraduate study, and gives students a useful insight into how their lecturers disseminate their own research.

JUST offers a useful platform for developing and continuing ideas and research investigations. The traditional dissertation and project work once marked, verified and archived is rarely accessed by others. A journal can be readily consulted by a current or future student undertaking similar investigative work, thereby enhancing the continuity of ideas.

The ability to write well is regularly cited as a top ten skill by graduate employers. Interpersonal skills, particularly the ability to present complex ideas clearly and succinctly, are also highly-valued. 'Writing for publication' provides an excellent vehicle for developing these skills when included as an aspect of the traditional dissertation or other pieces of coursework which focus on research investigations and the communication of findings.

Steve Rose, Academic Advisor to JUST

Despite various newspapers, politicians, and even governments denying that it is happening, climate change is one of the single greatest threats facing humanity today. In the last century, the average global temperature has risen by almost one degree Celsius; our best data predict that it will rise at least another one degree and perhaps as high as six or seven. The Earth has faced tougher challenges, and will doubtless survive, but it is unlikely that our present way of life will without drastic change.

All three papers published in this edition of JUST are about ways of combatting global warming's principle cause: the emission of greenhouse gases. Two papers battle it at the generation of power, firstly at power stations, by burning wheat straw to drive turbines, and another at finding effective, practical batteries for electric vehicles. The final paper demonstrates effective methods of drawing power directly from the sun, using mirrors to intensify its heat.

The University of Exeter is proud that its undergraduates help it to be a world leader in climate research. After all, who can honestly say they have never dreamed of helping to save the world?

Paul Gratrex, Editor

REQUIREMENTS AND CHALLENGES FOR ELECTRIC VEHICLE BATTERIES

BY P. KAVETHEKAR, A. LITTLEWORTH, H. POULTER, T. ROBSON, O. SMITH, & D. TRUDGEON

ABSTRACT

Electric vehicles (EV) have been touted as the future of motoring. Widespread utilisation of EVs would reduce CO₂ emissions and the associated effects of anthropological climate change. In addition, dependence on the finite resources of hydrocarbon fuels would be limited. As such, the development of safe, reliable, and durable batteries for EV applications is essential. Developing competitive batteries for this purpose presents challenges, as hydrocarbon fuels offer high energy densities in an easily transferable form.

It has been found that, as EV battery design has progressed, research is largely looking towards the use of lithium-ion batteries, encased in a composite material such as fibre reinforced plastics, and potentially incorporating the battery into the structural fabric of the vehicle. It is also found that ecological impacts associated with EV batteries can be severe. If the future of battery powered EVs is to be a clean and environmentally sound alternative to hydrocarbons, these impacts need to be addressed.

INTRODUCTION

This report investigates some of the issues faced by EV battery designers, starting with requirements at the design phase, and then considering operational issues such as range and lifespan, the availability of the materials used in battery technologies, and the environmental impacts associated with

the extraction and use of these materials. The most promising battery technology currently available is then identified.

MATERIAL SELECTION PROCESS

This section of the report is concerned with material selection for the EV battery. This has been split into two parts: material selection for the electrochemical cells; and material selection for the battery housing.

ELECTROCHEMICAL CELLS

The battery is characterised by the reactions that occur at each electrode: the cathode (+ve) is oxidised (loss of electrons) and the anode (-ve) is reduced (gain of electrons). This potential difference drives electrons through the electrical circuit as the cell tries to reach equilibrium. The electrolyte completes the circuit within the battery by allowing ions to flow.

From Figure 1 (next page) it is clear that lithium-based batteries offer the highest energy densities; however, NiMH is comparable in terms of volume. This is perhaps why NiMH has been chosen for the Toyota Prius, although NiMH is much more susceptible to battery memory problems than lithium technologies.

Lithium is the most reactive metal due to its electrochemical potential, which gives it its high energy density. In its pure form, however, it is unstable and unsafe, as it is “highly flammable [and] reacts violently

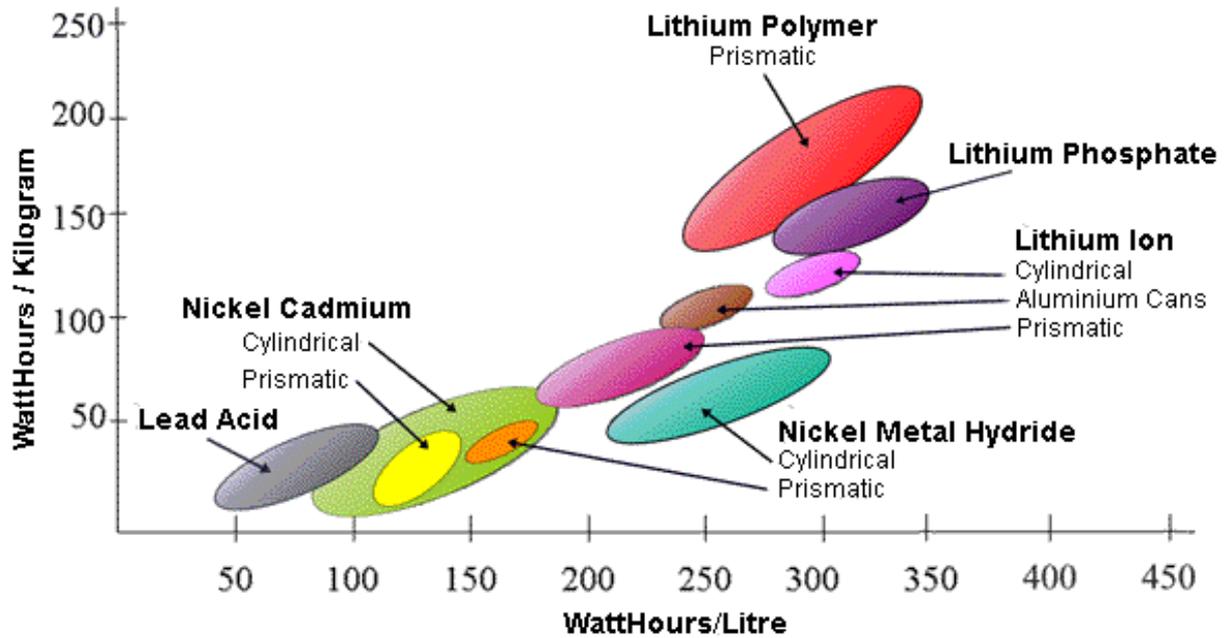


Figure 1: Energy density^[2].

with water, liberating highly flammable gases^[1]. It is therefore combined in compounds with other elements, the most common of which are compared in Table 1. In spite of this, lithium batteries require more extensive circuitry whilst charging and discharging.

Electrodes

The larger the surface area in contact with the electrolyte, the greater the supplied current can be. Lead acid batteries for SLI (starting, lighting & ignition) are not designed to go below a 50% DoD (depth of discharge) as they are recharged by the alternator. They have a greater number of thinner plates compared to deep cycle batteries which are designed to be fully discharged. It has fewer, thicker plates to be

able to withstand the heat that occurs during charging^[2].

The benefits of current hydrocarbon fuels are their high energy density and their liquid state. These make transport, storage, and re-fuelling relatively quick and simple. This is why the development of liquid electrodes is exciting for the future of EVs. It is being described as a “rechargeable fuel”^[21] and could be comparable with the convenience of hydrocarbon fuels in its delivery. Furthermore, it would allow for different vehicles (assuming the same battery composition) to use this method, leading to greater scalability as battery

Table 1: Lithium ion cathode chemistry comparison (used with carbon anodes)^[2].

CATHODE MATERIAL	TYPICAL VOLTAGE (V)	ENERGY DENSITY		THERMAL STABILITY
		Gravimetric (Wh/kg)	Volumetric (Wh/L)	
Cobalt Oxide	3.7	195	560	Poor
Nickel Cobalt Aluminium Oxide (NCA)	3.6	220	600	Fair
Nickel Cobalt Magnesium Oxide (NCM)	3.6	205	580	Fair
Manganese Oxide (Spinel)	3.9	150	420	Good
Iron Phosphate (LFP)	3.2	90-130	333	Very Good

swapping is dependent on a ready supply of an identical battery.

Electrolytes

The electrolyte must be able to conduct ions, especially for high power applications. Traditionally, this was an aqueous liquid, such as sulphuric acid in lead acid batteries. However, this is not suitable for a lithium based battery, so a non-aqueous organic lithium salt is used. This also eliminates the production of hydrogen and oxygen from the hydrolysis of water if over charged^[2]. Liquid electrolytes require a more substantial case to protect from damage due to leakage. Using AGM (absorbed glass matting) like a sponge to hold the liquid is one method of reducing this problem; another is using a gel electrolyte, but this is not ideal for fast charging as any gases released can cause permanent damage.

The best electrolyte in terms of safety, cost, weight, and design flexibility is a polymer, as it is a solid state and does not require the protection of liquid electrolytes. Unfortunately, compared with a liquid, the thickness of the polymer between electrodes is increased. It also has a higher internal resistance, and cannot discharge current as quickly, which is why its main use is portable electronics which don't require high currents^[2]. However, there are hybrid polymer cells which also contain liquid or gel to help mitigate this.

There is no doubt that lithium-based batteries are the right choice due to their superior energy to weight ratio. Currently lithium polymer is not as developed, and is more expensive, but could be the clear choice in the future due to its design flexibility and relative safety.

BATTERY HOUSING

In order to design EV battery housings the specification of the product needs to be addressed. A design statement for this element of the battery design could be:

‘An outer casing is required for an electro-chemical battery that is able to withstand high impact, high heat loads, and is a good insulator. It must also be lightweight and cost effective.’

These considerations then need to be categorised, as in Table 2, into constraints and objectives, with constraints being a limit and objectives being desirable outcomes. By following these, initial material choice can be made using material charts.

CONSTRAINTS	OBJECTIVES
High Young's modulus	Low cost per unit volume
High Strength	Lightweight
High fracture toughness	
High/low thermal conductivity	
High electrical resistivity	

Table 2: Battery housing constraints and objectives.

Figure 2 (next page) can be used to identify materials able to withstand high impacts whilst retaining low densities. It can be seen that metals, technical ceramics, and composites have the highest modulus. Of these, carbon-fibre-reinforced-polymer (CFRP) is the lightest. This process can then be repeated using fracture toughness/strength, yield strength/fracture toughness, strength/cost per unit volume, and thermal conductivity/electrical resistivity charts. Table 3 (next page) shows the best choice of material for each constraint and objective.

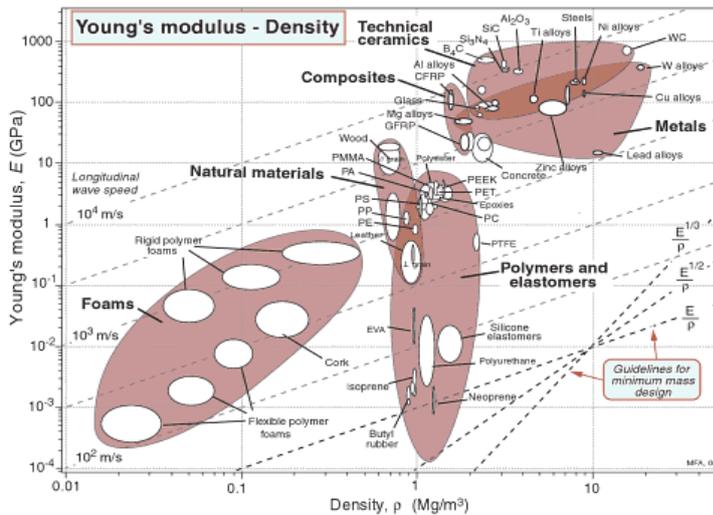


Figure 2: Young's modulus/density chart^[3].

Table 3: Material choice related to constraints and objectives.

CONSTRAINTS	OBJECTIVES
High Young's modulus – metals, CFRP	Low cost per unit volume – al. alloys, carbon steel, stainless steels
High Strength – metals, CFRP	Lightweight - CFRP
High fracture toughness – alloy/stainless steels	
Thermal conductivity – polymer foams (low), steels (high)	
High electrical resistivity – polymer foams	

Until recently, the trend in battery casings was for steels or aluminium alloys with foam insulation. The metals are easy to form and comparatively cheap; however, they are also heavy, with the casing making up around 15% of the battery weight. The use of lighter reinforced plastics has been researched with thermosets and thermoplastics reinforced with fibres, increasing the tensile strength and improving fracture toughness^[4]. The low thermal conductivity of the plastics allows elimination of the foam barrier, and connectors can be integrated into the design to provide insulation against temperature variances. The use of CFRP reduces housing weight by 25-35%^[5]. DuPont are currently making plastics for EV battery casings that reduce weight by up to 40%^[6].

Current research is using materials to make structural batteries (i.e. using load bearing parts of the vehicle as an integral energy storage unit^[7]).

OPERATIONAL ISSUES

This section focuses on four areas related to EV batteries. The first of these is range, which is one of the factors preventing widespread use of EVs. Current EVs cannot match the range of combustion engine based vehicles. Although the range of an EV is dependent upon motor efficiency, road type, and vehicle weight, in terms of the battery alone the potential range is directly related to energy density. A battery with high energy density will provide greater range.

EV batteries can be expensive and inconvenient to replace, making lifespan an important factor. This problem may be reduced through designing EVs with easily replaceable battery modules, or battery rental schemes such as Nissan currently employ with their Leaf model. Long lifespans are desirable in order to reduce the

frequency with which batteries need to be changed.

Lifespans of rechargeable batteries are usually given in terms of the number of charge/discharge cycles available at 80% DoD. However, it is more relevant to EVs to ascertain the mileage that a battery can achieve during its life. In order to compare the lifespan of different battery types, the energy density has been multiplied by the number of cycles available. This provides a figure for the energy available per kilogram over the life of the battery, which is directly related to the obtainable mileage (Table 4).

Most current EVs suffer from long recharge times, which is inconvenient for the user. Many battery types will incur damage and attenuation of lifespan if recharged too quickly. A battery type that can be safely and quickly charged without causing damage is therefore desirable.

EV batteries must be durable, as any damage caused to battery can decrease the lifespan and cause safety problems. It is important that EV batteries have low maintenance requirements and operational temperature ranges sufficient to cover the range of environments the vehicle will be exposed to. Many types of battery also suffer damage and/or reduced lifespan if overcharged or excessively discharged. However, these problems can be avoided by on-board Battery Management Systems (BMS) which prevent overcharging and unwanted DoD levels^[8]. BMS can monitor

the state of charge (SoC) of the battery and prevent excessive charge/discharge.

From the issues identified above, it can be seen that the ideal battery for EVs would have a high energy density, lifespan, recharge rate and durability whilst requiring little maintenance. Table 4 shows a comparison of the main types of battery under consideration for use in EVs.

Currently, the most promising battery type for EV applications is the lithium-ion battery. It has the highest energy density, requires little maintenance, and has a reasonable recharge rate and operational temperature range. In addition, lithium-ion batteries do not suffer from memory effect, which affects nickel cadmium and nickel metal hydride batteries. This causes decreased capacity if the battery is recharged after only partial discharge.

There are, however, issues with lithium-ion batteries. For example, they are prone to ageing if stored at temperatures above 15°C and can fail after only three years if stored incorrectly. Also, lithium-ion batteries are relatively fragile. Although BMS can be used to identify battery faults at an early stage and prevent damage^[8], the fragility of this battery type is potentially a safety issue due to the risk of sudden damage caused by a road traffic accident.

Table 4: Comparison of battery types for EV application^{[9][10][11]}.

BATTERY TYPE	ENERGY DENSITY (WH/KG)	SERVICE LIFE (NO. OF CYCLES)	LIFETIME ENERGY DENSITY (KWH/KG)	OPERATIONAL TEMPERATURE RANGE (°C)	RECHARGE RATE	LEVEL OF MAINTENANCE
Lithium Polymer	155	600	93	0 to 60	Medium	Low
Lithium Ion	160	1200	192	-20 to 60	Medium	Low
Nickel Cadmium	80	2000	160	-40 to 60	Low	High
Nickel Metal Hydride	120	1500	180	-20 to 60	Medium	High
Lead Acid	50	800	40	-20 to 70	High	Medium

COST AND AVAILABILITY

The availability of raw materials has a direct impact on their cost. For EVs the cost and availability of materials can be a deciding factor when selecting batteries. The availability of materials can be characterised into physical and political availability.

Physical availability concerns the quantity of the raw material within the earth's crust. In order to use a material for electric vehicle batteries it is important to consider the physical quantity and ease of access to it. For example, if there is a large reserve of a desirable raw material, but the reserve is difficult to extract, it will be costly and perhaps not possible to obtain. There is a relationship between cost and raw material supply and demand. If the demand for a material is high and the supply small then the material will be more expensive. However, if the raw material resource is plentiful but the demand is low, then prices will drop.

Political availability is related to the location of known reserves of a material. If they are located in an area of political uncertainty it may be challenging and potentially impossible to access the source. If resource availability is low, the price of the material increases. If the price of the material becomes too high, this will have financial implications on an EV battery's material selection.

Lithium-ion batteries are seen as the front runner for use in EVs, because they are seen as "chemically superior to other batteries"^[12]. The key lithium-ion raw materials are lithium, cobalt, nickel, and manganese^[13]. It is therefore important that these raw materials are available in large quantities and that they are accessible

politically as well as physically. It is estimated that there are "4.1 million tons of lithium reserves in the world"^[13]. This is a conservative estimate and is seen as enough lithium to supply 1.3 billion electric vehicles^[13]. The countries with major lithium reserves are Argentina, Chile, Bolivia and China^[13]; any political uncertainty in these countries could potentially influence the availability and price of lithium.

Like lithium, there is currently little concern over the availability or cost of nickel. However, 80% of global production of manganese originates from South Africa^[13]. Due to the production of this material coming predominantly from one country, prices could increase at a rapid rate if there is any political uncertainty in the region. At the moment, however, manganese costs are low, making lithium manganese batteries an attractive option in terms of cost.

Cobalt is a very expensive material. This is largely because "more than two-thirds of the world's cobalt is supplied by the Democratic Republic of the Congo"^[14]. The DRC is a country that has been experiencing severe political uncertainty and war for many years. As a result, mining in this country is high risk, and material prices high. Also, it is not possible to access all of the potential resources in the DRC because of these problems. There are also ethical issues associated with mining in the region due to the ongoing violence.

Table 5 (next page) shows that lithium cobalt oxide cathode materials are the most expensive, and lithium manganese dioxide cathode materials are the cheapest option. If the project objectives involve minimising cost it is likely battery materials with lower costs will be selected. The cheapest electric

battery material won't always be selected though, as the material properties and chemical properties of the material are vitally important, and it is essential that material performance constraints are met.

CATHODE CHEMISTRY	COST (\$/KG)	COST (\$/KWH)
LiCoO ₂	30-40	57-75
Li (NiCoAl)O ₂	28-30	50-55
Li (NiCoMn)O ₂	22-25	30-55
LiMnO ₂	08-Oct	20-25
LiFePO ₄	16-20	25-35

Table 5: Lithium-ion cathode material costs^[12].

ENVIRONMENTAL CHALLENGES

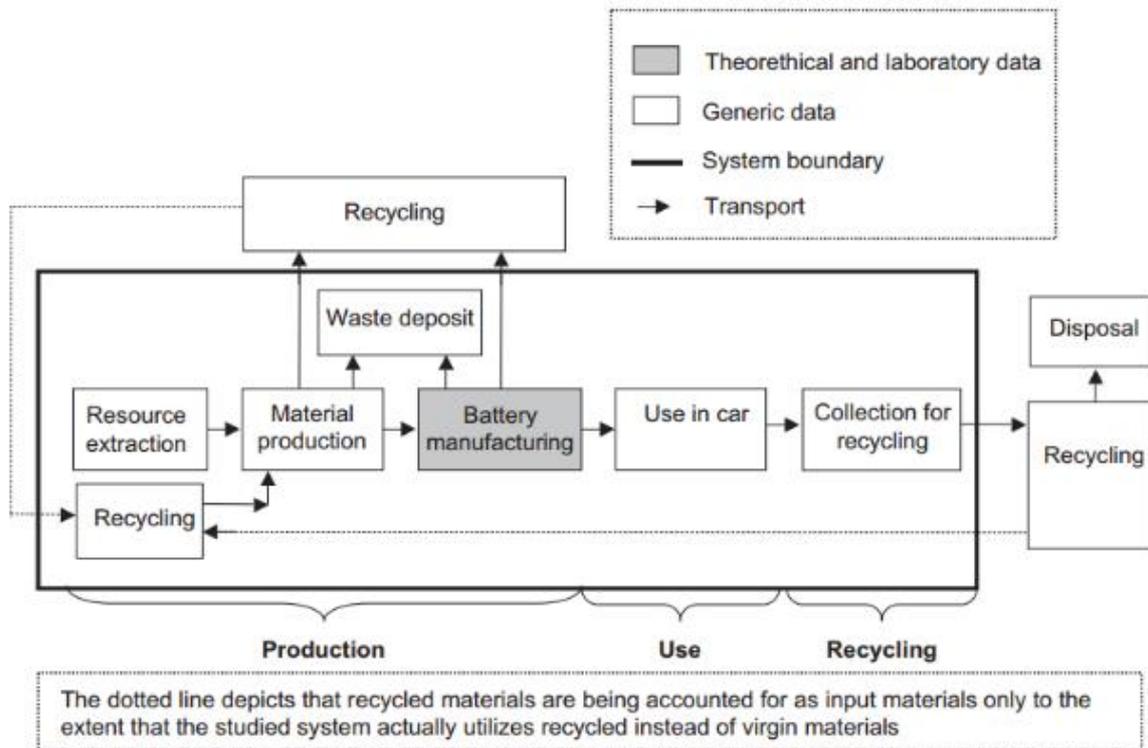
Electrification of the world's transport systems allows for reduced use of hydrocarbons as transport fuels. Globally, 27% of energy is consumed by transport, 94% of which is oil based^[15]. Although the majority of electricity worldwide is produced from fossil fuels, electric vehicles can utilise electricity generated from renewable sources. This has positive environmental impacts, such as reducing

emissions of CO₂ and other pollutants, and the environmental hazards involved in the extraction and transportation of oil, such as spills and groundwater contamination^[16]. How environmentally friendly a battery is depends on the battery type. Figure 6 shows the lifecycle of a typical EV battery.

Reducing the harm caused to the environment during extraction processes is the first step to ensuring the battery is as environmentally friendly. Metal casings require mineral extraction and polymer casings require oil extraction. As metals can be recycled more efficiently and more times than plastic^[17], it could be argued that metal casings are more environmentally friendly, but this also depends on other aspects, such as how much material is used per battery and its lifespan.

Longer battery life reduces environmental impact as batteries are not replaced as often.

Figure 6: EV battery life cycle analysis^[20].



Lithium-ion phosphate expected lifespan is 10 years. It is estimated that lithium-manganese spinel batteries could reach 40 year lifespans with correct optimisation^[18]. Increasing the number of charge/discharge cycles increases the life of the battery, decreasing its environmental impact. When EV lithium-ion batteries only hold up to 80% of their charge they are considered too depleted for automotive use, but can be used for grid electricity storage when supply exceeds demand, to be released when required. This allows the battery to serve a purpose and be used to its full potential before recycling.

Lead-acid batteries have been the basis for EV batteries in the past but convergence on lithium-ion has seen the batteries decreasing in size and increasing in lifespan. In total, 96% of the materials in lead-acid car batteries can be recycled^[19]. Hybrid cars such as the Toyota Prius use nickel metal hydride batteries of which a similar amount can be recycled. Specialist recycling facilities for EV components are in their infancy as the technology is new. A dedicated lithium-ion battery recycling centre is to be opened in the U.S. by lead-acid battery recycling company Toxco^[19].

As the cost of petrol and diesel rise, EVs become more popular as an alternative to traditional vehicles. As such, awareness has increased of EVs as a reliable, eco-friendly future for transport. Unfortunately, EVs also have some disadvantages, one of the biggest problems being that during the process of EV battery manufacture toxic waste is produced which is harmful to production workers and the surrounding natural habitats.

CONCLUSION

In the past, lead-acid batteries were the dominant battery and are still widely used to perform SLI (starter, lighting & ignition) functions due to their ability to deliver high currents at low cost. However, their low energy density and long charge times means that they are unsuitable as the primary mover of an EV. Currently, lithium-ion batteries appear to be the best choice for EV applications due to their high energy density and relatively cost, although there are problems with the ecological impacts of this battery type.

It is important that environmental concerns are taken seriously, and that eco-friendly design is a focus in the production of EVs. It is vital that the ecological impacts of the extraction, manufacturing and disposal processes of EV batteries are assessed in order to ensure that they are as environmentally friendly as possible.

Safety concerns are of paramount importance in EV battery selection, and lithium-ion batteries are relatively fragile when compared with other battery types such as lead-acid. However, by using high strength battery casings comprising of CFRP in conjunction with BMS these concerns can be allayed. Another advantage of using CFRP casings is that it could allow batteries to be integrated into the body of the vehicle itself, although this is still in the research stage.

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MATERIAL CONSTRAINTS FOR CONCENTRATING SOLAR POWER

BY O. FELTHAM, S. GOMM, M. MAST, M. STADDON, & K. TAM

ABSTRACT

This report investigates the material constraints in Concentrating Solar Power (CSP), focusing on the materials that constitute the reflector design. It analyses the traditional silver mirror design and compares this with modern silver/aluminium thin film developments. The relevant material properties of both designs are considered and compared, finding that silver offers better reflective characteristics (5% greater); however, aluminium is more abundant and so a design trade-off is identified between efficiency and commercial availability. The report concludes that for the future expansion of CSP further development and use of aluminium thin film is necessary.

INTRODUCTION

This report investigates the material constraints of the reflectors in CSP technology. Currently, CSP technology uses silver in the mirror design due to its high reflectivity and malleability; however, the current volatile market and resource scarcity suggests an alternative material for the future large-scale development of CSP is vital. Current research and development looks at aluminium as an alternative, and this report examines the properties of both materials with regard to the design trade-off.

CSP TECHNOLOGY

What is CSP?

CSP utilises mirrors and lenses to concentrate a large area of sunlight onto a smaller area. This magnified area of sunlight is converted to heat and can be used to power a heat engine, such as a steam turbine or Stirling engine, to produce electricity.

Currently there are three technologies used in CSP: the parabolic trough; the dish collector; and the solar power tower. The trough technology uses a series of parabolic reflectors to focus sunlight onto a pipe filled with a heating fluid, usually oil, which runs through a heat exchanger to drive a heat engine. The troughs are positioned from north-south and rotate on their length axis to track the sun from east to west. The second technology uses a giant dish on a dual-axis tracking system to concentrate the sunlight onto a focal point; this intense concentration of heat is then used to drive a Stirling engine to produce electricity. The final technology uses a field of mirrors mounted on separate two-axis tracking systems, called heliostats. These focus the sunlight onto a single focal point located on a tower in the centre of the heliostat field; this extremely high temperature can be used to drive a heat engine.

While solar energy can be thought of as unlimited, materials on Earth are not; the main constraint for the future development of CSP is the material of the mirror.

Main Properties of Interest

CSP has been developed since the first 1MW installation in 1968^[1]; initially, all reflectors were based on a standard glass silver mirror design, due to its high albedo characteristics and the already established mirror industry. However, corrosion and installation difficulties have led to the development of solar mirror films which substitute the glass with polymer layers, reducing weight and improving reflectivity characteristics. The increase in Silver prices has highlighted the possible need to re-design the reflector and substitute the reflective surface with another metal. Aluminium has similar reflective qualities to silver, and therefore many companies have started manufacturing aluminium substitutes needed to allow the up scaling of this technology.

Silver Mirrors

Traditional mirror designs comprise of approximately 4mm of low-iron glass which are silvered on the reverse with a layer approximately 100nm thick; several layers of protective coating are then applied producing a reflectance of around 93.5%^[2]. The presence of iron impurities in glass, specifically Fe^{2+} , can have detrimental effects on mirrors reflectance due to a large absorption band centred at 1000nm^[3]. To mitigate this problem, iron can be converted from the 2+ to 3+ oxidation state, reducing the absorption of the mirror glass. Another drawback of thick glass mirrors is the difficulty in producing parabolic shapes required in trough systems; this makes the manufacture, transportation, and installation process costly and time-consuming. Traditional mirrors have a protective rear surface, made of copper or lead, which gives lives in excess of 15 years^[4]. However, due to environmental

concerns, these traditional materials are no longer used. It is unclear how these changes may affect mirror lifespans.

Thin glass mirrors have also been developed, with a thinner 1mm glass layer, producing a solar-weighted reflectance of between 93-96%. However, similarly to thick glass mirrors, research carried out at the NREL has concluded that the substitution of lead and copper with new protection layers has dramatically reduced the lifespans of these mirrors.

Recently, materials companies have developed silver metallised acrylic films that can be applied directly to the reflector backing by adhesive. This adds the flexibility of quick application to most smooth surfaces of any shape, and dramatically reduces the weight and cost of the mirror. 3M has developed *Solar Mirror Film 1100* with reflectance of 94%; after 17 years of outdoor testing at the NREL the reflectance has only reduced by 3%^[5]. Other companies, such as ReflecTech, are also pioneering the development of solar films. Their 0.1mm thick mirror film features multiple layers of polymer films with an inner silver layer. This improves specular reflectance, as well as protecting the silver layer from oxidation and UV radiation^[6]. Solar mirror films are currently the most advanced silver reflective technology, offering a lightweight and flexible design that is easy to manufacture, transport, and install. Further research of this technology needs to be undertaken to determine if any further deterioration occurs to the reflector when exposed to outdoor environments for longer periods of time.

Aluminium Mirrors

The successful German company Alanod has developed MIRO-SUN[®], a thin-film

aluminium product designed to meet the requirements for the reflector components in concentrated thermal, photovoltaic, and solar power technologies, such as parabolic troughs. The company has shipped more than one hundred million square feet of solar absorptive surfaces since 2009, claiming the top spot in producing and shipping selective absorbing surfaces for the solar thermal industry and expects production to continue to rise in the U.S solar thermal market as a result of governmental incentives^[7].

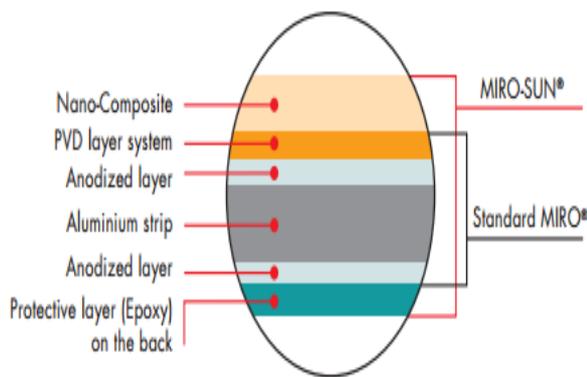


Figure 1: MIRO-SUN® Layer System^[8].

As can be seen in Figure 1, the film consists of an aluminium strip, anodised on both sides, and with layers (antireflection, absorptive and IR-reflection) applied to the back using a physical vapour deposition technique (PVD). The antireflection and metal oxide absorption layers ensure high solar absorption (α) whilst the infrared reflecting layer ensures low thermal emission (ϵ). For corrosion protection a nano-composite is applied to the top surface and an epoxy layer is applied to the back. This results in a product with around 94% total light reflectance (89% at AM 1.5) (see *Appendix* for details) and a high abrasion resistance suitable for outdoor applications such as an arid zone CSP^[9].

MATERIAL PROPERTIES AND THEIR RELEVANCE TO CSP

Table 1 (next page) shows the different material properties of aluminium and silver. The table attempts to give an indication of the factors that may be involved in the screening process of a material. By showing properties in it that may not be relevant to CSP technologies, however, common material parameters are also considered.

As was concluded in the introduction, the parameters that are important to consider for CSP technologies are reflectivity, cost, and malleability.

The table shows that silver is 5-10% more reflective than aluminium. This is the main parameter of interest in CSP technologies, as it is a direct indication of power production in the plant. This supports the fact that silver is the historically more used reflective material.

Counteracting this is the fact that silver is close to 1,000 times more expensive than aluminium. This is a major factor when comparing the two different types of reflective materials, and, due to the volatility of the precious metals market, this is an issue that is discussed in more detail below (see *Appendix*).

The malleability of the reflective material is an important factor in applying the reflective coatings, as it is an indication of how easily the material deforms under compressive forces. This is an especially useful characteristic, as the reflective materials are usually hammered and rolled into the desired shape of the reflectors (for trough systems, these are parabolic), and must deform but not fracture.

PROPERTIES	ALUMINIUM	SILVER
Reflectivity	90%	95-99%
Malleability	High	High
Cost (\$/kg)	2.4-2.7	1,850-2,000
Chemical reactance	Low	Low
Thermal expansion ($\mu\epsilon/^\circ\text{C}$)	21-24	19.5-19.9
Melting point ($^\circ\text{C}$)	500-650	957-967
Density (kg/m^3)	2,500-2,900	10,500-10,600
Maximum Service Temperature ($^\circ\text{C}$)	120-200	100-190
Embodied Energy (MJ/kg)	22-30	140-170

Table 1: Material properties of aluminium vs. silver^[10].

As CSP technologies are typically used in locations with very high ambient temperature, and by concentrating the solar radiation become even hotter than this, it is of great importance that all the materials of the technology remain stable through higher temperatures. Although the maximum service temperatures of the reflector materials in question are relatively low ($\sim 100^\circ\text{C}$) this factor is not of great importance as it merely shows the temperature after which the materials strength greatly declines. As the reflective coating of the reflectors in CSP is not in itself a weight carrying part of the full assembly, its strength is not considered to be of a high importance in the screening process.

The melting points of aluminium and silver are $\sim 570^\circ\text{C}$ and $\sim 960^\circ\text{C}$ respectively. As the reflector is reflecting up to 95% of incident radiation, the only source heating the reflector comes from convection and conduction from the rest of the assembly and the environment ($\sim 50^\circ\text{C}$). These temperatures are within limits of melting the reflective material.

The thermal expansion of the material is important, as the reflective coating is contained within the protective coatings surrounding it. If the material expands too

much in relation to its surroundings, it could cause fractures and cracks in the materials. Both aluminium and silver have thermal expansion coefficients of about $20\mu\text{-Strain}/^\circ\text{C}$. This is to say that, for every degree Celsius of heating, the material expands by 2×10^{-5} of its original dimension. Assuming the material used in the reflector is spread across a length of 5 metres and the temperature increases by 50°C , this amounts to an increase in length of 5mm. This change in length is assumed to be acceptable, especially when considering that the other materials used in CSP technologies have similar thermal expansion coefficients (see *Appendix*) and would therefore expand at a similar rate, thereby reducing the stresses caused.

The embodied energy in the primary production of silver is over six times that of aluminium. On consideration, the embodied energy of the reflector can be seen as negligible, as the reflective element of the entire CSP system is small. When considering the reflective material over the lifespan of a CSP system, the extra reflectance and energy generated will mitigate the extra embodied energy in the production of silver.

TRADE-OFF

Previous studies have shown that CSP technology has a favourable life cycle assessment with a high lifetime energy return and low environmental impact^[11], and as such the expansion of the technology would address future energy supply and CO₂ emission issues. However, if the use of CSP is to be scaled up, the availability of the materials required must be considered.

In general, most of the materials needed for CSP are commonplace, and those that are not can be substituted for similar materials, allowing for CSP up-scaling, but with a design trade-off in some cases. For instance, the need for silver as the main component in the reflectors in CSP systems could be problematical due to both a price rise, fuelled by a sudden demand increase, and a shortage of reserves to sustain production levels. A suitable substitute for silver is aluminium, which reduces the overall cost of CSP plant, but comes with a 5% decrease in the efficiency of the reflector; a 'trade-off' is made between reflectance and availability. The 2010 values for reserves, resources, and production of component materials are shown in Figure 2. The reserve life shows

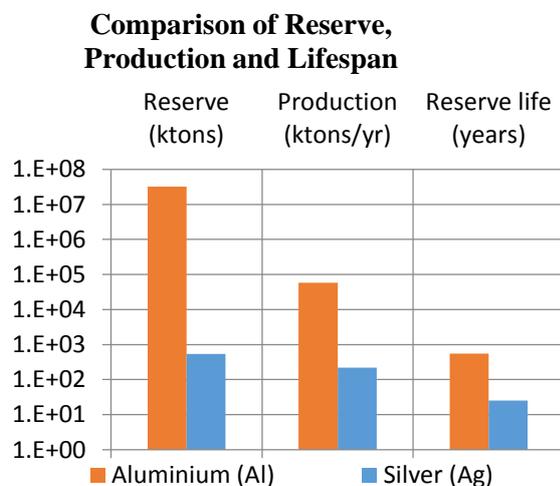


Figure 2: Resource comparison.

how many years the present reserves can supply the current demand before being exhausted^[12].

FUTURE AVAILABILITY

Prices

Silver rarely exists in its pure form, and over 70% of the silver produced is as a by-product from other mining operations^[13]. As a consequence, the price of silver is highly volatile and silver prices change every minute on the global investment market. Figure 3 below shows that the price of aluminium has remained stable historically, and follows the world's inflation rate with a net present value close to the market value. Conversely, silver does not follow the same pattern as the global economy, making it a much more expensive choice for CSP technology than aluminium.

Price Fluctuation of Silver and Aluminium

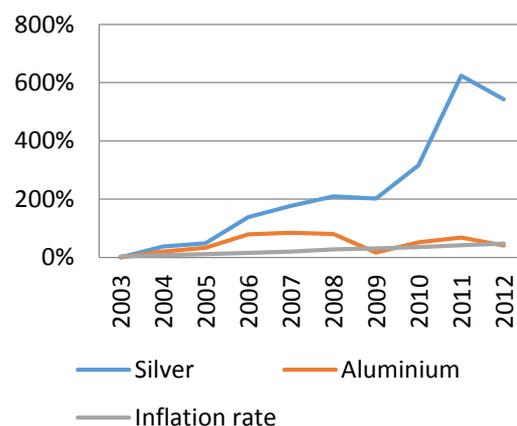


Figure 3: Cumulative price changes of materials vs. inflation rate.

Availability

Aluminium is one of the most abundant elements on earth; however, it does not exist in a pure form, and is energy intensive to process. The world produces about 50,000 tons of aluminium each year from bauxite, making it a readily available and cheap metal which is also suitable for a wide range of applications^[14]. Recycling aluminium only requires 5% of the energy needed to extract it from ore and over 75% of the world's aluminium is recycled and circulated between different products, making it a more sustainable material^[15].

As well as being the rarer metal, silver is mostly mined north of the Tropic of Cancer; however, most solar radiation is received south of it. The limited global deposits are sometimes situated far from favourable CSP locations, resulting in supply limitation and increased transportation cost.

A recent mining industry report from SRSrocco Report has found that, although mining operations are getting larger, the yield of silver is dropping, causing the price and carbon footprint to increase.

CONCLUSION

- Traditional silver mirror technology is outdated and not viable for the expansion of CSP due to corrosion issues, as well as the weight and fragile characteristics which make them cumbersome for transport and instalment.
- The main material properties to consider in CSP are reflectivity (due to the direct correlation to power production), thermal properties, and malleability.
- Modern CSP technology utilises silver and aluminium thin film reflectors.
- Silver mirror film technology offers high reflectivity and is more adaptable and made corrosion resistant by using a polymer film, producing lifespans of over 17 years. Aluminium film has a slightly lower reflectivity than silver (5%), but is cheaper and more abundant, with lower extraction energy requirements and higher recyclability.
- The design trade-off, therefore, is between reflectance and availability and associated cost with an expansion of CSP requiring a move toward Aluminium reflectors.

It would be interesting to widen the report's scope to consider other materials within CSP, such as the use of polymers, and the potential benefits of composites to replace structural parts.

APPENDIX

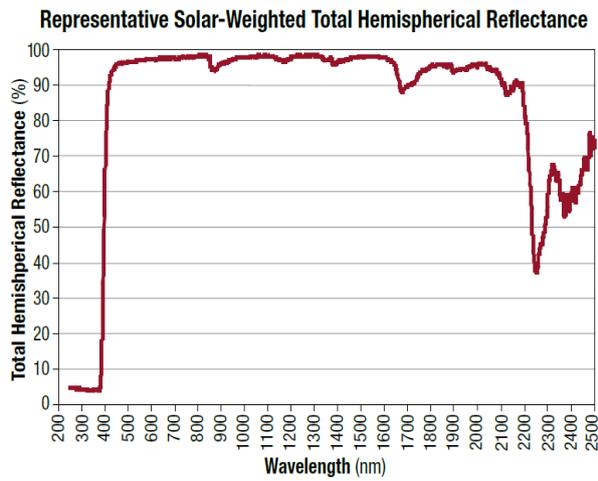


Figure 4: Solar reflectance of the 3M Solar Mirror Film 1100^[16].

Solar Reflectance
MIRO-SUN® weatherproof reflective 90

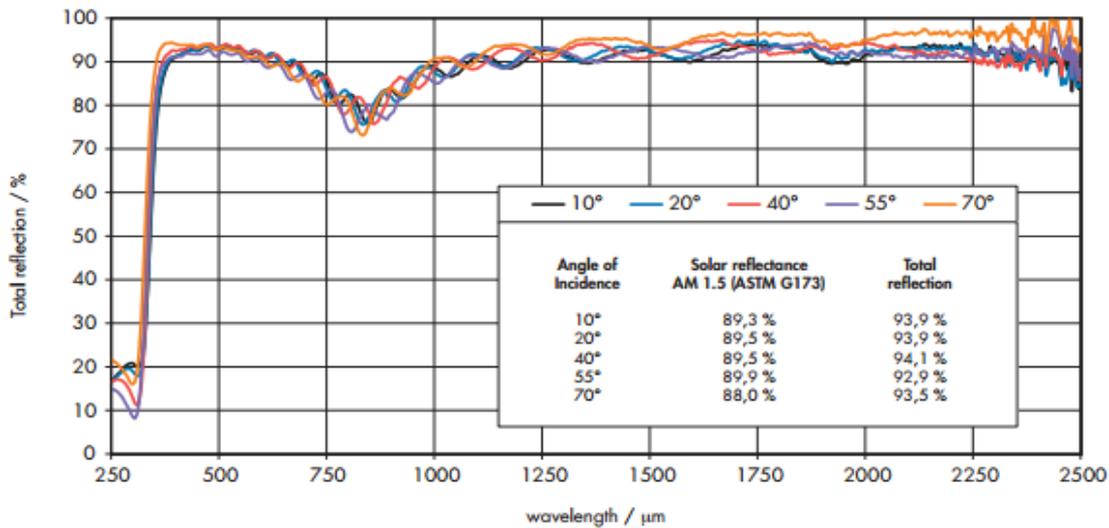


Figure 5: Solar reflectance of the MIRO-SUN® aluminium reflector^[17].

Low-Carbon Steel	11.5-13
Cast Iron	10-12.5
Cement	6-13

Table 2: Thermal Expansion Values for other Common Materials in CSP.

COST CALCULATIONS BASED ON PARABOLIC TROUGH:

$$\text{Price of Steel} = 0.7 \frac{\$}{\text{kg}}$$

Amount of Steel used per GW of installed power = 240,000 tons

$$\text{Cost of Steel for 1GW Installation} = 0.7 \frac{\$}{\text{kg}} * 240,000,000 \text{ kg} = \$168\text{m}$$

$$\text{Price of Silver} = 2000 \frac{\$}{\text{kg}}$$

Amount of Silver used per GW of installed power = 13 tonnes

$$\text{Cost of Silver for 1 GW installation} = 2000 \frac{\$}{\text{kg}} * 13,000 \text{ kg} = \$26\text{m}$$

COST CALCULATIONS BASED ON CENTRAL TOWER:

Amount of Steel used per GW of installed power = 65,000 tons

$$\text{Cost of Steel for 1GW Installation} = 0.7 \frac{\$}{\text{kg}} * 65,000,000 = \$45.5\text{m}$$

Amount of Silver used per GW of installed power = 16 tons

$$\text{Cost of Silver for 1GW Installation} = 2,000 \frac{\$}{\text{kg}} * 16,000\text{kg} = \$32\text{m}$$

For a parabolic trough the cost of steel amounts to about 6 times the price of silver used in the plant. For the central tower configuration the cost of steel is about 1.4 times the cost of silver.

PRICE AND COST ESTIMATION OF SILVER AND ALUMINIUM

	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Silver^[18]										
Mine Production (ton)	16930.3	17395.3	18064.3	18180.5	18883.6	19362.7	20230.2	21338.7	21460.6	22311.1
Recycling (ton)	5556.5	5633.1	5746.4	5845.7	5755.0	5692.6	5664.2	6486.4	7317.0	7197.9
Total Production (ton)	25225.4	24780.3	26980.2	26251.7	25883.1	25920.0	26339.5	30509.8	29466.5	29718.8
Total Recycled (%)	23%	23%	23%	24%	23%	22%	25%	25%	28%	30%
Industrial Demand (ton)										
Industrial Demand (ton)	10444.0	11047.8	12198.8	12842.3	13783.5	13916.8	11441.9	14194.6	13828.9	13208.0
Photography (ton)	5468.6	5068.9	4544.4	4031.3	3333.9	2871.8	2248.1	2044.0	1873.9	1638.6
Jewellery (ton)	5295.7	5318.4	5341.1	5003.7	5210.6	5077.4	5066.1	5465.8	5287.2	5261.7
Silverware (ton)	2412.5	1936.3	1973.1	1797.4	1743.5	1695.3	1559.2	1496.9	1369.3	1272.9
Coins & Medals (ton)	1012.1	1202.0	1134.0	1128.3	1125.5	1851.2	2233.9	2817.9	3353.7	2628.0
Global Demand (ton)	24630.1	24570.5	25191.4	24803.0	25199.9	25412.5	22549.2	26022.0	25715.9	24006.4
Price (£1000/ton)										
Price (£1000/ton)	103.93	142.50	154.71	247.93	286.93	321.86	314.14	432.00	752.36	667.50
Price rise based on 2003	-	37%	12%	90%	38%	34%	-7%	113%	308%	-82%
Cumulative (%)	-	37%	49%	139%	176%	210%	202%	316%	624%	542%
Parabolic Trough (£mil/GW)	1.351	1,852	2.011	3.223	3.730	4.184	4.083	5.616	9.780	8.677
Aluminium										
Primary Production (ton) ^[19]	27986.0	29857.0	31905.0	33938.0	38132.0	39971.0	37706.0	42353.0	45789.0	47787.0
£/kg	0.86	1.03	1.14	1.54	1.58	1.55	1.00	1.30	1.44	1.21
£/ton	860	1,031	1,140	1,544	1,584	1,547	1,002	1,304	1,440	1,213.68
Price Rise	0	20%	13%	47%	5%	-4%	-63%	35%	16%	-26%
Cumulative	0%	20%	33%	80%	84%	80%	16%	52%	68%	41%
Parabolic Trough (£1000/GW) ^[20]	11.18	13.40	14.82	20.07	20.59	20.11	13.02	16.95	18.72	15.78
World Inflation Rate Based										
on 2003 (%)	3.70	3.70	4.04	4.13	4.68	7.22	3.10	4.79	6.62	5.68
Cumulative (%)	3.70	7.40	11.44	15.58	20.26	27.47	30.57	35.36	41.98	47.66

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MATERIAL SOLUTIONS FOR CORROSION & FOULING IN BIOMASS (CO-)FIRING

BY J. ADAM, H. CADDELL, C. GARLAND, C. MITCHELL, & P. PETRUNEAC

ABSTRACT

During combustion of wheat straw, mineralogical changes occur, which lead to variation in the physical, chemical and textural properties of the ashes formed in the superheater tubes. Inorganic elements are of significant importance, as they have a direct implication in the superheater tubes corrosion. When biomass is co-fired with coal, the reaction of sulphur from the coal and the alkali species from the biomass becomes important.

Corrosion to the superheater tubes can cause losses to productivity and economic value of the operation. Common mitigation methods are to co-fire biomass with fossil fuels like coal, the addition of additives in to the combustion chamber, and methods of coating the affected surfaces of superheater tubes.

Material selection is vital for the efficient operation and lifespan of superheated tubes. The Ashby method of material selection provides a logical process to find the optimum material for a specified application. Using this process alongside material research gives a strong indication of suitable materials that meet the design and operational criteria.

INTRODUCTION

The burning of fossil fuels is the fundamental core of global energy production, accounting for 80% of all energy produced^[1]. The fact that this figure

is so high means that there is great scope for reducing the total CO₂ in the atmosphere by means of improvements in low carbon energy generation.

Governments around the world have introduced legislation to encourage the development of lower emission energy production. In the UK this is done through issuing Renewable Obligation Certificates (ROCs) to electricity generators using renewables. ROCs are sold to electricity suppliers who need to meet their quota set by Ofgem^[2].

The implementation of these incentives has caused 16 major UK coal-firing plants to convert to biomass co-firing, in order to be eligible for ROCs^[3]. Conversion only requires a small amount of modification in order to make burning biomass along with coal possible. Depending on the type of biomass co-fired, the power station will be awarded between 0.5 and 1 ROC per MWh^[4].

Whilst co-firing is an effective means of reducing greenhouse gas emissions, the combustion of biomass does bring its own problems. The composition of biomass can be problematic, it often has high moisture content, meaning it will not combust as easily as other fuels. Another issue is that it contains high concentrations of alkali and chlorine, and inorganic elements which, when combusted quickly, sublimate to gas, forming hydrogen chloride and potassium chloride^[5]. High quantities of these gases are associated with increased deposit formation within the system, leading to

increased rates of corrosion^[6].

This report will investigate the required material qualities of a superheater tube, and the causes of the corrosion, mainly examining co-firing of wheat straw. Once identified, we will look at methods of combatting this corrosion, and, most importantly in the goal of corrosion prevention, the material choice and the methodology behind its selection will be explored, particularly focussing on the Ashby method of material selection.

SUPERHEATER TUBES

“Steam superheaters are widely used in steam generators and heat-recovery steam generators (HRSGs). Their purpose is to raise steam temperature from saturation conditions to the desired final temperature, which can be as high as 1,000 °F [540 °C] in some cases. When used in steam turbines, superheated steam decreases the steam heat rate of the turbine, and thus improves the turbine and overall plant power output and efficiency. Additionally, the use of superheated steam results in little or no moisture at the turbine exit, and moisture at this stage can cause serious damage the turbine blades^[7].”

The superheater tubes perform a vital function in thermal power stations by carrying steam through the boiler to heat it via conduction through the walls of the pipe. The pipes have to carry high pressure steam through a high temperature environment containing corrosive chemical compounds released during the combustion of biomass fuels. These operating

conditions determine the main properties necessary for this type of application: high thermal conductivity; high melting point; high yield strength and stiffness; and high creep resistance.

Corrosion, the gradual destruction of a material due to chemical action, is the dominant issue concerning superheater tube failure. The corrosion is caused by the reaction of chemicals, produced during the combustion process, and the surface of the pipe. The resulting flaws act as stress concentrators that greatly accelerate the creep failure of the component. This issue is more severe for biomass co-firing power stations because of the more reactive chemical compounds produced. The major shortcoming of materials currently used for superheater pipes is insufficient corrosion resistance to these compounds, and this is leading to the premature failure of coal-fired power stations that have introduced co-firing without a superheater refit. The industry has not yet settled on a suitable material to be used in these circumstances.

FACTORS AFFECTING CORROSION

Biomass composition plays a pivotal role in the combustion process. Different sources present different compositions which have diverse reactions according to their particles. Carbon, oxygen, and hydrogen are the main constituents of all biomass with little variation among different sources. During the combustion process, along with the main constituents, the presence of inorganic elements can be identified and corrosive gases such as HCl and KCl are formed and released in the combustion environment. High amounts of gas (especially KCl) cause deposit formation on the superheater tubes^[9].

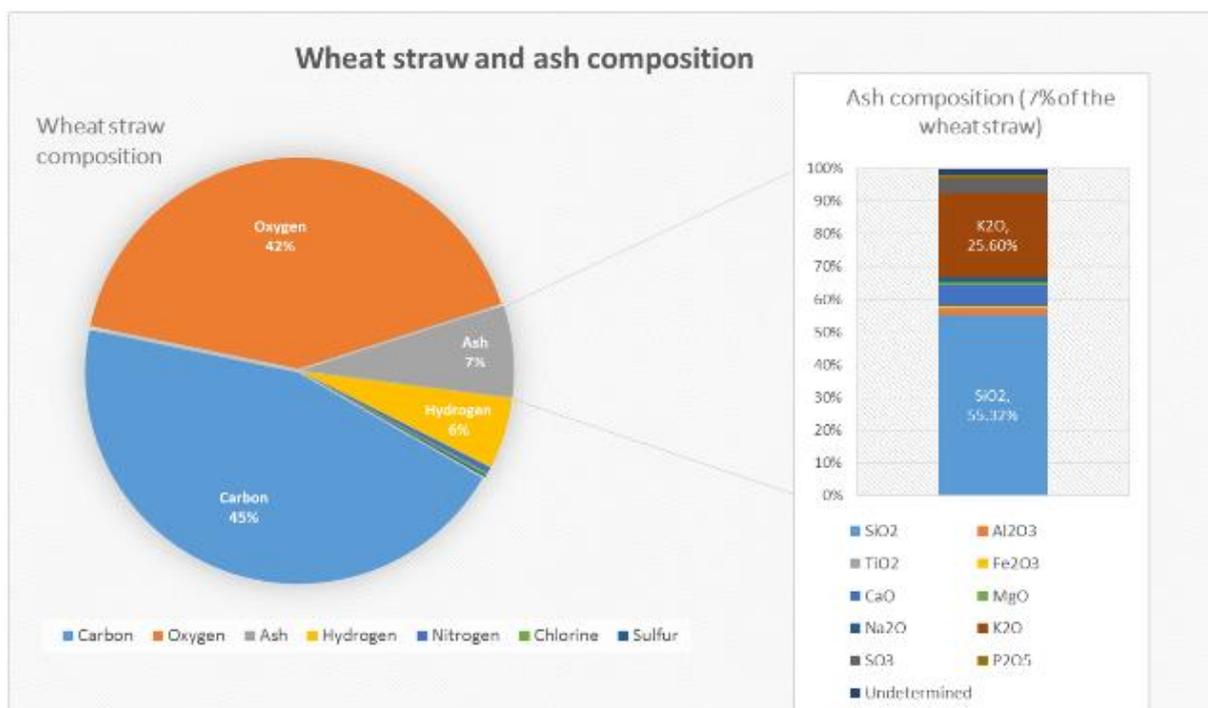
Biomass fuels such as straw are ‘rich in alkali metals (K and Na) which are mainly present as simple salts and organic compounds and chlorine’^[10]. Wheat straw is a preferable form of biomass because it ‘does not contribute to the greenhouse effect and produces an ash which can be returned to the soil’^[11]. However, this ash has a significant effect upon the physical properties of the superheater tubes.

Figure 1 below presents the total wheat straw composition and the inorganic composition within the released ash. The most abundant inorganic elements in the ash are silica (SiO_2) and potassium oxide (K_2O) which form molten condensates. The combustion of wheat straw leads to condensation of the molten silicates, which are most likely to cause the corrosion and fouling in the combustion process: ‘Because the protective layers of oxides can be relatively soluble and/or reactive in silicate slags, metals in combustion systems are vulnerable to chemical attack when silicates are present’^[11]. Moreover, unexpected corrosion could occur due to

the high volatility of the alkali metals. In addition, the presence of potassium chloride (KCl) in the deposit ‘is expected to play a major role in the mechanism of selective chlorine corrosion’^[12].

Co-firing straw with coal has created some technical challenges due to the ash composition of straw. The fly ash with a high KCl content can induce problems such as ash deposit formation and boiler corrosion. It has been discovered that ‘KCl in the deposit can cause corrosion where chlorides attack the chromium and iron in the steel leaving a nickel rich skeleton’^[13]. Another important interaction between the biomass and coal during the co-firing is the reaction of the sulphur in the coal with the alkali species from the biomass. Since the problems during the coal and straw co-firing are mainly due to K and Cl content within the ashes, the content and specification of the K and Cl is of a paramount importance.

Figure 1: Wheat straw composition^[8].



METHODS OF PREVENTING CORROSION

MITIGATION

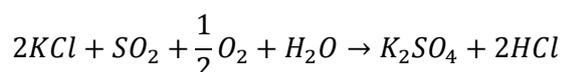
Corrosion to tubes within a superheater system is a big problem for the burning of biomass fuels. This can lead to expensive maintenance costs, which may occur regularly, if the initial material selection for the tubes does not consider the process contained within them.

Various methods of mitigation can also be adopted to prolong the corrosion period of the tubes, giving a longer working life and reduced maintenance time and costs.

Co-combustion of Straw with Coal

The oxidation of biomass superheater tubes due to chlorine deposition on the surface of the tubes is a large problem regarding corrosion within the superheater system. The introduction of the right mixture of a sulphur-rich fuel like coal to the initial burning process of the biomass fuels like wheat straw can help with the prolonging of the corrosion period or the reduction of the overall corrosion.

The introduction of the additional fuel can help by producing sulphate when the fuel is combusted; the sulphates react with alkali chlorides released during the combustion of the biomass fuel to produce alkali sulphates and hydrochloric acid in the combustion chamber, as seen in the equation below.



The alkali sulphates form deposits on the superheater tubes and act like a protective barrier to the penetration of gaseous chlorine to the metallic tubes. The alkali sulphates are considered less corrosive

compared to alkali chlorides, and reduce the penetration of the chlorine due to the dense structure of the compound. This method of mitigation is most suited to tube containing stainless steel in temperatures of around 500 °C^[14].

The Mixture of Additives

The introduction of additives is also a method of reducing the gaseous alkali chlorides released during bio-mass combustion. Usually, sulphur-containing additives are used in this process, and react in a similar manner to the co-firing of biomass and coal. This process consists of an aqueous solution of ammonium sulphate being sprayed in the turbulent zone at the entrance of the superheater to induce sulphation of the gaseous alkali chlorides. Another additive that can reduce the formation of alkali chlorides is molybdenum salts, as shown in a report by 'Schofield'^[15] which demonstrates the reaction of the alkali metal and the salt to produce $X_xMo_2O_7$ compounds.

Aluminosilicates found in kaolin bind with alkali metals of the alkali chlorides to produce either kalsilite or leucite depending on other substances present within the reaction. The two substances formed have melting points above 1500 °C when pure, which is usually well above the combustion temperatures of bio-mass. The production of the high melting point compounds traps the chlorine within the compound, stopping the corrosion reaction with the metallic surface of the superheater tubes. Due to the high chemical inertness and relatively small specific surface of kaolinite limiting the binding of alkalis, kaolinite can be replaced with halloysite. Halloysite is an aluminosilicate clay mineral consisting of silicone tetrahedra and aluminium octahedra forming single plates with a

space between layers which traps alkali metals between the layers, stopping the formation of alkali chlorides in ash deposits.

Methods of Coating Tubes

The aim behind coating the tubes of a superheater is to protect the metallic surface from corrosion. To achieve this successfully, the coating must be thermodynamically stable within the range of the operation temperature, it must be thick, even, and have a dense molecular structure that can withstand penetration from chlorides, and have a good interaction with the metallic surface.

A widely used method of applying this approach is the high velocity oxygen fuel (HVOF) thermal spray process, which forms an effective barrier against high temperature corrosion. It is used in a wide range of industrial combustion applications due to its intrinsic film characteristics, such as high density, low oxide levels, and

increased thickness^[17]. This makes them superior to coatings obtained by other spraying process, such as plasma spraying^[18].

Nanostructure Technologies

Nanostructures are a potential method of protecting superheater tubes from the effects of corrosion and fouling, and there are two methods of producing nanocrystalline structure using metallic materials. The top-down method uses severe plastic deformation (SPD) to reduce the structural grain size of a metallic material by subjecting a material to a large shear force, resulting in the production of a nanocrystalline metallic alloy. “The bottom-up approach is focused on the development of nanocrystalline coatings from nanocrystalline powders such as in the HVOF process, or spray-based processes, or on nanocrystalline films grown directly on the substrate, such as physical vapour

Table 1: Co-firing plants in Denmark^[19].

PLANT DESCRIPTION	TYPE	STEAM TEMP. (°C)	PRESSURE (MPa)	SIZE (MW _{TH})	COMMISSIONED
Haslev	Grate-fired	440	6.7	20	1989
Slagelse	Grate-fired	450	6.7	32	1990
Rudkøbing CHP 100% straw	Grate-fired	450	6.1	10.7	1990
Masnød CHP – almost 100% straw	Grate-fired	520	9.2	33	1996
Ensted CHP					
100% straw boiler	Grate-fired	470	20.1	80	1998
100% woodchip	Grate-fired	470-540	20.1	15	1998
Maribo Saksøbing CHP: 100% straw	Grate-fired	540	9.3	33	2000
Avedøre 2 (bioboiler: 100% straw)	Grate-fired	540	30	105	2001
Fyn 8: 100% straw	Grate-fired	540	12	117	2009
Grenå 50% CFP straw, 50% coal	CFB	505	9.2	80	1992
Strustrup suspension fired coal plant modified for coal + 10% straw	Suspension fired	540	25	830	2002 rebuilt Unit 4 2005 rebuilt Unit 5
Avedøre II (main boiler: oil + gas + wood)	Suspension fired	540-580	30	800	2001
Herning Wood + gas	Grate-fired	515	11.5	288	2002 rebuilt to biomass
Amagar I multifuel (straw pellets, coal, wood pellets, heavy fuel oil)	Suspension fired	560	18	350	2009

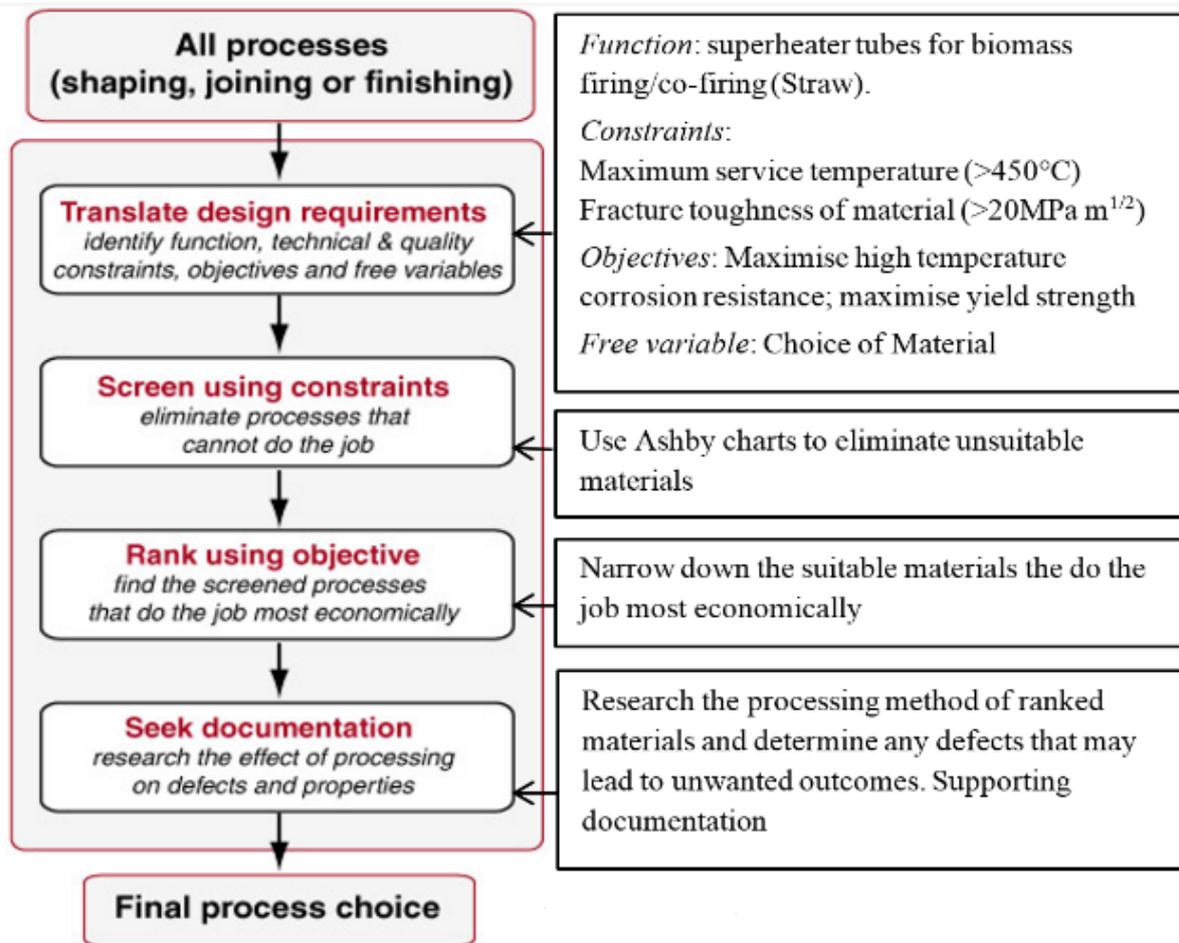


Figure 2: Ashby material selection process^[16].

deposition or chemical vapour deposition methods (CVD)^[15].

The advancement of nanostructure technology is exploring alternative methods of corrosion prevention. Using this technology to enhance the fundamental structure of the superheater tube material means corrosion resistance could be built in, thereby reducing the need for additives in the fuel. More research into the effectiveness of nanostructure technologies on thermal power station superheater tubes is required before the techniques discussed in the report can be introduced.

METHODS OF MATERIAL SELECTION

Ashby Method of Material Selection

The Ashby method for material selections (shown in Figure 2) is utilised to determine the most suitable material for superheated tubes, considering the parameters described in previous sections.

To meet the main objective, materials selected need to encourage a build-up of a stable protective oxide layer, whilst maintaining the constraining factors. Constraining factors are fixed variables that are utilised to screen out materials that are not suitable for the stated application.

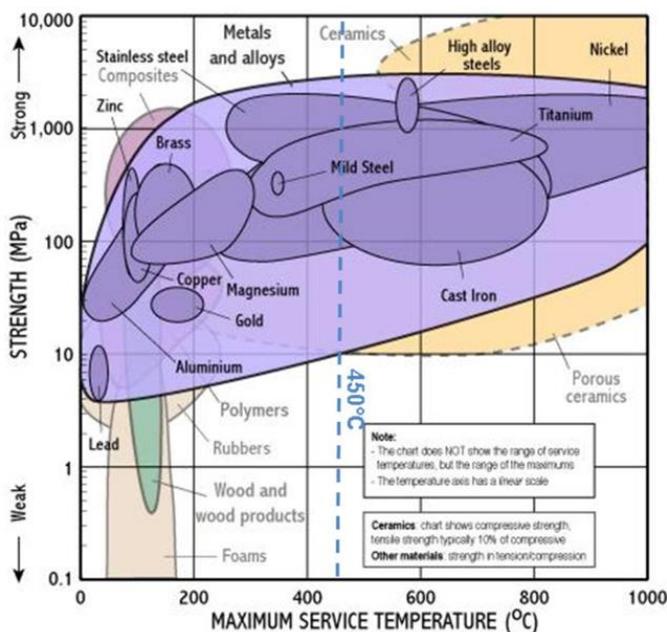
The Ashby material selection charts give an initial basis to start the screening stage of the material selection process. ‘One reason for the dominance of metals in engineering

is that they almost all have values of K_{1C} (fracture toughness) above $20 \text{ MPa}\cdot\text{m}^{1/2}$, a value often quoted as a minimum for conventional design^[20]. This information screened out almost all materials apart from metals for the desired application, with an indication that alloys are a feasible choice.

The maximum service temperature of the material has to be greater or equal to 450°C for firing and co-firing straw material. This can be seen in Table 1 (page 28), which shows biomass and co-firing plants in Denmark. Steam temperature is important when determining the optimum material for super-heated tubes, a small temperature gradient can greatly affect the lifespan of the selected material.

When TP347H (corrosion resistant steel) is used as superheated tubes for straw firing, Pinders states that ‘reducing the final steam temperature by 10°C will increase the anticipated tube life from approximately 43,000 hours to 130,000 hours^[21].

The maximum service temperature ($^\circ\text{C}$) against strength (MPa) chart in Figure 3 displays the grouping of general metals and alloys. This provides data which can be



used to screen out unwanted metals. It can be seen that materials that are viable are situated to the right of the blue dashed line. Figure 3 therefore suggests that a nickel alloy has great characteristics that meet both constraints. Other materials, such as cast iron, titanium, stainless steel, and alloy steels, should also be considered.

The screening process has reduced the possible materials available for superheater tubes. A further reduction can be made by investigating specific materials in each group. Researching materials used specifically for straw fired applications from relevant material will reduce the number of metals and alloys for the ranking stage.

Nickel and chromium encourage the build-up of protective oxide film which helps decrease the corrosion rate of superheated tubes; both materials can be utilised simultaneously as alloying elements to increase corrosion resistance. Using this as a base line, materials with high contents of nickel and chromium were selected for the ranking stage. Choi states ‘X20CrMoV121 steel has been widely used for superheater and re-heater tubes of power plants due to its improved creep strength and higher oxidation resistance^[23]; for this reason, X20 steel has been selected for the ranking process, with consideration for a low nickel content.

Table 2 (next page) shows the eight materials which have been selected for the ranking stage, data in table provided from research papers and accumulated in table format by Antunes and Oliveira.

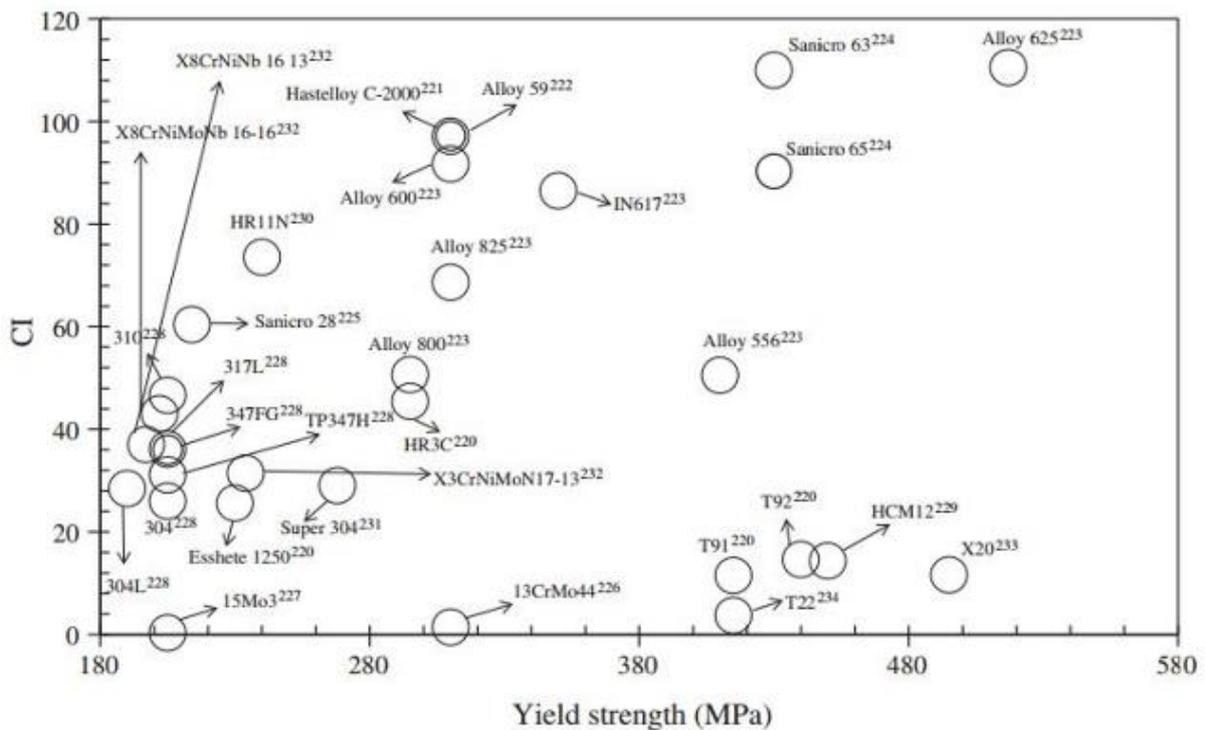
Figure 3: Ashby material selection for strength against maximum service temperature^[22].

MATERIAL	COMPOSITION (WT. %)											
	NI	CR	Mo	Nb	Ti	Al	C	Cu	Si	V	Mn	Fe
Alloy Steel X20	0.47	10.3	0.80	-	-	-	0.18	0.20	0.30	0.30	0.80	Bal
Stainless Steel 310	21.1	25.4	0.10	-	-	-	0.02	0.10	0.40	-	1.70	Bal
Stainless Steel HR3C	20.0	25.0	-	0.40	-	-	0.10	-	0.75	-	≤2.00	Bal
Alloy 625	61.0	21.5	9.00	3.60	0.20	0.20	0.05	-	0.20	-	0.20	2.00
Sanicro 65	61.3	20.7	8.30	-	-	-	0.01	-	0.40	-	0.40	Bal
Inconel 617 (IN617)	Bal.	22.0	9.0	-	-	-	0.07	-	-	-	-	<1.00
Hr11N	38.0-42.0	27.0-30.0	0.50-1.50	-	-	-	≤0.03	-	≤0.60	-	≤2.00	Bal
Alloy 59	Bal	22.0-24.0	15.0-16.5	-	-	0.10-0.40	-	-	<0.10	-	<0.50	<1.50

Table 2: Composition of materials selected for ranking^[15].

The specific materials can now be ranked using the two objectives outlined in Figure 3. Antunes and Oliveira have produced a useful chart (Figure 4) comparing the corrosion resistance against the maximum yield strength (MPa), where CI is the corrosion resistance index.

Figure 4: Material selection chart for corrosion resistance (CI) against yield strength^[15].



When considering corrosion resistance, the materials ranked as follows:

Alloy-625⇒Alloy-59⇒ Sanicro-65
 ⇒ IN617⇒HR11N⇒ Stainless-steel-310
 ⇒ HR3C⇒X20.

The yield strength properties are ranked as follows:

Alloy-625⇒X20⇒Sanicro-65⇒IN617
 ⇒ Alloy-59⇒HR3C⇒HR11N
 ⇒Stainless-steel 310.

The ranking has shown that the optimum material for superheated tubes in straw-fired applications would be alloy 625, which ranked highest for both objectives, followed by Sanicro 65. The results correspond to the high nickel content in these materials, as shown in Table 2.

The creep factor of the superheated tubes needs to be investigated to maximise the efficiency of the firing process. 'It is estimated that 10% of all power-plant breakdowns are caused by creep fractures of boiler tubes... In general, 30% of all tube failures in boilers and reformers are caused by creep'^[24]. Information was supplied by the special metals corporation stating 'High tensile, creep, and rupture strength; outstanding fatigue and thermal-fatigue strength; oxidation resistance; and excellent weldability and brazeability are the properties of INCONEL alloy 625'^[25].

CONCLUSION

It has been shown that the corrosion of superheater tubes in biomass co-firing power stations is directly linked to the chemical composition of the combusted fuel. With regard to biomass fuels, the levels of inorganic elements, alkaline chlorides, and sulphur are particularly important when considering the corrosive effects.

The findings show that co-firing of coal and biomass results in less corrosion than a 100% biomass combustion, although corrosive gases are still produced. Current mitigation techniques are to remove chlorine in the gas and replace it with sulphur, and then use the product to form a barrier around the tubes.

The required material qualities were found to be:

- High thermal conductivity;
- High melting point / retain strength at high temperatures;
- High yield strength & stiffness;
- High creep resistance;
- Be malleable;
- Corrosion resistive.

Once identified, these qualities became the constraints in the material selection process, with the objective of maximising the high temperature corrosion resistance. Alloy 625 was found to be a favourable choice of material based on the results. An interesting finding was that very small temperature increases can drastically affect the lifespan of superheater tubes.

Finally, it should be noted that further research is required regarding superheater corrosion. Co-firing of biomass is a relatively new subject, and, although much has been done to find preventative methods, the fundamentals of the transport of chlorine across the oxide scale is not yet fully understood. The development of effective mitigation methods requires a comprehensive understanding of the subject.

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