

CNS&E

Current Natural
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Peer-reviewed, Multidisciplinary Journal



<http://doi.org/10.63015/cnse-2025.2.1>

Volume 2 Issue 1, February 2025 (Special Themed Issue)

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Chief Editor's Message

Green Hydrogen for Earth Sustainability

Prof R K Kotnala

FNASC, FIGU, FMSI

Chief Editor, Current Natural Sciences & Engineering, Journal (CNS&E)

DOI: <https://doi.org/10.63015/1h-kotnala.2025.2.1>

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I feel thrilled to publish a special vol 2, issue 1 of CNS&E journal on Green Hydrogen for Earth Sustainability, Feb 2025, which is the need of the hour for the earth sustainability. The editorial responsibility of this issue has been entrusted to Prof K K Pant, Director IIT Roorkee, whose distinguished expertise in Green Hydrogen production and allied fields immensely benefited CNS&E Journal. Editorial team, myself and CNS&E Journal are grateful to Prof Pant for agreeing to work for such a burning issue of Green Hydrogen production challenges & constraints.

Since, we all are aware of the prevailing adverse condition of our environment and facing a grave situation of abrupt climate change & severe health issues due to unlimited carbon emissions to the atmosphere, which is not restricted to one region of earth but its impact is prevalent globally ! How to combat such a challenge within a short time ? The only immediate worldwide unanimous solution has emerged to make use of a cleanest energy source, green hydrogen, for the need of energy by replacing fossil fuels usage that can fulfil the commitment to environmental sustainability and hydrogen stands at the forefront of this transition. At present most of the hydrogen produced in the world is generally consumed by the petrochemical fertilizer and chemical processing industries. Due to the boost in the hydrogen economy, the use of Hydrogen as future fuel in the automobile sector will also stimulate the need for hydrogen. Hence, the use of hydrogen in industries, automotives etc holds immense promise as a clean, versatile fuel with zero carbon emissions. In the present scenario, the whole world is in dire need of ~300 million tonnes/year production of green hydrogen to achieve Net Zero Carbon emissions by 2035 for the earth's sustainability.

Thus, even today worldwide scientists are in pursuit of green hydrogen generation by new techniques. Although at such a crucial & crisis situation, one of the best solution for green hydrogen & electricity production is from Prof R K Kotnala & Dr Jyoti Shah's revolutionary invention of Hydroelectric Cell device, which is internationally validated through >87 original research papers & US/Indian patents in last six years. That is why, CNS&E has taken initiative to publish a special theme issue on Green Hydrogen for the Earth Sustainability!

The special theme issue consists of the following papers :

"Thermochemical Conversion of Agro -Waste for Green Hydrogen Production" manuscript elaborates different techniques for hydrogen production with a focus on a matured biomass gasification to produce hydrogen because it has the advantage of recovering energy from waste biomass. It also briefed about merits & demerits of the different techniques and current status of Hydrogen demand globally and in the perspective of Indian demand as well.

"Beyond Silos: A Unified Approach to Decarbonisation through Hydrogen Integration", the present manuscript explains critical global challenges in detail for hydrogen production capacity and comparisons by suggesting a few recommendations and the pathways for enabling a decarbonised future powered by clean, sustainable hydrogen energy.

"Green Energy Generation from the Industrial Waste Red Mud as Hydroelectric Cell", the authors in this manuscript have taken an inventive scientific novel approach that shows how huge quantities of red mud can be disposed of by converting red mud to energy material based Hydroelectric cells which is a sustainable solution to save the environment. Otherwise its improper disposal is contaminating land, water, and air which pose alarming environmental challenges.

"Trial of pilot scale nanofiltration unit for improvement of precipitation circuit at Tummalapalle Mill" A new concept of recycling a major fraction of leached uranium liquor has been adopted to increase the concentration of mother liquor from the leached slurry belt filter. A special useful effort has been made to increase the concentration of clarified mother liquor using a laboratory model of a nanofiltration unit at UCIL Tummalapalle and the reproducibility of the data has been established in this manuscript.

"Exploring the Potential of CFBC Ash in Sustainable Building Materials: A Review" This review is focused on generation of CFBC ash, characterization of CFBC ash and advancement in processing techniques with focus on current and potential applications via waste management for industrial and societal benefits particularly for use in the construction industry. Authors have taken a very important example from India being the 2nd largest ash producer in the world including petroleum coke fly ash with annual generation of 1,00,000 MT in an oil refinery located in Madhya Pradesh. It mainly emphasises on the utilization of CFBC ash as a very crucial for environmental protection and sustainable development.

"The Impact of Stress on Education: Understanding the Consequences and Finding Solutions" In CNS&E Education Watch Report, the author has described stress and education as intricately linked, with the pressure to perform well academically often taking a toll on students' mental and emotional well-being. Further, it has pointed out some of the causes of stress in education and the role of educational institutions.

Prof R K Kotnala.

Hydrogen as a Catalyst for Sustainability: Decoding the Value Chain

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DOI: <https://doi.org/10.63015/1h-kkpant.2025.2.1>



Prof. K.K. Pant

The escalating global demand for energy, propelled by rapid economic expansion and population growth, has intensified dependence on fossil fuels, resulting in heightened greenhouse gas emissions and accelerated resource depletion. This pressing scenario underscores the urgent need to transition from conventional energy systems to renewable energy alternatives. Hydrogen has emerged as a compelling energy carrier, poised to facilitate a shift toward a sustainable, low-carbon future. Unlike carbon-based synthetic fuels, hydrogen offers the potential for a carbon-neutral or even carbon-negative lifecycle when produced from renewable energy sources. This review provides a comprehensive and systematic analysis of the hydrogen economy, detailing its value chain from production to practical application and elucidating its potential to support sustainable development.

The analysis encompasses a variety of hydrogen production methodologies, including established techniques such as steam methane reforming and innovative approaches such as electrocatalysis, photocatalysis, biomass conversion, and non-thermal plasma-enhanced dry reforming of methane. This review critically evaluates the processes of hydrogen production, storage, transportation, and utilisation, emphasising its vital role in decarbonising key sectors. Various production methods are assessed based on their efficiency, economic feasibility, and environmental impact, with renewable-driven electrolysis identified as a particularly promising pathway.

In addition, the review examines hydrogen storage and transport technologies, including high-pressure compression, cryogenic liquefaction, and chemical carriers such as liquid organic hydrogen carriers (LOHCs) and metal hydrides, evaluating their technical feasibility and scalability. Furthermore, the study explores the applications of hydrogen in industrial processes, transportation, and power generation, highlighting its potential to substitute carbon-intensive energy sources. Insights from initiatives such as India's National Green Hydrogen Mission are incorporated, addressing critical challenges, including high production costs, infrastructural constraints, and technological limitations.

Progress in material science, process optimisation, and collaboration among academia, industry, and policymakers is essential for surmounting these challenges. Finally, this review delineates key research and development priorities, underscoring the necessity for coordinated efforts to establish hydrogen as a foundational element of a sustainable, low-carbon energy system.

Thermochemical Conversion of Agro-Waste for Green Hydrogen Production

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Volume 2, Issue 1, February 2025

Received: 18 February, 2025; Accepted: 25 February, 2025

DOI: <https://doi.org/10.63015/1h-2457.2.1>

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Abstract: The thermochemical conversion of agro-waste presents a sustainable pathway for green hydrogen production, addressing both energy and environmental challenges. Agricultural residues, such as crop straw, husks, and forestry waste, are abundant and rich in carbon content, making them viable feedstocks for hydrogen generation. Key thermochemical processes include pyrolysis, gasification, and hydrothermal liquefaction, each offering unique advantages in converting biomass into hydrogen-rich syngas. Gasification, in particular, operates at high temperatures with controlled oxygen or steam to enhance hydrogen yield while minimizing tar formation. Advanced catalysts and sorbents further improve hydrogen selectivity and carbon capture efficiency. Process optimization, including temperature control, catalyst selection, and reactor design, is crucial in maximizing hydrogen output and minimizing impurities such as CO and CH₄. Integrating carbon capture and storage (CCS) technologies enhances the sustainability of hydrogen production by reducing greenhouse gas emissions. Additionally, hybrid approaches combining thermochemical methods with biological or electrochemical processes offer the potential for improved efficiency and scalability. Despite its promise, challenges remain, including feedstock variability, high capital costs, and the need for technological advancements in process efficiency. Research efforts focus on developing cost-effective catalysts, optimizing reaction conditions, and utilizing artificial intelligence for process control. Policy support, investment in bio-refinery infrastructure, and life cycle assessment studies will be critical for commercializing this approach. Thermochemical conversion of agro-waste thus emerges as a promising strategy for producing green hydrogen, contributing to the global transition toward sustainable and carbon-neutral energy systems.

Keywords: Agro-waste, biomass, carbon-neutral, green hydrogen, sustainability, thermochemical conversion

1. Introduction

The petrochemical fertilizer and chemical processing industries have a significant share in the consumption of hydrogen produced worldwide. Due to the boost in the hydrogen economy, hydrogen as a future fuel in the automobile sector will also

stimulate the need for hydrogen [1]. However, hydrogen is the most abundant element in nature; it cannot be freely available, and thus, rather than fossil fuel, it must be produced from another renewable energy source. The most common technique for hydrogen production these days is hydrocarbon-steam

reforming or coal gasification for industrial processes, which require steam and hydrocarbons [2], [3]. Thus, hydrogen produced in this manner cannot be considered a renewable or clean gas as it is produced from hydrocarbon fuels and causes similar carbon dioxide emissions.

As the reduction of the greenhouse effect and independence from fossil fuels have become priorities for the world, new sustainable ways of hydrogen gas production need to be studied. In this direction, biomass gasification can produce hydrogen because it can recover energy from waste biomass [4]. Also, this process can be used to produce hydrogen, fuels, and many value-added chemicals. Thus, biomass gasification offers flexibility toward the input feedstock and output final products. The production of green hydrogen as fuel results in the generation of only energy and water as products without the emission of carbon or any toxic gas; thus, it is considered a clean fuel. Further, it is a much safer fuel than LPG, NG, gasoline, and diesel owing to its low density [5], [6], [7].

Biomass can be considered a prominent form of energy because it has around 10–14% share in the global energy supply [8], [9], [10]. Also, biomass contributes to up to 90% of total energy demand in the rural and remote areas of developing countries across the globe [11], [12]. In the coming future, it will remain the primary source of energy requirement for developing countries because it is expected that more than 80% of the world population will reside in the rural and remote areas of developing countries by 2050 [13], [14].

There are various methods available for biomass wastes to hydrogen production, but at present, most of the methods are either on a laboratory or pilot scale. The gasification of biomass to produce hydrogen is one of them. Gasification of biomass is a mature technology and has been used for more than 100 years for syngas and biochar

production with the help of various modes of gasifiers. The gasification process requires high temperature ($>700\text{ }^{\circ}\text{C}$) and a gasifying agent to convert the waste biomass into syngas, a mixture of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), and hydrogen (H_2) [15]. Tar and biochar are also produced during the gasification process. Thermal cracking in the presence of oxygen can be used to convert the tar, and a water gas shift reactor can be used to enhance hydrogen production. Pressure swing adsorption or membrane separation can separate the hydrogen from syngas. Hydrogen yield from gasification also depends on biomass's physical and chemical properties. So, the production of hydrogen from waste biomass requires process optimization and the identification and characterization of biomass through which the optimum yield of the hydrogen gas can be produced.

The use of hydrogen in the future will increase rapidly to overcome the problem of CO_2 emission and become a carbon-neutral environment worldwide. Global hydrogen demand was around 115 Mt in 2020, which is expected to increase to 200 Mt in 2030 and 530 Mt in 2050, and the demand for hydrogen in India would represent almost 10% of the global hydrogen demand [16]. India's annual demand for hydrogen was 6 MT in 2020, majorly for petro-refining, ammonia, and methanol production. These two applications currently account for more than 80% of the consumption of hydrogen, primarily derived from natural gas using steam methane reforming. As per the Ministry of Steel report, around 35% of the steel production in India is produced from the DRI-based plant only [17]. In India, most of the hydrogen (100%) is produced by using natural gas while simultaneously emitting the CO_2 into the environment. Around 11 kg CO_2 per kg of H_2 from SMR and 20 kg CO_2 per kg of H_2 from coal gasification are produced [18]. The use of up to 5 MT of green hydrogen per year

can reduce the 11 MT per year consumption of natural gas or around 25 MT of coal per year while simultaneously reducing the 34 million tonnes of CO₂ emission per year from natural gas or 57 million tonnes CO₂ emission per year from coal gasification by 2030, respectively [19], [20].


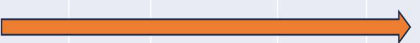
As can be seen from Table 1, if the current demand for all the fossil fuels, i.e., crude oil, coal, and natural gas, is hypothetically replaced by hydrogen, then about 276 MTPA of hydrogen will be needed. There will also be a corresponding reduction in CO₂ emission by about 2725 MTPA if the hydrogen is green. The prediction shows the strong need to replace fossil fuels in current applications with fuels like hydrogen.

Table 1: Market demand for green hydrogen and equivalent CO₂ savings per annum [21]

| Fossil Fuel type | Annual Indian Demand | Green H ₂ requirement for replacement | Equivalent CO ₂ savings due to replacement |
|------------------|----------------------|--|---|
| Coal | 430 MTPA | 143 MTPA | 1625 MTPA |
| Crude Oil | 250 MTPA | 83 MTPA | 740 MTPA |
| Natural Gas | 130 MTPA | 50 MTPA | 360 MTPA |
| Total | 810 MTPA | 276 MTPA | 2725 MTPA |

Hydrogen from renewable energy via water electrolysis is one pathway for green hydrogen, but equally critical for India is to build a hydrogen economy using hydrogen from solid fuels like coal, pet coke, and solid waste, including MSW and biomass [22]. Based on preliminary analysis and the proposed technology route discussed in this chapter, hydrogen can be produced at a competitive cost—under ₹200/kg—nearly half the cost of hydrogen generated through renewable energy and water electrolysis using current state-of-the-art methods. The colour code of hydrogen with greenhouse gas emission from the production process and the

acceptance level of the different processes

| Colour Code | Brown | Grey | Blue | Turquoise | Green |
|---|--|-------------------------|--|-----------|--|
| Energy Source | Coal or lignite | Natural gas | Any non-renewable energy source | Methane | Any renewable energy source |
| Process of getting hydrogen | Gasification | Steam methane reforming | Steam methane reforming and carbon capture & storage | Pyrolysis | Electrolysis of water and biomass gasification |
| Highest to lowest greenhouse gas emission |  | | | | |
| Lowest to highest acceptable level |  | | | | |

can be seen in Table 2.

Table 2: Colour code of hydrogen with greenhouse gas emission and acceptance level of different processes

This study presents a comprehensive analysis of agro-waste thermochemical conversion for green hydrogen production, emphasizing the gasification pathway. Unlike conventional studies that focus on brief discussions related to individual thermochemical pathways, this work provides a detailed assessment of the gasification process and the reactions involved, hydrogen storage and safety, cost of production, and the challenges associated with the production. Further, an advanced gasification scheme is proposed for maximizing the hydrogen production from biomass through water gas shift reaction, tar conversion to yield more syngas through catalytic cracking, and separation and purification of the hydrogen through pressure swing adsorption techniques and other low-temperature separation methods. By addressing critical challenges such as feedstock variability, process economics, and environmental impact through a multidisciplinary approach, this study contributes to developing a cost-effective, scalable, and carbon-neutral hydrogen production pathway from agricultural residues.

2. Agro-waste feedstock potential

For hydrogen production, abundant and low commercial value agriculture waste such as crop residue waste, rice straw, wheat straw, sugarcane bagasse/trash, cotton stalk, sorghum stover, etc., can be used effectively. Using these materials as a feedstock for hydrogen production can solve waste management problems or stubble burning of agro residue in rural areas by simultaneously decreasing pollution and other environmental hazards. Various properties of agro-waste required to be considered during gasification are listed in the Fig. 1.

India, a major agrarian society, generates a lot of agro residues. Overall, India produces approximately 686 MMT (million metric tonnes) of crop residue biomass in the form of stacks, roots, trashes, husks, and yard trimmings on an annual basis, of which 234 MMT (34% of gross) are estimated as surplus for bioenergy generation and available in distributed form [23]. According to the MNRE report, it is estimated that 750 MMT of agricultural and forestry biomass is generated annually in India. The surplus biomass available in India is around 230 MMT out of the total available, with the potential of 28 GW of energy production [24]. From the observation of data from 2010–11 to 2015–16, the survey covered production statistics of the primary selected crops such as wheat straw, rice straw and husk, sugarcane leaf and bagasse, gram, soybean, groundnut castor, etc. Based on the survey, it is estimated that the annual average biomass generation from these crops was around 683 million tonnes [25]. It was also found that more than 80% of biomass is generally produced from rice straw and husk (33%), wheat straw (22%), sugarcane tops and bagasse (17%), and cotton (8%) [26]. The majority of biomass was produced in Uttar Pradesh, Maharashtra, Madhya Pradesh, Punjab, and Gujarat, and these all

were the top five states of India generating biomass [27].

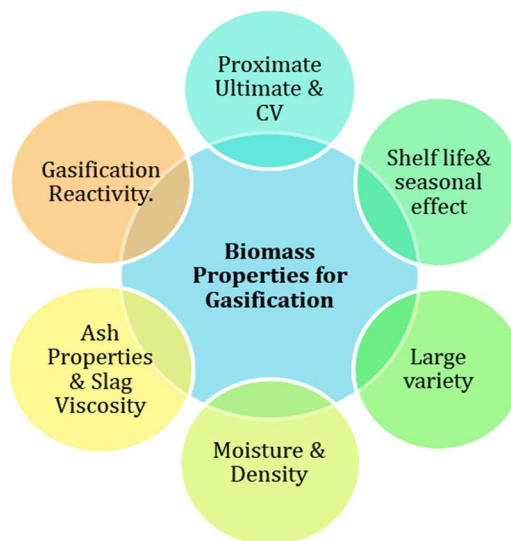


Fig. 1: Various properties of agro-waste

3. Gasification process for conversion of agro-waste

It is a thermo-chemical process involving multiple chemical reactions wherein a carbon-containing feedstock, such as agro waste, is converted into synthetic gas in a partial supply of air, oxygen, or steam. The process operates at sufficiently high temperatures ($>600 - 1000\text{ }^{\circ}\text{C}$) to thermally degrade the biomass waste to yield the hydrogen-rich syngas [15], [28]. Several advantages are associated with gasification, such as the increased heating value of fuel by the rejection of non-combustibles like nitrogen and water, reduction in oxygen content of the fuel, exposure to H_2 at high pressure or exposure to steam at high temperatures and pressures where H_2 is added to the product will raise the products relative hydrogen content (H/C ratio) [29]. Biomass feedstock has a variation in moisture content during the different seasons and in the different parts of the country. The feedstock quality, especially the moisture content, plays a significant role in the quality of the product after gasification; less than

20% moisture content generally seems reasonable for a good quality product [30], [31]. An overview of the different production processes, types of hydrogen storage, and various modes of hydrogen transportation with end applications can be seen in Fig. 2.

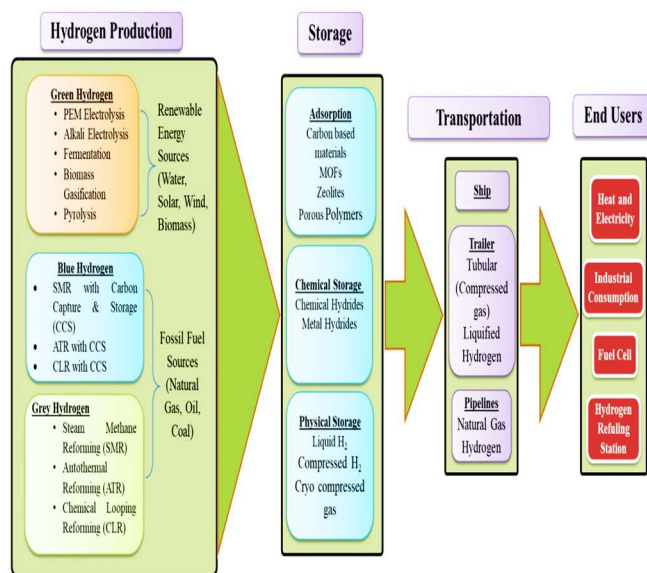
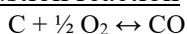


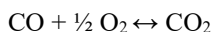
Fig. 2: Overview of hydrogen production to end-use

Conversion of biomass in a typical gasifier system is mainly carried out by four different stages: drying, pyrolysis, gasification, and combustion [32]. Many reactions of different natures (i.e., endothermic or exothermic, etc.) are simultaneously carried out in these four zones. The reactions inside the gasifier are complicated and can be found in reaction no. R1 to R8 [33], [34]. These reactions are generally classified into five types: i) carbon reactions, ii) oxidation reactions, iii) shift reactions, iv) methanation reactions, and v) steam reforming reactions [28], [35], [36], [37].

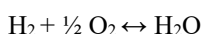
Combustion reaction



$$\text{Heat of Reaction} = -122 (\text{kJ/mol}) \quad (\text{R1})$$

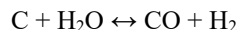


$$\text{Heat of Reaction} = -283 (\text{kJ/mol}) \quad (\text{R2})$$

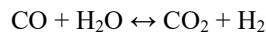


$$\text{Heat of Reaction} = -248 (\text{kJ/mol}) \quad (\text{R3})$$

Water gas shift reaction

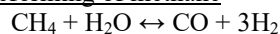


$$\text{Heat of Reaction} = +136 (\text{kJ/mol}) \quad (\text{R4})$$



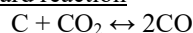
$$\text{Heat of Reaction} = -35 (\text{kJ/mol}) \quad (\text{R5})$$

Steam reforming of methane



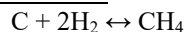
$$\text{Heat of Reaction} = +206 (\text{kJ/mol}) \quad (\text{R6})$$

Boudouard reaction



$$\text{Heat of Reaction} = +171 (\text{kJ/mol}) \quad (\text{R7})$$

Hydrogasification



$$\text{Heat of Reaction} = -74.8 (\text{kJ/mol}) \quad (\text{R8})$$

High purity near green hydrogen with a higher production rate can be produced from the advanced biomass gasification system, as can be seen in Fig. 3. The syngas produced after the gasification of biomass generally contain a high amount of tar, which can be converted into more syngas by increasing the temperature, and the process is called the thermal/catalytic cracking of tar. This can be done by adding oxygen to the gas, leaving the gasifier during thermal cracking. After the thermal cracking operation, the temperature of the gas stream will be lowered to around 250 °C by water quenching. Then, solid particles will be removed using a bag-house filter.

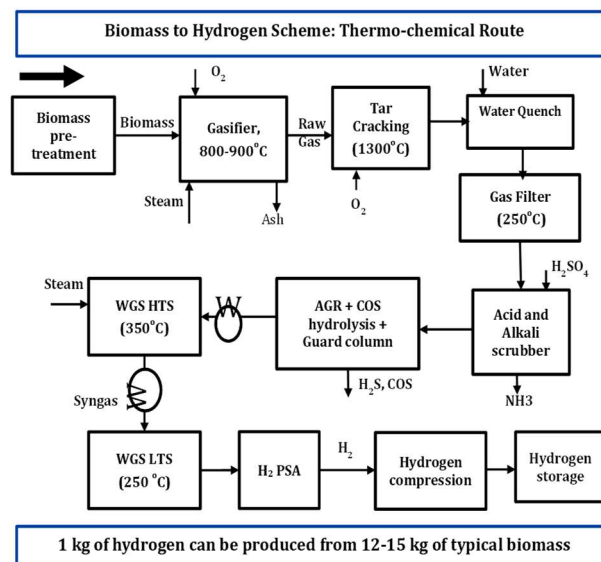


Fig. 3: Proposed route for biomass to hydrogen production

To maximize the yield of hydrogen, water gas shift (WGS) conversion process is

required. This conversion shifts the carbon monoxide (CO) present in the syngas to carbon dioxide (CO₂) and additional hydrogen (H₂) via reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$), which is an exothermic in nature and known as the water gas shift reaction (WGSR). Typically, 1 kg of biomass feed requires 1 kg of steam during the WGSR. The reaction is favored at lower temperatures and higher steam content. Still, based on the varying temperature conditions, the WGSR can be called High-Temperature Shift Conversion (HTSC), Medium Temperature Shift Conversion (MTSC), Low-Temperature Shift Conversion (LTSC), and Sour Gas Shift Conversion (SGS) [26], [38]. Based on the syngas characteristics or as per final product quality requirements, any one or pair of shift conversion reactions can be used. The SGS conversion process typically utilizes a bed of cobalt molybdenum catalyst. The syngas typically enter the SGS reactor at 230-260 °C temperature. A high-temperature shift reaction is generally carried out at 350-450 °C, whereas a low-temperature shift can be carried out at 250 °C temperature [39], [40].

After WGSR, Pressure Swing Adsorption (PSA) is used to recover and purify the hydrogen from the hydrogen-rich gas stream coming from WGSR. PSA is an effective tool for producing pure hydrogen from syngas. The technology used in the PSA process generally relies on the differences in the adsorption properties of different gases to separate them under pressure. The PSA tail gas containing the impurities can then be sent into a burner for process heating and steam generation. The crude hydrogen obtained from the gasifier is a complex mixture of hydrocarbons, heavy chemicals, and moisture. Removal of such impurities from hydrogen is essential to hydrogen energy utilization. Other separation methods could also be employed for hydrogen purification and separation, such as low-temperature

separation methods (cryogenic distillation and low-temperature adsorption) and membrane separation methods (inorganic membrane and organic membrane).

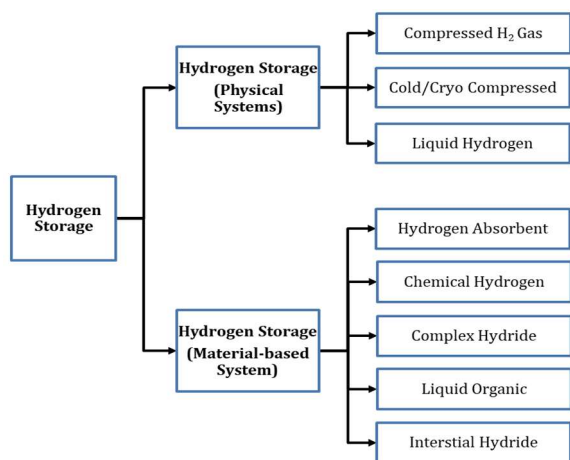
Applying a specific purification method depends upon the types and amounts of impurities. The impurities such as sulfide, HCHO, and HCOOH can be effectively eliminated using low-temperature adsorption. However, it is a complex method that requires high energy consumption and is suitable for small-scale operations. Metal hydride separation and palladium membrane separation methods are feasible when the separation of gas source with a high content of inert components is required, but the purification efficiency is low. New membrane technologies such as carbon molecular sieve membranes, ionic liquid membranes, and electrochemical hydrogen pump membranes have recently been developed, but their industrial implementation is limited. The pressure swing adsorption (PSA) technique is the most common and frequently adopted hydrogen purification technology widely used in coal gasification and natural gas reforming processes because of its long service life and economic feasibility [41]. In most PSA processes, activated carbon and zeolite have been used as an adsorbent to remove critical impurities of CO₂ and CO from the crude hydrogen [42], [43].

4. Hydrogen storage and safety

The pure hydrogen stream from the PSA can be compressed to the typical dispensing pressures of 350 or 700 bar using booster pumps and filled into the cylinders or storage tanks [44], [45]. These cylinders will then be dispatched to the customers. If the gas grid is available, the hydrogen will be boosted to a suitable pressure and injected into the gas grid. Hydrogen can operate fuel cell-based vehicles in either molecular form or combined form (say methanol, ammonia,

or DME). However, this would require suitable infrastructure for storing, distributing, and dispensing hydrogen (both in molecular and combined form).

Storage of hydrogen can be done either in the form of compressed gas or the form of liquid. High pressure of the order of 350–700 bar is required to store the hydrogen in the gaseous state [46], [47]. On the other hand, cryogenic temperature is required to store the hydrogen liquid state because hydrogen has a boiling point ($-252.8\text{ }^{\circ}\text{C}$) at atmospheric pressure. The other hydrogen storage options are adsorption on the solid surface or absorption within the solid [38], [48]. Different methods of hydrogen storage



are shown in Fig. 4.

Fig. 4: Various methods of hydrogen storage

Biomass gasification is a fairly complex technology, and hydrogen production plants based on biomass gasification must comply with various guidelines and national laws. Each process step has to be carefully considered for its Health, Safety, and Environmental constituents during the planning, engineering, construction, and operation stages. Identifying process safety and risk assessment is an essential activity during biomass gasification. Globally, it is gaining interest as the most cost-effective tool for

identifying safety requirements and reducing risk during operation. People dealing with gasification plant construction and operation generally recognize the risk assessment requirements, but due to lack of experience and resources, they did not assess the risk quantitatively. Using advanced safety techniques and tools during the gasification plant design and operation, many key issues related to safety can be easily identified. Implementing and incorporating essential safety features during the initialization step of plant design will result in safe operation during production. This will not only meet the necessary legislative standards but also satisfy the criteria of ALARP (As low as reasonably practicable) while handling the various raw materials properly. However, there can be several events of hazards that may occur with various consequences. But, the most critical issues are (i) fire and explosion hazards during the operation, (ii) operation failures due to various reasons, and (iii) unplanned release of hazardous liquids, chemicals, and gas.

5. Production cost of hydrogen from various methods

The cost of hydrogen production from different methods was analyzed based on various assumptions and market surveys, and the same is summarized in Table 3. It is possible to produce 1 kg of hydrogen from 12-15 kg of raw biomass followed by a thermochemical conversion route. The proposed technology (Fig. 4) for biomass waste gasification has some unique features, such as the capacity to produce 100 kg of hydrogen from 1.2-1.5 TPD of MWS/biomass with 85-95% conversion efficiency. With this high efficiency, the proposed pathway can convert all the available agricultural biomass to hydrogen energy. One kilogram of biomass is capable of producing approximately 85 grams of hydrogen. One kg of biomass can produce 0.6

Table 3: Cost of hydrogen production

| Parameters | Water splitting (high-pressure electrolyzer) [49] | Steam-Methane reformation (SMR) [50] | Methane Pyrolysis (The new process) | Coal gasification (high ash India coal) [50], [51] | Biomass waste to hydrogen |
|------------------------------------|---|--------------------------------------|---|---|--|
| Yield (kg of H₂) | 1 kg of hydrogen /55-60 kWh | 1 kg of hydrogen/3 kg of Methane | 1 kg of hydrogen/ 4.2 kg of Methane | 1 kg of hydrogen/19.2 kg of HAIC | 1 kg of hydrogen/15 kg of biomass |
| Primary energy cost | At Rs 3/kWh | 18 – 41.4 Rs/kg of natural gas | 18 – 41.4 Rs/kg of natural gas | 1.8-3.5 Rs/kg of HAIC Imported is nearly the same on eq. cal. basis | If the MSW cost is zero. Others are governed by policy |
| Energy costs/MJ | Rs 0.83/MJ _e | 0.36-0.84 Rs/MJ | 0.36-0.84 Rs/MJ | 0.11-0.24 Rs/MJ | 0-0.2 Rs/MJ |
| Cost of hydrogen | 240-300 Rs/kg | 200-300 Rs/kg | 200 Rs/kg | 120-160 Rs/kg | 120-160 Rs/kg |
| CO₂ emission | Associated with electrolyzer manufacturing | 8.07 kg of CO ₂ / Kg | 1.67 kg of CO ₂ / kg of hydrogen | 21 kg of CO ₂ per kg | Carbon neutral and hence zero |

kWh of energy and may yield a maximum of 3 Rs. revenue; while converting it to hydrogen, we can get approximately proposed technology 0.093 kg of hydrogen and a revenue of 15/- Rs. five times higher revenue. After successfully demonstrating the indigenized technology, the total cost is Rs. 150 per kg.

6. Challenges linked with the implementation of green hydrogen

The development of low-cost indigenous technology for hydrogen production from biomass/agro-waste is hindered by several challenges, as summarized below [52], [53], [54], [55].

- **Feedstock Variability and Availability:** Agro-waste composition varies significantly based on crop type, location, and

seasonal changes, affecting process efficiency and hydrogen yield. High moisture and ash content in some residues can reduce conversion efficiency and lead to operational issues such as slagging and fouling in reactors.

- **High Capital and Operational Costs:** Thermochemical processes, especially gasification and hydrothermal liquefaction, require advanced reactors, catalysts, and separation units, increasing capital investment. The cost of biomass collection, transportation, preprocessing (drying, grinding, etc.), and storage adds to the overall expenses.
- **Process Optimization and Efficiency:** Achieving high hydrogen selectivity while minimizing by-products (CO, CH₄, tar, and char)

requires precise temperature control, optimized catalysts, and effective reactor design. Tar formation in gasification remains a critical challenge, necessitating advanced tar-cracking catalysts or secondary reforming processes.

- **Catalyst Deactivation and Development:** Catalyst performance deteriorates over time due to sintering, carbon deposition, and poisoning from impurities in agro-waste feedstocks. Developing cost-effective, durable, regenerative catalysts is crucial for improving long-term process efficiency.
- **Carbon Emissions and Sustainability Concerns:** Although thermochemical processes can integrate carbon capture and storage (CCS), ensuring a net-zero or negative carbon footprint remains challenging. Effective utilization of biochar and CO₂ by-products is essential to enhance overall sustainability.
- **Integration with Renewable Energy and Hybrid Approaches:** Hybridizing thermochemical methods with biological or electrochemical processes can enhance efficiency, but technological integration remains complex. Ensuring a stable and renewable energy supply (e.g., for steam or plasma gasification) is necessary to maintain proper "green" hydrogen production.
- **Policy, Economic, and Market Challenges:** Inconsistent government policies, subsidies, and carbon pricing mechanisms impact the economic feasibility of agro-waste-based hydrogen production. Competing with fossil-fuel-derived hydrogen, which remains cheaper due

to existing infrastructure and subsidies, presents a significant economic barrier.

- **Life Cycle Assessment and Environmental Impact:** Comprehensive life cycle assessments (LCA) are needed to evaluate the true environmental impact of thermochemical conversion, considering land use, energy input, and emissions. Managing waste by-products such as ash and heavy metals is crucial to minimize ecological risks.

7. Conclusions

The thermochemical conversion of agro-waste offers a sustainable and efficient route for green hydrogen production, utilizing abundant agricultural residues to address energy and environmental challenges. Processes such as pyrolysis, gasification, and hydrothermal liquefaction enable the transformation of biomass into hydrogen-rich syngas, with gasification being particularly effective in maximizing hydrogen yield while minimizing by-products. Despite challenges such as feedstock variability, high capital costs, and process optimization complexities, a key aspect for the future lies in exploring advanced catalysts and sorbents that could improve hydrogen selectivity while simultaneously capturing carbon emissions, thereby increasing overall process sustainability. Further, policy support, infrastructure investment, and life cycle assessment studies will be critical in facilitating large-scale commercialization. As the world transitions toward cleaner energy systems, thermochemical conversion of agro-waste presents a viable and impactful solution for achieving sustainable hydrogen production and reducing carbon emissions.

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Beyond Silos: A Unified Approach to Decarbonisation through Hydrogen Integration

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Volume 2, Issue 1, February 2025

Received: 15 December, 2024; Accepted: 29 January, 2025

DOI: <https://doi.org/10.63015/1h-2450.2.1>

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Abstract: Renewable sources like hydrogen ignite hope as the world wrestles with surging energy demands, dwindling fossil fuels, and choked skies. Hydrogen fuel, versatile in both gaseous and liquid forms, boasts applications from fuel cells and internal combustion engines to powering industries. Global hydrogen production currently stands at 0.1 gigatonnes, primarily for industrial applications like metal refining. Despite its promise, hydrogen remains a fledgling player in the global energy mix. High production costs, with water electrolysis four times costlier than steam reforming, pose a significant hurdle. Also, hydrogen's low volumetric density necessitates efficient compression, liquefaction, and storage advances. Public awareness of the scope of turquoise and blue hydrogen should be actively pursued. With this background, the present article discusses critical global challenges in detail and suggests recommendations and pathways for enabling a decarbonised future powered by clean, sustainable hydrogen energy.

1. Introduction

The global drive for alternative and renewable energy sources is fuelled by two primary concerns: ensuring energy security by reducing reliance on imported fossil fuels and mitigating climate change through reduced carbon emissions. Global warming due to fossil fuels-led greenhouse gas emissions makes the transition to renewable fuels imperative [1]. Innovation in technologies can facilitate optimal usage of existing resources, protect the environment and promote sustainable development. Challenges remain while significant progress has been made – for instance, global renewable energy capacity surpassed fossil fuel capacity in 2021. These include limitations in large-scale energy infrastructure, underdeveloped ecosystems for electric vehicles, and dependence on critical minerals [2].

With an energy density of 122 MJ/Kg (2.75 times more than gasoline), hydrogen presents a compelling option for future energy systems (Kaur et al. 2024). Some of the significant properties of hydrogen as a fuel are mentioned in Table 1. The lower heating value (LLV) of 120 MJ/Kg and higher heating value (HLV) of 119.9 MJ/Kg compared to diesel's 44.8 MJ/Kg (LLV) and 42.5 MJ/Kg (HLV), positions hydrogen as a strong contender for the title of "ultimate energy source for the 21st century [3–5]. Hydrogen, with abundant reserves, high calorific value and a non-carbon-based energy source, is eco-friendly, renewable and versatile and is important for a smoother transition in the energy sector (Zhou et al. 2022). Based on sources of raw materials, chemical, physical or biological processes can be employed to produce hydrogen. Both chemical and physical processes for hydrogen production require specific

reaction conditions and are thus energy-exhaustive processes. Biologically produced hydrogen, though low in cost, carries a long duration of time [9]. To produce Hydrogen, a commonly employed process is steam methane reforming (SMR) or coal gasification without carbon capture (Grey H) [10]. In addition to this, steam methane reforming (SMR) or coal gasification with carbon capture (Blue Hydrogen), methane pyrolysis (Turquoise Hydrogen), and electrolysis of water or biomass pyrolysis (Green Hydrogen) are also alternative routes of hydrogen production [11].

Table 1: Properties of Hydrogen Fuel

| Fuel | LLV (MJ/Kg) | HLV (MJ/Kg) | Reference |
|----------|----------------|----------------|-----------|
| Hydrogen | 120 | 119.9 | [7-8] |
| Methane | 55.5 | 50 | [8] |
| Ethane | 51.9 | 47.8 | [8] |
| Gasoline | 47.5 | 44.5 | [8] |
| Diesel | 44.8 | 42.5 | [8] |
| Methanol | 20 | 18.1 | [8] |

Alkaline electrolyzers are the most favourable cost-effective, mature technology and most widely used, with reported efficiencies ranging from 63-70%. Proton Exchange Membrane (PEM) electrolyzers, with a slightly lower level of commercial maturity, also exhibit comparable efficiency levels within the same range (63-70%). Solid Oxide Electrolyzer Cells (SOECs), with higher energy conversion efficiency (74-86%) and higher cost, are still at the demonstration stage of development [12].

Hydroelectric cell is an innovative alternate technology to produce clean hydrogen at ambient temperature, eliminating the need for light, acid, or alkali. Laboratory-scale studies on hydrolytic cells have shown

encouraging results with the production of large volumes of hydrogen (1.856 mmol/h). The study on the effectiveness of hydrolytic to produce fast hydrogen has shown that zinc anode and silver cathode immersed in deionized water, coupled with a nanoporous lithium-substituted magnesium ferrite catalyst and driven by external voltage, presents a promising pathway for sustainable hydrogen generation [13].

Globally, about 95 Mt of hydrogen was produced annually in 2022, nearly two-thirds of which is derived from reforming natural gas, with lower environmental benefits. It has been reported that there is a critical need to rapidly scale up green hydrogen production technologies like electrolysis [14].

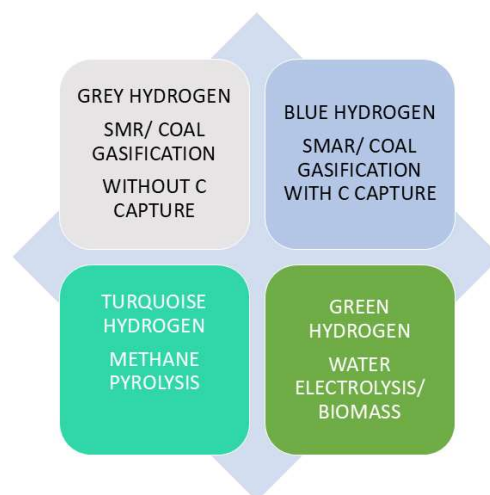


Figure 1: Colour codes for Hydrogen

Debates persist regarding the preferred production method, with the oil, gas, and coal industries favouring "blue" hydrogen. At the same time, wind and solar sectors advocate for "green" hydrogen to expand their markets. Additionally, natural gas-producing countries also lean towards blue hydrogen. Globally, nations have designed strategies to move towards other sources of hydrogen, depending on available national resources and infrastructure, to gain maximum environmental benefits. Thus,

the present study delves into the potential and challenges of hydrogen as a clean, alternative, non-carbon fuel. It explores its viability for large-scale deployment and a smooth transition to a net-zero global future.

1. Global Hydrogen Policy Landscape

Driven by a desire for clean energy, countries worldwide are turning to hydrogen and have announced their national hydrogen policies [15]. While Japan was the first to announce its national hydrogen policy, other Asian nations like India are also developing hydrogen programs. Europe, a major hydrogen consumer, is heavily invested in production and storage technologies with a goal of carbon neutrality by 2050. International collaboration between research institutions, industries, and governments is crucial to achieve this ambitious target. Hydrogen valleys, where the entire hydrogen supply chain is clustered, and public-private funded projects like HEAVENN, showcase the promising future of hydrogen in a global clean energy transition [16].

3. Challenges for the Hydrogen Economy

3.1 Transition to Green Hydrogen:

Most hydrogen is produced through fossil fuels, which questions the greening of the whole value chain. To provide long-term solutions, the need of the hour is impetus to Green Hydrogen eco-system development. While solar and wind energy are available widely at competitive prices, it is essential to support the manufacturing of green hydrogen globally.

3.2. Economies of Green Hydrogen Production:

Total cost includes fixed cost like cost of electrolyser, and land procured. The operational cost consists of raw materials like water, utilities (electricity), labour employed, maintenance and repair. The cost depends on the type of technology used, with water electrolysis an expensive technology compared to other technologies (Table 3).

Table 2: Global Nations with Hydrogen Policies [17]

| Country | Major Policy Guidelines |
|-----------|---|
| Australia | The Australian Clean Hydrogen Trade Program (ACHTP) of AUD 150 million was initiated in 2022 to support the growth of a clean, innovative, safe and competitive Australian hydrogen industry. |
| Canada | Hydrogen production through electrolysis as well as from natural gas with carbon capture, utilization, and storage (CCUS) receives Investment Tax Credit in 2024 |
| China | State-owned Sinopec Green Hydrogen Plant initiated with an aim to produce 20,000 tonnes of hydrogen through financial investment of 2.6 billion yuan (2022) |
| EU | Homegrown hydrogen production of 10 GW supported through 17.5 GW by 2025 of electrolysers, storage and port facilities |
| India | National Green Hydrogen Mission (2023) for annual production of 5 MMT of GH by 2030 |
| Japan | The annual budget 2024, announced the development of hydrogen supply chain through funding of 25 billion yen |
| UK | Green Industries Growth Accelerator program with financial support of GBP 960 million for net zero sectors through offshore wind, networks, CCUS, hydrogen and nuclear (2024) |
| USA | Department of Energy has initiated \$100 million grant program for low-carbon energy technologies (2021) |

Specifically in Indian scenarios, the report by Department of Science and Technology (DST), India shows that electrolysis of water required for production of GH involves higher cost of production (Rs 433/kg) than steam methane reforming of Rs 150/kg.

Table 3: Cost of Hydrogen Production through different technologies [18]

Table 4: Cost for Hydrogen production in India [19]

| Hydrogen production method | Cost (USD/ kg hydrogen produced) |
|----------------------------|----------------------------------|
| Photobiolysis | 1.84-2.27 |
| Dark fermentation | 1.02-2.70 |
| Gasification | 0.93-2.83 |
| Pyrolysis | 1.47-2.57 |
| Steam reforming | 1.25-3.50 |
| Water electrolysis | 3.01-4.51 |

3.3 Standards for Hydrogen:

The development of the hydrogen economy

| Hydrogen production method | Cost (Rs/ Kg) |
|----------------------------|----------------|
| Steam methane reforming | 150 |
| Coal gasification | 245 |
| Biomass Gasification | 258 |
| Biomass microbial | 813 |
| Electrolyser | 433 |

hinges on the establishment of clear standards that guarantee reliability, safety, and traceability and foster a robust global market, translating into significant economic benefits. While ISOTC197 deals with standards for hydrogen, PESCO (Petroleum Explosives Safety Organisation) has established Static & Mobile Pressure Vessels Rates 1981,

Explosive Act 1854, 2008, and Gas Cylinder Rules 2004.

The establishment of ISO/TS 19870, which provides a methodology for evaluating greenhouse emissions from the production, condition, and transport of hydrogen, is a step towards evaluating the environmental impacts of the hydrogen economy. However, since hydrogen can be produced from various sources and finds applications in multiple fields, evaluation of overall emissions and carbon foot printing under different scopes is a complex task and needs detailed international guidelines (Figure 2).

However, hydrogen-specific rules and regulations pertaining to gas refilling, storage, and transport vary from country to country. More integration among global certifications is needed. Revised globally acceptable regulations, codes, and standards for the hydrogen sector need to be formulated. Certification methods for cross-border certificates for hydrogen trades are yet to be available. While future regulatory frameworks are uncertain, there are inconsistencies in certification and standardization, posing significant barriers to investment.

3.4 Infrastructure for Sustainable Green Hydrogen Deployment

Electrolyzers, the workhorses of green hydrogen production, account for 40% of the total cost and are crucial to unlocking this clean fuel's potential. Securing a reliable and affordable supply is crucial, particularly in developing nations like India, where most electrolyzers are imported (often with in-house assembly). Raw materials are concentrated in just a few countries. This limited geographic spread throws a wrench into efforts to build robust electrolyser manufacturing capabilities worldwide. The widespread adoption of

green hydrogen hinges on overcoming this supply chain bottleneck.

Fertilizers as well as in other sectors such as Data Centers, Cold Storage, Gated Communities, etc. Hydrogen can be used in

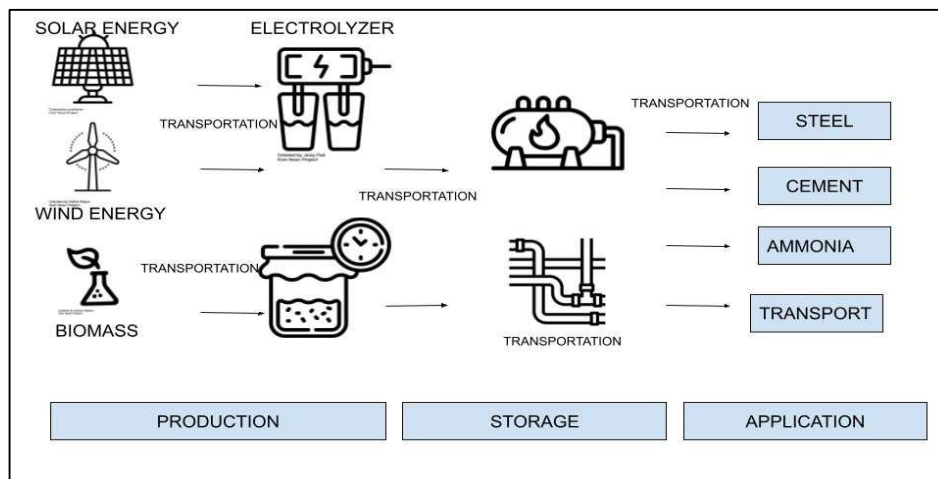


Figure 2: Different Segments of Hydrogen Eco-system

Pipelines, cryogenic storage facilities, trucks, and export ports must be strengthened globally. Presently, hydrogen can be stored in cylinders with 350 bar capacity in India, which needs to be developed to type 4 cylinders with 700 bar capacity. There is a strong need for research for the development of hydrogen storage materials as well as systems development. Storage of hydrogen composite tanks is found to be the most viable option. Companies like Hexagon are the world's largest manufacturers of composite tanks. The size of hydrogen tanks allowed internally, and face issues with hydraulic retest every 3 years. Global standards that should be followed should be well-established. Also, rules and regulations related to safety systems should be documented. Hydrogen purification systems and heating and cooling applications for Hydrogen compression are in the stages of development.

3.5 Hydrogen Application Development

There are ample green hydrogen offtake possibilities in industrial sectors such as Mobility, Fine chemicals, Steel, and

vehicles to power fuel cells in zero-emission cars with a potential for high-efficiency [20].

Industrial applications of hydrogen are already well-established. Hydrogen is widely used in the synthesis of ammonia and nitrogenous fertilisers [21]. Petroleum refineries use hydrogen to lower the sulfur content of fuels [22]. The modern steel industry is leaning on hydrogen to become environment-friendly and its decarbonisation goals through phasing out coal with hydrogen in processes such as direct reduction of iron (DRI) for conversion of iron oxides to metallic iron. The application of ammonia-blended hydrogen-fuelled engines is still in the pilot stages, which can further broaden and adaptation of hydrogen [23]. Hydrogen also finds application in the hydrogenation of the food and oil industry to enhance their stability and avoid spoilage [24].

Some of the potential uses of hydrogen include its application in powerplants where hydrogen can also be converted into electricity in a conventional fuel cell [25]. Further, to meet high energy demand and

reduce intermittency in the solar and wind energy sector, hydrogen is also considered as a medium of additional storage [24].

Furthermore, with higher energy efficiency and lower environmental impacts, the mobility sector has shown keen interest in integrating hydrogen as a fuel source, on a global scale. Some of the commercially launched projects have shown promising results, propelling further research in the domain [26]. However, the adoption of hydrogen in the transport sector needs simultaneous development in multiple sectors. First, the infrastructure for hydrogen refueling is underdeveloped and costly, hindering widespread adoption. Fuel cell vehicles (FCVs) have higher initial costs due to expensive materials and low production volumes, making them less competitive with battery electric vehicles (BEVs). Process development to lower energy losses during production, compression, storage, and conversion needs detailed investigation.

3.6. Capacity Building

The hydrogen sector is experiencing explosive growth, with new production plants and applications developing rapidly. Research and development is also flourishing, fueled by the promise of clean energy. However, the workforce must gain the specialised knowledge and experience required for these cutting-edge hydrogen production technologies. This skills gap threatens to stall the sector's momentum, creating a bottleneck between innovation and large-scale implementation. The availability of a skilled workforce equipped with the latest hydrogen technologies is paramount for the sector's continued success.

4. Conclusions

To strengthen the GH sector, we need a continuous supply of Solar and wind energy, which is already available at

enough and competitive cost. Taking examples from the solar PC sector, establishing large-scale GH production plants will help reduce overall costs in the long term. Joint research ventures to share resources and expertise are needed to accelerate innovation across every aspect of hydrogen production, storage, transportation, and application. JRVs will help in avoiding duplication of effort and maximizing resource utilization. Innovations like hydrogen-powered vehicles and infrastructure, such as hydrogen refuelling stations and pipelines, will accelerate widespread adoption. Converting waste biomass into green hydrogen holds immense potential that demands further exploration. Biohydrogen offers a promising approach to tackling climate change by reducing greenhouse gas emissions (GHG) and boasting an energy efficient process. However, research on improving the strains of microorganisms used in the conversion is crucial to make this method truly competitive with conventional methods. Global funds dedicated to technological breakthroughs are essential to fuel these collaborative efforts. These funds should prioritize research in critical areas like seawater electrolysis, wastewater electrolysis, advanced storage materials, and transportation. The ambitious global hydrogen economy requires a robust knowledge base. To achieve this, fostering partnerships for data recording and sharing is crucial. The whole value chain can be validated by pooling data from various stakeholders from cradle to grave, i.e., renewable energy producers to run electrolyzers to end-users. The digitalisation of every step in the form of a hydrogen passport will serve as a valuable tool to evaluate carbon foot printing and assist in identifying challenges, accelerating the global journey towards a hydrogen-powered future.

To develop trained manpower, bridging the gap between educational institutes and industries is essential. There are some positive examples. For instance, industries like Greenzo are establishing electrolyser and GH production capacity near Ahmedabad (India). The industry is collaborating with nearby universities to provide students with invaluable hands-on experience in cutting-edge hydrogen production technologies. In addition, they are working with educational institutions to develop comprehensive theoretical courses specifically focused on green hydrogen technology. This will ensure a well-rounded understanding for future industry leaders.

Therefore, a multi-dimensional approach focusing on infrastructure development is essential for boosting the ecosystem for hydrogen deployment. Scaling up green hydrogen production and utilising existing turquoise and blue hydrogen will help explore more avenues for hydrogen utilization. Different strategies for hydrogen, production, storage and applications can be devised and implemented depending on local resources.

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Green Energy Generation from the Industrial Waste Red Mud as Hydroelectric Cell

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Volume 2, Issue 1, February 2025

Received: 10 February, 2025; Accepted: 26 February, 2025

DOI: <https://doi.org/10.63015/2hec-2455.2.1>

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Abstract: Red Mud is a highly alkaline and toxic waste product generated in large quantities during alumina refining. Huge quantities of red mud are improperly disposed off regularly, contaminating land, water, and air which pose alarming environmental challenges. Converting red mud to energy material for hydroelectric cell is a sustainable solution to save the environment. Red mud is translated to defective and porous structure by adding ZnS through solid state reaction process. Dislocation density in red mud crystallite found to be increased from 5.93×10^4 to 13.03×10^4 by adding ZnS due to defects creation. SEM images clearly show increase in porous microstructure of the composite. Red mud based hydroelectric cell generated current 8 mA, and voltage 0.96 V that increased to 13 mA and 0.98 V by 10 wt% ZnS addition. Charge transfer resistance of red mud drastically decreased from 80.7Ω to 4.4Ω , thus decreased the activation loss and increased the current generated in red mud-ZnS composite. Transforming red mud into hydroelectric cell presents a sustainable waste-to-energy solution that could revolutionize energy security and environmental pollution.

Keywords: Red mud, Hydroelectric Cell, Green electricity, Defects, Waste utilization

1. Introduction: Continuous efforts to boost industrialisation and economic growth has put the environment on the back seat. The after effects of rapid urbanization that took place in the last few decades are now coming out at an alarming stage. The massive amount of waste generated by factories, refineries, industries, manufacturing units, energy production and other sectors is creating nuisance in the environment. Untreated waste disposal creates more harm by polluting the land, water and soil. One such industrial waste is Red Mud (RM), a residue produced during alumina refining by Bayer process. Solid waste red mud is highly alkaline complex mixture of many oxides that is generated in huge amounts in alumina refineries all over the world. For every tonne of refined alumina, around 1.5-2 tonnes of red mud is produced as a residue. Red mud, having pH 10-13, is highly toxic for all the life forms as

well as the environment [1]. Red mud typically comprises 65-70% iron oxide, 40-50% aluminium oxide, and 15-25% titanium dioxide, with variations based on the bauxite source, along with many heavy metals like arsenic, lead, cadmium, mercury etc. Most of this hazardous waste, which also contains valuable materials, ends up in landfills or stored in massive man-made ponds. These create problems for the nearby living beings. Globally, there are more than 100 operational Bayer process plants, collectively generating a stockpile of over 3.5 billion tonnes of bauxite residue. The continuous and rapid accumulation of this by-product poses a significant threat to human health, plant life, and the environment. The toxic effects of such a waste product have compelled scientists and researchers to think about its utilization instead of disposal.

Over the time red mud have been utilized for the extraction of iron, titanium, and other rare earth elements through a variety of pyrometallurgical, direct reduction, and hydrometallurgical processes [2,3]. Red mud exhibits a pronounced capacity as an adsorbent for the effective sequestration of heavy metal, non-metal, and organic contaminants, as well as synthetic dyes from aqueous effluents [4,5]. Waste red mud is transformed into a high-performance supercapacitor electrode through mechanical milling, exhibiting excellent capacitance and stability, offering a sustainable solution for its disposal [6]. In spite of the growing research for its utilization and recycling, industrial applications of red mud remain limited, with only 3-4% of total generation being utilized in sectors such as cement production, brick manufacturing, and iron ore supplementation.

An ingenious step in this direction is transforming the solid waste red mud into green energy generating device Hydroelectric Cell (HEC), that holds a high potential for its useful disposal [7]. The Hydroelectric cell works on the principle of water splitting by metal oxides/ferrites at room temperature [8]. Strategically created surface defects and nanopores enhance the water splitting efficiency of the material and aids in green electricity generation [9–14]. In this direction, present research work investigates the potential of red mud (RM), an industrial waste product, for water splitting without using any acid/alkali or light. Using a simple solid state reaction method, 10 and 20 weight % ZnS was added to Red Mud, creating oxygen deficiencies and nano-porosity within its structure. The structure, morphology and power generation capacity of the Red mud based Hydroelectric cells have been studied by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), V-I polarization curves and Electrochemical Impedance Spectroscopy (EIS).

2. Materials & Method: The raw material, solid waste red mud was collected from a leading alumina refining company and washed with distilled water until a neutral pH 7 was obtained. Red mud and its composite with 10 and 20 wt % ZnS (Thomas Baker; 97% purity) were hand grinded with methanol solvent in a pestle-mortar for 30 minutes. The grinded powder was pressed in the shape of 1 inch square pellets and sintered at 800 °C for 2 hours. From the sintered pellets, Hydroelectric cells were fabricated by attaching zinc electrode on one face and conducting silver paste in comb pattern on the other face of the square pellet. Samples were labelled as RM (red mud), RMZ1 (10 wt % ZnS-Red Mud) and RMZ2 (20 wt % ZnS-Red Mud).

3. Characterization: The material properties have been studied using different characterization techniques. The X-ray diffraction spectra has been recorded on Bruker D8 Advance XRD with a 0.154 nm Cu-K α radiation. The morphology of different samples has been studied using SEM images taken on Carl Zeiss Scanning Electron Microscope. The current-voltage characteristics of the fabricated Hydroelectric cells have been recorded using the Keithley 2430 1 kW power source meter. The ionic diffusion of different species and charge transfer phenomenon in the cell was investigated by Electrochemical Impedance spectroscopy using Wayne-Kerr 6500B impedance analyser, in the frequency range 20 Hz to 120 MHz.

4. Results and Discussion:

4.1. X-ray Diffraction (XRD): The crystalline phase and structural parameters of the samples have been determined through XRD measurements. The XRD spectra of RM, RMZ1 and RMZ2 are given in figure 1(a). Most XRD peaks of red mud match well with that of rhombohedral Fe₂O₃ confirmed by the ICDD card number 04-007-9266. A few peaks could also be indexed to ICDD card number 04-009-8445 indicating presence of AlFeO₃ phase [7]. On

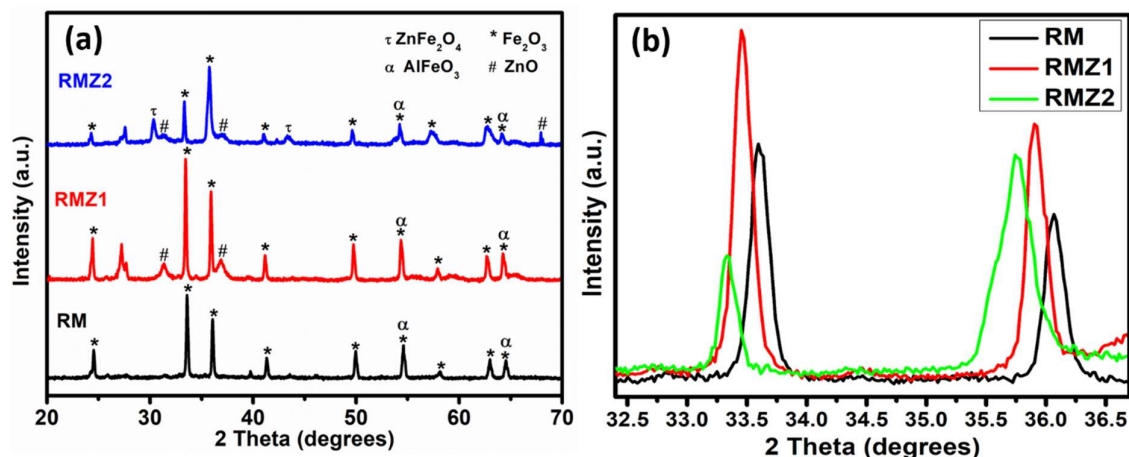


Figure 1. (a) X-ray diffraction pattern of Rm, RMZ1 and RMZ2; (b) Peak shifting in (104) and (110) peaks of RM on doping ZnS.

addition of 10 weight % ZnS in Red mud, two peaks of hexagonal wurtzite ZnO can be observed in the XRD spectra of RMZ1, that has been matched with the JCPDS card number 036-1451 [15]. XRD spectra of RMZ2 shows two additional peaks of zinc ferrite (ZnFe_2O_4) along with that of ZnO. The XRD peaks of ZnFe_2O_4 has been verified with ICDD card number 00-077-0011 [16].

The distortion created in the Red mud lattice structure on addition of ZnS can be seen in peak shifting and broadening in figure 1(b), that shows the peak shifting towards lower 2 theta values. It indicates tensile strain developed in red mud due to stretching of interplanar spacing by ZnO incorporation. Peak widening in case of RMZ2 indicates smaller crystallite size that has been further verified by SEM images.

Addition of ZnS has created defects by reducing Fe_2O_3 in the form of SO_2 gas during sintering. The crystallite size, dislocation density and microstrain has been evaluated using the Debye-Scherrer equation (eqn 1), Williamson-Smallman equation (eqn 2) and Stokes-Wilson equation (eqn 3) respectively [17,18].

$$D = \frac{K\lambda}{\beta \cos \theta} \dots \dots \dots (1)$$

$$\varepsilon = \frac{\beta}{4 \tan \theta} \dots \dots \dots (2)$$

$$\delta = \frac{1}{D^2} \dots \dots \dots (3)$$

Here, D is the crystallite size, K is the Scherrer constant having value 0.9, λ is the wavelength of the Cu-K α radiation (0.15406 nm), β is the full width at half maxima (in radians), θ is the diffraction angle (in radians), ε is the micro strain and δ is the dislocation density. Crystallite size, dislocation density and microstrain of all samples have been listed in table 1. An increase in dislocation density and microstrain in the red mud HEC supports water adsorption and splitting, resulting in enhance current generation.

Table 1: Crystallite size, dislocation density and microstrain of RM, RMZ1 and RMZ2.

| Sample | Crystallite size (nm) | Dislocation density ($\times 10^4$) | Microstrain ($\times 10^4$) |
|--------|-----------------------|---------------------------------------|-------------------------------|
| RM | 41.179 | 5.93 | 2.671 |
| RMZ1 | 40.961 | 6.76 | 2.705 |
| RMZ2 | 33.817 | 13.03 | 3.885 |

Zinc sulfide (ZnS) undergoes oxidation to zinc oxide (ZnO) during the sintering process at temperatures exceeding 500 °C. The resultant ZnO subsequently reacts with ferric oxide (Fe_2O_3), the primary constituent of red mud, to form zinc ferrite (ZnFe_2O_4). Literature suggests that the nucleation and growth of zinc ferrite commence at approximately 700 °C and completes at

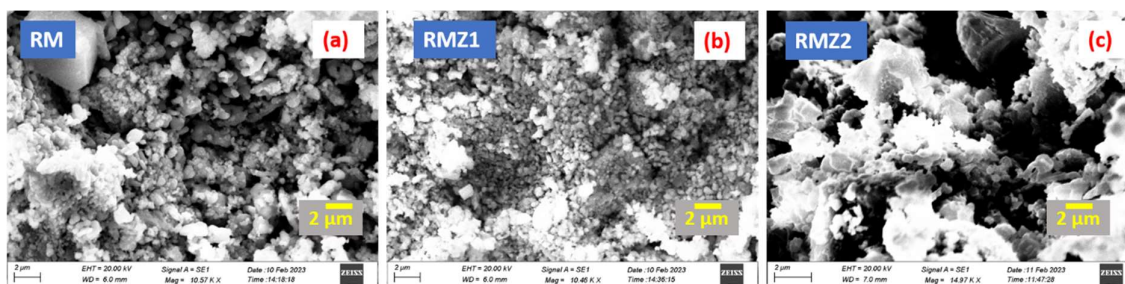


Figure 2. Scanning Electron Microscopy images of (a) RM, (b) RMZ1 and (c) RMZ2.

1300 °C [19]. At a sintering temperature of 800 °C, the initial formation of a disordered zinc ferrite structure is observed. The tendency for zinc ferrite formation is directly correlated with zinc oxide concentration [20]. Consequently, no ZnFe_2O_4 diffraction peaks were detected in the X-ray diffraction (XRD) pattern of RMZ1, while two distinct ZnFe_2O_4 peaks were evident in the XRD pattern of RMZ2 due to an elevated ZnO content arising from higher ZnS content. The disordered zinc ferrite phase along with other oxide components serve as active sites for adsorption and chemidissociation of water by the material, promoting electricity generation in Red mud based Hydroelectric cell.

4.2. Scanning Electron Microscopy (SEM): Scanning electron microscopy has been used to study the particle morphology and pore distribution across the material surface. It can be inferred from the electron micrographs, Figure 2, that all samples consist primarily of nanospheres with a broad particle size distribution. Average particle size has been evaluated using ImageJ software, with RM, RMZ1 and RMZ2 having an average particle size of 0.84, 0.58 and 0.37 μm respectively. Red Mud (figure 2(a)) shows mostly spherical nanoparticles distributed unevenly across the surface. The particle size decreases with increased concentration of ZnS in Red Mud as can be observed in figure 2(b) and (c). Small pores are uniformly distributed throughout the microsphere matrix in RMZ1, whereas RMZ2 shows a highly agglomerated nanoparticle morphology with extensive void spaces. Adding ZnS in RM

led to enhanced porosity and surface area facilitating higher surface water adsorption and splitting hence power generation by RMZ1 Hydroelectric cell.

4.3. Mechanism of Green Electricity generation by Hydroelectric Cell:

Hydroelectric cell working is based on surface defects like unsaturated surface cations and oxygen vacancies to interact with the water molecules at the material surface. The electrostatic interaction between the surface dangling bonds and dipolar water molecule results in heterolytic splitting of water molecule into H^+ and OH^- ions. This forms a monolayer of chemisorbed OH^- ions on the HEC surface, over which multilayers of water molecules are formed through hydrogen bonding. In the physisorbed layers, H^+ ion interacts with other water molecules and migrate via Grotthuss proton hopping mechanism [21]. Since H^+ ion cannot exist alone, it binds with another water molecule to form H_3O^+ i.e. hydronium ion. During chemidissociation and Grotthuss proton hopping, some hydronium ions get trapped in the nanopores in the material. These hydronium ions generate an electric field inside the nanopore which leads to physidissociation, thus continuing the water splitting process at the surface. The hydroxide ions (OH^- ions) migrate towards the anode (zinc electrode) where zinc oxidation releases two electrons, simultaneously forming zinc hydroxide [22]. The electrons move via the external circuit towards the cathode (inert silver electrode) where hydronium ions accept electrons and get reduced to hydrogen gas and water [23]. The electrochemical reactions are summarised in equations 4-6.

At surface: $4 \text{H}_2\text{O} \rightarrow 2 \text{H}_3\text{O}^+ + 2 \text{OH}^-$
------(4)

Anode: $\text{Zn} + 2 \text{OH}^- \rightarrow \text{Zn}(\text{OH})_2 + 2 \text{e}^-$
 $E_{\text{ox}} = 0.76 \text{ V}$ -----(5)

Cathode: $\text{H}_3\text{O}^+ + 2 \text{e}^- \rightarrow \text{H}_2 + \text{H}_2\text{O}$
 $E_{\text{red}} = 0.22 \text{ V}$ -----(6)

The power generated by Red mud and ZnS doped Red mud hydroelectric cells is given in table 2. The cell performance has been further studied by plotting V-I polarization curves of all the samples.

Table 2: Current, voltage and power generated by RM, RMZ1 and RMZ2 HECs.

| Composite | Current (mA) | Voltage (V) | Power (mW) |
|----------------------------|--------------|-------------|------------|
| Red Mud (RM) | 8.7 | 0.96 | 8.35 |
| 10 wt % ZnS-Red Mud (RMZ1) | 13 | 0.98 | 12.74 |
| 20 wt % ZnS-Red Mud (RMZ2) | 10 | 0.92 | 9.2 |

4.4. V-I Polarization Curves: The voltage drop as a function of increasing load has been studied by plotting V-I polarization curves of all samples. The different voltage loss regions observed in the polarization curves, shown in figure 3, provide insights into the operational characteristics of these HEC device. Experimental results indicate an open circuit voltage (V_{oc}) of 0.96 V for RM, 0.98 V for RMZ1 and 0.92 V for RMZ2, given in table 2. The short circuit current of 8.7 mA observed in RM has been increased to 13 mA and 10 mA in ZnS doped RMZ1 and RMZ2 respectively. Analysis of polarization curves reveals three distinct voltage loss regions. The initial region, at low current densities, primarily reflects activation losses. This voltage drop is attributed to the energy required for water splitting and associated electrochemical processes [24]. The region AB marked in figure 3 represents activation losses due to the sluggish charge transfer at the material-electrode surface. Diminished activation loss region has been observed after doping

ZnS in Red mud. Enhanced surface defects

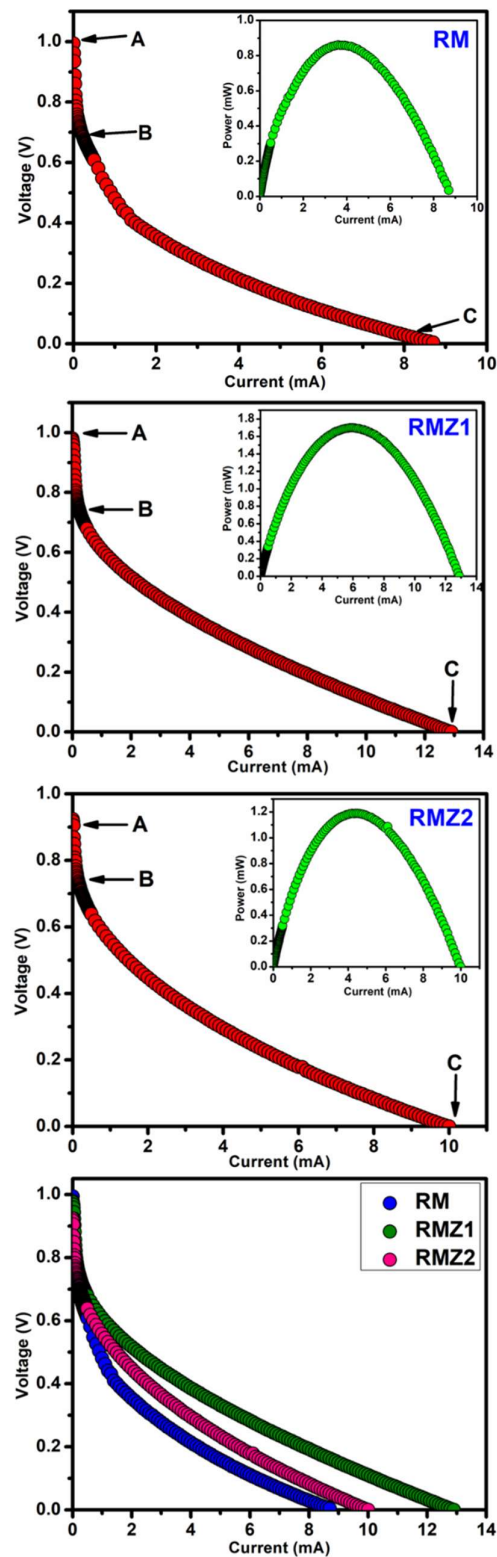


Figure 3. V-I polarization curves of RM, RMZ1 and RMZ2. Last figure presents a comparison of voltage and current relationship in all the samples

and porosity accelerates water chemidissociation at the HEC surface providing large number of ions at the electrode.

The intermediate region BC, exhibits Ohmic losses due to the material's internal resistance faced by the migrating hydronium and hydroxide ions inside the porous structure. At high current densities, concentration losses dominate as ion accumulation on electrode surfaces becomes significant, which is not observed in our case. This might be due to the rapid consumption of ions in the electrochemical reaction at the two active electrodes [12].

The comparative V-I polarization plot of the three samples shows the least voltage losses and hence maximum power generation capacity of RMZ1 Hydroelectric cell.

4.5. Electrochemical Impedance Spectroscopy (EIS): Water splitting as well as the electrochemical reactions occurring in the Hydroelectric cell are limited by the ion movement at and across the material surface. To study the kinetics of charge transfer at electrode-material interface as well as the ionic diffusion inside the bulk material, electrochemical impedance spectroscopy has been carried out.

Nyquist plots of the three wet red mud-ZnS HECs are given in figure 4. Red mud Nyquist plot exhibits a distinct semicircle at high frequency region and a larger incomplete semicircle at lower frequencies. The high-frequency semicircle corresponds to the material's bulk resistance due to grain boundaries and second semicircle is due to impedance faced by the charge transfer reaction at the material-electrode interface [25]. In addition to the semicircle, a slanting tail is also visible in the Nyquist plots of ZnS doped red mud, that represents Warburg impedance region. This low-frequency Warburg impedance is indicative of mass transfer limitations due to hindered ionic diffusion within the material near the electrode surface [26].

In order to determine the individual resistive and capacitive contribution of various species, Nyquist plots have been fitted using EIS Spectrum software. Equivalent circuits models employed in fitting have been depicted in figure 4. The fitting parameters of various circuit elements are given in table 3. Different contributions to impedance spectrum includes, the bulk resistance (R_1), grain boundary resistance (R_2), charge transfer resistance (R_3) and Warburg diffusion (W). The deviation from an ideal capacitive behaviour has been modelled using constant phase elements (P_1, n_1, P_2, n_2) [27].

Doping ZnS into red mud resulted in a decrease in all resistance values, suggesting accelerated ion transport kinetics. The enhanced water adsorption and dissociation capacities of RMZ1 and RMZ2 can be attributed to their smaller particle size, larger surface area, and increased porosity. The lattice defects introduced by ZnS doping facilitates rapid chemisorption and unimpeded charge transfer. The distorted lattice structures of RMZ1 and RMZ2 promotes the diffusion of H_3O^+ and OH^- through the pellet. All these factors collectively contribute in greater power generation capacity of ZnS doped Red mud Hydroelectric cells.

Table 2: Equivalent Circuit fitting parameters for RM, RMZ1 and RMZ2 HECs Nyquist plots.

| | RM | RMZ1 | RMZ2 |
|----------------------|-----------------------|--------------------|-----------------------|
| R₁ | 24.53 | 11.84 | 16.09 |
| R₂ | 6.53 | 2.92 | 12.00 |
| R₃ | 80.78 | 4.48 | 5.04 |
| W | - | 91.68 | 55.00 |
| P₁ | 0.03×10^{-4} | 5×10^{-4} | 39.5×10^{-4} |
| n₁ | 0.64 | 0.54 | 0.53 |
| P₂ | 0.00843 | 0.000475 | 0.000569 |
| n₂ | 0.27 | 0.79 | 0.43 |

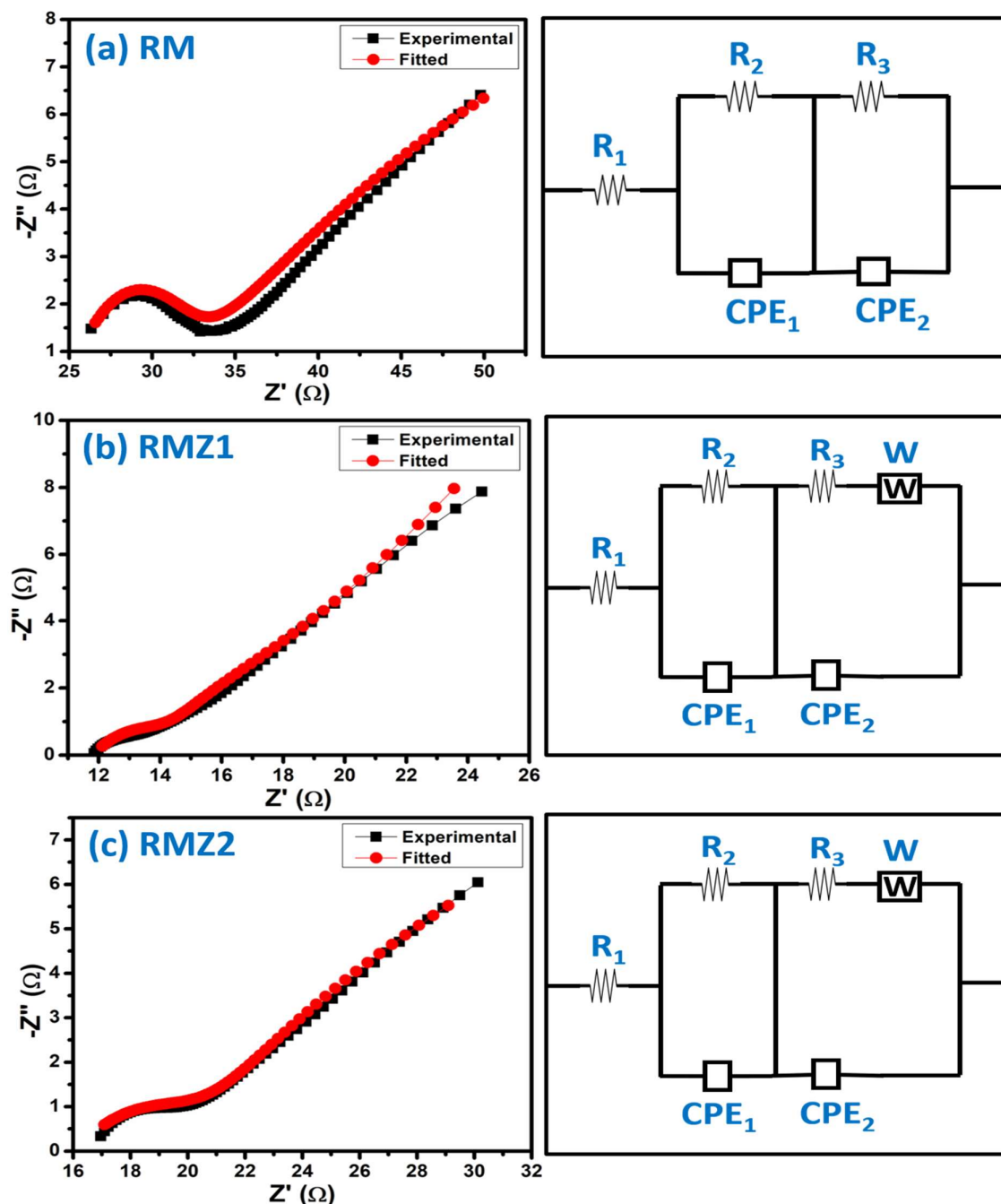


Figure 4. Nyquist plots and corresponding electrical circuit of (a) RM, (b) RMZ1 and (c) RMZ2.

5. Conclusions: In the present study red mud, a toxic industrial waste product, has been transformed into Hydroelectric cell that generates green electricity by water splitting. The red mud Hydroelectric cell's performance has been enhanced by doping zinc sulfide (ZnS) at 10 wt% and 20 wt% concentrations in red mud. XRD analysis revealed significant structural changes in red

mud after ZnS doping, including lattice distortions and microstrain arising due to the formation of ZnO and zinc ferrite phases. SEM analysis depicts a reduction in particle size from 0.84 μm in pure red mud (RM) to 0.37 μm in the 20% ZnS-doped sample (RMZ2), along with increased porosity. Activation and Ohmic losses are substantially reduced in RMZ1 and RMZ2

as evidenced by the V-I polarization curves indicating more efficient water splitting and ion transport. The 10 wt% ZnS-doped sample (RMZ1) achieved the highest power output of 12.74 mW, compared to 9.2 mW for RMZ2 and 8.35 mW for pure red mud (RM). EIS spectroscopy results validate the enhanced ionic conductivity and reduced resistance in ZnS doped red mud samples, which is attributed to their smaller particle size, larger surface area, and increased porosity. Hence, the present study shows that the hazardous red mud waste can be effectively translated into a valuable material for clean energy production in the form of Hydroelectric cell. The strategic incorporation of ZnS successfully enhanced the water-splitting capabilities through increased surface defects and porosity. This approach not only addresses the environmental concerns associated with red mud disposal but also presents a sustainable pathway for its utilization in green energy generation.

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Trial of Pilot Scale Nanofiltration Unit for Improvement of Precipitation Circuit at Tummalapalle Mill

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Volume 2, Issue 1, February 2025

Received: 28 January, 2025; Accepted: 25 February, 2025

DOI: <https://doi.org/10.63015/7n-2453.2.1>

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Abstract: Alkaline pressure leaching is used in the Tummalapalle Uranium Ore processing plant due to the ore's high carbonate content (85%). About 70% of the uranium-laden liquor from the leached slurry filter is recycled to repulp the pre-leach filter cake, increasing the mother liquor concentration. This creates a large inventory of concentrated slurry, affecting precipitation efficiency and settling characteristics. Higher mother liquor concentration may improve settling after precipitation. A laboratory nanofiltration unit at UCIL Tummalapalle was tested to enhance clarified mother liquor concentration. Preliminary experiments showed reproducible results, suggesting an increase in uranium concentration from 0.5 gpl to 0.9 gpl. This process reduces leach liquor recycling, improves wash liquor flexibility, and operates with lower leach liquor values. This paper presents pilot-scale nanofiltration trials at Tummalapalle Mill, which could enhance U_3O_8 recovery. Further study is needed to assess water balance for full-scale implementation.

Keywords: Uranium; Tummalapalle Mill; Nano Filtration Skid; Ultra Filtration; Precipitation; Alkali Leaching.

Nomenclature:

| | |
|------|---|
| AERB | Atomic Energy Regulatory Board |
| CNSC | Canadian Nuclear Safety Commission |
| CPL | Clarified Pregnant Liquor |
| ED | Electrodialysis |
| EPA | Environmental Protection Agency |
| EU | European Union |
| HP | High Pressure |
| IAEA | International Atomic Energy Agency |
| LP | Low Pressure |
| LPD | Liters per Day |
| NF | Nanofiltration |
| NRC | Nuclear Regulatory Commission |
| NTU | Number of Transfer Units |
| OSHA | Occupational Safety and Health Administration |
| REEs | Rare Earth Elements |

| | |
|------|--------------------------------------|
| RO | Reverse Osmosis |
| SDI | Silt Density Index |
| SDU | Sodium Diuranate |
| SS | Stainless Steel |
| TDS | Total Dissolved Solids |
| TSS | Total Suspended Solid |
| UCIL | Uranium Corporation of India Limited |
| UF | Ultrafiltration |

1. Introduction and Literature Survey:

Inorganic membranes have been explored extensively for their potential to reject uranium from both fresh and saline waters (Lin et al., 2019a). The feasibility of using nanofiltration (NF) to remove uranium from groundwater under environmentally relevant conditions has been evaluated, highlighting its effectiveness in contaminated environments (Verma & Loganathan, 2024). Scaling up NF processes through pilot trials has been

proposed as a critical step towards wider industrial adoption (Guerra et al., 2023). From an economic perspective, electrodialysis (ED) emerges as a more cost-effective solution due to its lower energy requirements and high membrane durability, which minimizes replacement expenses (Guerra et al., 2024). Existing active mine water treatment technologies have been comprehensively reviewed, offering valuable insights into current practices (Wolkersdorfer, 2022). Furthermore, there is a growing trend among mining companies to adopt technologies to reuse water within internal circuits (Witecki et al., 2022). The potential recovery of rare earth elements (REEs) from acid mine drainage has also been investigated, with advancements in precipitation strategies yielding an 8% improvement in REE recovery and a 2.8-fold increase in purity (Mwewa et al., 2022); (Liu et al., 2024). A review by (Yadav et al., 2022a) discusses prospects in this domain, emphasizing ongoing innovations. In the fabrication of nanofiltration membranes, techniques such as phase inversion and interfacial polymerization have been utilized to enhance performance (Mahmoud & Mostafa, 2023). For uranium and thorium separation, chitosan–polypropylene membranes (C–PHF–M) have demonstrated precise selectivity, with thorium dioxide retained almost entirely. At the same time, aluminum is recovered as sodium aluminate during filtration (Man et al., 2024). The behavior of extractable alkali metal complexes with specific ligand mixtures has also been characterized (Bezdomnikov et al., 2024). While some promising approaches have been proposed, further validation at industrial scales remains necessary (Pola et al., 2022). Membrane technologies are being increasingly studied for lithium recovery, with lithium phosphate precipitation yielding an impressive 84% recovery from salt solutions containing around 200 ppm lithium (Annunzi et al., 2023). Finally,

uranium removal using NF membranes has achieved remarkable performance, with a rejection rate of 99.83% and a permeate flux of 71.1 L/(m²·h) (Meng et al., 2023). The economic and operational trade-offs between nanofiltration (NF) and electrodialysis (ED) in uranium extraction from alkaline leach liquor primarily stem from differences in energy consumption, selectivity, scalability, and cost-effectiveness. Both technologies are used to concentrate and separate valuable elements such as uranium from leachate, but they operate on different principles and have varying impacts on industry operations. Below is an in-depth comparison:

1. Principle of Operation: The nanofiltration (NF) membrane filtration process works by using semi-permeable membranes to separate ions, molecules, and particles based on their size and charge. In uranium extraction, NF is typically employed to separate uranium and other monovalent ions from the alkaline leach liquor. Electrodialysis (ED) is an electrochemical process, that uses an electric field to drive the migration of ions through selective ion exchange membranes. In ED, uranium and other ions are separated based on their charge, with cations (positively charged ions) moving through cation-exchange membranes and anions (negatively charged ions) passing through anion-exchange membranes.

2. Energy Consumption: Energy consumption in NF primarily depends on the transmembrane pressure required to push the liquid through the membrane. The pressure can be significant but is often lower than electrodialysis. For uranium extraction, NF tends to have moderate energy requirements, especially when compared to ED. Electrodialysis, on the other hand, typically consumes more energy due to the need for an electric current to drive ion migration. The energy requirement is proportional to the ion concentration and the number of ion-exchange membranes used. While ED can

be highly efficient for specific ion separations, it generally has a higher operational energy cost compared to NF. From an energy perspective, NF tends to be more cost-effective due to lower energy consumption, especially for large-scale operations where energy costs are significant.

3. Selective Separation: NF membranes can be designed to selectively separate uranium and other ions based on their size and charge. However, NF membranes may have lower selectivity compared to ED, as they might not effectively differentiate between ions with similar charge or size. Electrodialysis has high selectivity, especially for ions with distinct charges. ED membranes can selectively separate cations like uranium ions from the solution. This is particularly useful for industries where purity or specific separation of ions is important. If high purity of uranium or specific ion separation is critical, ED might be the better choice despite higher energy costs. However, for more general applications where perfect selectivity is not as crucial, NF can be more cost-effective.

4. Scalability and Flexibility: Nanofiltration systems are generally more scalable, easier to operate, and more flexible for handling large volumes of alkaline leach liquor. They can be operated continuously, and membrane fouling (a major issue in many filtration processes) can be mitigated with regular cleaning procedures. While ED systems can also be scaled, they tend to be more complex to operate and maintain. The ion-exchange membranes in ED can be susceptible to scaling and fouling, requiring more frequent maintenance and specialized cleaning, which can lead to higher operational downtime and costs. NF is often more attractive for large-scale operations due to its ease of scaling and lower maintenance needs, making it a more stable option in terms of long-term costs.

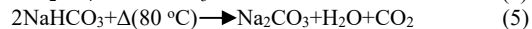
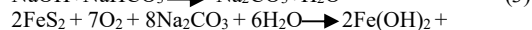
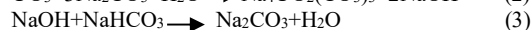
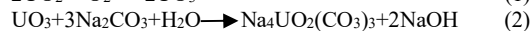
5. Capital and Operational Costs: The capital investment for NF is typically lower than for electrodialysis, especially in terms of membrane costs and system complexity. Operating costs are lower due to lower energy usage and reduced maintenance requirements. The capital investment for ED systems can be higher due to the need for multiple ion exchange membranes, electrodes, and power supplies. Moreover, operating costs can be higher because of the greater energy consumption and more frequent maintenance due to membrane fouling. NF usually has a lower upfront capital cost and lower ongoing operational costs compared to ED, making it more economically viable for many industries that need to extract uranium in bulk or where cost efficiency is a priority.

6. Environmental Impact and Waste Management: NF systems produce a concentrate that contains the uranium and other solutes. Proper disposal or further treatment of this concentrate is necessary to prevent environmental contamination. However, the system itself has a smaller environmental footprint due to its lower energy consumption. Electrodialysis systems generate waste in the form of brines or concentrated waste streams. This requires effective waste management practices to ensure minimal environmental impact. The higher energy use can also result in a larger carbon footprint, especially if the energy is sourced from non-renewable sources. Environmental considerations and waste disposal costs are factors that can affect the overall economics of the operation. NF may have the edge in terms of lower energy consumption, but both processes need to manage waste effectively.

7. Product Recovery and Purity: While NF is effective at concentrating uranium, the purity of the recovered uranium can sometimes be lower compared to ED, as some unwanted ions may coalesce with the uranium in the permeate. Electrodialysis offers the potential for higher-purity

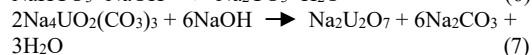
uranium recovery due to its more selective ion separation capabilities, ensuring that the final product is enriched to the desired level. Industries that prioritize the high purity of uranium may find ED to be more economically advantageous in the long term, despite its higher operational costs. NF is likely to be more economically favorable for large-scale uranium extraction, especially when the operation focuses on minimizing energy costs, simplifying maintenance, and maintaining operational flexibility. Its lower capital and operational expenses make it an attractive option for cost-conscious industries. ED may be more appropriate when very high selectivity, purity, and effective ion separation are necessary, despite its higher initial investment, energy consumption, and maintenance needs. In summary, the choice between NF and ED depends on the specific requirements of the uranium extraction process, including factors such as desired product purity, scalability, energy costs, and long-term operational feasibility. For most industries, NF tends to offer better economic efficiency, while ED excels in processes where purity and ion selectivity are critical.

1.1 Alkali leaching process & chemical reactions: Sodium bicarbonate generation takes place as per exothermic reactions (1,2,3,4) inside a pressurized autoclave which helps in the completion of chemical reactions in the presence of oxygen (S. T. , S. V. K. Reddy B.N.K., 2024). For autoclave operations, low concentration NaHCO_3 is sufficient, and it benefits product precipitation.



Filtration of autoclave discharge slurry takes place after alkali leaching for solid-liquid separation. Filtrate goes to the clarification unit for removal of remaining

TSS (Thamida S.K., 2023). In the precipitation stage, bicarbonate is first neutralized with caustic soda (reaction 6). Precipitation of clarified liquor takes place for precipitating sodium diuranate in the presence of 48% conc. NaOH (reaction 7) (Rajesh L., 2018).



1.2 R&D activities at Tummalapalle Mill: Tummalapalle project processes low-grade uranium ore. Although it is one of the largest ore reserves, still it is the main challenge for the R&D team to improve concentration using various existing technologies (Sharma V. K., 2023). A team of engineers conducted several experiments for the enhancement of U_3O_8 concentrations which are as follows:

1. Candle Filtration
2. Centrifugation
3. Ultra Filtration
4. Re-Dissolution
5. Ion Exchange
6. Nano Filtration

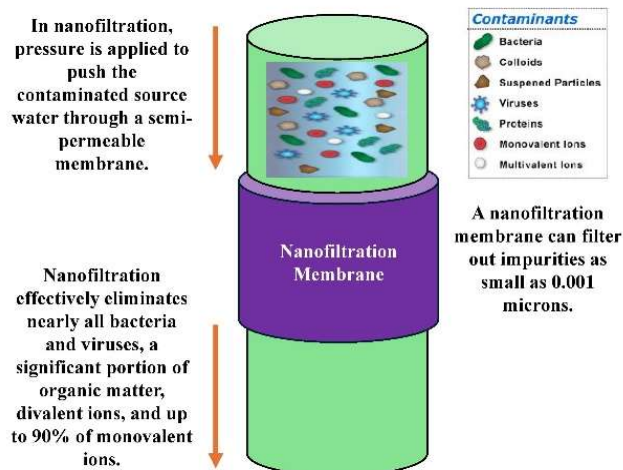


Figure 1. Working function of nanofiltration membrane

1.3 Membrane Separation: Membrane separation processes operate without heating and therefore use less energy than conventional thermal separation processes

such as distillation, sublimation, or crystallization (Rani N., 2009). The separation process is purely physical, and both fractions (permeate and retentate) can be used. Cold separation using membrane technology is widely used in food technology, biotechnology, and pharmaceutical industries (Tiwari R., 2008). Furthermore, using membranes enables separations to take place that would be impossible using thermal separation methods. The challenges for the membrane system for such applications are as under (Rajesh L., 2019):

3.1 The membrane system does not handle high salt concentration due to osmotic pressure limitation.

3.2 Membrane systems need highly clarified liquor with a very low NTU/SDI index.

3.3 High temperature is not conducive to membrane life.

1.4 SaltOut Technology: It was noticed that the membrane process can help in achieving the desired concentration of product starting from low concentrations (Sharma V.K., 2008b). Membranes can also assist in the separation of salt, purification of process stream, and recycling of liquor. A comprehensive study of the current process was made to apply technology at other points (A. Ghaddar, 2008). A new process scheme with SaltOut Technology which may avoid the recycling of liquors to achieve high concentration in CPL and facilitate recycling of salts into the process was used in Tummalapalle Mill (Sharma V.K., 2008a).

1.5 Objectives of nanofiltration at Tummalapalle Mill: The main objectives of nanofiltration at Tummalapalle Mill are as follows (Sharma V.K., 2022):

1. The recycling loop can be avoided.
2. Increase in concentration of process liquor.
3. U_3O_8 Recovery Enhancement.
4. Improved floc generation inside product thickener.

5. Improved settling characteristics at product thickener.

6. Control on TSS present in process liquor.



Figure 2. (a) Top view of nanofiltration membrane used for the trial, (b) Side view of nanofiltration membrane used for the trial.

1.6 Technical Justification of Nanofiltration Selection: The selection of nanofiltration (NF) over other membrane technologies like reverse osmosis (RO) and ultrafiltration (UF) for uranium extraction from alkaline leached liquor is based on several factors related to the specific properties of these membranes, their performance in processing uranium-laden streams, and the operational requirements of the extraction process. Below is a detailed discussion covering the technical, economic, and operational considerations in selecting nanofiltration for uranium extraction:

1. Membrane Characteristics

a. Nanofiltration (NF)

- **Pore Size:** Nanofiltration membranes have pore sizes in the range of 1-10 nanometers. This size allows NF membranes to selectively reject divalent ions (such as uranium) while allowing monovalent ions (e.g., sodium and potassium) to pass through. This is a key feature for uranium extraction from alkaline-leached liquors.
- **Ion Selectivity:** NF membranes exhibit selective permeability to ions based on their charge and size. Uranium ions, which are typically in their divalent form (UO_2^{2+} or $UO_2(OH)_2$), are effectively rejected by NF membranes, making them ideal for concentrating uranium while allowing the passage of less valuable ions.

- **Pressure Requirement:** NF membranes typically operate at lower pressures than reverse osmosis membranes, making them more energy-efficient in certain applications.

b. Reverse Osmosis (RO)

- **Pore Size:** RO membranes have a much smaller pore size (typically around 0.0001 microns) compared to NF. While they are highly effective at removing almost all ions, including both monovalent and divalent ions, the rejection of monovalent ions (like sodium) is not desirable in some cases.
- **Energy Requirement:** RO membranes require high pressure (up to 60-80 bar) to overcome osmotic pressure and achieve effective separation. The high energy demand makes RO less economical for certain applications like uranium extraction, where the goal is the selective removal of divalent ions.
- **Water Recovery:** RO typically operates with a lower water recovery rate than NF membranes. Since uranium extraction often involves the handling of large volumes of solution, lower water recovery can lead to significant waste generation.

c. Ultrafiltration (UF)

- **Pore Size:** UF membranes have larger pores (typically in the range of 10-100 nanometers), making them suitable for separating larger particles, such as suspended solids, colloids, and larger molecules. However, UF is not selective enough to remove dissolved ions like uranium, especially in its divalent form.
- **Limited Ion Rejection:** UF does not effectively reject dissolved species like uranium ions, which makes it unsuitable for uranium extraction in leached liquor where divalent metal ions need to be separated from the solution.

2. Uranium Extraction Process

- **Alkaline Leaching of Uranium:** In uranium extraction, the ore is treated with an alkaline solution (such as sodium carbonate or sodium hydroxide) to leach uranium into solution as soluble complexes. This results in a liquor

containing uranium in the form of uranyl ions (UO_2^{2+}) and other alkali metal ions like sodium or potassium.

- **Selective Removal of Uranium:** The goal of using a membrane process is to selectively remove or concentrate uranium from the leachate while allowing other components to pass through. Since uranium in leach liquor exists predominantly as divalent uranyl ions, a membrane that is selective for divalent ions but passes monovalent ions (e.g., sodium) would be ideal.

3. Performance Considerations

a. Ion Rejection

- **Nanofiltration:** NF membranes provide selective rejection of divalent ions like uranium while allowing monovalent ions such as sodium to pass. This selective rejection ensures that uranium can be concentrated without excessive removal of beneficial monovalent salts, which is crucial for maintaining the chemical balance in the leach liquor.
- **Reverse Osmosis:** RO membranes would reject almost all ions, including the monovalent ones, which would result in a very concentrated stream of uranium but also waste a significant amount of the alkali salts (such as sodium) that are essential for the leaching process. The rejection of monovalent ions could also result in operational challenges, such as scaling and fouling.
- **Ultrafiltration:** UF does not effectively reject dissolved ions such as uranium. It is primarily used for separating larger particles and suspended solids, making it unsuitable for applications requiring the removal of dissolved metal ions.

b. Operational Efficiency

- **Energy Consumption:** NF membranes operate at much lower pressures (typically 5-20 bar) compared to RO membranes, making them significantly more energy-efficient for processes like uranium extraction from leachate. The reduced energy demand is especially important in large-scale industrial applications, where

energy costs can significantly impact the overall economy.

- **Water Recovery:** NF systems tend to have higher water recovery rates compared to RO systems, meaning they produce more permeate (clean water) relative to waste (concentrated uranium solution). This higher recovery is beneficial in reducing water consumption and minimizing waste generation.

c. Membrane Fouling

- **Nanofiltration:** While NF membranes are generally less prone to fouling than RO membranes due to their larger pore size, fouling can still occur due to the presence of organics, suspended solids, or high concentrations of certain salts in the leachate. However, the fouling tendency is typically lower for NF than for RO, and periodic cleaning can restore membrane performance.
- **Reverse Osmosis:** RO membranes are more prone to fouling, especially in complex solutions like alkaline leachate that may contain organic matter, salts, and other impurities. The need for frequent cleaning and replacement of RO membranes can increase operational costs.
- **Ultrafiltration:** UF membranes may suffer from fouling due to the accumulation of colloidal particles or other macromolecules. However, since they do not offer significant ion separation, they are not suitable for uranium extraction where ion selectivity is crucial.

4. Economic Considerations

- **Capital and Operational Costs:** The capital cost for NF systems is generally lower than for RO systems due to the lower pressure requirements and less complex infrastructure. Additionally, the operational costs for NF systems tend to be lower due to the reduced energy consumption, which is a critical consideration for large-scale uranium extraction.

- **Membrane Lifespan and Maintenance:** NF membranes, while still requiring maintenance, tend to have a longer lifespan than RO membranes because they are exposed to lower operating pressures. This results in reduced frequency of replacement and lower maintenance costs in the long run.
- **Waste Generation:** RO systems tend to produce a high volume of brine or concentrated waste, which can be difficult to dispose of, particularly in regions with strict environmental regulations. NF membranes produce less waste, making them a more environmentally friendly option.

5. Suitability for Uranium Extraction

Nanofiltration is particularly well-suited for uranium extraction from alkaline leached liquors due to:

- Its ability to selectively reject divalent uranium ions while allowing essential monovalent ions (like sodium and potassium) to pass through.
- It lowers energy requirements compared to reverse osmosis.
- Higher water recovery and lower brine production, which reduces waste handling.
- Its economic advantages, including lower capital and operational costs, especially in large-scale operations.
- Its relative resistance to fouling compared to RO membranes, reduces maintenance costs.

In conclusion, nanofiltration (NF) is an ideal membrane technology for uranium extraction from alkaline leached liquor due to its selective rejection of uranium while permitting the passage of monovalent ions. NF membranes operate at lower pressures, consume less energy, and offer higher water recovery rates compared to reverse osmosis, making them more cost-effective for large-scale operations. Furthermore, NF systems generate less waste and are less prone to fouling, ensuring a more efficient and sustainable process. On the other hand, reverse osmosis is energy-intensive and rejects both monovalent and divalent ions,

which can disrupt the chemical balance in the leachate, while ultrafiltration is not effective for ion separation. Therefore, nanofiltration stands out as the most suitable membrane technology for uranium extraction in this context.

2. Material & Methods: Three SS316 tanks of capacity 1000 liters and one tank of capacity 200 liters are present in the nanofiltration skid (fig. 3). Tank 1 filled with clarified pregnant liquor (CPL) received after filtration of leached liquor received from autoclaves. Ultra filtration takes place initially inside tank 1 with the help of a ceramic filtration unit (Lin et al., 2019b). This ultra-filtration helps with the removal of foreign objects that may be present in CPL. It decreases the load on the main nanofiltration membrane (Sharma V.K., 2020). This ultra-filtered liquor goes to tank 2. Liquor of tank 2 is used as feed for the main nanofiltration skid. All pumping operation takes place by HP pump which may operate at a maximum 8 m³/hr flow and 60 bar pressure (Sharma et al., 2024). Initially, the LP pump starts manually which is designed for a maximum 8 m³/hr flow and 2 bar pressure. The air may be released by opening drain valves at the suction and discharge side (K. T. S. , S. V. K. Reddy B.N.K., 2022). LP pump requires proper suction to the HP pump to avoid starvation/liquid hammering. The HP pump starts after starting the LP pump (Sharma et al., 2023). Feed from tank 2 passes through the nanofiltration membrane and the concentrate goes to tank 3 after filtration. Permeate goes to tank 4 after nanofiltration. This cycle continues until the HP pump automatically stops when tank 3 reaches its maximum capacity of 200 liters. The heat exchanger is available in a skid for heating/cooling of process liquor based on requirements (fig. 3). Approximately 4 hours take the completion of one complete cycle (Sriharsha P., 2023). A sampling of feed, concentration, and permeate for 21 cycles was completely taken, and concentrations of sodium carbonate, sodium bicarbonate, and

uranium oxide were analyzed in the CR&D lab (table 1,2&3).

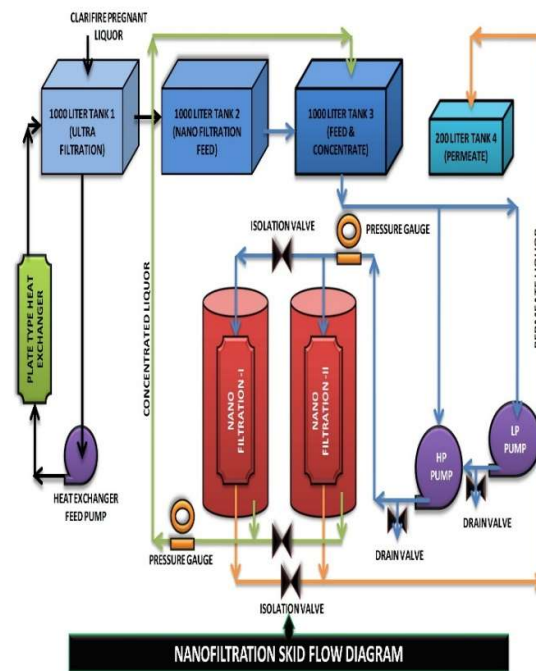


Figure 3. Flow diagram of nanofiltration skid.

Table 1. Design parameters of nanofiltration skid

| Parameter | Input | Output | Side Stream |
|---------------------------------|-------------|----------|---------------|
| Flow | >100 gpd | >100 LPD | Corresponding |
| Product | 0.1-0.3 gpl | 4 gpl+ | <0.1 gpl |
| TSS | 2-10 ppm | NA | <10 ppm |
| Na ₂ CO ₃ | 5-10 gpl | <1 | <1 |
| NaHCO ₃ | 10-20 gpl | <2 | >20-40 gpl |
| Na ₂ SO ₄ | 30-40 gpl | NA | NA |
| pH | 8-10 | 8-10 | 8-10 |
| Temperature | 25-60 °C | 25-60 °C | 25-60 °C |

3. Results & Discussions:

3.1 Operating parameters of nanofiltration skid:

The control panel board displayed various parameters (Rajesh N.V., 2023). Below mentioned parameters were noted down in various time intervals (table 1). The average pH of the liquor was observed at 9.5

Table 2. Process Parameters of Nanofiltration Skid Trial

| Sl. No. | Process Parameters | Unit | 11:00 am | 11:30 am | 12:00 pm | 12:30 pm | Avg. Value |
|---------|--------------------------------|---------|----------|----------|----------|----------|------------|
| 1 | Feed/Concentrate Tank-3 Volume | liter | 581 | 475 | 419 | 350 | - |
| 2 | Nanofiltration Pressure | bar | 7.5 | 7.6 | 7.6 | 7.6 | 7.6 |
| 3 | Permeate Flow | lit/min | 1.59 | 1.60 | 1.58 | 1.58 | 1.59 |
| 4 | Feed/Concentrate Tank-3 Temp. | °C | 37 | 37 | 38 | 39 | 38 |
| 5 | Permeate Tank-4 Temp. | °C | 27 | 28 | 28 | 28 | 28 |

3.2 Nanofiltration skid trial results:

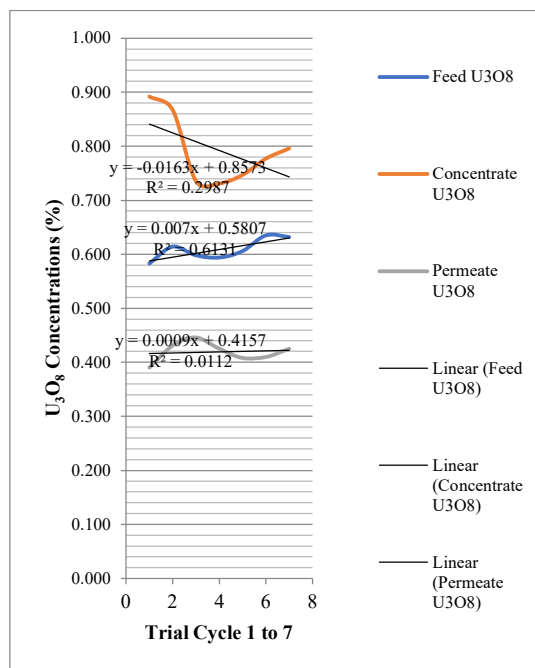
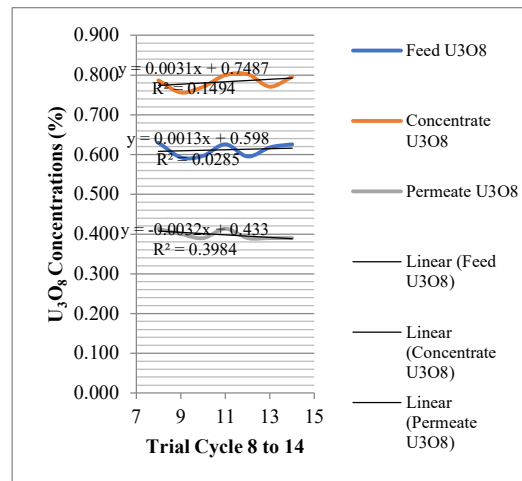
Sodium carbonate and sodium bicarbonate are the main reagents used for alkali pressurized leaching-based Tummlapalle uranium processing plants. U_3O_8 is the main content of the Tummalapalle Mill product (sodium diuranate). The concentration of these parameters was analyzed for various trials of nanofiltration skid (table 2,3&4). Figures 4,5&6 represent the compositions for various trials (Sarkar Suman, 2022). Initial values of U_3O_8 were in the range of 0.5 to 0.6 gpl in feed (Rao M.S., 2019b). After several trials, it rose to 0.8 to 0.9 gpl in concentrate. It is satisfactory results on the initial level. However, it was observed that the concentration of U_3O_8 in permeate was not as desired. It creates further selectivity scope of the nanofiltration membrane (Sreenivas T., 2010).

Table 3. Chemical compositions of Trial – I

| Contents | Unit | Feed | Concentrate | Permeate |
|------------|------|--------|-------------|----------|
| Na_2CO_3 | gpl | 4.810 | 8.020 | 6.420 |
| $NaHCO_3$ | gpl | 15.260 | 13.980 | 13.980 |
| U_3O_8 | gpl | 0.583 | 0.892 | 0.390 |

Table 4. Chemical Compositions of Trial - II

| Contents | Unit | Feed | Concentrate | Permeate |
|------------|------|--------|-------------|----------|
| Na_2CO_3 | gpl | 6.420 | 4.810 | 6.420 |
| $NaHCO_3$ | gpl | 15.260 | 15.260 | 15.260 |
| U_3O_8 | gpl | 0.614 | 0.867 | 0.431 |

**Figure 4:** U_3O_8 analysis graph for samples of feed, concentrate, and permeate received from nanofiltration pilot scale trial cycles no. 1 to 7**Figure 5:** U_3O_8 analysis graph for samples of feed, concentrate and permeate received from nanofiltration pilot scale trial cycles no. 8 to 14

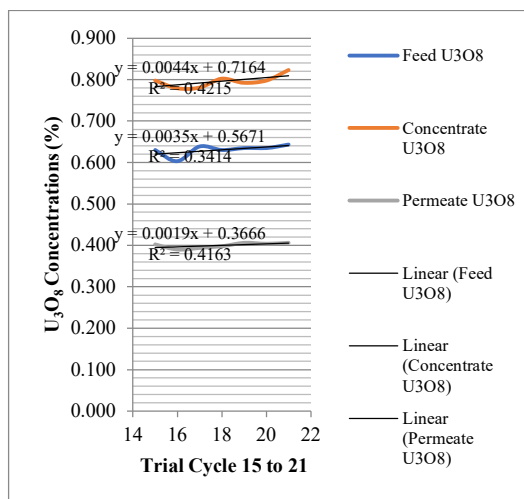


Figure 6. U_3O_8 analysis graph for samples of feed, concentrate and permeate received from nanofiltration pilot scale trial cycles no. 15 to 21

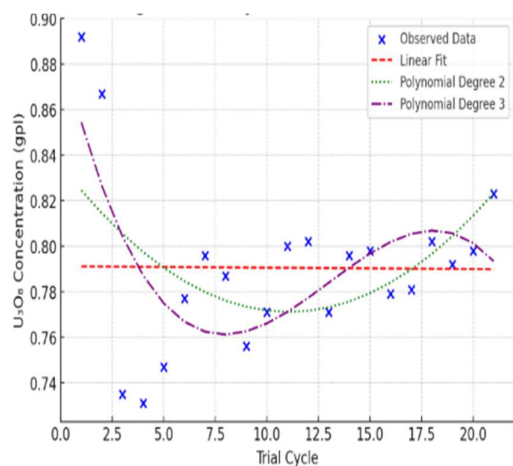


Figure 6. Regression analysis of U_3O_8 concentrations

3.3 Validation of U_3O_8 Concentration

Increase: The study originally claimed that U_3O_8 concentration varied from 0.5-0.6 gpl in the feed and 0.8-0.9 gpl in the concentrate. To statistically validate this claim, a paired t-test was conducted to compare feed and concentrate U_3O_8 concentrations across multiple trials. The results showed a t-statistic of -19.59 and a p-value of 1.61×10^{-14} , which is well below the 0.05 threshold, indicating that the increase in U_3O_8 concentration is statistically significant. These findings support the conclusion

that the nanofiltration process enhances uranium concentration.

3.4 Reproducibility and Standard Deviation Analysis:

To assess the reproducibility of the results, the standard deviation of U_3O_8 concentration in the concentrate was calculated across multiple trials. The mean U_3O_8 concentration in the concentrate was found to be 0.791 gpl, with a standard deviation of 0.038 gpl. This relatively low standard deviation suggests a consistent increase in concentration across trials, confirming the reliability of the process.

3.5 Regression Analysis and Data Representation:

Regression modeling was performed to evaluate the trends in U_3O_8 concentration changes. The results of different regression techniques are as follows:

- **Linear Regression:** $R^2 = 0.0001$, indicating a very poor fit with no clear trend.
- **Polynomial Regression (Degree 2):** $R^2 = 0.219$, showing weak correlation.
- **Polynomial Regression (Degree 3):** $R^2 = 0.385$, providing a slightly better fit but still indicating significant variability. Given these results, the low R^2 values suggest that additional factors may be influencing U_3O_8 concentration trends, raising concerns about data reliability. Further investigation into operational conditions (e.g., temperature, pressure fluctuations) is recommended to improve predictive modeling.

4. Conclusions:

4.1 Process modification scope after nanofiltration installation:

The nanofiltration skid trial demonstrated its potential for enhancing the separation efficiency in uranium processing at the Tummalapalle plant. The average operational parameters, including pH, temperature, and pressure, remained

stable across multiple trials, ensuring consistent process conditions. Key findings include the increased concentration of U_3O_8 in the concentrate from 0.5–0.6 gpl to 0.8–0.9 gpl, marking a significant improvement at the initial stages of implementation (Yadav et al., 2022b). The results revealed that while the permeate U_3O_8 concentration did not meet the desired specifications, the findings provide valuable insights for optimizing the nanofiltration membrane's selectivity. Additionally, the chemical composition analyses indicated that sodium carbonate and sodium bicarbonate concentrations varied across the feed, concentrate, and permeate streams, which could influence overall separation efficiency (Mahmoud & Mostafa, 2023b). This study highlights the efficacy of nanofiltration technology in improving uranium recovery while emphasizing the need for further refinement of membrane properties to achieve better selectivity. Future work should focus on membrane customization and parameter optimization to address the observed challenges, paving the way for more efficient and sustainable operations in uranium processing plants. Redissolution of SDU cake in liquor takes place before precipitation of process liquor (Rao M.S., 2019a). The nanofiltration unit may be installed after clarification. It may help in increasing liquor concentration and finally effective

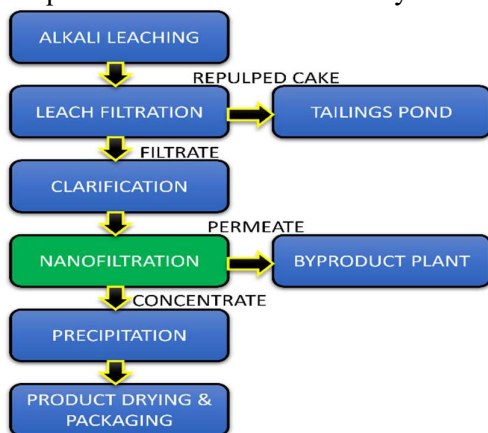


Figure 7. Scope of process modification at Tummalapalle Mill after nanofiltration

addition of caustic lye in a series of tanks (fig.7).

4.2 Limitations of nanofiltration:

Nanofiltration is the least used method of membrane filtration in industry as the membrane pores sizes are limited to only a few nanometers. A main disadvantage associated with nanotechnology, as with all membrane filter technology, is the cost and maintenance of the membranes used. Repairs and replacement of membranes are dependent on total dissolved solids, flow rate, and components of the feed. Tests were conducted to check the performance of membranes for repeated use to establish membrane life, efficiency, and amenability for regeneration. Sensitivity analysis and reproducibility tests were also conducted for the performance of the membrane at various concentration levels of salts. This pilot unit is also required to generate higher concentration liquor to determine the threshold concentration for better precipitation and settling of SDU precipitate. The flux also needs to be optimized for the given input liquor. The performance of a nanofiltration (NF) membrane for uranium extraction in an alkaline leach liquor environment at a uranium ore processing unit is influenced by variations in water composition. Here's how different factors can impact NF membrane performance:

1. Effect of Total Dissolved Solids (TDS) and Ionic Strength: Higher TDS and ionic strength increased ionic concentration (Na^+ , CO_3^{2-} , HCO_3^-) can lead to greater osmotic pressure, reducing the permeate flux and affecting uranium rejection efficiency. Lower TDS reduces osmotic pressure but may lead to lower uranium concentration in the concentrate, affecting overall recovery.

2. Influence of Carbonate and Bicarbonate Levels: Uranium in alkaline leach liquor primarily exists as uranyl carbonate complexes ($UO_2(CO_3)_3^{4-}$, $UO_2(CO_3)_2^{2-}$). Higher Na_2CO_3 / $NaHCO_3$

Concentrations can enhance uranium solubility but might reduce membrane selectivity by increasing the passage of uranium into the permeate. Lower carbonate levels may cause lower uranium solubility, potentially leading to membrane fouling due to the precipitation of uranium or other salts.

3. Presence of Competing Ions (Ca^{2+} , Mg^{2+} , SO_4^{2-}): Calcium and Magnesium can form insoluble carbonates or hydroxides, leading to membrane scaling and reduced efficiency. Sulphate (SO_4^{2-}), if present in significant amounts, can interfere with uranium rejection due to complexation or precipitation effects.

4. pH Variations: Higher pH (>10) enhances uranium rejection but can lead to carbonate scaling on the membrane surface. Lower pH (<9) may reduce uranium rejection efficiency as uranium complexes become less stable and can dissociate.

5. Temperature Effects: Higher temperatures can increase membrane permeability but may also degrade membrane material over time. Lower temperatures reduce diffusion rates, lowering uranium flux through the membrane.

6. Organic and Colloidal Contaminants: Organic matter (humic/fulvic acids) and fine colloids can lead to membrane fouling, requiring frequent cleaning. Pre-treatment methods such as filtration or chemical dosing (e.g., antiscalants) might be necessary to maintain performance.

4.3 Regulatory Challenges in Implementing Nanofiltration in an Operational Uranium Mill: Implementing nanofiltration (NF) technology in an operational uranium mill for improving U_3O_8 concentration in alkaline leach liquor presents several regulatory challenges. These challenges primarily arise due to the strict

environmental, safety, and radiological controls governing uranium processing facilities. Below are key regulatory considerations:

1. Radiation Safety and Worker Protection Regulations: Regulatory agencies (e.g., AERB, IAEA, EPA, NRC, CNSC) impose strict radiation dose limits for workers handling uranium-containing solutions. The NF membrane system must comply with radiation shielding and dose monitoring standards. NF processes can lead to aerosolization of uranium during pressure-based filtration, requiring adequate ventilation and containment measures.

2. Environmental Compliance and Waste Management: NF generates concentrate and permeate streams, with the concentrate containing higher uranium levels. Proper usage and recycling must comply with radioactive regulations. Alkaline leach liquors contain sodium carbonate, bicarbonate, and trace metals. Zero liquid discharge can be followed by the recycling of entire liquor into the plant.

3. Regulatory Approval for Process Modification: Modifying an existing uranium mill to include NF technology requires approval from regulatory bodies such as the Nuclear Regulatory Commission (NRC) in the U.S., or equivalent authorities in other countries. Detailed risk assessments, including radiation impact studies, are required. Pilot studies may be mandated to prove that NF improves U_3O_8 concentration while meeting safety and performance standards. Data must be submitted to regulators, demonstrating uranium recovery rates, membrane life expectancy, and potential scaling/fouling issues.

4. Chemical Handling and Transportation Regulations: Alkaline leach solutions involve Na_2CO_3 and NaHCO_3 , requiring adherence to chemical

storage and handling standards set by OSHA (U.S.) or REACH (EU). Nanofiltration offers a promising method for improving U_3O_8 concentration in alkaline leach liquor, but its implementation in uranium mills faces stringent regulatory challenges. Compliance with radiation safety, environmental laws, chemical handling regulations, and public engagement requirements is essential. A proactive approach involving pilot studies, risk assessments, and regulatory engagement can help facilitate successful adoption.

Acknowledgment: We thank the management of Uranium Corporation of India Limited, Tummalapalle. We also thank **Shri Manoj Kumar**, Director (Technical) and **Shri B.C.Gupta**, Company Secretary, UCIL, for their valuable suggestions for improvement and CR&D activities at Tummalapalle Mill. Additionally, we express our appreciation to Dr. T. Sunil Kumar, HOD, and the esteemed Professors from the Department of Chemical Engineering, Indian Institute of Technology Tirupati, for their invaluable guidance in academic and research endeavors.

Conflict of Interest: Authors declare No conflicts of interest.

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Exploring the Potential of CFBC Ash as Sustainable Building Material: A Review

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Volume 2, Issue 1, February 2025

Received: 15 February, 2025; Accepted: 26 February, 2025

DOI: <http://doi.org/10.63015/2e-2456.2.1>

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Abstract: Increasing use of CFBC technology for combustion of petroleum coke and other low calorific fuel offers high fuel efficiency and reduced coal utilization. India being the second largest ash producer in the world including petroleum coke fly ash with annual generation of 1,00,000 Metric Tons in an oil refinery located in Madhya Pradesh, India. The demand for its proper utilization and management is going up day-by-day. Coupled with the country's growing population and expanding infrastructure, the demand for construction materials is also increasing. The production of conventional material results in substantial CO₂ emission. Previous studies have discussed application of CFBC ash as cement (OPC, calcium sulphoaluminate, magnesium oxysulphate), concrete (AAC, RCC, NAAC), solid waste based zero cement binder (fly ash replacement of portland cement, AAC, magnesium sulphate cement, aggregates) have been discussed. However, challenges associated with CFBC ash are its porous and loose morphology, high water requirement, self-cementitious property and expansibility, which limits its potential uses and pose substantial challenges to human society. This review is focused on generation of CFBC ash, characterization of CFBC ash and advancement in processing techniques with focus on current and potential applications via waste management for industrial and societal benefits particularly for use in construction industry.

Keywords: CFBC Ash; Waste Management; Building Material; Societal Benefit; Sustainable Development

1.0 Introduction:

Global coal consumption is projected to rise by over 50% by 2030 and developing countries like India are likely to show an increase of more than 97% [1,2]. Due to this reason, coal gangue, sub-bitumen, lignite, peat, petcoke and other low-grade fuel are also used as coal substitute in thermal power stations which results in excessive emissions of CO₂, SO₂, and NO_x which pose serious risk to human, plants and animal health and limit the sustainable ecological development [3]. Hence, CFBC technology is gaining popularity as it effectively processes a blend of low-grade fuels with diverse quality, composition and moisture levels. Within the boiler,

limestone is added for in-situ desulfurization [4] and sand bed is suspended with the fuel by high-velocity air stream under fluidization. The bed material plays crucial role in enhancing heat transfer and minimizing temperature gradient confirming optimal turbulence at operating temperature between 700–900°C. This makes CFBC technology highly efficient and environment friendly [5,6]. The use of CFBC technology has increased globally due to low combustion temperature, reduced pollutant emissions, broad fuel compatibility, effective combustion and high desulfurization efficiency [7] which results in generation of CFBC ash. The residual CFBC ash that is discharged in

large quantities is an important issue to consider as it can cause severe environmental pollution and ecological damage. Additionally, long-term storage of the ash can contaminate groundwater and soil quality [8]. Therefore, utilization of CFBC ash is very crucial for environmental protection and sustainable development.

Reported literature has detailed about utilization of CFBC ash, its physico-chemical characteristics and its present and future application with focus on utilization of CFBC ash in building materials or construction industry [5,9-12]. As reported in literature, author has reviewed various potential application of CFBC ash in agriculture, construction materials, adsorbent materials, waste stabilization and also addressed the limitations associated with CFBC ash [5]. Another author provided the comprehensive review of coal fly ash by detailing its generation, physico-chemical properties, global hazards and summarizing by present and future applications along with their advantages and disadvantages [13]. Previous articles focused on utilization of CFBC ash as construction material and related issues. This review aims to bridge the gap by examining recent advancements in processing techniques and focusing on existing and future applications including its utilization in the construction sector.

1.1 Generation of CFBC Ash:

The global annual generation of fly ash consisting of both pulverized coal combustion (PCC) and circulating fluidized bed combustion (CFBC) were reported as 750 million tons per annum (MTPA) in 2012 which increased to 904 MTPA by 2020 [14] whereas in India, the total fly ash (PCC and CFBC) production has increased from 83 MTPA in 2002 to 228 MTPA by 2020 marking nearly 175% increase during the last 18 years [15]. The future projections of ash generation will reach between 300 and 400 MTPA by 2025. The annual generation of petcoke fly ash from

the Oil Refinery located in Madhya Pradesh is around 1,00,000 metric tons per annum which includes 70,000 metric tons per annum of petcoke fly ash (PCFA) and 30,000 metric tons per annum of Bed Ash (BA).

India has the third largest coal-power generating capacity in the world, providing for more than 70% of the total power demand in the country. Growing coal based power generation backed by domestic coal demand will further boost ash generation over the next decade. Even with the latest 83% ash utilization rate mainly going into cement, mine-filling/land-filling, bricks, blocks, tiles, infrastructure and concrete, around 17% of the annual ash generation (about 38 million tons) goes unutilized and is disposed into ash ponds/dykes and more than 1.6 billion tons of legacy ash is lying in ponds/dykes across the country.

2.0 Characterization of CFBC Ash:

The knowledge of detailed physico-chemical characterization of CFBC ash plays an important role for its disposal and utilization in scientific manner. The properties of CFBC ash are mainly determined by combustion condition and type of fuel used. Although CFBC boilers offer considerable fuel flexibility, most CFBC ash originates from thermal power plants that use coal or a blend of coal with other low-grade fuels, biomass, municipal solid waste and petcoke. This review mainly focuses on CFBC ash derived from different types of coal blended with petroleum coke.

2.1 Physico- Chemical Characterization:

The colour of CFBC ash is generally greyish in colour and varies from blackish to brownish colour based on the raw material used. The addition of limestone results in relatively light colour. The higher unburnt carbon content was responsible for darker colour of CFBC ash. The reddish-brown colour of CFBC ash indicates the presence of iron content mainly hematite

[16]. The CFBC ashes possess broad particle size distribution with an average particle size ranging from 12.4 -43 μ m [17-19]. The fineness of ash mainly depends on type of fuel, fuel combustion ratio and combustion process. In CFBC boiler, pulverized coal gets properly fluidized with bed material followed by crushing, combustion and heat exchange which results in more fineness in CFBC ash [20] that around 53% of CFBC ash particles have particle size distribution between 0.1 to 16 μ m. The specific gravity and Blain fineness of CFBC ash were found in the range of 2.50-2.80 and 2880– 3050 cm^2/g respectively [21-24] whereas the BET surface area of CFBC ash are observed in the range of 2.5– 67 m^2/g [17,24]. The CFBC ash usually has high pH which makes it alkaline in nature which is due to the presence of high calcium content.

The chemical composition of CFBC ash mainly consist of SiO_2 , Al_2O_3 , SO_3 , CaO , Fe_2O_3 with minor contents of Na_2O , K_2O and MgO as summarized in **Table 1** which are main elemental oxides in CFBC ash as

reported in literature. Generally, CFBC ash generated by desulfurization process has high content of SO_3 and CaO and has almost linear proportionality. The observed linear increase in sulfur content with calcium content is attributed to the desulfurization process. i.e., addition of limestone/dolomite in- situ for adsorption of emitted SO_2 in boiler. The loss on ignition (LoI) is generally higher in CFBC ash which contributes to more unburnt carbon, sulfur-binding agents and sulfur-binding products in ash which is due to low combustion temperature of CFBC boiler as compared to other boilers. Apart from this, fluidization rate of CFBC also influences loss on ignition. As fluidization rate increases, amount of unburnt carbon gradually increases. Hence decarbonization treatment is performed on CFBC ash with higher LoI [25]. The content of SiO_2 , SO_3 , CaO and LoI varies significantly due to factors such as difference in combustion condition and type of fuel used [26] (coal, petcoke and other fuel blend with coal) and quantity of desulfurizing agent used.

Table:1 Elemental Oxides in CFBC Ashes [27-48]

| Metal Oxides | Minimum (wt%) | Maximum (wt%) |
|-------------------------|---------------|---------------|
| CaO | 1.40 | 56.80 |
| SiO_2 | 0.22 | 53.50 |
| Al_2O_3 | 0.10 | 50.98 |
| SO_3 | 0.50 | 40.60 |
| Fe_2O_3 | 0.10 | 27.9 |
| MgO | 0.15 | 7.10 |
| Na_2O | 0.10 | 1.17 |
| K_2O | 0.34 | 0.55 |
| LoI | 2.75 | 14.70 |

1

2.2 Mineralogical Content:

The key mineralogical phases found in CFBC ash are Anhydrite (CaSO_4), Portlandite ($\text{Ca}(\text{OH})_2$), Quartz (SiO_2), Calcite (CaCO_3), Quicklime (CaO) and Hematite (Fe_2O_3) [47-51]. CFBC ash typically has higher proportion of crystalline phases due to lower combustion

temperature used in CFBC boilers compared to other types of boilers.

The proportions of amorphous and crystalline phases in CFBC ash were determined using X-Ray Diffraction (XRD). The crystalline phases range between 25% to 63% while the amorphous content of CFBC ash was estimated to be

between 57% to 82% [14]. Quicklime and Anhydrite are also found as CFBC boilers use limestone for desulfurization. Quartz is originally present in the fuel and Calcite is produced by reaction between Lime with CO_2 in the air. Portlandite is formed when free lime of CFBC ash comes in contact with air and react with water vapour during storage whereas Calcite and Lime is formed due to addition of desulphurization agent during the combustion in CFBC boiler [20,47,10].

The combustion of low grade coal in CFBC boiler leads to increase in SO_2 emission which results in increase in lime content. It is reported that higher levels of SO_3 and lime contribute positively to enhance self-cementitious strength [11]. It is also confirmed from previous studies that CFBC ash contain Calcium, Aluminum and Silicon as reactive component and the hydration product of these components lead to formation of Portlandite and Ettringite in the initial stage and the layer gets converted into Calcium Silicate Hydrate (C-S-H) and Gypsum [20,47,49]. It was also noticed that fly ash from various Thermal Power Plants vary in properties due to different fuel blending ratio and different combustion conditions.

2.3 Morphological Properties:

The morphology of CFBC ash mainly consists of irregular block or rod-shaped particles that are flaky, angular and loose, porous surface [47,50-52]. The main reason for irregular shape is combustion temperature of CFBC boiler which is in range of 700-900°C. This temperature range could not melt irregularly shaped ash particles into spherical shapes resulting in irregular microstructure of unburnt carbon particles, Anhydrite, Calcite, Lime [18] in CFBC ash. Furthermore, Limestone

degradation and CO_2 emission during the reaction phase might cause surface loosening [20,53,54]. The high water requirement of CFBC ash along with its loose and porous structure prevents it from being used in accordance with fly ash treatment procedures. Hence, CFBC ash has greater water requirement for normal consistency as compared to Ordinary Portland Cement.

3.0 CFBC Ash as Building Material:

The generation of large amounts of CFBC ash causes serious problems in terms of its safe disposal and storage as it has negative impact on environment like ground water contamination, environmental pollution occupying large space including farmlands thus wasting resources. Therefore, proper management and potential utilization of CFBC ash is very important to protect environment and sustainable development. Various researchers have reported and discussed the application of CFBC ash as cement substitute material in Ordinary Portland Cement, Magnesium Oxysulphate and Calcium Sulfoaluminate in concrete like Autoclave Aerated Concrete, Non-Autoclave Aerated Concrete, Roller Compacted Concrete. Apart from this, CFBC ash is used as zero cement binder along with various industrial solid wastes like Coal Fly Ash, Blast Furnace Slag, Tailings etc. Currently, broad areas of application of CFBC ash in construction application include Roller Compacted Concrete, Light Weight Aggregate/Foam Concrete, Portland Pozzolana Cement replacement, Concrete, Bricks and Geopolymer. The key contributions by various researchers on the application of CFBC ash in civil infrastructure materials are summarized in **Table 2**.

Table 2: Summary of Applications of CFBC Ash as Building Material

| No. | Application | Raw Material | Additives | Properties | Ref. |
|-----|-------------|--------------|------------------|-------------------|---------|
| 1. | Cement | CFBC Ash | OPC, Class F fly | Water absorption, | [55-59] |

| | | | | | |
|----|---------------------------------|----------|--|---|---------------|
| | | | ash, GBF slag, limestone filler, Portland cement, commercial gypsum | Compressive, tensile, flexural strength, elasticity modulus, elasticity modulus, particle size, XRD, SEM. | |
| 2. | Zero Cement Binder | CFBC Ash | Fly ash, ground granulated blast furnace slag (GGBS), silica fume, recycled aggregates | Compressive strength, heat of hydration, initial - final setting time, thermal analysis, microstructure study. | [40,41,60-67] |
| 3. | Autoclaved Aerated Concrete | CFBC Ash | Fly ash, cement, superplasticizer (polycarboxylate), lime | Dry density, pore structure, compressive and specific strength and hydration products. | [49,68-71] |
| 4. | Non-Autoclaved Aerated Concrete | CFBC Ash | Aluminate cement/ Portland cement/ PCC fly ash, cement, phosphogypsum | Compressive strength, morphological, volume stability, drying shrinkage, frost resistance and thermal conductivity. | [72-75] |
| 5. | Roller Compacted Concrete | CFBC Ash | Cement, river sand, OPC, coarse aggregates, gravel | Compressive, Flexural Strength, setting time, sulphate resistance, density, thermal conductivity, microstructural analysis. | [76,77] |
| 6. | Light Weight Aggregate | CFBC Ash | Glass powder, perlite tailing powder, bentonite, calcium carbonate, oil-contaminated drill cuttings (OCDC), quicklime. | Cylinder strength, water absorption apparent density, softening coefficient, bulk density. | [78,79] |
| 7. | Concrete | CFBC Ash | Cement, river sand, coarse aggregate, gravel, slag. | XRD, Thermal analysis, Compressive and Flexural Strength. | [40,80] |
| 8. | Alkali Activator/ Geopolymer | CFBC Ash | Sodium Hydroxide, Sodium Meta Silicate, Metakaolin. | Compressive Strength, Microstructure, FTIR, Physico chemical Properties. | [81-85] |

3.1 Ordinary Portland Cement:

Conventionally, fly ash is known for its

effectiveness as mineral admixture and has been extensively utilized in Portland

Pozzolana Cement. Similarly, CFBC ash has been used as a mineral additive in Portland Cement. Research on its effects on physico- mechanical properties of cement-based composites has emerged as key area of research for its resource utilization in building materials. The findings of few researchers in terms of properties reported that expansion of CFBC ash reduces shrinkage of cement mortar [55] and another study concluded that CFBC ash can increased the hydration rate of Tricalcium Silicate and enhances the early formation of Ettringite (AFt) and thus results in improvement of mechanical properties of cement [56]. It is highlighted how activators can enhance the hydration process of cement by generating Portlandite ($\text{Ca}(\text{OH})_2$) which in turn activates the pozzolanic reaction of CFBC ash resulted in formation of Calcium Silicate Hydrate (C-S-H) gel with lower Aluminum to Silicon ratio positively influencing cement hydration and improving its early strength [57]. A study conducted in 2019 has explored that grinding CFBC ash to a fineness comparable to cement enhances its pozzolanic activity making it a suitable replacement for cement clinker [58]. It was also reported in the literature that when CFBC ash is combined with other materials, it leads to the formation of significant quantities of Ettringite and Silicates. This reaction driven by sulfate ions and free lime results in reducing shrinkage/self-shrinkage in the material [59].

3.2 Zero-Cement Binder:

The production of one ton of cement results in release of 800 kg of CO_2 significantly contributing to global atmospheric pollution and emissions of greenhouse gas. The cement industry accounts for 8% of global CO_2 emission [60]. As a result, the development of alternative binders involves using solid waste materials like coal fly ash, CFBC ash and GGBFS which has emerged as a key area of investigation in the area of solid waste and construction materials

owing to its efficacy as supplementary and alternative cementitious material. It is distinguished by its high utilization efficiency and lower carbon emissions associated with its production process. Numerous researchers have investigated the development of zero-cement binders by utilizing various forms of solid waste.

Previous study demonstrated that CFBC ash with varying free lime content can be used to develop zero- OPC binders. These binders form hydration products similar to conventional cement. Free- CaO content ranges from 9.0% to 17.0% which to ensures desirable setting characteristics and compressive strength along with pre-hydration controlled free- CaO content and improved performance. Mineral admixtures like fly ash, silica fume and GGBFS further enhanced strength and durability [61]. Researchers has developed an eco-binder by combining Circulating Fluidized Bed Combustion Fly Ash (CFBCFA) with Ground Granulated Blast Furnace Slag (GGBFS) without incorporating Ordinary Portland Cement or alkaline activators. The hydration products formed were included Ettringite, Calcium-Silicate-Hydrate and Aluminum-modified Calcium Silicate Hydrate gel. The maximum achieved compressive strength after 28 days was 75 MPa [62]. Prior to this study, it is also investigated that mortars (SCA) made from CFBC fly ash (CA) and slag (S) exhibited good sulfate resistance and strength reduction restricted to approximately 15% or less [41]. Additionally, it is also demonstrated that the eco-binder SCA paste achieved appropriate setting time and adequate strength with compressive and tensile strengths of 80 MPa and 4.6 MPa respectively at 28 days. The hydration products includes Ettringite, C-S-H and C-S-A-H which formed a dense, self-cementitious microstructure leading to lower ultimate drying shrinkage compared to Ordinary Portland Cement paste[40]. Study conducted in 2019 found that adding brown coal fly ash to GGBFS accelerates early hydration, reduces setting time and

increases early compressive strength. Additionally, increasing the fly ash content resulted in a 20% reduction in setting time and a 22% improvement in compressive strength [63].

Few researchers examined a ternary blended no-cement mortar consist of Class F Fly Ash, GGBFS and CFBC Ash. They found that while the mortar demonstrated good durability and heat resistance below 400°C both its weight and compressive strength significantly decreased at temperatures exceeding 600°C. Strength loss is minimal up to 400°C and its weight reduction occurs at 800°C in a study conducted in 2018 [64]. Study carried out in 2017 investigated zero-cement mortar made from CFBC ash, Blast Furnace Slag and recycled aggregates achieving up to 50 MPa compressive strength after 91 days with an optimal mix of CFBC 75:25. The mortar exhibits excellent durability, including enhanced resistance to chloride diffusion, frost, carbonation and sulfuric acid [65]. Some authors reutilized waste co-fired fly ash through CFBC boiler as an alkali activator in combination with GGBFS to create an eco- friendly binder. The reported best mix i.e, 30% CFFA and 70% GGBS attained 31.43 MPa compressive strength which is 72.4% of the Ordinary Portland mortar strength. This results in the formation of C–S–H and C–A–S–H gels resulting from the reaction between CaO with H₂O, SiO₂ and Al₂O₃ [66] whereas some explored the use of CFBC bottom ash in controlled low strength materials (CLSM). Laboratory tests on various mixture proportions showed that incorporating fly ash and GGBS with bottom ash improves flowability, setting time, compressive strength and water absorption [67]. These findings indicate that secondary products like fly ash, ground-granulated blast furnace slag, silica fume and recycled aggregates can be effectively utilized in promoting sustainable development. It is suggested that CFBC ash-based zero-OPC binders can be used as sustainable

alternative to traditional cements for reducing CO₂ emissions and for utilizing industrial waste.

3.3 Autoclaved Aerated Concrete:

Autoclaved aerated concrete (AAC) is a lightweight precast building material that contains air bubbles throughout its structure, giving it a cellular composition. Some researchers tried to use CFBC ash for making AAC and suggested that addition of CFBC ash can bring several benefits to AAC. In previous study conducted by few researchers indicates that feasibility of substituting up to 50% fly ash in cementitious materials without experiencing a substantial reduction in compressive strength. Microstructural analysis validated the integration of aluminum ions into the C-S-H phase with consistent presence of crystalline Tobermorite [68]. In 2015, it has been reported that incorporation of CFBC ash in AAC with the addition of superplasticizer Polycarboxylate (PCE) can significantly influence the material's properties. Optimal PCE content and Water to Powder (W/P) ratios are critical for maintaining desirable rheological properties and effective gas-foaming which in turn affect the porosity and overall performance of the AAC [49]. The utilization of CFBC ash in AAC is feasible and can lead to improved properties and the density of AAC with CFBC ash was slightly lesser as compared to traditional AAC indicating potential benefits in terms of lightweight construction materials as reported in study conducted in 2021[69]. Further, microstructural analysis revealed changes in the pore structure and hydration products suggesting alterations in the concrete's internal structure.

It was also concluded by researchers that the use of 16wt% lime as a partial replacement of cement in AAC results in improvement of compressive strength with presence of Tobermorite crystals microstructure which contributes in

property improvement [70]. However, beyond this, the microstructure of AAC is adversely affected. Hence, previous studies suggest that creating aerated concrete serves as an optimal approach for recycling CFBC ash and producing concrete. Previous study addressed the challenge of high water absorption in CFBC ash and investigated its feasibility in preparing AAC concrete which indicated that the water-reducing effect of superplasticizers enhance the slurry's rheology to synchronize with the gas generation rate of aluminum powder, thereby optimizing pore structure, reducing the number of harmful pores (<50 nm) and improving product strength [71]. High water content introduces numerous uneven macropores whereas low water content hampers cement hydration, reducing the formation of C-S-H gel and Tobermorite. A balanced combination of water content and water-reducing agent improves AAC strength without significantly altering bulk density.

3.4 Non-Autoclaved Aerated Concrete:

Non-Autoclaved Aerated Concrete (NAAC) is a type of lightweight concrete that is not cured in an autoclave. Aerated concrete typically comprises of cement, lime, gypsum, sand and small amount of pore-forming agent i.e., aluminum powder on reaction with lime generating hydrogen gas and various fine bubbles that are evenly distributed throughout the matrix [72,73]. This results in lightweight, porous concrete with good thermal insulation properties and fire resistance. In comparison to traditional autoclaved aerated concrete, non-autoclaved aerated concrete offers significant advantages in streamlining the manufacturing process and lowering production costs. Currently, CFBC ash has been utilized in the production of both AAC and NAAC.

Research study performed in 2013 identified the Coal Fly Ash (CFA) as the primary raw material for NAAC. The study involved rheological, physical, chemical,

microstructure and mechanical analysis to assess the impact of raw materials on NAAC properties. The optimal composition was found to be 65.5% CFA, 22% cement and 10% lime with an ideal particle size range of CFA between 9.6 μ m and 23.9 μ m and the key minerals were needle shaped like Ettringite and floccular pattern of C-S-H [74]. Few researchers have also explored the utilization of CFBC ash to prepare foam concrete with 60°C steam curing for 24 hours. The optimal mix was found to be 70% CFA, 8% Quicklime, and 2% Aluminate cement. The addition of Aluminate cement or Quicklime accelerated the setting and hardening process of the slurry. For better compressive strength, finer CFA and lower w/s ratio were preferred. The resulting foam concrete exhibited good compressive strength, resistance to frost and thermal conductivity [75].

3.5 Roller Compacted Concrete:

Roller-compacted concrete (RCC) is a type of concrete that is laid and compacted using machinery similar to that employed for asphalt pavement. Few authors explored the preparation of RCC using CFBC ash through replacement of fine aggregates. Author reported that replacement of CFBC ash with 5% as fine aggregate at 75g/cm² of roller compaction pressure increased water absorption and reduced initial surface absorption, improved compressive strength, tensile strength and sulphate resistance of RCC [76]. In 2019, other author has reported that 10% CFBC ash replacement as fine aggregates and rolling pressure of 100g/cm² enhances the development of flexural strength, reduces the initial and the final setting time by 30%-60% and 16%-20% respectively [77]. Based on SEM and XRD results, it was confirmed that increasing the amount of CFBC ash as a substitute for fine aggregate led to an improvement in the density of C-S-H gel and gradual increase in the content of Portlandite.

3.6 Aggregates:

Research undertaken in 2020 found that Calcium Sulfate in CFBC ash acts as a foaming and fluxing agent promoting the formation of vitrified surface and porous cellular structure during sintering process. This in turn, leads to a substantial decrease in water absorption and apparent density of the Ceramsite. Optimized process yielded 700-grade lightweight CFBC ash Ceramsite with 50–70% content of CFBC ash and cylinder strength of 5.3MPa [78]. In the same year other authors has investigated the feasibility of co-mechano-chemical treatment of CFBC ash, oil-contaminated drill cuttings (OCDC) and quicklime to develop non-sintered lightweight aggregates and reported that light weight aggregates exhibit high cylinder compressive strength of 17.87 MPa and low water absorption rate of 6.28%. These properties were achieved under optimal conditions of water addition, steam-curing (60°) and steam- curing time (12hr). The co-mechano-chemical treatment effectively enhanced the pozzolanic activity of CFBC ash thereby contributed in enhancement of strength [79].

3.7 Concrete:

Several researchers have examined the application of CFBC ash for the preparation of roller compacted concrete (RCC). It is dry and stiff form of concrete which doesn't have slump. Several studies have explored the utilization of CFBC ash in various type of concrete which are summarized in **Table 2**. They investigated CFBC ashes from coal combustion at three thermal power plants using them as cement binder additives in concrete with 20% to 30% weight substitution and observed the decrease in Portlandite content and moderate alterations changes in Ettringite content in CFBC ash incorporating cement pastes as confirmed through XRD and thermal analysis. The study concluded that addition of CFBC ash increases C–S–H gel and crystalline Ettringite content and also enhances hydration products without

significantly altering the qualitative phase composition of cement paste [80].

3.8 Geopolymer:

Geopolymers were initially introduced by French Scientist Joseph Davidovits in the late 1970s to describe inorganic polymers formed by the geopolymerization process. The study conducted in 2011 tested the potential application of CFBC ash in ceramic tile manufacturing through the sintering technique. Specimen were moulded using extrusion fired at 1050°C and tested for microstructure and physical properties. Various properties were evaluated for plasticity, water absorption and mechanical strength [86]. Later in 2020, another author studied the impact of partially substituting Pulverized Coal Combustion (PCC) fly ash with Circulating Fluidized Bed Combustion (CFBC) ash in alkali-activated materials utilization different molar concentration (4M, 5M, and 6M) of Sodium Hydroxide along with Sodium Silicate solution. The research revealed strong correlation between the compressive strength and Sodium Hydroxide molarity of CFBC ash based alkali-activated materials with the relation that higher molarity resulting in greater compressive strength[82].

In 2010, few authors reported that low-reactive CFBC ash can be effectively used as a raw material for geopolymer production by enhancing their reactivity through an alkali fusion process and balancing the Na/Al ratio with an additional Aluminosilicate source such as high-reactive Metakaolin (MK) with dense and homogeneous microstructure [83]. The higher alkali activator ratio (i.e. sodium silicate to sodium hydroxide) enhanced compressive strength and produced dense, homogeneous composites, while lower ratio resulted in weaker materials with more Calcium Hydroxide [84]. It was also investigated that addition of high calcium coal based ash to grinding CFBC ash enhanced the properties of CFBC ash based geopolymer composite as PCC fly ash is

rich in glassy phases which easily released Si and Al ions when treated with alkali solution and hence facilitating the formation of a linking network in geopolymeric composites [85].

4.0 Conclusions:

Based on the extensive research on characterization and utilization of CFBC ash, the study highlights its wide- ranging potential application across various sectors. Among these the most promising areas of application with lot of encouraging research have been reported in its use in cement and non- cementitious building materials including aerated concrete, geopolymers, synthetic light weight aggregates and other non- structural construction materials. Key findings from this research include:

1. CFBC ash shows significant potential as mineral admixture in Portland cement offering several advantages which includes the acceleration of hydration, reduction of shrinkage, enhancement of pozzolanic activity and early strength improvement. Research findings indicate that CFBC ash can lessen cracking by minimizing shrinkage, promote hydration of Ettringite (Aft) and Tricacium Silicate(C_3S) for early strength and to facilitate pozzolanic reactions through activators. It can also be serves as an effective clinker replacement after mechanical activation.

2. CFBC ash and other industrial by-products such as fly ash, GGBS and recycled aggregates is a viable alternative to conventional portland cement. These materials significantly reducing CO_2 emissions. According to research, CFBC ash based zero cement binders have excellent durability, compressive strength and environmental resistance. These binders create hydration products that are similar to conventional cement however perform better and making them a viable option for sustainable building materials.

3. CFBC ash shown its capability to replace conventional ash without cement

compromising strength in autoclaved aerated concrete (AAC). It contributes to improves pore structure, reduces density and formation of beneficial hydration products like Tobermorite. Optimal use of superplasticizers and water-to-powder ratio is important for maintaining desirable properties. As result, CFBC ash serves as a valuable material for lightweight, durable and sustainable AAC thereby promoting industrial waste recycling in construction.

4. CFBC ash effectively replaces fine aggregates in roller-compacted concrete (RCC) enhancing its compressive, flexural strength, tensile strength and sulfate resistance while reducing initial surface absorption and setting times. Optimal replacement levels and compaction pressures further improve C-S-H gel density and Portlandite content and enhancing overall RCC's performance and sustainability. It also acting as foaming agent thus improves lightweight aggregates by reducing density and water absorption. Co-mechano-chemical treatment increases its pozzolanic activity and strength along with sustainable aggregates like Ceramsite.

5. The manufacturing of geopolymer from CFBC ash exhibits considerable promise. The compressive strength of alkali-activated materials is significantly influenced by the sodium hydroxide concentration with higher concentrations producing superior outcomes. Furthermore, alkali fusion can be used to activate low-reactive CFBC ash for geopolymerization, specially when paired with aluminosilicates like metakaolin, resulting in dense, high-strength composites.

5.0 Future Research Prospects:

It has been noticed that despite of extensive research has been done on CFBC ash for its application in various field these is always a scope for improvement. Some challenges associated while using CFBC ash in construction applications which needs to be optimize and overcome like water-cement

ratio, curing conditions and blending ratios to maximize the potential utilization of CFBC ash. Additionally, more research needs to be done to enhance strength, durability and workability. Further, the application of CFBC ash through geopolymerization can be more explored. There is a great variation in results due to varying composition of ash and there is no standard available till date which could also be explored and optimized to ensure consistent performance in various applications.

Acknowledgement:

The authors are grateful to Prof. Avanish Kumar Srivastava, Director, CSIR-AMPRI, Bhopal for granting the permission to publish this work.

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Education Watch Report

The Impact of Stress on Education: Understanding the Consequences and Finding Solutions

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Volume 2, Issue 1, February 2025

Received: 28 January, 2025; Accepted: 20 February, 2025

DOI: <https://doi.org/10.63015/6t-2452.2.1>

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Abstract: Stress has become a significant factor affecting students' academic performance, mental well-being, and overall development. Educational stress arises from various sources, including academic pressure, high expectations, competitive environments, and personal challenges. This paper explores the impact of stress on education, highlighting its consequences on cognitive function, motivation, and emotional stability. Studies suggest that excessive stress leads to anxiety, burnout, poor concentration, and even physical health issues, ultimately hindering learning outcomes. To mitigate these negative effects, effective stress management strategies must be implemented in educational institutions. Solutions such as mindfulness practices, time management training, counseling services, and supportive learning environments can help students cope with stress. Additionally, a balanced approach to assessments and promoting extracurricular activities can enhance student well-being. Understanding the link between stress and education is crucial in fostering healthier learning experiences. By addressing stressors proactively, educators, parents, and policymakers can create a more supportive academic atmosphere, ensuring students achieve their full potential without compromising their mental health.

1. Introduction: Stress is an unavoidable aspect of modern education, affecting students at all levels. With increasing academic demands, competitive environments, and high expectations from teachers, parents, and society, students often experience overwhelming pressure. While a certain level of stress can be beneficial in motivating students to perform better, excessive and prolonged stress can have detrimental effects on their cognitive abilities, emotional well-being, and overall academic success.

This paper explores the impact of stress on education, focusing on how it affects students' concentration, memory, motivation, and mental health. It also examines the broader consequences of academic stress, such as anxiety, burnout, and reduced learning efficiency. Furthermore, the study highlights practical strategies to help students manage stress effectively, including mindfulness techniques,

better time management, access to counseling services, and supportive teaching methods.

By understanding the relationship between stress and education, educators, parents, and policymakers can work together to create a more balanced and supportive learning environment. Addressing these challenges will not only improve academic performance but also promote students' overall well-being and personal growth.

2. Rationale: Education plays a crucial role in shaping an individual's future, yet many students face significant stress that hampers their academic performance and overall well-being. The increasing pressure to excel in studies, meet deadlines, and balance extracurricular activities can create a high-stress environment, negatively impacting students' mental and physical health. This research seeks to explore the effects of stress on students' learning abilities, emotional

stability, and academic achievements while identifying effective coping mechanisms.

Understanding the impact of stress on education is essential for educators, parents, and policymakers to develop strategies that promote a healthier and more supportive learning environment. By addressing stress-related challenges, institutions can help students enhance their productivity, maintain motivation, and achieve academic success without compromising their mental health. The findings from this study will contribute to the growing conversation on student well-being and provide insights into sustainable solutions that foster resilience and better stress management in educational settings.

3. Objectives:

3.1. The primary aim of this study is to examine the impact of stress on education and identify effective strategies to mitigate its negative effects. The specific objectives include:

3.2. To analyze the causes of stress in students – Identifying key factors such as academic pressure, high expectations, workload, peer competition, and personal challenges.

3.3. To evaluate the consequences of stress on academic performance – Examining how stress affects concentration, memory retention, problem-solving skills, and overall learning outcomes.

3.4. To assess the emotional and psychological effects of stress on students – Exploring its impact on mental health, including anxiety, depression, burnout, and motivation levels.

3.5. To identify effective stress management strategies – Investigating techniques such as mindfulness, time management, counseling, physical activities, and supportive learning environments.

3.6. To provide recommendations for reducing stress in educational settings – Suggesting measures that educators, parents, and

policymakers can implement to create a healthier and more balanced academic experience.

3.7. By achieving these objectives, this study aims to contribute to the development of stress-free and more effective learning environments for students.

4. Review of Literature: Stress in education has been widely studied by researchers, with various studies highlighting its causes, effects, and potential solutions. This section reviews key literature on the topic, focusing on the relationship between stress and academic performance, psychological well-being, and coping mechanisms.

Stress and education are intricately linked, with the pressure to perform well academically often taking a toll on students' mental and emotional well-being. Chronic stress can have severe consequences on students' cognitive, emotional, and social development, ultimately affecting their academic achievement and overall quality of life.

Accordingly to a research, secondary/high school (defined here as junior/lower secondary education and senior/upper secondary education)] (UNESCO, Citation2012) and tertiary (defined here as post-secondary education) (UNESCO, Citation2012) it was self-report by students experiencing ongoing stress relating to their education, which we refer to as academic-related stress, such as pressure to achieve high marks and concerns about receiving poor grades. For example, the Organisation for Economic Co-operation and Development (OECD) recently conducted a survey involving 72 countries and consisting of 540,000 student respondents aged 15–16 years. On average across OECD countries, 66% of students reported feeling stressed about poor grades and 59% reported that they often worry that taking a test will be difficult. The OECD further found that 55% of students feel very anxious about school testing, even when they are well prepared. As many 37% of students reported feeling very

tense when studying, with girls consistently reporting greater anxiety relating to schoolwork compared to boys (OECD, Citation2017). This data demonstrates that education and academic performance are a significant source of stress to students. The impact of this ongoing academic-related stress to student outcomes and well-being has not been comprehensively explored. Therefore, the current narrative review explores the impact of academic-related stress on students' academic performance, mental health and well-being.

5. Academic-related stress and mental health:

Previous research indicates that self-reported stress is associated with the presentation of anxious states and lower well-being (Carter, Garber, Ciesla, & Cole, Citation2006; Kessler, Citation1997; Robotham & Julian, Citation2006). The recent above-mentioned OECD survey reports that secondary students who self-report higher levels of academic-related stress also report lower well-being, measured using psychological, social, cognitive and physical components (OECD, Citation2015). A systematic review of 13 studies showed that in individuals undertaking higher education, self-reported levels of stress are associated with poorer quality of life and well-being (Ribeiro et al., Citation2017). Ongoing stress also precipitates the development of more serious mental health issues such as anxiety and depression (Kessler, Citation1997; Moylan, Maes, Wray, & Berk, Citation2013). The prevalence of anxiety is as high as 35% in tertiary students (Bayram & Bilgel, Citation2008; Eisenberg, Gollust, Golberstein, & Hefner, Citation2007; Ozen, Ercan, Irgil, & Sigirli, Citation2010) and the prevalence of depression is 30% (Ibrahim, Kelly, Adams, & Glazebrook, Citation2013). The reciprocal relationship between stress and depression and anxiety is well established (Dantzer, Citation2012; Dantzer, O'Connor, Lawson, & Kelley, Citation2011; Maes, Citation2008). Indeed, major stressful life events are one of the best predictors of the onset

of depression (Kendler et al., Citation1995; Kessler, Citation1997). Accordingly, in young people the first onset of depression is often preceded by major life stressors (Lewinsohn, Allen, Seeley, & Gotlib, Citation1999).

6. Causes of Stress in Education: Several studies have identified academic pressure as a primary source of stress among students. According to Lazarus and Folkman (1984), stress arises when individuals perceive demands exceeding their coping abilities. In an academic setting, factors such as heavy workloads, tight deadlines, high expectations from parents and teachers, and peer competition contribute to heightened stress levels (Misra & McKean, 2000). Additionally, research by Deb, Strodl, and Sun (2015) found that students experiencing financial difficulties, social pressure, or inadequate support systems are more vulnerable to stress.

7. Effects of Stress on Academic Performance:

Research has consistently shown that excessive stress negatively affects students' cognitive abilities and learning outcomes. Yerkes and Dodson (1908) proposed the Yerkes-Dodson Law, which suggests that moderate stress can enhance performance, but excessive stress impairs concentration, memory retention, and problem-solving skills. A study by Kohn and Frazer (1986) found that chronic stress leads to burnout, reduced motivation, and academic disengagement. Furthermore, Hattie et al. (1996) indicated that stress contributes to test anxiety, resulting in lower academic achievement and impaired cognitive functioning.

8. Psychological and Emotional Impact of Stress:

Stress not only affects academic performance but also has severe emotional and psychological consequences. According to Selye (1976), prolonged stress can trigger emotional exhaustion, anxiety, and depression. A study by Arnett (2000) revealed that high levels of academic stress correlate with mental health disorders, including sleep disturbances and low self-esteem. Additionally, Beiter et al. (2015)

found that university students experiencing excessive stress are more likely to suffer from social isolation and decreased overall well-being.

9. Coping Mechanisms and Stress Management Strategies: Several studies have explored effective stress management techniques for students. Mindfulness-based interventions, such as meditation and relaxation exercises, have been found to reduce stress and improve focus (Kabat-Zinn, 1990). Additionally, time management skills, including goal setting and prioritization, help students handle academic workloads more effectively (Britton & Tesser, 1991). Support systems, such as counseling services and peer mentoring programs, have also been identified as crucial in reducing academic stress (Regehr, Glancy, & Pitts, 2013).

10. Research Methodology: This study aims to explore the impact of stress on education, its consequences, and potential solutions. The research methodology outlines the approach used to collect, analyze, and interpret data to achieve the study's objectives.

10.1. Research Design:

A mixed-methods approach will be used, combining both qualitative and quantitative methods. This will allow for a comprehensive understanding of the causes, effects, and coping strategies related to academic stress.

10.2. Population and Sampling

Target Population: Students from various educational levels (high school, college, and university) will be studied to understand the prevalence and effects of stress.

Sample Size: A sample of approximately 100–200 students will be selected for the survey, along with 10–15 educators and counselors for qualitative insights.

Sampling Technique: A random sampling method will be used to ensure a diverse and representative group of students from different academic backgrounds and environments.

10.3. Data Collection Methods

Survey Questionnaires: Structured questionnaires will be distributed to students to assess their stress levels, academic performance, and coping mechanisms. A Likert scale will be used to measure stress intensity.

Interviews and Focus Groups: Semi-structured interviews with educators, psychologists, and counselors will provide qualitative insights into student stress and recommended solutions.

Secondary Data Analysis: A review of existing literature, academic reports, and previous studies will support data validation and provide additional perspectives.

10.4. Data Analysis

Quantitative Data: Statistical tools such as SPSS or Excel will be used to analyze survey responses, identify patterns, and measure correlations between stress levels and academic performance.

Qualitative Data: Thematic analysis will be conducted on interview transcripts to identify key themes and insights on stress management strategies.

10.5. Ethical Considerations

Confidentiality: Participants' identities and responses will be kept confidential to protect their privacy.

Informed Consent: All participants will be informed about the study's purpose and their right to withdraw at any time.

Bias Reduction: The research will ensure objective data collection and analysis to maintain credibility and reliability.

10.6. Limitations of the Study

Self-Reported Data: The study relies on participants' self-assessment of stress, which may be subjective.

Sample Size Constraints: A limited number of participants may not fully represent all educational institutions.

External Factors: Personal life stressors outside of academic settings may influence results.

10.7. Limitations

The study may not fully account for individual differences in stress tolerance.

Factors beyond academics (e.g., personal life issues) may influence results.

The findings may be more relevant to specific educational systems and may not be universally generalizable.

11. Expected Outcomes

This study aims to provide a comprehensive understanding of how stress impacts education and to identify effective solutions for managing it. The expected outcomes include:

11.1. Identification of Key Stress Factors

The study will highlight the main sources of academic stress, such as exams, workload, peer competition, and parental expectations.

It will also explore external stressors like financial constraints and social pressure.

11.2. Understanding the Effects of Stress on Academic Performance

The research is expected to show how excessive stress negatively affects students' concentration, memory, problem-solving abilities, and overall academic achievement.

It will provide evidence on how stress leads to decreased motivation, test anxiety, and burnout.

11.3. Assessment of Psychological and Emotional Consequences

The study will explore the link between academic stress and mental health issues such as anxiety, depression, and emotional exhaustion.

It will analyze the long-term effects of chronic stress on students' well-being.

11.4. Evaluation of Effective Coping Mechanisms

The findings will identify stress management techniques that students use, such as time management, relaxation methods, and seeking social support.

The effectiveness of institutional interventions, such as counseling services and mindfulness programs, will also be assessed.

11.5. Recommendations for Stress Reduction Strategies

The study will provide practical solutions for students, educators, and policymakers to reduce academic stress.

Strategies may include curriculum modifications, improved support systems, and better stress awareness programs.

11.6. Contribution to Educational Policy and Student Well-being

The research is expected to contribute to discussions on improving the learning environment and making education less stressful.

Schools and universities may use the findings to implement student-friendly policies that promote mental health and academic success.

12. Conclusion: Stress in education is a widespread issue that affects students at all academic levels. While a certain level of stress can enhance motivation and performance, excessive stress has been shown to negatively impact students' concentration, memory, problem-solving skills, and overall academic success. Beyond academics, chronic stress contributes to mental health challenges such as anxiety, depression, and emotional burnout, which can hinder personal development and long-term well-being.

This study has explored the primary causes of academic stress, including heavy workloads, competitive environments, parental and societal expectations, and financial pressures. It has also examined the consequences of stress on both academic performance and emotional health, emphasizing the need for proactive interventions.

To create a more supportive educational environment, institutions, educators, and policymakers must implement strategies that help students manage stress effectively. Time management training, mindfulness programs, access to mental health support, and flexible assessment methods can all play a role in reducing stress levels. Additionally, fostering a balanced curriculum that integrates extracurricular activities, social support systems, and open communication between students and educators can contribute to a healthier learning experience.

Ultimately, addressing academic stress is not just about improving grades—it is about nurturing well-rounded individuals who can handle challenges with resilience and confidence. A holistic approach to education, one that prioritizes both academic excellence and emotional well-being, is essential for preparing students for future success in both their personal and professional lives.

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3048-460X**

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