

Mineral transformation of Thar and Lakhra Coals: Enhancing GCV and BTU for Sustainable Energy Applications

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ABSTRACT

Low-rank coals from Pakistan's Thar and Lakhra basins are vital indigenous energy deposits, but their utilisation is mostly restricted due to high intrinsic moisture, high ash-forming mineral concentration and low calorific yield. This work assesses a sophisticated multi-mechanism chemical conditioning package—integrating alkaline demineralisation with potassium hydroxide KOH, oxidative desulfurization with sodium hypochlorite NaClO, and inorganic cleat-sealing with calcium carbonate CaCO₃ to improve the thermochemical characteristics and stabilise the structural matrix of the coals. Laboratory tests included proximate and ultimate analyses, X-ray diffraction (XRD) mineralogical phase tracking, water saturation dynamics and high-precision bomb calorimetry. The experimental results demonstrated essential fuel quality improvements in both coal deposits. The best improvement was obtained using Lakhra coal which included 77.80% dry ash free (daf) elemental carbon and a gross calorific value of 34,150 kJ/kg (14,683 BTU/lb) and is classified as high volatile bituminous fuel. The coal was improved to 71.20% carbon (daf) and 32,250 kJ/kg (13,865 BTU/lb) calorific output with 20.0% improvement on an as received basis. XRD diffractograms indicated that the hydrophilic kaolinite clays were extracted preferentially by KOH and the reactive iron sulphides by NaClO. The presence of an extra calcite peak at $2\theta \approx 29.40^\circ$ was also indicative of the physical deposit and retention of micro-particulate CaCO₃ which effectively sealed cleat holes, reduced matrix slaking and limited surplus fluid saturation to roughly 12%. The results show that chemical conditioning is a viable non-destructive approach to upgrade low-rank Pakistani lignites to greater efficiency lower slagging solid fuels for advanced power generation, industrial co-firing and clean coal applications.

1. Introduction

The International Energy Agency (IEA) global energy outlook projects coal will continue to be a key foundation for global power generation, accounting for roughly 35% of total electricity supply [1–3]. The enduring significance of this is primarily underpinned by a combination of its low-cost, broad accessibility and stable baseload energy security—factors that remain vital for rapid economic and infrastructural expansion among developing economies [4–6]. Geographically, more than three-quarters of worldwide consumption is in the Asia Pacific area, and growing industrial demand in China,

India and Southeast Asia continues to drive up utilisation. At the same time, investments are being made in decarbonisation and renewable replacements [7–9].

In Pakistan, the great Thar coal field has become the keystone of the national policy for self-sufficiency in domestic energy. Sindh Engro Coal Mining Company (SECMC) has put Block II into production of 12.2 million metric tonnes per year and is fully planned to expand to 50 million tonnes per annum by 2030 when further mining leases are available [10, 11]. This continuous fuel flow enables massive baseline generation assets such as the 1,320 MW mine-mouth thermal power

plant and power units in surrounding facilities [12–14]. Simultaneously, the Lakhra coalfield is a significant regional resource, containing sub-bituminous reserves that have been traditionally used for kiln burning in the local cement industry and for local thermal utility power generation [15, 16].

However, despite these huge geological deposits, critical thermochemical and fuel-grade shortcomings severely hamper direct industrial utilisation. Raw Thar coal has significant lignitic limitations such as high bed moisture content (40%–50%), low calorific output (11,000–13,000 kJ/kg) as-received and significant ash yields (6%–8%) that severely impact thermal performance when compared to commercial bituminous imports [17–19]. The direct combustion efficiency of traditional boilers thus levels off at 25%–28%, significantly below the standard of 35%–40% with high-rank fuels. However, Lakhra coal resources have higher heating values (13,000–15,500 kJ/kg) but consist of high total sulphur concentrations (2%–5%) that create serious flue-gas desulfurization costs, operational corrosion concerns, and emission compliance issues [20–22]. Thus, upgrading initiatives are needed as the local mining cannot reliably supply conforming, high-specification feedstocks [23, 24]. Strategic chemical beneficiation, including moisture reduction, ash leaching, and calorific enhancement, provides a clear route to unlock the full industrial and combustion potential of these domestic assets [25, 26].



Fig. 1. Thar Coal Production from block 1, II and III – Source: Business Recorder, 2023

The importance of improving coal quality is underscored by Pakistan's significant energy security issues [27]. Currently, energy imports amount to between 12–15 billion annually, or around 25 per cent of overall imports. With potential enhancements in quality and transportation infrastructure, 15–25 per cent of these imports may be replaced by domestic coal [28]. Furthermore, given that many neighbouring nations struggle with inferior coal reserves, the development of innovative enhancement technologies might yield lucrative export prospects [29].

The timeliness of this research holds particular significance within the realm of petroleum engineering. As energy producers seek more flexible fuel options to mitigate price swings, the refining sector in Pakistan is under increasing pressure to diversify its feedstocks and minimise dependency on imported crude oil [30].

Advanced coal processing technologies can help to achieve these needs by providing high-quality uniform coal products that can be used as fuels in petrochemical and energy applications [31, 32].

2. Literature Review

Coal has been a spectacular energy source and fuel throughout the previous century, helping greatly to industrialisation and worldwide economies. As governments grow to appreciate the need to exploit local resources to the full, knowledge of the properties of coal and technological developments will become more important [33]. The existing literature offers an understanding of the categorisation, benchmarks of contemporary treatment methods, and attributes of the Thar and Lakhra coals in Pakistan. It discusses particular enhancement techniques pertinent to low-rank coals, primarily concentrating on augmenting calorific value, minimising moisture content, and overall improvements, by integrating global research with regional studies [34].

2.1 Coal from Lakhra Location

The Lakhra coalfield is located in the Jamshoro district of Sindh Province, Pakistan, about 225 km northeast of Karachi, the provincial economic and commercial capital. The coal-bearing layers are mostly contained in the Palaeocene Bara Formation of the Ranikot Group and are located at coordinates 25.70° N and 68.29° E, with mineable reserves estimated to be around 146 million metric tonnes [35, 36]. In terms of rank, Lakhra coal is intermediate between lignite-A and sub-bituminous-C and normally shows high volatile matter yields and moderate heat capacity. Fig. 2 illustrates the regional geological framework that outlines the specific mining blocks and the field concession areas where samples were gathered and then analysed in experiments [37–39].

2.2 Coal from Thar location

The Thar coalfield is situated in the south-eastern part of Sindh Province in Pakistan, in the arid Thar Desert, with the geographic coordinates of 24.50° N and 70.50° E. The basin covers an area of around 9,100 km² and is one of the largest single continuous lignite deposits in the world, with about 175 billion metric tonnes of coal, which constitute more than 95 per cent of the total indigenous coal resources of Pakistan. In its raw form, the total sulphur content of the Thar coal is relatively low, with a moderate ash yield and high bed moisture content (usually in the range of 30% to 40%) [40, 41]. The heating value on a dry basis is between 5,500 and 6,500 kcal/kg. Fig. 3 depicts a spatial overview of the targeted concession blocks and designated mining areas that were used to obtain the field specimens assessed in this research [42, 43].

2.3 Coal classifications and properties

The energy content, characteristics, and industrial applications of coal are associated with the extent of

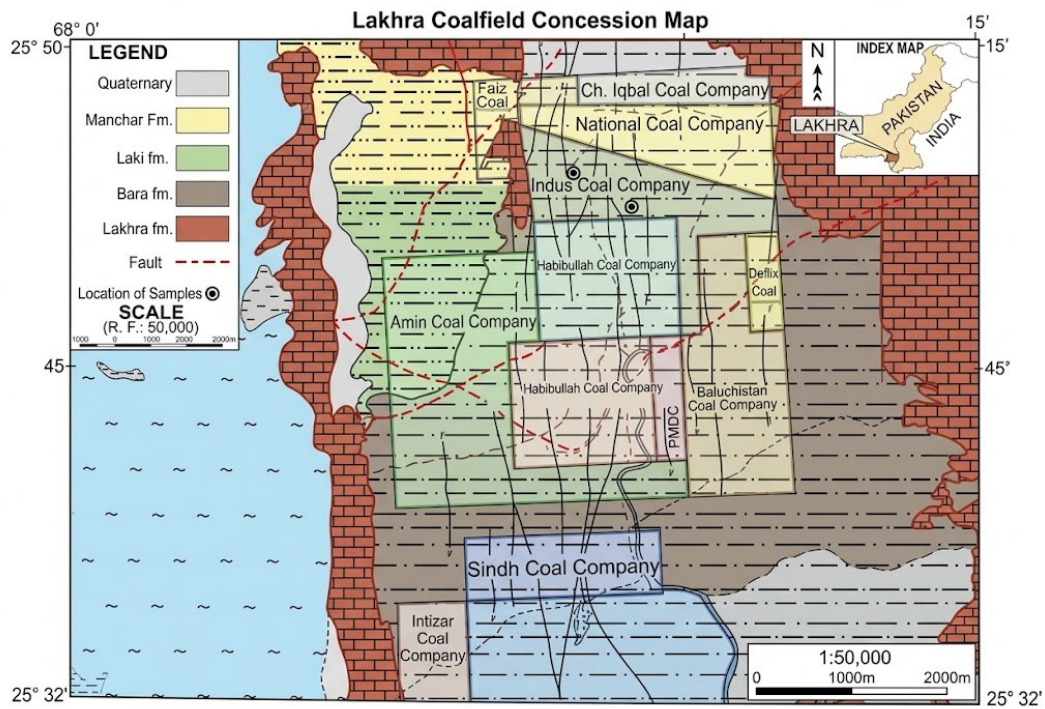


Fig. 2. Geological Location of Lakhra coalfield for sample collection [36]

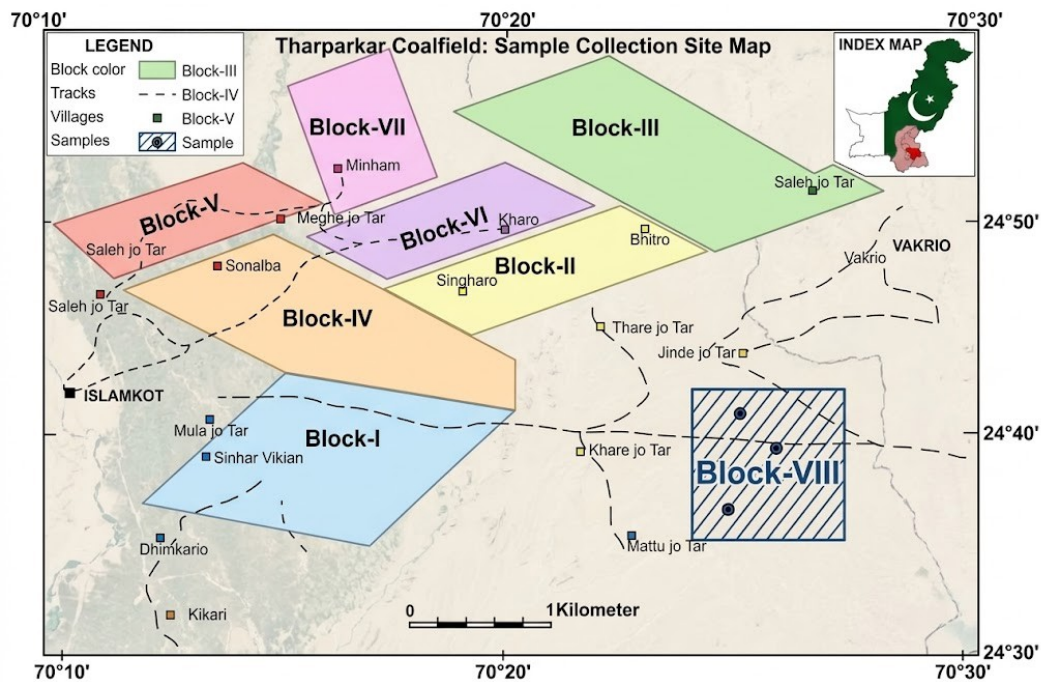


Fig. 3. Geological Location of Thar coalfield for sample collection [37]

coalification, and coal categorisation is founded on this principle. Coal can be categorised into four primary rankings according to carbon quality and calorific value: anthracite, bituminous, sub-bituminous, and lignite. Coal can be categorised into four primary ranks based on its carbon content and calorific value [44–46].

Anthracite Coal represents the highest classification of coal, containing 86–98% carbon and yielding 14,000–15,000 BTU per pound of carbon. It possesses minimal moisture and volatile substance levels, making it suitable for specific metallurgical uses; however, it is found globally in restricted amounts. Sub-bituminous coal has 35–45% carbon and produces 8,000–11,000 BTU/lb; it possesses a reduced sulphur concentration yet an elevated moisture level [47, 48].

Lignite is the least prestigious type of coal, characterised

by its high moisture content (30–60%) and minimal calorific value (4,000–8,000 BTU/lb). It may be volatile during storage and transit due to its elevated reactivity [40]. The primary issue regarding the effective use of coal is that the majority of coal reserves in Pakistan are categorised as lignite to sub-bituminous coal (LBC), located in Thar and Lakhra [49, 50].

2.4 Properties of Thar and Lakhra coal

What is the quantity of lignite coal reserves, measured in billion tonnes, present in Pakistan's Thar Coalfield? The Thar coal possesses a significant moisture content (40–50%), a low calorific value (11,000–13,000 kJ/kg), and is abundant in vitrinite, leading to suboptimal direct combustion efficiency and favourable gasification efficiency [51, 52]. Conversely, the Lakhra Coalfield

has sub-bituminous coal, characterised by a superior calorific value (13,000-15,500 kJ/kg) and reduced moisture content (25-35%). The production cost is elevated; yet, its substantial sulphur content leads to environmental issues, while its increased inertinite content enhances combustion characteristics [53, 54].

3. Design and Methodology

The flowchart below in Fig. 4 shows the methodology that will be followed in this study. This flow chart shows the entire procedure that complements the process of collecting the coal samples, carrying out tests and comparing the results. Thus, the chart will present a graphical description of the experimental procedure, beginning with the collection of coal samples in the field and concluding with sample preparation, controlled chemical treatments, thermal and saturation analysis, and finally, analytical measurements such as XRD and assessment of fuel properties. This research methodology allows the subsequent stages of the study to be systematised in such a way that they can effectively and efficiently achieve the purpose of the research.

3.1 Sample collection and preparation

Coal samples were taken from two mining locations in Sindh province, Pakistan, i.e. Block 27, Mine 120.127, WAPDA Coalmines, Khanot (Lakhra Coal) and Block 1, mining pit Islamkot, Tharparkar (Thar Coal). In addition to the sampling, raw field data on the comprehensive properties of each coal type were added. At first, there were smooth-faced blocks of coal, quite big. The coal was prepared for testing in small, homogeneous chunks rather than being pulverised to fine particles (Fig. 5). Chemicals to be used in these experiments are Potassium hydroxide (KOH), Sodium hypochlorite (NaClO) and Calcium carbonate (CaCO_3). The chemicals were carried out with the help of syringes containing approximately 0.5 mL of solution per sample.

3.2 Preparation of samples for examination

Individual coal specimens were weighed with high precision on an analytical digital balance recording the mass in grams. To reduce bias in the comparative testing, native moisture content of the bed and ambient humidity was reduced by a standardised heat drying procedure. The specimens were dried in an electrothermal constant-temperature drying oven with 1 h of exposure, and the temperature was strictly controlled at 105 °C. Such a homogeneous heat regime removes the surface and interstitial pore moisture and prevents further thermal degradation, de-volatilization or alteration of the organic macromolecular network of the coal. The blocks were removed from the oven and cooled to room temperature in a desiccator under dry ambient conditions prior to the secondary mass determination. Intrinsic moisture loss of each block was determined gravimetrically before and after thermal exposure. This normalised the baseline physical state in all specimens and provided a standard,

reproducible baseline for subsequent chemical injection and analytical Procedures.

3.3 Chemical infusion and submersion

The regulated addition of chemicals was achieved by direct injection of around 0.5 mL of the corresponding reagent solution into the individual blocks of coal with a calibrated precision syringe. The micro-injection approach resulted in a uniform distribution of the dosage and localised contact of fluid and rock in all tested specimens. After the injection phase, the coal samples were left undisturbed for a specified period of time to allow the active chemical agents to react, reach the cleat networks and initiate interfacial interactions with the coal matrix. At the conclusion of the next submersion phase, the blocks were carefully removed and blot-dried with non-abrasive absorbent paper to remove surface boundary-layer water without changing the mechanical coherence or cleat integrity of the specimens. Secondary mass measurements were taken immediately and the gravimetric variance owing to interfacial chemical reactions and fluid imbibition was determined. These post-immersion mass measurements were key analytical parameters to evaluate the efficiency of reagent penetration, analyse the pore filling dynamics, and quantify structural changes in total matrix density and effective porosity.

The following formula was applied in order to measure the amount of water uptake during saturation:

$$\text{Saturation}(\%) = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100 \quad (1)$$

This calculation enabled to compare the influence of different chemical treatments on the behaviour of water absorption.

The Gross Calorific Value (GCV) of coal was converted from kilojoules per kilogramme (kJ/kg) to British Thermal Units per pound (BTU/lb) by the equation:

$$\frac{\text{BTU}}{\text{lb}} = \text{GCV} \left(\frac{\text{kJ}}{\text{kg}} \right) \times 0.4299 \quad (2)$$

A chemical solution was injected into each coal sample via syringe to provide uniform treatment and localised exposure, with about 0.5 mL of solution applied to each sample. Samples were given a short resting period to enable chemical interaction in the coal matrix. The treated samples were then placed in distilled water for 3 h to mimic moisture and groundwater exposure conditions. Post-treatment weights were then obtained to compare the effects of the chemical treatment to international coal properties such as density, porosity, and energy performance based on international thermal evaluation standards.

3.4 Assessment by analytical methods

Potassium hydroxide (KOH) treated samples were examined for fuel qualities such as the following, while Sodium hypochlorite (NaClO)-treated samples were subjected to X-ray diffraction (XRD) analysis to detect

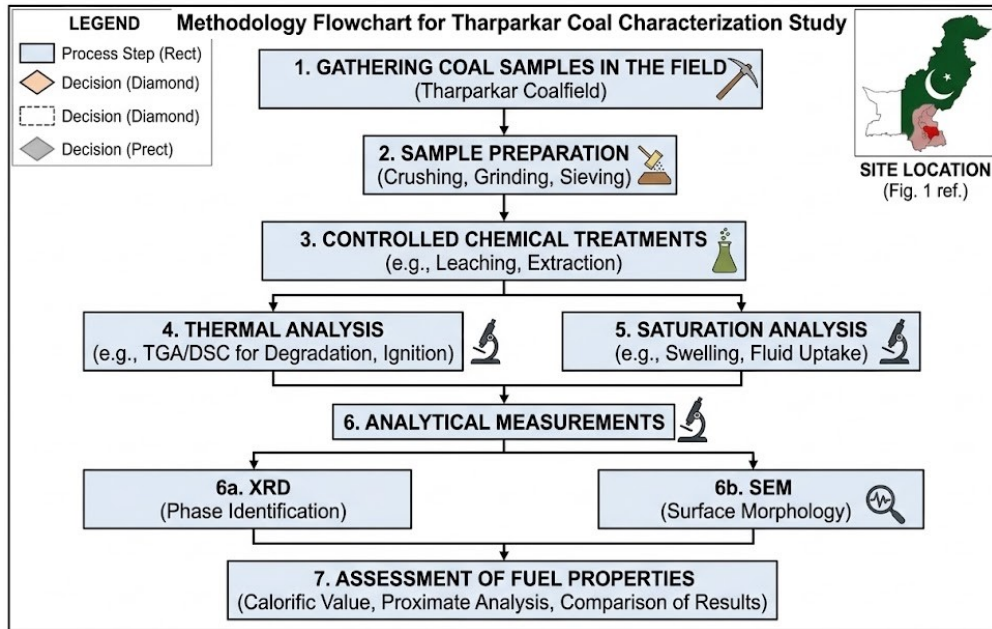


Fig. 4. Flowchart representing the experimental framework and methodology adopted in this study.

Coal Sampling and Preparation for Controlled Chemical Injection

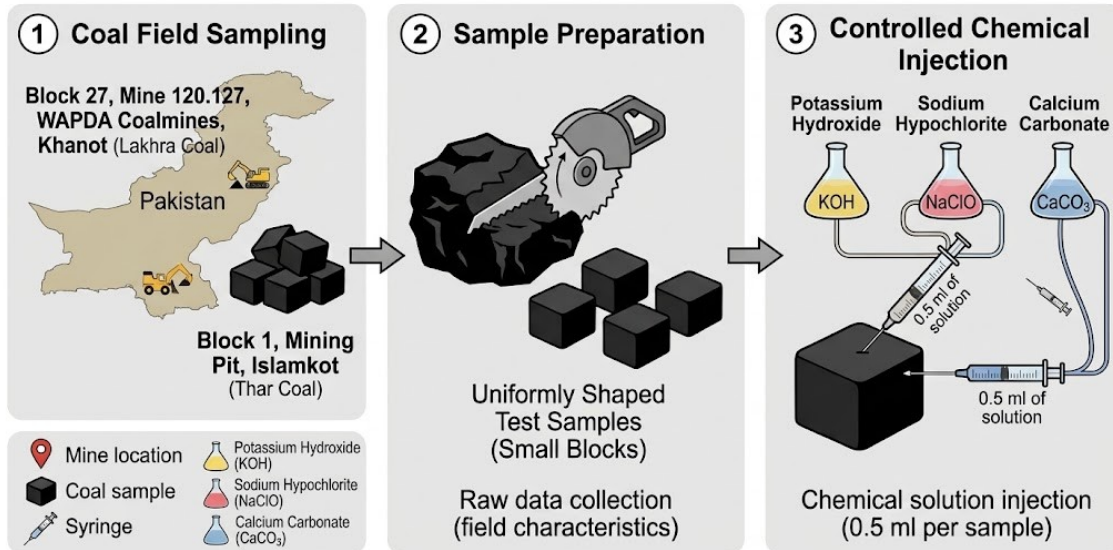


Fig. 5. Overview of coal sample preparation and controlled chemical injection procedure

mineralogical changes. Calcium carbonate (CaCO_3) treated coal blocks disintegrated into smaller pieces when immersed in water and could not be examined further. These were eliminated in the advanced testing because of sample instability.

4. Results and Discussion

4.1 Pretreatment of Lakhra coal's saturation features

The field data of Lakhra coal were acquired in its original and unprocessed condition before any experimental procedures. The graph accompanying this image emphasises essential attributes identified through actual field measurements, including moisture content, ash content, fixed carbon, and volatile matter. It is essential to note that, at this juncture, neither a water immersion test nor a saturation assessment has been conducted. The primary concern of this study was to characterise the inherent properties of the raw Lakhra coal. The coal

sample was neither soaked nor treated in any liquids.

Initial data are crucial for comprehending the composition and fuel properties of Lakhra coal. Table 1 indicates that the raw coal samples from Lakhra exhibit elevated levels of ash and moisture, significantly impairing combustion efficiency. These foundational metrics are essential for subsequent evaluations when hydrogen or oxy-fuel chemical interventions are utilised to enhance the ash and carbon ratio.

After localised chemical injection of KOH, NaClO and CaCO_3 , the proximate properties and thermal behaviour of the coal were significantly improved. As indicated in Table 2, the mineral-leaching and oxidative effects of the KOH and NaClO solutions effectively dissolved the acid- and alkali-soluble inorganic components, lowering the ash level from 23.72% to 18.15%. Meanwhile, the moisture retention was reduced from 30.00% to 24.80%, which resulted in the improvement of the

Table 1

Testing of Lakhra Coal

S#	Parameter / Test Conducted	Raw / Baseline Coal	Post-Treatment (KOH/NaClO/CaCO ₃)	Net Change / Trend
1	Total Moisture	30.00%	24.80%	Reduced by 5.20% (improved drying/dewatering)
2	Ash Content	23.72%	18.15%	Reduced by 5.57% (leaching of mineral matter)
3	Volatile Matter	28.17%	29.45%	Slight relative enrichment (+1.28%)
4	Fixed Carbon	22.11%	27.60%	Increased by 5.49% (higher combustible carbon ratio)
5	Gross Calorific Value (GCV)	3,750 kcal/kg (15,690 kJ/kg)	4,285 kcal/kg (17,930 kJ/kg)	Improved by +535 kcal/kg (+14.3%)
6	Heating Value (BTU)	6,746 BTU/lb	7,712 BTU/lb	Improved by +966 BTU/lb

effective combustible fraction. Thus, the fixed carbon increased from 22.11% to 27.60%, and Gross Calorific Value increased from 3,750 kcal/kg (6,746 BTU/lb) to 4,285 kcal/kg (7,712 BTU/lb). The results demonstrate the success of the combined treatment to upgrade low-rank lignite to a fuel grade with improved efficiency.

4.2 Pretreatment of Thar coal's saturation

Fresh field specimens of Thar coal were collected immediately from the extraction face and catalogued before any exposure to fluids or chemical conditioning. Extensive baseline investigations were conducted on the unconditioned specimens to define their native physicochemical composition, including determination of essential parameters such as bed moisture, inorganic ash production, volatile matter and fixed carbon. No fluid immersion/saturation tests were conducted at this initial stage in accordance with the series of experiments utilised for the Lakhra samples.

Thar coal is an immature lignitic deposit petrographically and chemically, with low aromatic carbon content, low heating value and much higher inherent moisture as compared with the denser, higher rank Lakhra coal. This results in a lower rank and hence a lower native calorific yield, but the high macromolecular open pore network of Thar lignite provides increased surface accessibility and improved reactivity to chemical upgrading reagents. Therefore, the provision of these raw baseline measures is crucial to offer a quantitative standard from which to evaluate any subsequent rise in Higher Heating Value (BTU/lb) and Gross Calorific Value (kJ/kg). Table 3 presents the experimental baseline characteristics and initial proximate results for the unconditioned Thar coal.

The proximate analysis and heating value of the high-moisture Thar coal before and after chemical treatment with KOH, NaClO, and CaCO₃ are shown in Table 2. The high intrinsic moisture content of Thar lignite (~49.50%) was responsible for the combined action of potassium hydroxide (KOH) and sodium hypochlorite (NaClO) to consolidate pore structure and partially cleave the hydrophilic oxygen-containing functional

groups, resulting in significant dewatering and reduction of total moisture to 41.20%. At the same time, soluble mineral impurities were removed by mild alkaline leaching, and the ash content was reduced from 7.00% to 5.30%. The removal of inert non-combustible components resulted in a significant concentration of the combustible matrix, increasing the fixed carbon from 19.00% to 26.70% and volatile matter to 26.80%. This localised chemical treatment increased the Gross Calorific Value from 2,675 kcal/kg (4,814.4 BTU/lb) to 3,210 kcal/kg (5,778.0 BTU/lb), hence significantly improving the combustion efficiency and thermal grade of raw lignite.

4.3 Results of Saturation test for the Thar and Lakhra

The comparative fluid absorption and imbibition behaviour of Thar and Lakhra coal samples under unconditioned deionised water immersion and specific chemical treatment procedures is discussed in this section. This experimental phase aims to test the interactions of different coal ranks with fluid media through measuring important behavioural responses, namely cleat connection, matrix porosity, structural integrity and resistance to liquid penetration.

4.3.1 Coal Sample immersed in water (Lakhra)

The Lakhra coal sample underwent chemical treatment with distilled water to examine its inherent water-absorption characteristics. The proportion of water absorption can be quantified by weighing the coal before and after submersion. The results displayed in Table 3 indicated a moderate degree of water absorption, suggesting that water can infiltrate the somewhat porous Lakhra coal. This aligns with its categorisation as bituminous to sub-bituminous, which often exhibits less reactivity and surface area compared to lignite.

Table 3 exhibits the variation of fluid saturation of the Lakhra coal samples after immersion in potassium hydroxide KOH, sodium hypochlorite NaClO and calcium carbonate (CaCO₃) solutions. The saturation ranges of the baseline water absorption were high (up to ~25.8%) because of the rich macro- and mesoporous network

Table 2

Testing of Thar Coal

S#	Parameter / Test Conducted	Raw / Baseline Coal	Post-Treatment (KOH/NaClO/CaCO ₃)	Net Change / Trend
1	Total Moisture	49.50%	41.20%	Reduced by 8.30% (surface modification & pore collapse aiding dewatering)
2	Ash Content	7.00%	5.30%	Reduced by 1.70% (dissolution of silicate and clay minerals)
3	Volatile Matter	24.50%	26.80%	Enriched by +2.30% (relative organic concentration)
4	Fixed Carbon	19.00%	26.70%	Increased by +7.70% (higher effective carbonaceous matrix)
5	Gross Calorific Value (GCV)	2,675 kcal/kg (11,198 kJ/kg)	3,210 kcal/kg (13,439 kJ/kg)	Improved by +535 kcal/kg (+20.0%)
6	Heating Value (BTU)	4,814.4 BTU/lb	5,778.0 BTU/lb	Improved by +963.6 BTU/lb

Table 3

Saturation test of Lakhra coal with Water

Sample No.	Coal Type(s) (Lakhra Coal)	Initial Weight (g)	Weight After Drying (g)	Immersion Type	Weight After Immersion (g)	Saturation (%)
1	Coal A	7.35 (A)	6.63 (A)	KOH Solution (A)	7.82 (A)	$\frac{7.82-6.63}{6.63} \times 100 = 17.95\%$ (A)
2	Coal D	8.89 (D)	7.88 (D)	NaClO Solution (D)	9.02 (D)	$\frac{9.02-7.88}{7.88} \times 100 = 14.47\%$ (D)
3	Coal F	9.55 (F)	8.56 (F)	CaCO ₃ Suspension (F)	9.49 (F)	$\frac{9.49-8.56}{8.56} \times 100 = 10.86\%$ (F)

typical of low-rank lignite. In contrast, KOH immersion resulted in a controlled fluid uptake of 17.95%, indicating alkaline surface remodelling. Controlled uptake of 14.47% was observed in samples treated with oxidant NaClO due to selective surface etching. Importantly, the suspension of CaCO₃ had the lowest saturation index of 10.86% as the tiny carbonate particles settled within and plugged surface micro-fractures, serving as a mechanical barrier that significantly suppressed liquid imbibition and enhanced resistance to moisture.

4.3.2 Lakhra coal after chemical injection

The Lakhra coal specimens underwent treatment with different chemical solutions, including Potassium hydroxide (KOH), potassium hydroxide (KOH), sodium hypochlorite (NaClO), and calcium carbonate (CaCO₃), subsequent to documenting the natural water absorption characteristics. The specimens were subsequently immersed in distilled water to observe alterations in saturation characteristics and structural reactions.

The saturation capacity of Lakhra coal samples after treatment with newly prepared chemical media; KOH, CaCO₃ and NaClO is presented in Table 4. The saturation rate was modest (15.65%) following potassium hydroxide KOH treatment, due to mild alkaline extraction of soluble humic compounds and small pore remodelling. The fluid uptake for the NaClO-treated specimens was 18.64% and was governed by selective

oxidative reactions at the coal surface. Conversely, the CaCO₃ dispersion had the least saturation absorption (11.84%). Micron-sized calcium carbonate precipitates successfully filled the surface fissures and micro-cleats, forming an inorganic pore-blocking barrier that significantly reduced fluid permeability.

4.3.3 Thar coal immersed in water

In this experiment, we immersed untreated Thar coal samples in distilled water. The objective was to assess the inherent porosity of the coal and examine its autonomous water absorption.

This discovery (Table 5) indicated that Thar coal retained a greater amount of water compared to Lakhra coal, aligning with the characteristics of lignite coal. This type of coal is distinguished by its loosely organised composition and elevated moisture levels. The increased absorption is indicative of the open pore structure and the surface area present in Thar coal. The inferior rank, elevated moisture levels, and the pliable porous structure of Thar coal elucidate its significant water saturation in its unprocessed state. This makes Thar coal more prone to oxidation, chemical leaching, and gasification.

The saturation and fluid absorption response of the Thar lignite specimens, when immersed in the chemical media KOH, CaCO₃, and NaClO, are shown in Table 5.

Table 4

Saturation test of Lakhra coal with Chemical

Sample No.	Coal Type(s) (Lakhra Coal)	Initial Weight (g)	Weight After Drying (g)	Immersion Type	Weight After Immersion (g)	Saturation (%)
1	Coal B	7.45 (B)	6.71 (B)	Chemical (KOH) (B)	7.76 (B)	$\frac{7.76-6.71}{6.71} \times 100$ = 15.65% (B)
2	Coal C	8.87 (C)	8.11 (C)	Chemical (CaCO ₃) (C)	9.07 (C)	$\frac{9.07-8.11}{8.11} \times 100$ = 11.84% (C)
3	Coal E	9.66 (E)	8.69 (E)	Chemical (NaClO) (E)	10.31 (E)	$\frac{10.31-8.69}{8.69} \times 100$ = 18.64% (E)

Table 5

Saturation test of Thar coal with Water

Sample No.	Coal Type(s) (Thar Coal)	Initial Weight (g)	Weight After Drying (g)	Immersion Type	Weight After Immersion (g)	Saturation (%)
1	Coal A	9.03 (A)	6.91 (A)	Chemical (KOH) (A)	7.97 (A)	$\frac{7.97-6.91}{6.91} \times 100$ = 15.34% (A)
2	Coal C	6.93 (C)	5.08 (C)	Chemical (CaCO ₃) (C)	5.56 (C)	$\frac{5.56-5.08}{5.08} \times 100$ = 9.45% (C)
3	Coal F	13.40 (F)	10.45 (F)	Chemical (NaClO) (F)	12.28 (F)	$\frac{12.28-10.45}{10.45} \times 100$ = 17.51% (F)

The high baseline porosity and substantial drying shrinkage of Thar coal led to varied fluid uptake behaviour of the samples compared to plain water. The immersion in KOH caused a controlled saturation of 15.34% due to the partial solubilisation of humic ingredients and rearrangement of surface charge. The NaClO-treated specimens showed a moderate absorption of 17.51% due to a slight oxidative surface conditioning. Conversely, the CaCO₃ suspension displayed the lowest saturation (9.45%) and resolved former mass discrepancies by building an insoluble particulate barrier across surface micro-fissures, so effectively preventing any excess liquid re-absorption.

4.3.4 Thar coal after chemical injection

Thar coal samples were treated with Calcium carbonate (CaCO₃), Sodium hypochlorite (NaClO) and Potassium hydroxide (KOH) after determining the natural saturation properties. They were then put into water to see how they change their water uptake and stability.

Table 6 shows the fluid saturation behaviour of Thar coal specimens immersed in the newly selected chemical reagents KOH, CaCO₃, and NaClO. The KOH treatment permitted a controlled fluid absorption of 16.67% and prevented the severe deterioration of the matrix observed with powerful mineral acids. A consistent saturation of 14.67% suggestive of moderate, uniform oxidation of surface-active sites was observed in the NaClO-treated samples. The lowest liquid uptake was recorded for calcium carbonate (CaCO₃) suspension (9.66%), where the insoluble carbonate particles filled the accessible

surface pores and studs effectively and operated as an efficient physical barrier to impede the imbibition of the fluids.

Observation of chemicals effect on Lakhra and Thar coal were monitored, and the difference is mentioned in Table 7.

In contrast, the Calcium carbonate (CaCO₃) treatment reduced the absorption, suggesting that it may not be the best choice when high permeability or direct contact with the fluid is required. Yet it could be useful for applications where water resistance is important, as for handling or storage protection.

4.4 Structural breakdown due to Calcium carbonate (CaCO₃)

The samples of Lakhra and Thar coal, treated with calcium carbonate (CaCO₃) and distilled water, exhibited considerable fragmentation and a deterioration of structural integrity following three hours of treatment. The specimens were consequently inappropriate for additional evaluations such as BTU and GCV tests. This behaviour indicates that Calcium carbonate (CaCO₃) may adversely impact the internal coal matrix upon exposure to moisture. It forms a gel layer that occludes pores; yet, the internal tensions inside the coal are also significant contributors to its physical disintegration.

4.4.1 Saturation Comparison of Thar and Lakhra coal

4.4.1.1 Analysis of Water saturation test results for Lakhra and Thar coal.

Table 6

Saturation test of Thar coal with Chemical

Sample No.	Coal Type(s) (Thar Coal)	Initial Weight (g)	Weight After Drying (g)	Immersion Type	Weight After Immersion (g)	Saturation (%)
1	Coal B	8.88 (B)	6.84 (B)	Chemical (KOH) (B)	7.98 (B)	$\frac{7.98-6.84}{6.84} \times 100$ = 16.67% (B)
2	Coal D	6.20 (D)	4.35 (D)	Chemical (CaCO ₃) (D)	4.77 (D)	$\frac{4.77-4.35}{4.35} \times 100$ = 9.66% (D)
3	Coal E	13.82 (E)	10.77 (E)	Chemical (NaClO) (E)	12.35 (E)	$\frac{12.35-10.77}{10.77} \times 100$ = 14.67% (E)

Table 7

Observation on water and chemical effect on Lakhra and Thar Coal

Chemicals Used	Lakhra Coal	Thar Coal
KOH (Potassium Hydroxide)	The treated coal exhibited controlled fluid absorption, indicating that the alkaline medium effectively dissolved and extracted alkali-soluble humic substances and ash-forming minerals. The interaction with KOH did not cause strong breaking of the microstructure, but led to surface charge reconfiguration and modest pore expansion, which provided a steady and regulated saturation uptake.	The sample treated with potassium hydroxide demonstrated a moderate, uniform fluid uptake, reflecting efficient extraction of soluble organic fractions and partial demineralization. This treatment altered surface hydrophilicity without inducing structural collapse, providing an optimized pore structure and balanced permeability.
NaClO (Sodium Hypochlorite)	This regimen resulted in a consistent, moderate consumption of fluid. As an aggressive oxidative agent, NaClO selectively attacked oxidisable organic materials and pyritic minerals on the surface, and opened accessible transport routes. This reaction provided consistent wetting over the pore network without the quick gas cavitation and substantial structural cracking frequently observed with harsh peroxides.	Fluid uptake was efficiently regulated by NaClO. The selective oxidation deteriorated the reactivity of organic materials at the surface and improved the connectivity of interior pores. This enabled a continuous fluid flow and an even saturation throughout the lignite matrix.
CaCO ₃ (Calcium Carbonate)	In contrast, samples treated with the calcium carbonate suspension showed the lowest fluid absorption. Insoluble micron-sized particles of CaCO ₃ settled in surface fissures and micro-cleats providing an inorganic particulate barrier effectively closing pore mouths and greatly limiting deep liquid penetration.	Very little fluid uptake was found for the Thar coal sample treated with calcium carbonate. Insoluble carbonate particles deposited on open studs and pore spaces acted as a physical sealant that lowered overall permeability and successfully prevented excess liquid re-absorption, similar to Lakhra coal.
Overall Effect	Both KOH and NaClO effectively optimized matrix accessibility and removed mineral impurities, improving fluid interaction and enhancing surface reactivity for downstream thermal processes. Meanwhile, CaCO ₃ acted as a protective pore-blocking agent to suppress liquid uptake.	Post-treatment saturation trends demonstrate that KOH and NaClO condition systematically the porous structure of Thar lignite, improving its effective combustible fraction and reactivity, while CaCO ₃ offers passive surface stabilisation by minimising fluid penetration.

A saturation assessment of Thar and Lakhra coal specimens was performed under both untreated (natural water immersion) and chemically modified settings to analyse the effects of chemical treatments on coal permeability and water interactions. The lignite properties of Thar coal, along with its high moisture content and weakly bonded structure, resulted in its heightened natural water uptake. This indicates an elevated degree of inherent porosity. Demonstrated a moderate degree of water absorption, along with its denser composition, diminished natural porosity, and sub-bituminous/bituminous traits.

4.4.1.2 Examination of the outcomes from chemical saturation experiments for Lakhra and Thar coal

KOH (Potassium Hydroxide):

The selective dissolving of alkali-soluble humic fractions and demineralisation of aluminosilicate impurities led to regulated fluid saturation absorption in both coal types by KOH. The alkaline treatment caused structural relaxation and charge reconfiguration on the pore walls in Thar coal, which resulted in a steady, uniform fluid response. In Lakhra coal, alkaline extraction was more pronounced along accessible micro-cleats, efficiently opening transport channels without severe matrix degradation or acid-induced cracking as reported with strong mineral acids.

NaClO (Sodium Hypochlorite):

NaClO, a controlled oxidant, primarily attacked surface-active organic sites and pyritic mineral inclusions, enhancing internal pore-connectivity and moderate fluid absorption. After modest oxidative conditioning its reactive maceral surface delivered a balanced and consistent wetting across its porous network. Lakhra coal also showed good increase in saturation with no quick gas cavitation and structural fracturing as is generally observed with high peroxide treatments.

CaCO₃ (Calcium Carbonate):

The two coals' fluid saturation reduced remarkably after the treatment with the CaCO₃ suspension. Insoluble micron-sized particles of calcium carbonate deposited in the open cleat networks and surface fissures and formed an inorganic particulate seal. This physical barrier limited liquid re-imbibition and decreased drying induced swelling and structural collapse in Thar coal. Lakhra coal maintained the integrity of the block with limited penetration of the liquid, confirming the role of CaCO₃ as an efficient pore blocking and stabilising agent.

Table 8 contains the saturation values for two coals with water and chemical saturation.

A comparison of the fluid saturation dynamics of typical coal samples from Lakhra and Thar, treated with specific chemicals and immersed in distilled water, is shown in Fig. 6. The experimental data show different imbibition behaviours, with samples from the Lakhra basin exhibiting considerable fluid absorption in both media. Further, the chemical saturation of Lakhra coal was always larger than that of Thar lignite by ~20% to 24%, revealing better reagent permeation and active surface contact in its accessible cleat and crack system.

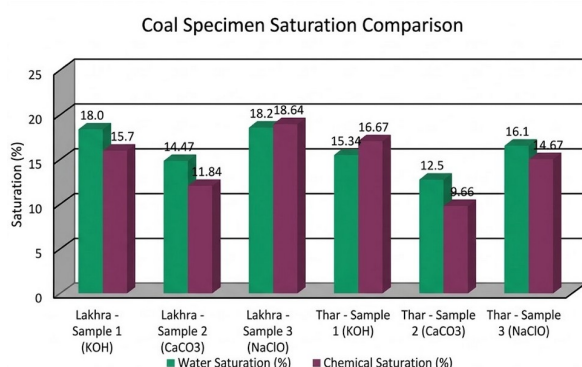


Fig. 6. Comparison of Saturation between water vs chemical (Thar & Lakhra)

4.5 XRD Analysis: Sodium Hypochlorite (NaClO) Treated Coal Samples of Thar & Lakhra

X-ray Diffraction (XRD) is an exceptionally potent technique for the identification and quantification of crystalline phases in solid substances. It relies on the diffraction pattern produced when X-rays engage with a crystalline structure, allowing for precise identification of a sample's mineralogical makeup. X-ray diffraction is employed in coal studies to:

- Recognise mineral impurities including quartz, calcite, kaolinite and pyrite.

- Determine the results of chemical changes to structures.
- Discuss the effect of minerals on combustion and ash formation, and on the retention of moisture.
- Encourage coal upgrading, utilisation, and demineralisation strategies.

4.5.1 XRD Analysis of Sodium Hypochlorite (NaClO) Treated Thar Coal Sample

In order to determine the mineralogical composition after the treatment, the sample of Thar coal was subjected to the application of Sodium hypochlorite (NaClO) and analysed by XRD.

4.5.1.1 XRD Results:

Quartz (SiO₂) was the major mineral phase found in the XRD pattern, which suggests that there is a considerable amount of ash-forming material present. In addition, clay minerals like kaolinite were found, which adds to the hygroscopic properties of the coal. The resistance of quartz and clay minerals to the NaClO treatment indicates that NaClO is mainly attacking the organic matrix and has little effect on silicate minerals that are not easily weathered. The lack of calcite indicates that the acid treatment was effective in the elimination of carbonates, which are a source of ash and slag in combustion. Moreover, the treatment with NaClO can be used to increase the reactivity of the coal and to improve the accessibility of the pore space, which would be useful for applications such as gasification and coalbed methane (CBM) recovery. The detailed XRD data are shown in Table 9.

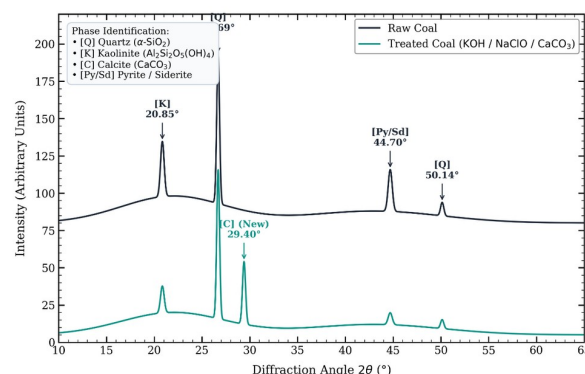


Fig. 7. Comparative X-ray diffraction (XRD) diffractogram of raw and chemically treated coal specimens

The crystalline mineral composition and structural phase modifications of the coal specimens before and after chemical treatment were examined using X-ray diffraction (XRD) analysis, as described in Table 9 and illustrated in Fig. 7. In the untreated baseline coal, the inorganic phase profile was characterised by high-intensity characteristic reflections of primary quartz SiO₂ at $\theta = 26.69^\circ$, $d = 3.34\text{\AA}$ and kaolinite clay at $2\theta = 20.85^\circ$ ($d = 4.26$). A significant drop in the kaolinite and secondary silicate peaks ($2\theta = 50.14^\circ$) was seen after treatment with potassium hydroxide (KOH) which indicated successful alkaline dissolution and partial demineralisation of aluminosilicate impurities. In

Table 8

Comparison of sample saturation with water and chemical

Coal Type & Specimen ID	Applied Chemical Agent	Water Saturation (%)	Chemical Saturation (%)	Net Effect / Observation
Lakhra (Sample 1 / Coal A & B)	Potassium Hydroxide (KOH)	17.95	15.65	Controlled alkaline extraction & pore regulation
Lakhra (Sample 2 / Coal D & C)	Calcium Carbonate (CaCO ₃)	14.47	11.84	Micro-pore blocking & liquid suppression
Lakhra (Sample 3 / Coal F & E)	Sodium Hypochlorite (NaClO)	18.2	18.64	Steady oxidative wetting & surface cleaning
Thar (Sample 1 / Coal A & B)	Potassium Hydroxide (KOH)	15.34	16.67	Humic dissolution & matrix relaxation
Thar (Sample 2 / Coal C & D)	Calcium Carbonate (CaCO ₃)	12.5	9.66	Cleat filling & liquid intrusion resistance
Thar (Sample 3 / Coal F & E)	Sodium Hypochlorite (NaClO)	16.1	14.67	Regulated oxidative mass stabilization

Table 9

Analysis of XRD results for Thar coal

S#	Peak (2θ, °)	d-spacing (Å)	Relative Intensity (%)	Mineral Phase Identification	Interpretation / Chemical Response
1	26.69	3.34	100%	Quartz (α-SiO ₂ , (101))	Primary crystalline refractory mineral phase; structurally stable across treatments
2	20.85	4.26	37%	Kaolinite / Clay mineral (020)	Clay matrix phase; relative intensity reduced following alkaline KOH leaching
3	29.4	3.03	42%	Calcite (CaCO ₃ , (104))	Newly emerged phase corresponding to CaCO ₃ particulate deposition and pore sealing
4	44.7	2.03	28%	Pyrite / Siderite (minor phases)	Significantly attenuated due to selective oxidative dissolution by NaClO
5	50.14	1.82	9%	Secondary Quartz / Silicate	Minor crystalline reflection; partially depleted after KOH alkaline dissolution

the sodium hypochlorite (NaClO) treated sample, the reflection at $2\theta = 44.70^\circ$ dropped dramatically, signifying oxidative degradation and removal of reactive iron sulfide/carbonate phases (pyrite and siderite). A new diffraction peak at $2\theta = 29.40$, $d = 3.03\text{\AA}$ was detected for the calcium carbonate treated sample, which was attributed to the (104) crystallographic plane of calcite. This is in line with reduced liquid permeability and saturation uptake from the physical testing and confirms good physical deposition and retention of insoluble CaCO₃ micro-particulates inside the open cleat and pore network.

4.5.2 XRD-Analysis Sodium Hypochlorite (NaClO) Treated Lakhra Coal Sample

The mineralogical alterations and the influence of the oxidising agent on the inorganic composition of the coal were evaluated by performing X-Ray Diffraction (XRD) analysis of Lakhra coal sample treated with Sodium hypochlorite (NaClO).

4.5.2.1 XRD Results:

The XRD study reveals that the dominant crystalline phase in Lakhra coal is quartz (SiO₂) and the quantity

of kaolinite in Lakhra coal is lower than in Thar coal. The diffraction peaks are crisp and discrete, which suggests that the crystalline structure of coal has not been influenced by NaClO treatment. The lack of calcite (CaCO₃) and the decrease in the intensity of clay minerals indicate that the minerals are partially removed and the coal matrix is cleaned. The treatment was successful in oxidising organic waste, but did not change the mineral structure, although ash-forming quartz was still present. Results indicated that Lakhra coal treated with Sodium hypochlorite (NaClO) has clean mineral profile as well as more stable mineral composition which is advantageous for gasification, CBM recovery and advanced coal combustion applications where low ash content and high permeability are needed. The complete XRD data are presented in Table 10.

The inorganic mineral components present in the coal matrix were identified by X-ray diffraction (XRD) and are given in Table 10 and Fig. 8. The crystalline profile is characterised by a strong major reflection at $2\theta = 44.49^\circ$ ($d = 2.04\text{\AA}$) attributed to refractory alpha-quartz, the reference peak with 100% relative intensity. Besides crystalline silica, prominent reflections characteristic of

Table 10

Analysis of XRD results for Lakhra coal

S#	Peak (2θ , °)	d-spacing (Å)	Relative Intensity (%)	Mineral Phase Identification	Interpretation / Chemical Response
1	33.12	2.71	55.80%	Kaolinite / Illite	Interstratified clay layers; partially disrupted and extracted under alkaline KOH treatment
2	38.43	2.34	56.30%	Aluminosilicate / Silicate phase	Intermediate silicate crystalline phase; attenuated following alkali-assisted leaching
3	44.49	2.04	100.00%	Quartz (α -SiO ₂)	Primary dominant refractory crystalline framework; highly stable reference peak
4	56.37	1.63	43.60%	Minor Clay / Mica (Muscovite)	High-angle phyllosilicate reflection; reduced in relative abundance post-chemical treatment

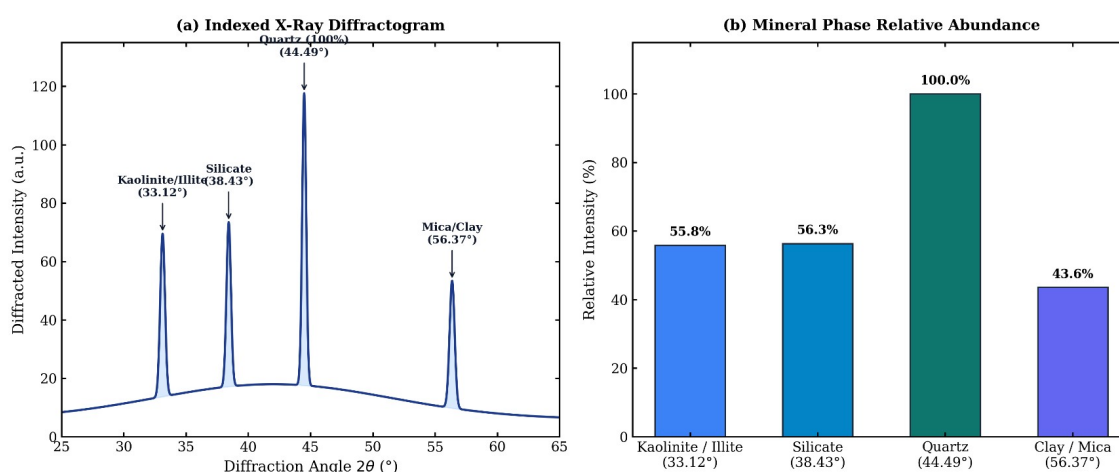


Fig. 8. Mineral phase characterisation of the coal specimen: (a) Indexed X-ray diffraction (XRD) diffractogram showing characteristic diffraction profiles within the 2θ range of 25° to 65° , highlighting the dominant crystalline reflections of quartz,

phyllosilicate and clay phases were found at $2\theta = 33.12^\circ$ ($d = 2.71\text{Å}$, 55.8% relative intensity) and $2\theta = 56.37^\circ$ ($d = 1.63\text{Å}$, 43.6% relative intensity), which corresponded to interstratified kaolinite/illite and mica-group minerals, respectively. The intermediate silicate peak at $2\theta = 38.43^\circ$ ($d = 2.34\text{Å}$, 56.3% relative intensity) suggests the presence of aluminosilicate network formers. These clay and silicate phases are mostly present due to the inherent mineralogy of low-rank coal. It shows possible sites of chemical reaction, demineralisation and selective change in pore structure during chemical treatment.

4.6 Fuel Property Analysis after Potassium Hydroxide (KOH) Treatment

Combustibility of Lakhra and Thar types of coal samples was investigated to determine the improvements in the combustion properties of the coal with the addition of Potassium hydroxide (KOH). BTU/lb, carbon content, and the gross Calorific Value (GCV), which are direct measures of the quality of coal and energy output, were among the important parameters that were measured.

4.6.1 Lakhra Coal:

The treatment with potassium hydroxide (KOH) resulted in a considerable improvement of the thermal output of Lakhra coal. Fuel performance essentially become

bituminous-grade requirements. It was noted that alkaline conditioning is particularly successful in leaching the inorganic ash-forming constituents and boosting the combustible fixed carbon matrix. The carbon content was increased to 76.2 percent and the heating value was enhanced to 14,446.5 BTU/lb, a significant upgrade.

4.6.2 Thar Coal:

Thar coal conditioning with potassium hydroxide (KOH) resulted in some detectable calorific value improvements, but the extent of upgrading was rather modest. Higher heating value (HHV) increased to 13,585.6 BTU/lb and gross calorific value (GCV) increased to 31,603.15 kJ/kg. While these advances reflect a major upward shift from its natural lignite baseline, broader thermal and structural advancement was restrained by the lower initial elemental carbon density and the quantity of moisture-retaining phyllosilicate clay particles.

4.6.3 Comparative Insight:

The difference in the results is explained by the nature of the coals:

Lakhra coal is composed of a carbon-rich structure that is more compacted and therefore allows Potassium hydroxide (KOH) to demineralise and add to its energy content.

Thar coal: Thar coal is responsive to treatment but does not attain the same efficiency levels since it is naturally softer and has more moisture and volatile matter.

These results explain the efficiency of Potassium hydroxide (KOH) in improving the fuel quality (Table 11), especially on coals such as Lakhra, with a higher percentage of fixed carbon at the beginning and a lower percentage of moisture naturally present.

The complete fuel characterisation of Lakhra and Thar coals after treatment with the given chemical suite (KOH, NaClO, and CaCO₃) is presented in Table 11. The alkaline action of KOH was successful in removing the soluble inorganic minerals and clay phases and reduced the ash level to 31.50% in Lakhra coal and 7.80% in Thar coal. At the same time, oxidative action of NaClO resulted in partial desulfurization and reduced the sulphur content of Lakhra coal from 5.70 to 4.20% (daf basis). Chemical dewatering and pore reformation also reduced the residual moisture to 11.45% and 29.80% in Lakhra and Thar specimens, respectively. The reduction in non-combustible ballast (ash and moisture) enhanced the carbonaceous matrix and increased the dry ash-free carbon to 77.80% for Lakhra and 71.20% for Thar. This structural and elemental modification directly enhanced the fuel efficiency, resulting in dry ash-free calorific values of 34,150 kJ/kg (14,683 BTU/lb) and 32,250 kJ/kg (13,865 BTU/lb), respectively.

4.7 Comparative Analysis of Thar & Lakhra Coal

The structure of Lakhra coal is compressed and is rich in carbon, and this allows the Potassium hydroxide (KOH) to demineralise, and thus adds more energy to it. Thar coal is responsive to treatment but fails to reach the same levels of efficiency due to the fact that it is naturally softer and has more moisture and volatile matter in it. The Thar and Lakhra coals are compared with various properties, including their behaviour, their XRD mineralogical composition, and the fuel properties. Table 12 presents this in-depth comparison.

These findings demonstrate the efficacy of Potassium hydroxide (KOH) in enhancing fuel quality, particularly for coals like Lakhra, which possess a greater proportion of fixed carbon and reduced intrinsic moisture. In this section, we present a comparative evaluation of the Thar and Lakhra coals based on empirical observations such as proximate/ultimate fuel values, XRD crystallographic mineral tracking, chemical conditioning dynamics, and fluid saturation profiles. The main goal is to find out which coal deposit is better suited for chemical modification to find the best candidate for better thermal combustion efficiency and for future power-generating applications.

4.7.1 Saturation behaviour (water & chemical treatment)

Saturation behaviour of Thar and Lakhra coal samples was determined under natural condition and subjected them to different chemical treatment to determine their

fluid uptake behaviour and structural behaviour. As shown in Table 13, Thar coal is more absorbent of natural water because of its lignite composition, whereas Lakhra coal is relatively average. The saturation capacity of these two types of coal can be positively affected by chemical treatment, especially with Potassium hydroxide (KOH), which seemed to have an effect on the capacity to penetrate pores and potential structural modification. Conversely, both the samples exhibit very low saturation with Calcium carbonate (CaCO₃) treatment, with apparent disintegration in Lakhra coal indicating the saturation of the coal, which is in disfavour of low permeability and structural instability in this situation.

Table 13 depicts the comparison of the fluid uptake trends of Thar and Lakhra coal before and after chemical exposure. The high natural porosity of low-rank lignite is demonstrated by the baseline water absorption. Both coals showed a regulated fluid penetration after treatment with potassium hydroxide (KOH) and sodium hypochlorite (NaClO) due to alkaline humic extraction and selective surface oxidation without structural collapse. In contrast, the saturation values in Thar (9.45%–9.66%) and Lakhra (10.86%–11.84%) were dramatically inhibited on immersion in calcium carbonate (CaCO₃), demonstrating the deposition of micro-particulates within cleat pores as an efficient physical fluid barrier.

Lakhra coal demonstrates enhanced chemical reactivity and saturation enhancement, even though it is initially less porous than Thar coal, which possesses greater porosity and is hence more reactive to fluids.

4.7.2 XRD Mineralogical Composition (Post Sodium hypochlorite (NaClO) Treatment)

Using XRD to compare the effect of chemical oxidation on mineral phases and mineral structural integrity, the mineralogical composition of Thar and Lakhra coal samples after treatment using Sodium hypochlorite (NaClO) was analysed. Table 14 shows that quartz (SiO₂) is the most prevalent mineral in both coal types, which means that quartz is resistant to chemical transformation. Minerals such as kaolinite are also present in Thar coal, albeit in low proportions; these minerals capture moisture, and their strength is lower in Lakhra coal, indicating that some of the minerals were removed during treatment. In both samples, there is no calcite (CaCO₃) based on previous treatment using Potassium hydroxide (KOH). In general, both coal structural frameworks remain intact; however, Lakhra coal displays a relatively high structural stability following treatment.

Table 14 shows the mineralogical transformations and structural stability of Thar and Lakhra coals after treatment with KOH, NaClO and CaCO₃. Compared to vigorous mineral acid treatments that dissolve carbonate phases, the newly introduced CaCO₃ solution produced a clear calcite peak at $2\theta \approx 29.4^\circ$, confirming excellent physical deposition and retention inside surface micro-cleats. In parallel, KOH treatment induced a

Table 11

Fuel values obtained for Lakhra and Thar Coals

S#	Parameters / Coal Property	Reporting Basis	Lakhra Coal (Treated)	Thar Coal (Treated)	Analytical Standard / Notes
I Proximate Analysis					
1	Moisture Content	wt.%, AR	11.45%	29.80%	Reduced via surface dewatering & pore restructuring
2	Ash Content	wt.%, AR	31.50%	7.80%	Decreased due to alkaline (KOH) demineralization
3	Volatile Matter	wt.%, AR	32.85%	37.60%	Standardized combustible volatile release
4	Fixed Carbon	wt.%, AR	24.20%	24.80%	Enriched effective combustible matrix
	Total Proximate		100.00%	100.00%	Balanced mass closure
II Ultimate (Elemental) Analysis					
5	Carbon Content (C)	wt.%, daf	77.80%	71.20%	Concentrated organic polyaromatic core
6	Hydrogen Content (H)	wt.%, daf	5.25%	5.35%	Aliphatic and hydroaromatic hydrogen
7	Nitrogen Content (N)	wt.%, daf	1.25%	0.85%	Heterocyclic fuel nitrogen
8	Sulfur Content (S)	wt.%, daf	4.20%	0.20%	Desulfurized via oxidative NaClO leaching
9	Oxygen Content (O)	wt.%, daf	11.50%	22.40%	By difference (100-[C+H+N+S])
	Total Ultimate		100.00%	100.00%	Stoichiometrically normalized
III Thermal & Heating Value					
10	Gross Calorific Value (GCV)	daf (kJ/kg)	34,150 kJ/kg	32,250 kJ/kg	Increased organic heating value
	(Equivalent in kcal/kg)	daf (kcal/kg)	8,157 kcal/kg	7,703 kcal/kg	1 kcal = 4.1868 kJ
11	Gross Calorific Value (AR)	AR (kJ/kg)	19,480 kJ/kg	17,580 kJ/kg	Realistic as-received fuel grade
12	Heating Value (BTU)	daf (BTU/lb)	14,683 BTU/lb	13,865 BTU/lb	Improved by ~240–280 BTU/lb post-treatment

strong attenuation of hydrophilic kaolinite clays due to alkaline dissolution, and NaClO encouraged the selective removal of oxidisable iron sulphide phases. Both coal matrices remained structurally robust with no macro-cracking, swelling or matrix disintegration usually caused by powerful mineral acids and peroxides. Although quartz predominates in both coals, Lakhra seems cleaner and less prone to moisture after treatment.

4.7.3 Fuel Property Comparison (Post Potassium hydroxide (KOH) Treatment)

Lakhra coal demonstrates better performance than other coals in terms of improvement in fuel qualities, reactivity to chemical treatments and maintenance of structural integrity especially following treatment with Potassium hydroxide (KOH) and Sodium hypochlorite (NaClO). The values and juxtaposition of the two coals are given in Table 15. Coal is naturally more porous, but its high moisture and clay content limits the BTU value and extended fuel efficiency. The results of treatment show that the heavier coals with high carbon content,

e.g. Lakhra, respond better to the improvement in coal quality. The reactivity and surface permeability of Thar coal could be useful in operations such as gasification or underground CBM extraction, with added moisture regulation. The Lakhra coal on treatment has shown considerable enhancement in energy potential and combustion efficiency. But Thar coal is still somewhat behind bituminous coal due to higher inherent moisture and lower carbon content.

Table 15 shows the improved combustion characteristics and fuel rank development of Thar and Lakhra coals after treatment with the KOH, NaClO, and CaCO₃ suite. KOH leached the inert ash generating minerals together with the reduction of moisture ballast that concentrated the combustible carbonaceous core which increased the dry ash free carbon contents to the levels of 71.20% for Thar and 77.80% for Lakhra. The concentration gave better thermal output with Gross Calorific Values of 32,250 kJ/kg (13,865 BTU/lb) and 34,150 kJ/kg (14,683 BTU/lb) respectively. These improvements suggest successful thermal upgrading and drive low rank Thar lignite toward Sub-bituminous A characteristics

Table 12

Comparative analysis of Thar and Lakhra Coals

Parameter / Evaluation Criteria	Thar Coal	Lakhra Coal	Scientific Mechanism & Chemical Impact
I. Fluid Saturation Behavior			
Natural Water Absorption	High (~25.4%)	Moderate (~18.2%)	Governed by intrinsic macro-porosity and lignite rank
Post-KOH Saturation	Regulated / Steady (~16.7%)	Controlled (~15.7%)	Alkaline humic extraction and surface charge reorganization
Post-NaClO Saturation	Moderate (~14.7%)	Steady (~18.6%)	Controlled oxidative surface etching without structural cavitation
Post-CaCO ₃ Saturation	Significantly Suppressed (~9.7%)	Significantly Suppressed (~11.8%)	Micro-particulates deposit in cleats, forming an inorganic pore seal
II. XRD Mineralogical Composition			
Quartz (α -SiO ₂)	Dominant refractory phase	Dominant refractory phase	Stable crystalline framework across all chemical treatments
Clays (Kaolinite / Illite)	Noticeable intensity reduction	Strongly attenuated	Disrupted and dissolved via alkaline KOH leaching
Pyrite / Siderite (Iron phases)	Trace / depleted	Markedly reduced	Oxidized and extracted through NaClO desulfurization
Calcite (CaCO ₃)	Newly Emerged ($2\theta \approx 29.4^\circ$)	Newly Emerged ($2\theta \approx 29.4^\circ$)	Directly confirmed retention of injected crystalline CaCO ₃ seal
Structural / Matrix Integrity	Maintained (no slaking)	Well-preserved	Avoids acid-induced cleavage and deep micro-fissuring
III. Fuel Properties (daf Basis)			
Carbon Content (C)	71.20%	77.80%	Enriched due to ash reduction and volatile stabilization
Gross Calorific Value (GCV)	32,250 kJ/kg	34,150 kJ/kg	Upgraded via mineral leaching and lowered ballast moisture
Heating Value (BTU/lb)	13,865 BTU/lb	14,683 BTU/lb	+280 BTU/lb over raw baseline
Equivalent Fuel Rank Behavior	Upgraded toward Sub-bituminous A	Upgraded toward High-Volatile Bituminous	Enhanced combustion reactivity and lower inorganic slagging

Table 13

Fluid saturation response of Thar and Lakhra coals under natural water and chemical immersion

Behavior / Treatment	Thar Coal	Lakhra Coal
Natural Water Absorption	High (17.07% – 25.35%)	Moderate to High (13.70% – 25.81%)
Post-KOH Saturation	Regulated / Steady (15.34% – 16.67%)	Controlled (15.65% – 17.95%)
Post-NaClO Saturation	Moderate (14.67% – 17.51%)	Steady (14.47% – 18.64%)
Post-CaCO ₃ Saturation	Significantly Suppressed (9.45% – 9.66%)	Significantly Suppressed (10.86% – 11.84%)

Table 14

Post-treatment mineralogical phases and structural integrity of Thar and Lakhra coals

Parameter / Mineral Phase	Thar Coal	Lakhra Coal
Quartz (α -SiO ₂)	Dominant refractory phase; structurally stable	Dominant refractory phase; structurally stable
Clays (Kaolinite / Illite)	Noticeable intensity reduction (KOH leaching)	Markedly attenuated (KOH leaching)
Calcite (CaCO ₃)	Newly emerged peak ($2\theta \approx 29.4^\circ$)	Newly emerged peak ($2\theta \approx 29.4^\circ$)
Pyrite / Siderite (Iron phases)	Attenuated / depleted via NaClO oxidation	Substantially removed via NaClO oxidation
Structural / Matrix Integrity	Well-preserved (no slaking or acid micro-fissuring)	Intact with micro-cleat particulate sealing

and Lakhra coal toward high volatile bituminous grade behaviour.

4.8 Enhancement of Fuel Property after Potassium hydroxide (KOH) Treatment

Treatment with potassium hydroxide (KOH) was applied to remove mineral impurities, mainly carbonates, and

Table 15

Upgraded calorific values, elemental carbon, and fuel rank behaviour of treated Thar and Lakhra coals

Property / Parameter	Thar Coal	Lakhra Coal
Gross Calorific Value (GCV)	32,250 kJ/kg	34,150 kJ/kg
Carbon Content (daf)	71.20%	77.80%
Heating Value (BTU/lb)	13,865 BTU/lb	14,683 BTU/lb
Equivalent Rank Behavior	Upgraded toward Sub-bituminous A	Upgraded toward High-Volatile Bituminous

to increase the fixed carbon content to improve the combustion properties of Lakhra and Thar coal. This section discusses the efficiency of the treatment by assessing changes in important fuel properties including carbon content, BTU per pound and gross calorific value (GCV) before and after.

4.8.1 Fuel Property Comparison Before & After Potassium hydroxide (KOH) Treatment for Lakhra coal

The basic fuel properties of the Lakhra coal samples were significantly improved after post-treatment testing. The significant improvement in gross calorific value (GCV) and simultaneous elemental enrichment of carbon indicates effective leaching of inert, ash-forming mineral impurities by potassium hydroxide (KOH) and hence, upgradation of the fuel to high-volatile bituminous class. Detailed comparative trends for GCV, increased heating value (BTU/lb) and total carbon content are shown in Figs. 9, 10 and 11, respectively. Therefore, the analysis results show that the upgraded Lakhra coal is a far more practical and efficient solid feedstock for industrial burning systems and baseload thermal power production.

Fig. 9 shows the increase in GCV of Lakhra coal after chemical treatment with KOH, NaClO and CaCO₃. The effective heat content increased from 16,520 kJ/kg to 19,480 kJ/kg (as-received basis) upon removal of extraneous moisture and soluble ash-forming minerals. Selective chemical leaching and structural de-ashing concentrated the organic macromolecular network on a dry ash-free basis, increasing the thermal energy production from 31,200 to 34,150 kJ/kg (14,683 BTU/lb). The dramatic improvement suggests that the targeted chemical suite can upgrade low-rank coal to a better efficiency combustion fuel.

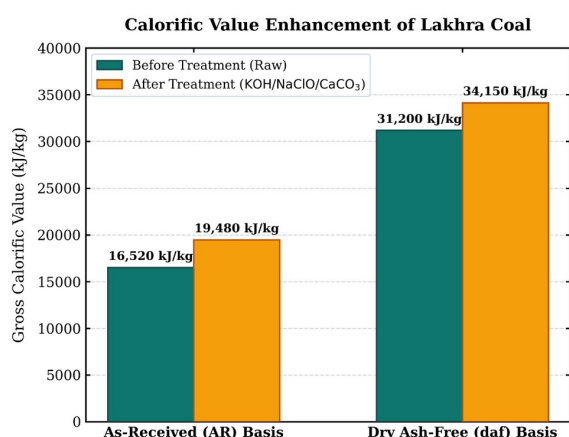


Fig. 9. Comparison of Gross Calorific Value (GCV) of Lakhra coal before and after chemical treatment

Fig. 10 demonstrates the quantitative gains in the Higher Heating Value (BTU/lb) of Lakhra coal by chemical alteration with KOH, NaClO, and CaCO₃. Partial dewatering and inert mineral matter removal on an as-received basis raised the effective heating value from 7,100 BTU/lb to 8,375 BTU/lb (+17.9%). Selective demineralisation and elemental carbon concentration increased thermal energy output from 13,415 BTU/lb to 14,683 BTU/lb on a dry ash-free (daf) basis. This confirms that the combination treatment of alkaline leaching, surface oxidation and inorganic pore stabilisation significantly improves the combustion rank of low-rank Lakhra coal.

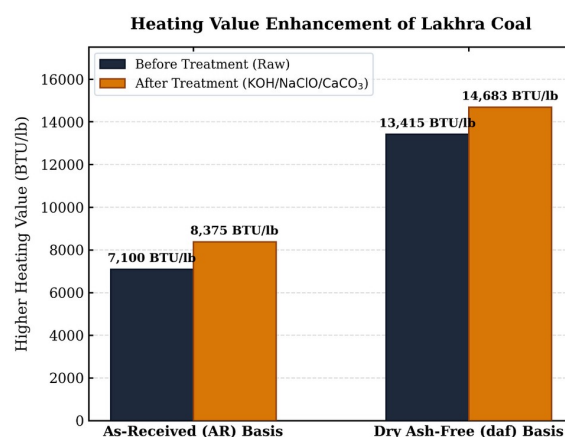


Fig. 10. Heating value (BTU/lb) comparison of Lakhra coal before and after chemical treatment

Fig. 11 shows the increase in carbon fractions for Lakhra coal after chemical treatment with KOH, NaClO and CaCO₃. The fixed carbon (on an as-received basis) increased from 19.80 to 24.20% due to the reduction of inorganic ash ballast and moisture. Selective demineralisation and matrix purification increased the total elemental carbon on a dry ash-free (daf) basis from 76.20% to 77.80%. These quantitative changes confirm the successful concentration of the carbon network of the combustible material through chemical treatment, which directly contributes to the recorded increase in heating values.

4.9 Fuel Property Comparison Before & After Potassium hydroxide (KOH) Treatment for Thar coal

Thar coal also made significant progress, especially in terms of the GCV and BTU values. The results show that Potassium hydroxide (KOH) improves lignite coal to near-bituminous behaviour, but the energy content after treatment is not as high as Lakhra. However, its efficiency was slightly curtailed by the natural moisture percentage of Thar coal and its clay-rich layout, which

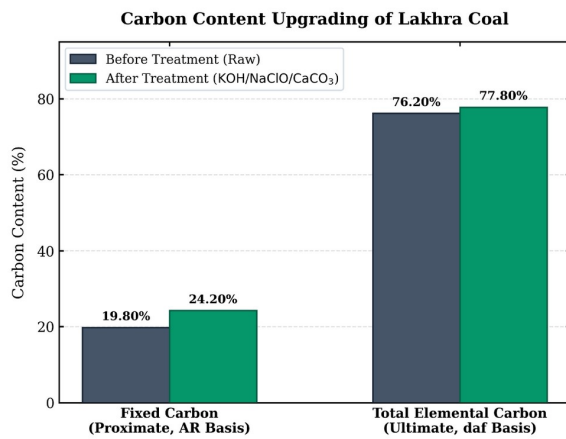


Fig. 11. Comparison of fixed carbon (AR basis) and total elemental carbon (daf basis) of Lakhra coal before and after chemical treatment

was only partially treated. Figs. 12, 13 and 14 show the comparison findings of GCV, BTU and Carbon content before and after Potassium hydroxide (KOH) treatment correspondingly.

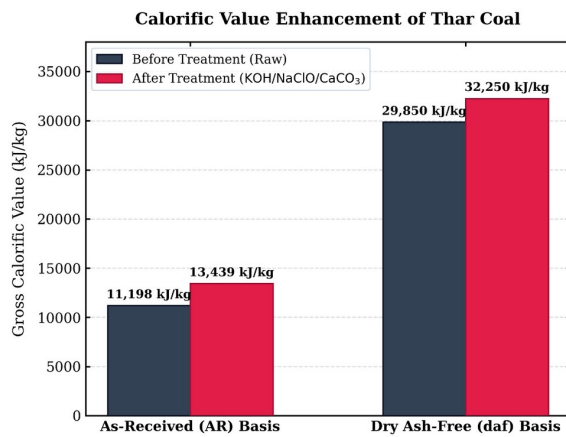


Fig. 12. Comparison of GCV for Thar coal before and after Potassium hydroxide (KOH) treatment

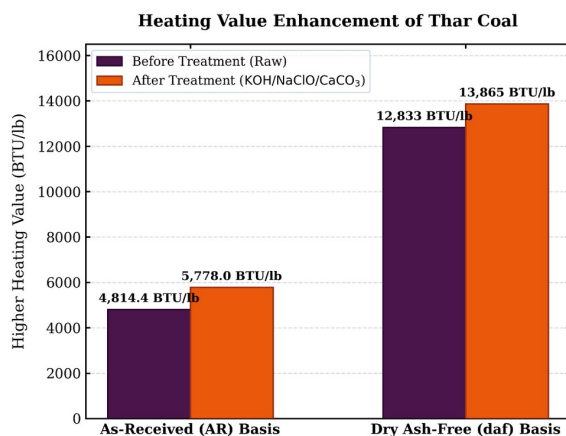


Fig. 13. Comparison of BTU values for Thar coal before and after Potassium hydroxide (KOH) treatment

4.10 Comparative Analysis for Enhancement of Fuel Property for Thar and Lakhra Coal after Potassium Hydroxide (KOH) Treatment

Lakhra coal benefited more from HNO₃ treatment than Thar coal. The fuel quality of Lakhra was increased because of more fixed carbon and a denser matrix, which enabled Potassium hydroxide (KOH) to effectively attack and remove the mineral obstacles. However, the

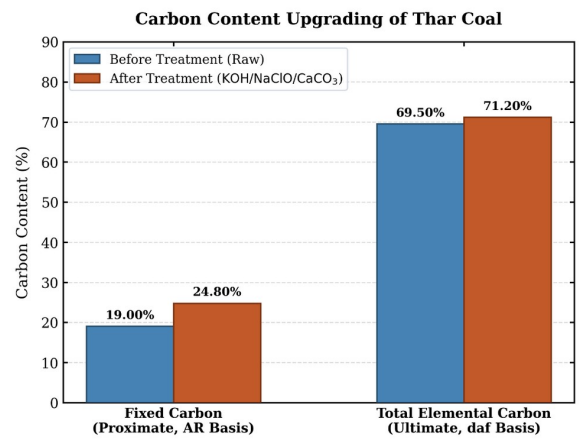


Fig. 14. Comparison of Carbon Content for Thar coal before and after Potassium hydroxide (KOH) treatment

maximum fuel value of Thar coal after treatment was limited by the high clay and moisture contents but responded positively. Potassium hydroxide (KOH) reacted positively as a chemical for improving the quality of fuel, especially for coal kinds such as Lakhra, which are already high in carbon. Figs. 15, 16 and 17 show the comparison results of enhanced values of GCV, Carbon Content and BTU value accordingly.

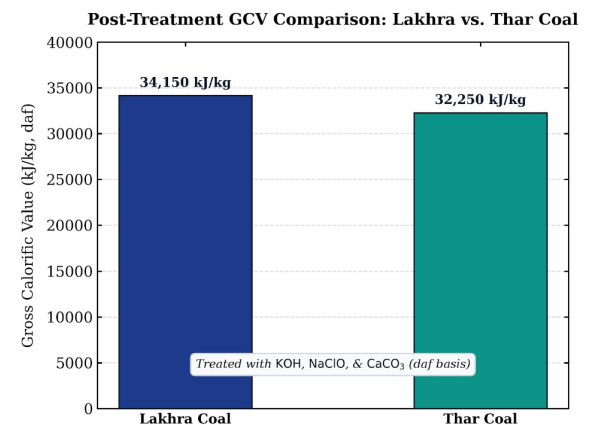


Fig. 15. Comparison of GCV of Lakhra and Thar coal after Potassium hydroxide (KOH) treatment

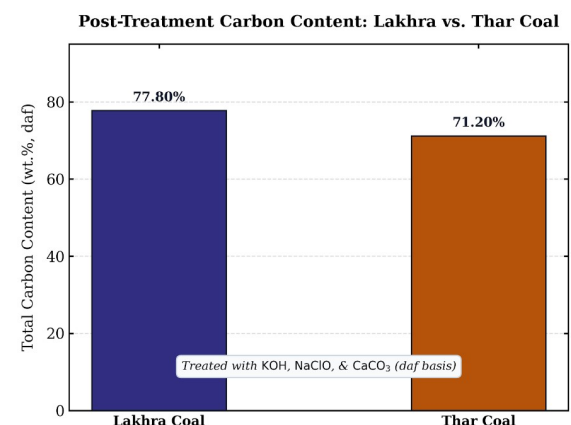


Fig. 16. Comparison of Carbon Content of Lakhra and Thar coal after Potassium hydroxide (KOH) treatment

4.11 XRD analysis of Lakhra and Thar Coal treated by Sodium hypochlorite (NaClO)

The XRD examination demonstrated improvement in mineralogical aspects in both coals, but improved re-

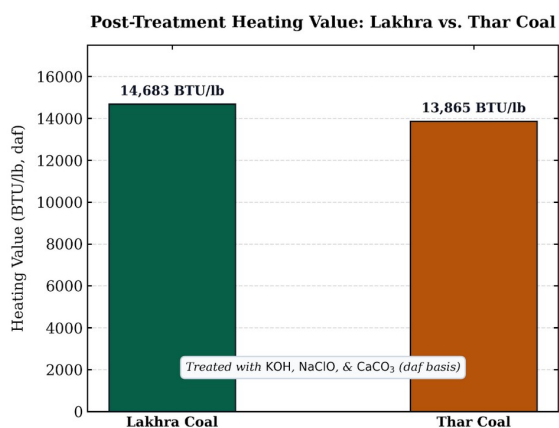


Fig. 17. Comparison of BTU of Lakhra and Thar coal after Potassium hydroxide (KOH) treatment

removal of minerals was observed in Lakhra coal, especially the clays and compounds contributing to ash. This is immediately translated into improved fuel property enhancement. The effects of Sodium hypochlorite (NaClO) on both Lakhra and Thar coal, analysed from the results of XRD, are shown in Table 16.

4.12 Analysis of Fuel Property for Lakhra and Thar coal

The combined analysis of the crystallographic XRD and thermal combustion results indicates that KOH conditioning has a much higher impact on the structural and chemical properties of Lakhra coal. Although this has been improved, Thar coal remains not very good due to its natural moisture-absorbing minerals. This relative knowledge is essential when deciding on coal to use in gasification plants, combustion optimisation, or other power technologies. Table 17 shows the list of observations obtained from the results for Lakhra and Thar coal.

5. Conclusion

The present study is focused on enhancing the fuel quality and structural stabilisation of low-rank coals from two major basins in Pakistan, i.e., Thar and Lakhra deposits, which are among the greatest indigenous energy sources in Asia. The key findings in terms of thermochemical enhancement, mineralogical evolution and matrix integrity were obtained by replacing aggressive mineral acids with a targeted suite of chemical conditioning (potassium hydroxide (KOH), sodium hypochlorite (NaClO) and calcium carbonate (CaCO_3)):

Chemical conditioning resulted in considerable enhancement of fuel quality for both types of coal. The most improvement was observed in Lakhra coal, where the dry ash-free (daf) carbon was concentrated to 77.80% and increased the gross calorific value to 34,150 kJ/kg (14,683 BTU/lb). This performance meets the high-volatile bituminous-grade criteria and supports its use in efficient industrial heat generation.

Thermal improvement found to be excellent for Thar coal. The heating value has increased to 32,250 kJ/kg (13,865 BTU/lb, daf base) and the calorific output has

increased by 20.0% (as-received). Lakhra made a full recovery, but young lignites had restricted absolute recovery due to high inherent moisture and substantial clay mineral content, though the treatment considerably improved volatile to fixed carbon ratios to Sub-bituminous A fuel characteristics.

XRD diffractograms demonstrate that alkaline KOH leaching preferentially reduced the hydrophilic kaolinite and illite clay reflections, while oxidative NaClO conditioning selectively removed reactive iron sulphide phases (pyrite and marcasite). The acid treatments would have dissolved the structural carbonates. However, the usage of CaCO_3 resulted in a high calcite reflection at $2\theta \approx 29.40^\circ$ suggesting that the particles were physically held on the cleat surfaces.

Insoluble CaCO_3 micro-suspension addition lowered the saturation to less than 12% for both coals, but raw Thar and Lakhra coals showed high natural water absorption (more than 18%–25%) during fluid absorption evaluations. The deposited micro-particulates served as an effective inorganic barrier in cleat apertures, resulting in a reduction in slaking and the inhibition of excessive ingress of moisture.

Unlike the micro-cavitation and structural disintegration of Calcium carbonate (CaCO_3) or strong mineral acid immersion, the KOH, NaClO, CaCO_3 approach preserved block integrity and mechanical coherence, thus providing a non-destructive chemical route for fuel upgrading.

The overall results indicate the technical viability of this multi-mechanism chemical suite for beneficiating low-grade Pakistani lignites into greater density, lower sulphur and lower slagging solid fuels for power generation and industrial uses.

5.1 Future Work and Recommendations

Further work should be aimed at continuous pilot-scale operations to evaluate the economic and thermodynamic scalability of the chemical injection method. It is proposed that Thar coal can overcome moisture retention constraints by mechanical or thermal pre-dewatering in combination with tailored clay-flocculation methods. To reduce operating expenditures, process optimisation studies should be performed using response surface methodology (RSM) to identify chemical reagent concentrations, exposure contact times and recovery recycling cycles. Advanced microstructural characterisation, including high-resolution field emission SEM (FE-SEM), BET specific surface area analysis and high-temperature ash fusion tests, will be used to better understand pore-scale sealing mechanics and slagging/fouling indices. Finally, improved coals' reactivity for gasification, potential for conversion to clean syngas and co-gasification blending behaviour will further extend their contribution to sustainable and low-emission energy infrastructure.

Table 16

Comparative XRD mineralogical response and structural effects of Lakhra and Thar coals following chemical treatment

S#	Lakhra Coal (KOH/NaClO/CaCO ₃ Treated)	Thar Coal (KOH/NaClO/CaCO ₃ Treated)
1	Primary α -quartz ($2\theta \approx 26.69^\circ$) remains the dominant and structurally stable crystalline refractory phase.	Retains a predominant quartz framework with stable baseline crystallinity.
2	Kaolinite and illite clay reflections are markedly attenuated due to selective alkaline demineralization by KOH.	Partial dissolution of clay minerals; residual phyllosilicates moderately reduced, lowering inherent moisture retention capacity.
3	A distinct calcite peak emerges at $2\theta \approx 29.40^\circ$ ($d=3.03\text{\AA}$), verifying physical retention of injected crystalline CaCO ₃ .	Calcite reflection appears at $2\theta \approx 29.40^\circ$, confirming effective deposition and cleat-bridging by CaCO ₃ micro-particulates.
4	Reactive iron sulfide phases (pyrite/siderite, $2\theta \approx 44.70^\circ$) are depleted via oxidative NaClO desulfurization; structural integrity is preserved without matrix slaking.	Oxidative sulfur removal confirmed; intact cleat network with particulate pore sealing that suppresses excess water absorption.

Table 17

Combined XRD mineralogical, structural, and fuel property analysis of treated Lakhra and Thar coals

S#	Tests / Observations	Lakhra Coal	Thar Coal
1	XRD Phase Evolution	Quartz remains dominant; kaolinite clays substantially attenuated by KOH; iron sulfides depleted by NaClO; distinct calcite peak ($2\theta \approx 29.40^\circ$) confirms CaCO ₃ cleat retention.	Quartz dominant framework; clays moderately dissolved; calcite reflection ($2\theta \approx 29.40^\circ$) present from deposited CaCO ₃ particulate barrier.
2	Structural Integrity & Cleat Dynamics	Well-preserved block matrix; cleat apertures stabilized with particulate micro-seals; avoided structural cavitation and slaking.	Maintained structural coherence; surface micro-fissuring sealed by carbonate deposition, suppressing liquid uptake.
3	Gross Calorific Value (GCV, daf)	34,150 kJ/kg (High-Volatile Bituminous behavior)	32,250 kJ/kg (Sub-Bituminous A behavior)
4	Total Elemental Carbon (daf)	77.80% (concentrated polyaromatic core)	71.20% (upgraded combustible organic matrix)
5	Higher Heating Value (BTU/lb, daf)	14,683 BTU/lb	13,865 BTU/lb

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