

Petrographical and chemical characteristics of cleaned oltu-stone waste for their potential use (as a semi-precious stone)

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ABSTRACT

Oltu-stone, a semi-precious stone found in the Oltu district of Erzurum, Turkey, is frequently used in the making of decorative ornaments. Approximately 90-95% of the Oltu-stone mined, consisting of substandard Oltu-stone because of mineral impurities and small fragment sizes, is considered Oltu-stone waste (OW). This waste is either discarded or burned, resulting in economic losses. The utilization of Oltu-stone waste (OW) as an alternative to standard Oltu-stone (SO) could reduce such losses. In order to see if Oltu-stone waste can be used as an alternative to standard Oltu-stone, it must first be cleaned of its inorganic impurities. After that, the cleaned Oltu-stone properties should be determined to compare their characteristics with standard Oltu-stone. In this study, the petrographic and chemical characteristics of cleaned Oltu-stone obtained by dense medium separation (float-sink method) were determined. The results indicated that the cleaned Oltu-stone was liptinite-rich coal with a small amount of huminite content. Also, it shows contorted suberinite cellular structure and has varying resinite content. Due to high liptinite content, cleaned Oltu-stone has a high volatile matter, i.e., 63-65%. The inorganic impurities in the Oltu-stone wastes were mainly quartz, calcite, pyrite, and clay mineral. After cleaning, most inorganics were separated, although pyrite and silicate minerals remained in trace amounts within the cellular structure. The FTIR results show the predominance of aliphatic hydrocarbons, low aromaticity, and low apparent maturity. It was determined that the cleaned Oltu-stone wastes have similar characteristics to the standard Oltu-stone and can be utilized for further processing as an alternative source.

1. Introduction

Oltu-stone is a semi-precious stone of organic origin that is found in the Oltu district of Erzurum province in Turkey. It is also known as black, amber jayet, jet, and gagat [1,2]. Oltu-stone does not show crystallinity and has a density close to that of coal, i.e., about 1.30 g.cm⁻³. Oltu-stone was reported to be comparable to jet in color, such as black, gray, green, or blackish brown [3,4], but differs in chemical properties [5,6]. Oltu-stone contains both organic and inorganic components. Mineral impurities diminish the stone

quality and harden the stone, whereas coal macerals are an integral component of the organic composition.

According to many research studies, Oltu-stone is composed of coaly materials [7-9], and is also considered black amber due to resin-rich content [3,10]. Toprak [11] discussed the genesis of Oltu-stone in detail and described it as suberinite-rich coal with reflectance values ranging between 0.45-0.49%. Other macerals like resinite, sporinite, and huminites are present in small amounts. In Oltu-stone, due to geochemical effects, the huminite and inertinite maceral elements were probably destroyed during

formation, leaving voids behind, but the liptinite component remained due to greater physical resistance [12,13]. All cell cavities in Oltu-stones were deformed and filled with silicates [11]. Amorphous and cryptocrystalline silicates arranged in a cellular structure, along with other inorganic materials and coal, as well as moisture loss, are considered to contribute to the hardness of Oltu stone [14].

Oltu-stone deposits occur in the Late Cretaceous Dutlu Formation, located northeast of Erzurum, Turkey [11]. Marly layers of the Dutlu formation, 70-80 cm thick, contain Oltu-stone in the form of thin, discrete horizons and lenses ranging in thickness from 3 to 15 cm [11,15]. Oltu-stone has high hydrogen index (HI) values (314-379 mg HC/g TOC) and is a Type II kerogen due to resin-containing terrestrial organic matter [16]. The use of Oltu-stone as a semi-precious stone was attributed to the presence of resin content. Based on the findings [8,16], Oltu-stone was classified as lignite to sub-bituminous coal due to its high volatile matter (63.86%), low reflectance values (0.24 - 0.30%), and low maturity level.

Mined Oltu-stone is cut easily to produce ornamental objects, such as prayer beads, rings, earrings, necklaces, and other jewelry [9,17]. One of the good properties of Oltu-stone is its softness when initially unearthed and getting harder when exposed to air due to the moisture content loss [11,15]. As a result, it is effortless to carve and polish. At Oltu-stone mines, the traditional mining methods are used, with local miners extracting the Oltu-stone by hand using tools like shovel and hammer. The waste materials produced during the extraction of Oltu-stone are primarily adjacent rocks. Following extraction, the Oltu-stone blocks, approximately 30 cm long in size, are transported out of the mines and broken into pieces using hand tools i.e., hammer. Then, mineral-containing Oltu-stone and standard Oltu-stone (mineral-free) are separated by hand. The standard Oltu-stone fragments are acceptable for final processing at the atelier (Oltu workshop) if they are at least 3cm thick. Most of the standard Oltu-stone is discarded as a waste as it is too small to produce ornamental products. Oltu-stone wastes (OW) comprise the fragments of mineral-containing Oltu-stone and standard Oltu-stone (discarded due to small sizes)[18-19]. Based on statistics, the market consumes about 1.6 tons of material which is triaged from approximately 8 tons of excavated material from the galleries. However, the 0.32-0.8 tons of material is transformed into a final jewelry product.

The increasing global emphasis on sustainable development and circular economy practices has

driven the need to explore value-added applications for industrial and mining wastes. Oltu-stone waste, typically considered a low-value by-product, presents an opportunity for waste valorization through effective cleaning and repurposing. Transforming such waste into a usable material aligns with sustainable resource utilization strategies and contributes to reducing the environmental footprint of mining activities. According to atelier data, Oltu-stone wastes account for 90-95% of the Oltu-stone extracted from mines. Such wastes of semi-precious stones may be treated by high-pressure binderless agglomeration, if there is enough resin content, to produce an alternative stone, as adopted for amber chips and powder [20]. Before using any processing technology to make use of the Oltu-stone waste, it is important to determine the waste constituents. According to washability data [21], the ash content in Oltu-stone wastes is 10-18%, which is greater than the ash content for standard Oltu-stone, i.e., 2.33%. In a previous study [21], a cleaned Oltu-stone with less than 2% ash was obtained by washing. Thereafter, the washed Oltu-stone was used to produce beads by thermal treatment and high-pressure agglomeration [19]. That agglomeration process can be further optimized if detailed characterization of cleaned Oltu-stone is available. Other than washing and thermal characteristics, no characterization data for cleaned Oltu-stone waste has been published. Therefore, various characterization methods must be used to examine the cleaned Oltu-stone and to compare it with standard Oltu-stone. This study aims to assess the petrographic and chemical characteristics of cleaned Oltu-stone wastes for their utilization as an alternative semi-precious stone.

2. Materials and Methods

2.1 Oltu-stone waste samples

Oltu-stone waste is generated at different stages, from mining to final processing, and can be categorized into three types such as rock waste, Oltu-stone waste from hand sorting and Oltu-stone waste from final processing of beads [18]. *Rock waste* consists of sandstone and claystone fragments, along with discarded Oltu-stone pieces, which accumulate inside mines during extraction. Oltu-stone waste from hand sorting is produced when large blocks are broken and manually sorted, generating elongated chips containing minerals and underdeveloped stone, as well as small-sized (<3 cm) high-quality fragments that are discarded due to size limitations. Oltu-stone waste from final processing arises during cutting, crushing, grinding, and polishing at ateliers, where fine powder waste is generated in small quantities. Understanding

these waste types is crucial for developing efficient utilization strategies. In this study, Oltu-stone waste samples from hand sorting were collected from Oltu district, Erzurum, for cleaning and characterization.

2.2 Dense Medium Separation

The total sample mass collected from the mines was 20 kg. Then, a 1 kg representative fraction was taken from the total sample mass using a riffle splitter. The sample was crushed to 1mm and cleaned Oltu-stone fractions were obtained by dense medium separation (float-sink) using ZnCl_2 solutions of different densities, i.e., 1.15, 1.20, 1.25, 1.30, 1.35, and 1.40 g.cm^{-3} . All fractions were then washed in distilled water, filtered, dried, and weighed. The ASTM standard D1374 method was used to determine the ash yield in float fractions. Oltu-stone is liptinite-rich coal in origin, and liptinite macerals are mainly separated below 1.25 g.cm^{-3} [22,23]. Therefore, three cleaned Oltu-stone fractions, below 1.25 g.cm^{-3} , were selected for this study, i.e., CO1 (-1.25+1.20 g.cm^{-3}), CO2 (-1.20+1.15 g.cm^{-3}), and CO3 (-1.15 g.cm^{-3}). The float is the recovered product, commonly referred to as the float yield, representing the lighter, coal-like fraction (likely Oltu-stone) separated at each density. For comparison, a hand-picked standard Oltu-stone (SO) obtained from the atelier was also investigated.

2.3 Analytical Procedure

2.3.1 Petrographic Investigation

Polished sections were prepared using METKON mounting resin for petrographic examination. Maceral analysis was conducted by identifying 500 points following the ingredients point-counting technique. Random reflectance was determined on polished sections under reflected white light and specific filters, utilizing a 50x oil-immersion objective attached to a Leica DM4000M microscope. To assess the fluorescence characteristics of liptinite macerals, a TIDAS CCD UV-NIR instrument coupled with a microscope was employed. The maceral analyses and measurements were made according to the nomenclature of ICCP [24].

2.3.2 Morphology

The morphology and elemental content of samples were studied by SEM inspect 50 (FEI company), coupled with an EDAX OCTANE (AMETEK Inc.). Polished and grain samples (<1mm) were coated with Au-Pd. These analyses include simultaneous backscattered imaging and elemental analysis of the sample.

2.3.3 Mineralogical Investigation

XRD analyses were performed using Rigaku ultima-IV powder XRD with Cu radiation. All samples were grounded in a disc grinder to obtain powder samples of 30 μm . Then, X-ray diffractograms of these samples were acquired over the 2θ range of 5° – 70° at a scanning rate of $1^\circ/\text{min}$. These diffractograms were evaluated by the Rigaku software database to detect carbon phases and mineral impurities.

2.3.4 Proximate and Ultimate analysis

The proximate analysis was performed on Perkin Elmer STA6000 equipment using the micro-TGA procedure given by [25]. For ultimate analysis (C, H, N, S), LECO TruSpec micro CHNS analyzer was used with different calibration standards i.e., Sulphamethazine LCRM, Cystine LCRM, and BBOT. The respective tests were repeated three times on each sample. The test results were averaged to estimate the values of each element in each sample. Oxygen (O) content was calculated by the difference method.

2.3.5 Functional groups analysis

FTIR spectra were recorded by using Spectrum-II (Perkin Elmer) spectrometer coupled with DRIFT (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) accessory. The scanning region ranged from 4000 cm^{-1} to 450 cm^{-1} (Mid-infrared region), with 32 scans at 4.0 cm^{-1} resolution. Then, specific regions were evaluated by a curve-fitting tool using Peak-fit software for low absorption bands and overlapping peaks [26]. Peak positions and their integrated area were calculated from the second derivative of the experimental spectrum, and the fitted peak shape was generated using a Gaussian approach. For measurement, powdered samples (<30 μm) were prepared from Oltu-stone wastes, cleaned Oltu-stone fractions, and standard Oltu-stone.

3. Results and Discussion

3.1 The yield of the density fractions

Laboratory methods for separating maceral and mineral impurities from coal include hand-picking, float-sink with dense liquids, density-gradient centrifugation [27], and reflux classifier [23]. The float-sink technique takes advantage of the differences in the densities of maceral or maceral groups. It is easy to use, and even it does not require expensive equipment. Fig. 1 represents a typical washability curve of the cleaned Oltu-stone obtained from the float-sink method at different densities using a ZnCl_2 solution. Compared to CO1 and CO3, CO2 has the highest float yield i.e., 53.71%. The cumulative float

yield (CFY) increases sharply from 1.15 g.cm⁻³ to 1.25 g.cm⁻³ (Fig.1). The cumulative float yield obtained at 1.25 g.cm⁻³ density is 82.64%, indicating the presence of a high amount of liptinite macerals in Oltu-stone wastes. Liptinite macerals make Oltu-stone suitable for use in ornamental products as a semi-precious stone[28]. The cumulative ash in a float at 1.25 g.cm⁻³ is approximately 1.5% less than standard Oltu-stone, i.e., 2.33% reported by [21].

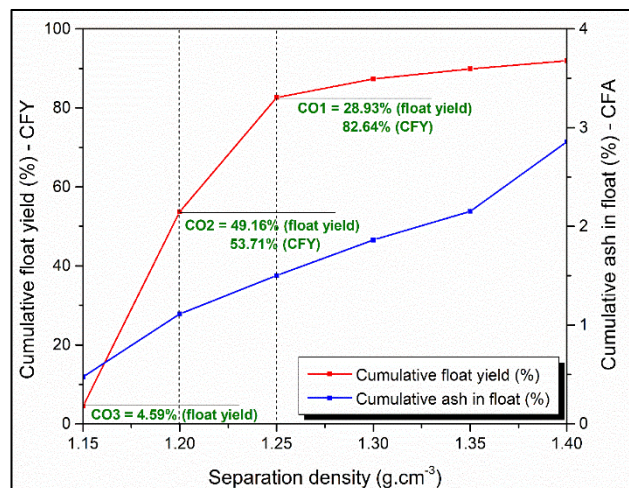


Fig. 1. Washability curve of Oltu-stone wastes at different densities.

Random reflectance measurements of Oltu-stone samples were carried out on huminite macerals

(containing embedded resinous material), giving R_{mean} 0.39-0.41%. Petrographic analysis (Table 1) indicated that cleaned Oltu-stone waste has abundant liptinite content, a small number of huminite macerals, and mineral impurities, indicating its potential use as a semi-precious stone [28]. The cleaned Oltu-stone was further investigated to look at the liptinite maceral group. Fig. 2(a) shows that the suberinite has contorted shapes with poor fluorescence and rarely broken cell structures, unlike common rounded shapes as previously reported by [11]. That is probably due to the samples taken from various tectonically affected environments. These shape deformations may occur due to the compaction of the cellular structure during formation and thermal effect ("rank increase"), which reduces the fluorescence also. In Fig. 2(b), the inorganics are seen within the cellular structure, and the outer rims are huminites (lighter color). Inorganics such as pyrite and silicate minerals (clay and quartz) were observed in all fractions of cleaned Oltu-stone. Pyrites were seen within the cellular structure, with a size range of approximately 1-10 μm . It is always difficult to separate these fine inorganics by dense medium separation (float-sink) due to encapsulation in the cell cavities [29].

Table 1. Maceral and inorganic content of Oltu-stone samples and their reflectance values.

Samples	Huminite	Liptinite	Inertinite	Inorganics (%)		Reflectance (R_{mean} %)
	(%)	(%)	(%)	clays, silicates	Pyrite	
OW	16	75	0	6	3	0.38
SO	21	73	0	4	2	0.41
CO1	22	72	0	3	3	0.40
CO2	23	75	0	-	2	0.39
CO3	20	78	0	-	2	0.39

Resinite is a resin-rich maceral and belongs to the liptinite group. It appears black to dark grey in reflected white light in low-rank coal [30]. Siliceous minerals and resinite may exhibit similar color appearances under white light but are distinguished by fluorescence. Cleaned Oltu-stone waste has varying resinite content, such as primary cell resinite and secondary resinite. The primary cell filling resinite is observed as globules within the huminite (Fig. 2(c) and Fig. 2(d)), and some cavities, probably formed much later, moved from other places. The fluorescent color of secondary resinites in Fig. 2(f) is much brighter, which is most likely exsudatinite. Although

some researchers [29,30] distinguish between exsudatinite and secondary resinite, both types are collectively referred to as resinite in the present discussion to align with the study's focus on ornamental utilization. This approach, also adopted in previous studies [28]. Having both resinites together in the same environment reveals various depositional conditions and maturation effects, as reported [33]. The variable resinite content and embedded huminite cause color variations [34]. Also, some fine-sized resinites are difficult to see under blue light due to accumulation within the liptinite and huminite macerals or in inorganic impurities, consistent with the study of [35]. Resinites can be melted, dissolved, and

rehardened [30] due to their thermoplastic properties. Therefore, resinite can work as a binder if cleaned Oltu-stone is used for high-pressure agglomeration, as practicing for semi-precious stone processing [20].

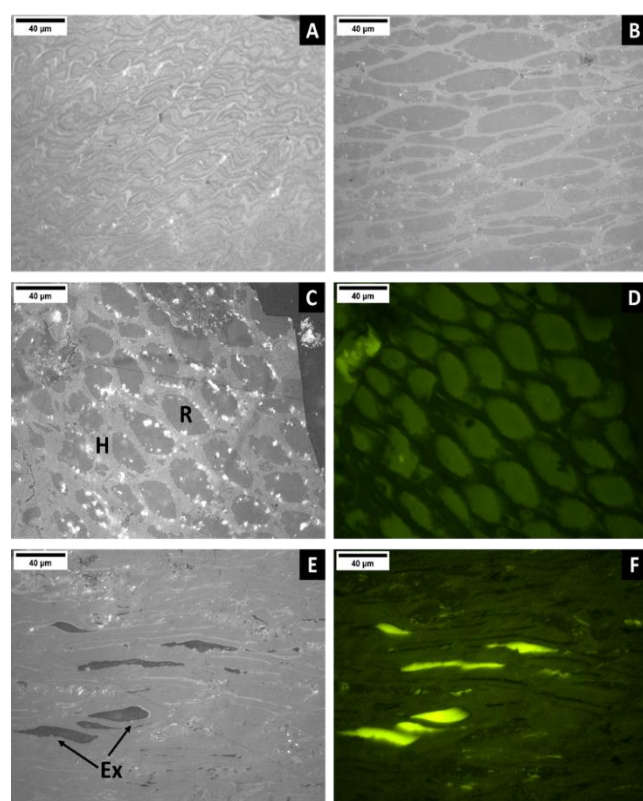


Fig. 2. Microphotographs of cleaned Oltu-stone, a). The contorted cellular structure of suberinite (under white light). b). Oval-shaped cellular structure, inorganics (in cell filling), and huminite (at the boundary). c). Primary cell filling resinite (R) within the huminite (H). d). Panel-C under blue light excitation. e). Secondary resinite (exsudatinite-Ex). f). Panel-E under blue light excitation. All scale bars = 40 microns (R = resinite, H = huminite, Ex=exsudatinite).

3.3 Morphology and elemental content

SEM analysis is the best method to observe the morphology and elemental content, but it is difficult to distinguish the organic components such as coal macerals. Based on atomic number contrast, mineral matter appears lighter gray to white, while organic matter appears dark gray in backscattered electron mode. Image magnification and contrast are essential factors in identifying maceral types under SEM. Liptinites are distinguished by their dark relative gray level, similar to how they appeared in reflected white light (Fig. 2), whereas huminites occurred as a matrix maceral with a medium gray level, as reported previously [18]. The resinite globules within the huminite matrix are shown in Fig. 3(a). Many authors [30] stated that resinite bodies sometimes contain gas bubbles of varying sizes. It was observed that the cell filling resinite has some cracks and cavities, which may have formed due to escaping of gas bubbles or due to polishing during sample preparation. Moreover,

the Cleaned Oltu-stone exhibits the bark-like texture as a primary texture (Fig. 3(b)) and contains mineral impurities such as framboidal pyrite, quartz, and clay minerals shown in Fig. 3(c) and Fig. 3(d). Some quartz and clay were not separated, remained in particle cavities, and were observed in CO1 only. The encapsulated bodies of framboidal pyrite (approximately 5-10 μm in size) were observed in all cleaned Oltu-stone samples. These findings support the XRD results presented in the next section.

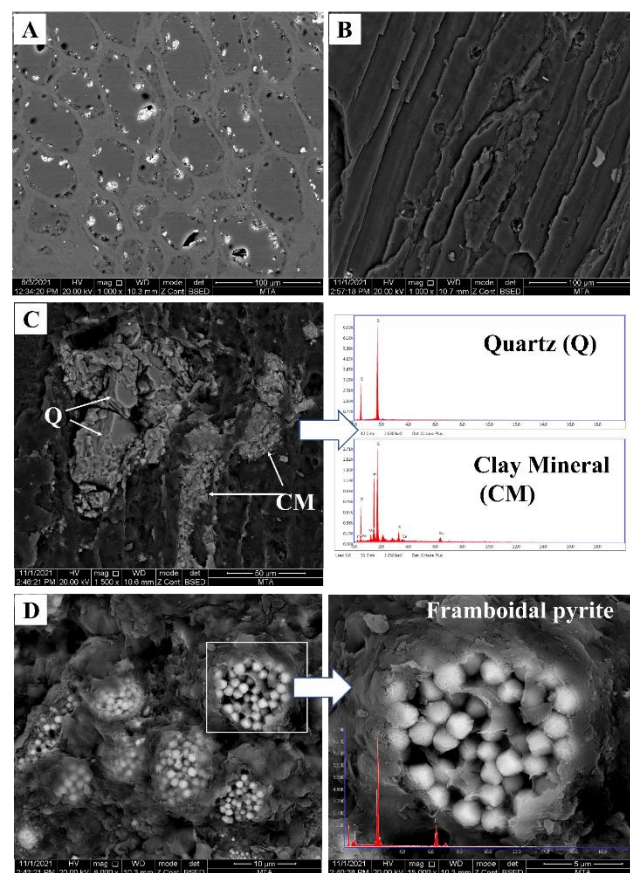


Fig. 3. SEM-EDS analysis of cleaned Oltu-stone fractions. a). primary cell filling resinite b). primary bark-like texture. c). quartz and clay are present in particle cavities, with EDS spectrum. d). framboidal pyrite in form of enclosed bodies.

3.4 Mineralogy

Fig. 4 shows the X-ray diffractogram of Oltu-stone wastes (OW), cleaned Oltu-stone (CO) samples, and standard Oltu-stone (SO). The mineral diffraction bands of clay minerals (like kaolinite), quartz, pyrite, and calcite, were detected in Oltu-stone wastes. Quartz was found to be the most abundant mineral in Oltu-stone waste. After cleaning, the quartz band was significantly reduced, whereas the pyrite band was less affected. It indicates that quartz is largely separated during dense medium separation. However, as observed in SEM images, pyrite remains within the enclosed bodies in fine sizes (Fig. 3(d)). Apart from mineral content, all samples exhibit highly disordered material in coal in form of amorphous carbon at $10-25^\circ$. Chen [36] explained this region ($2\theta=10-25^\circ$) and

revealed the presence of aliphatic and aromatic carbon atoms in coal. Compared to SO, the CO samples revealed nearly the same carbonaceous and mineral phases.

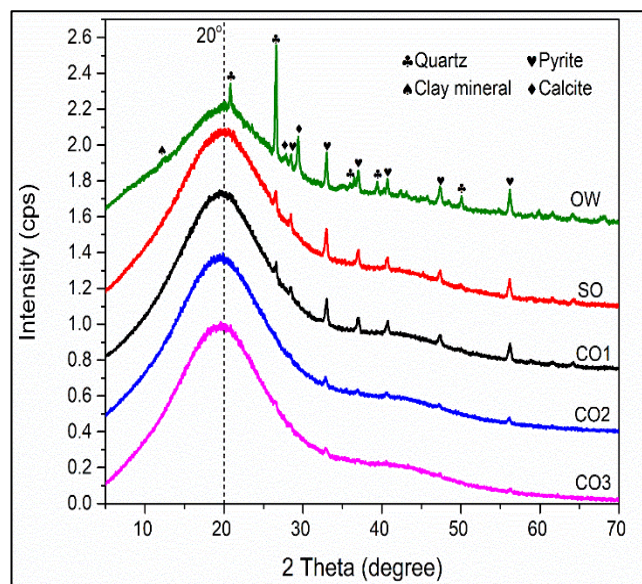


Fig. 4. X-ray diffractogram of Oltu-stone samples

3.5 Proximate and Ultimate analysis

Fig. 5 represents the proximate analysis of cleaned Oltu-stone waste using micro-TGA methods, while Table 2 contains the numerical data of the proximate and ultimate analyses. In the previous study [21], ash was used as a criterion for the washability of Oltu-stone waste. Apart from ash, other parameters, particularly volatile matters, should be evaluated. Cleaned Oltu-stone waste has a high volatile content (63-66%) due to the dominant group of liptinite macerals. Liptinite macerals are highly reactive [31,38,39,40] and possess thermoplastic properties. As a reason, the thermal behaviour of cleaned Oltu-stone under an inert environment is worthy of being investigated. Based on the TGA curve (Fig. 5), the

cleaned Oltu-stone starts to decompose at 250 °C. Therefore, it must be treated below this temperature for further processing, e.g., high-pressure agglomeration.

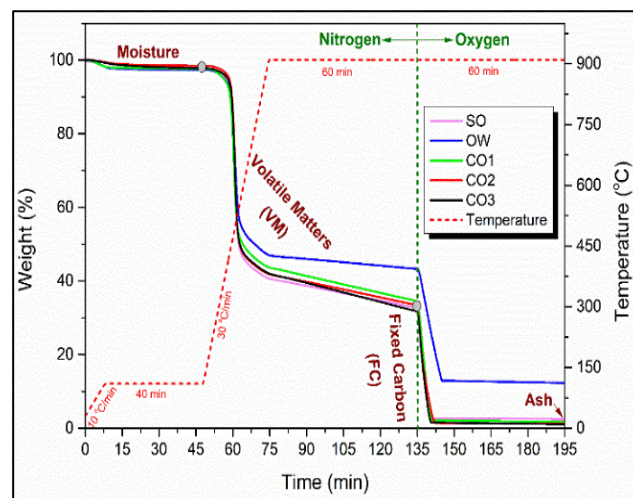


Fig. 5. Proximate analysis of Oltu-stone samples by the micro-TG method.

In ultimate analyses of cleaned Oltu-stone, the decrease in sulfur content with decreasing dense-medium density (Table 2) comparable with the declining trend of pyrite diffraction bands (Fig. 4). Therefore, it infers that the sulfur present in cleaned Oltu-stone is mainly inorganic sulfur, i.e., pyrite. Moreover, the standard Oltu-stone has a slightly high H/C ratio compared to Oltu-stone wastes and cleaned Oltu-stone. In cleaned Oltu-stone, a little increasing trend in the H/C ratio with decreasing dense medium density can be seen. The increased atomic H/C ratio suggested an increase in the aliphatic portion. According to the petrographic system based on reflectance values and elemental composition of coal [40], cleaned Oltu-stone is considered lignite to sub-bituminous coal. The same coal rank for Oltu-stone was defined in previous studies [8,16].

Table 2. Proximate and ultimate analyses of Oltu-stone samples

(Basis: OW and SO are as-received, and Cleaned Oltu-stones are dry basis)

(Basis: OW and SO are as received, and Cleaned Ota stones are dry basis)									
ID	Proximate Analysis			Elemental Analysis					Atomic ratio
	%			%					
	VM	Ash	FC	C	H	N	S	O*	
OW	54.02	12.3	30.9	70.3	5.64	0.5	2.23	9.03	0.96
SO	64.5	2.5	30.2	77	6.33	0.41	1.99	11.77	0.99
CO1	63.03	1.78	32.79	76.9	6.12	0.44	1.98	12.78	0.96
CO2	64.9	1.22	32.28	75.3	6.08	0.48	0.41	16.51	0.97
CO3	65.94	1.1	30.7	74.1	6.06	0.52	0.6	17.62	0.98

VM= volatile matters, FC=fixed carbon, C=carbon, H=hydrogen, N=nitrogen, O=oxygen
H/C = atomic ratio, * by difference method,

3.6 Functional Group analyses

FTIR spectroscopy is a highly effective technique for analyzing the structural composition of coal and identifying the presence of various chemical functional groups. Fig. 6 illustrates the FTIR spectra for Oltu-stone waste, purified Oltu-stone fractions, and standard Oltu-stone. The spectra exhibit comparable absorption bands and peaks, except for Si-O absorption (3700 , 1105 , and 1035 cm^{-1}), which is evident in the samples. These specific bands disappear in the cleaned Oltu-stone due to the removal of silicate minerals during the dense medium separation process, aligning with previous findings [41]. The FTIR spectra of all examined samples highlight aromatic rings, aliphatic side chains, and oxygen-containing functional groups. In the purified Oltu-stone, aliphatic CH stretching dominates within the $2800\text{--}3000\text{ cm}^{-1}$ range, including 2956 cm^{-1} (CH_3 asymmetrical stretching), 2921 cm^{-1} (CH_2 asymmetrical stretching), and 2853 cm^{-1} (CH_2 symmetrical stretching) [42]. Additionally, aliphatic deformation and rocking vibrations appear at 1443 cm^{-1} , 1370 cm^{-1} , and 1325 cm^{-1} . The $\text{C}=\text{C}$ stretching vibrations occur at approximately 1500 cm^{-1} and 1610 cm^{-1} in the aromatic system and nucleus, respectively [43]. The peaks within the $900\text{--}700\text{ cm}^{-1}$ range correspond to C-H out-of-plane vibrations in aromatic rings, while the absorption at 3020 cm^{-1} represents C-H stretching in the aromatic nucleus [44]. Functional groups containing oxygen, such as those found in the $1740\text{--}1690\text{ cm}^{-1}$ region, include aliphatic esters ($1740\text{--}1730\text{ cm}^{-1}$) and aromatic carbonyl or carboxyl ($\text{C}=\text{O}$) groups ($\sim 1710\text{--}1690\text{ cm}^{-1}$) [45]. Additionally, a band at 1875 cm^{-1} , likely associated with carbonyl or carboxyl groups, has been reported in earlier studies [46]. The absorption at 1660 cm^{-1} is linked to exocyclic double bonds or conjugated carbonyls, indicating a degree of immaturity in liptinite macerals, especially resinite [47]. The region between $1300\text{--}1100\text{ cm}^{-1}$ corresponds to C-O stretching vibrations, characteristic of carboxylic acids, phenols, alcohols, and ethers, with a strong absorption at 1260 cm^{-1} [48]. Moreover, OH groups are visible within the $3600\text{--}3100\text{ cm}^{-1}$ range, which could be attributed to various hydrogen bonding interactions, such as OH-N, cyclic OH tetramers, OH-O ether, self-associated OH-OH n-mers, and OH- π bonds [49].

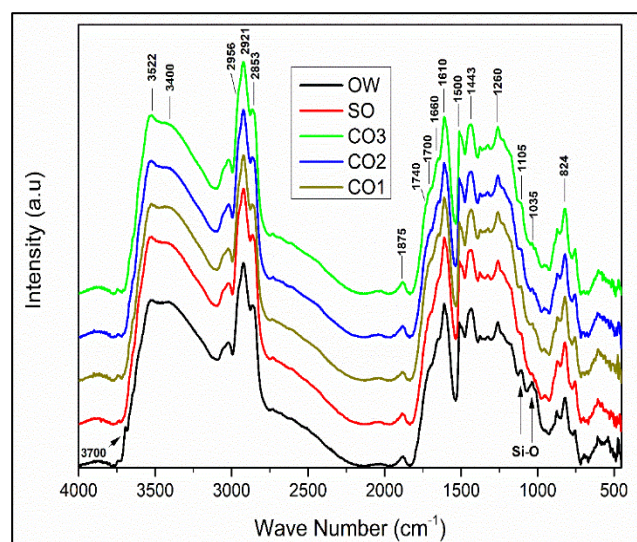


Fig. 6. DRIFT-FTIR spectra of Oltu-stone samples

When comparing the Oltu-stone wastes with cleaned Oltu-stone, the differences lay in the relative intensities of FTIR spectra. The difference between the relative intensities of the functional group is not apparent. To further investigate the chemical structure variations between the cleaned Oltu-stone fractions and Oltu-stone wastes, the FTIR spectra were curve fitted by deconvolution of the following regions: $3100\text{--}2800\text{ cm}^{-1}$, $1800\text{--}1540\text{ cm}^{-1}$, and $1540\text{--}980\text{ cm}^{-1}$ (as mentioned in supporting information). The integrated area of the fitted peaks was used for semi-quantitative analyses of FTIR parameters [51,52,53], listed in table 3. It is observed that the cleaned Oltu-stone has nearly identical values of structural parameters compared to standard Oltu-stone (Table 4). The chain length ratio provided insight into the typical length of aliphatic and alkyl side chains on aromatic rings [53]. In cleaned Oltu-stone fractions, CO3 has the highest value of chain length ratio (1.46) compared to CO1 and CO2. It is seen that the chain length ratio is increasing with a decrease in dense medium density. The recovery of the aliphatic portion accompanies the increase in chain length ratio from high to low densities, reflecting increased liptinite content (particularly resinite). In general, liptinite contains the longest and least branched chain length compared to other macerals groups. Besides, the aromaticity (AR) and degree of condensation (DOC) are very low due to low aromatic structures. Index A, in Table 3, is mainly evaluating the hydrocarbon-generation potential. The ratio for different cleaned Oltu-stone fractions varied 0.55–0.56, indicating the high potential for hydrocarbon generation, as stated by [54].

Table 3 FTIR semi-quantitative indices.

Semi-quantitative index		Index calculation
1	Aliphatic chain length (AL)	$\frac{CH_2}{CH_3} = \frac{A_{(-2920)}}{A_{(-2950)}}$
2	Aromaticity (AR)	$\frac{CH_{ar}}{CH_{al}} = \frac{A_{(3000-3100)}}{A_{(2800-3000)}}$
3	Degree of aromatic ring condensation (DOC)	$\frac{CH_{ar}}{C = C} = \frac{A_{(3000-3100)}}{A_{(-1500)} + A_{(-1600)}}$
4	Hydrocarbon generation potential (A)	$\frac{CH_{al}}{CH_{al} + C = C} = \frac{A_{(2800-3000)}}{A_{(2800-3000)} + A_{(-1500)} + A_{(-1600)}}$
5	Coal maturity (M)	$\frac{C = O}{C = O + C = C} = \frac{A_{(1650-1800)}}{A_{(1650-1800)} + A_{(-1500)} + A_{(-1600)}}$

“A” corresponds to the integrated area of the corresponding peaks

The apparent maturity is assessed by the ratio between oxygen-containing groups (C=O) and aromatic groups (C=C). It is observed that the apparent maturity of cleaned Oltu-stone samples is approximately the same as standard Oltu-stone. In cleaned Oltu-stone, it is noticed that the value of apparent maturity (M) has decreased with increasing the dense medium density. That decrease in the ratio indicates that the amount of matured coal is increased [53]. Chakravarty [55] stated that coal maturity negatively relates to the aliphatic chain length ratio. In

this study, the lowest density fraction (CO3) has a high chain length ratio and low apparent maturity than other density fractions (CO1 and CO2). Semi-quantitative and qualitative analysis of FTIR spectra found that cleaned Oltu-stone has the longest aliphatic chain length, low aromaticity, low maturity level, and great potential for hydrocarbon generation. In contrast to standard Oltu-stone, the cleaned Oltu-stone has exhibited approximately similar chemical structures, based on the qualitative and quantitative analysis.

Table 4. Semi-quantitative analyses of functional group ratios derived from FTIR spectra.

Semi-quantitative Index	Calculated values				
	CO1	CO2	CO3	OW	SO
Aliphatic chain length (AL)	1.40	1.42	1.46	1.44	1.35
Aromaticity (AR)	0.05	0.06	0.05	0.05	0.05
Hydrocarbon generation potential (A)	0.55	0.55	0.56	0.55	0.56
Degree of aromaticity ring condensation (DOC)	0.06	0.07	0.07	0.06	0.06
Apparent maturity (M)	0.46	0.47	0.50	0.48	0.47

4. Conclusion

In this study, the cleaning of Oltu-stone waste was carried out using a float-sink method with zinc chloride solution at varying densities. Three fractions with densities below 1.25 g/cm³ were selected for analysis, and their petrographic and chemical properties were compared with those of standard Oltu-stone.

The cleaned Oltu-stone samples primarily consist of liptinite macerals (72-78%), with a minor presence of huminite (20-23%) and an ash content of less than

2%. Liptinite was particularly concentrated in the fraction below 1.25 g/cm³, resulting in a cumulative float yield of 82.64%, which is a favorable proportion for potential applications. The processed Oltu-stone waste contains macerals such as contorted suberinite, primary cell-filling resinite, and secondary resinite, specifically exsudatinitite. Due to the high liptinite content, especially resinite, the purified Oltu-stone exhibits a significant volatile matter content of around 63-65%.

The raw Oltu-stone waste includes mineral contaminants like quartz, clay, calcite, and pyrite. XRD analysis confirmed that quartz and calcite were largely removed during processing, though pyrite remained trapped within enclosed structures. SEM imaging revealed that most of this pyrite appears as framboidal pyrite. FTIR analysis indicated that the refined Oltu-stone is rich in aliphatic hydrocarbons, has a low degree of aromaticity, and exhibits strong potential for hydrocarbon generation with relatively low thermal maturity.

The findings from this study provide essential insights into the characteristics of cleaned Oltu-stone waste, validating its similarity to standard Oltu-stone and reinforcing its suitability for reuse. By conducting a detailed petrographic and chemical analysis, this work supports the previously demonstrated high-pressure agglomeration approach and offers a foundation for optimizing that process. As such, the study contributes to waste valorization efforts and promotes circular economy strategies by turning mining by-products into useful and economically valuable materials.

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