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SINTERING OF JORDANIAN OIL SHALE UNDER SIMILAR CONDITIONS OF FLUIDIZED BED COMBUSTION SYSTEMS

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Abstract. *Oil shale in Jordan and elsewhere faces many obstacles that hinder its utilisation. Recent developments of the utilization of Jordanian oil shale include the establishment of power generation companies that depend on the technology of atmospheric fluidized bed combustion systems (FBC). Sintering is believed to have been the main cause of many operational problems of FBC systems. This work investigates the sintering propensity of ash obtained from oil shale from Jordania's largest oil shale deposit El-Lajjun, when combusted at different temperatures, as well as major mineral transformations as a function of temperature. The results obtained by the pressure drop sintering technique showed that the sintering temperature is a strong function of the combustion temperature. Two regions of sintering were found: a low temperature sintering region and a high sintering temperature region. The low sintering temperature region starts at around 700 °C where it is believed to be due to the sintering of limestone. On the other hand, the high sintering temperature region, which starts at 900 °C, is believed to be due to the sintering of the wollastonite formed. Scanning Electron Microscope (SEM) images and Brunauer–Emmett–Telle (BET) measurements confirm these findings.*

Keywords: *oil shale ash, sintering, pressure drop sintering, FBC.*

1. Introduction

The growing shortage of high-grade fossil fuels and the increase in their cost together with recently introduced environmental regulations demand new, highly efficient, cost-effective methods for power generation. In this context, the fluidized bed combustion (FBC) system is one of the most promising technologies.

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The higher efficiency, low emissions, and low capital cost of the fluidized bed combustion system make it very competitive for power generation. Fluidized bed combustion systems also have the ability to convert wastes into an energy source by utilizing the heat transfer characteristics of the fluidized bed technology. On the other hand, some operational problems are encountered during fluidization of some fossil fuels.

Several problems accompany the combustion of coal in FBC reactors. These problems are mainly caused by agglomeration of bed particles with ash deposits leading to defluidisation of the bed, ash deposition on gas circuits, and blockage of hot gas cleaning systems. The early operation of the Wakamatsu demonstration plant in Japan in 1993 showed the following minor operational problems: plugging of fuel piping and nozzles, cracking of spurge tubes, gas leakage from hot gas piping, cracking of ceramic filters, cyclone plugging, and entrainment of fine ash particles [1].

The agglomeration observed in fluidized bed systems occurs mainly because of particles sintering. Sintering refers to the welding of adjacent particles, usually under heating. It normally involves the development of strength of these particles. This phenomenon can occur at temperatures much below the melting temperature because crystalline material can behave like amorphous materials at certain temperatures [2].

The term "sintering" is used to describe particle-particle agglomeration under heating. There is no exact definition for sintering; some definitions state that sintering is the bonding of adjacent surfaces of particles in a mass of powder [3]. Others refer to sintering as the thermal treatment of powder compact for the purpose of increasing strength or as an operation which increases the cohesion between the particles in a green or pre-sintered compact or powder performed at elevated pressure. However, all agree on the principle of formation and binding as driven by excess surface energy. Hausner [3] reports that sintering of certain materials begins at temperatures equal to 40–50% of the melting temperatures of those materials.

Sintering of fuel ash depends largely on the nature and composition of the ash as well as temperature of operation. In a recent study on Estonian oil shale in a bench scale fluidized bed combustion system [4], it has been shown that the sintering temperatures of oil shale ash are substantially lower than their deformation temperatures. This has caused defluidisation of the FBC particularly during the firing up stage, indicating the importance of sintering in the operational problems of FBC when utilizing oil shale as the solid fuel.

Sintering temperatures of oil shale ash were found to depend on its chemical composition [5, 6]. The chemical composition of ash fractions is mainly presented in terms of the contents of SiO_2 and CaO. A special method was elaborated for determination of the sintering temperature of Estonian calcium-rich oil shale ash [7]. This method correlates the sintering temperature Ts with the ratio $SiO_2/CaO = m_0$. The sintering temperature of oil shale ash was described by a simple empirical equation for a basic oil shale ash [7]:

$$Ts(K) = 1530 - 366 \cdot m_0. \qquad (1)$$

The composition of Jordanian oil shale is universally unique due to the high contents of minerals (> 55%), particularly calcite and sulfur [8]. Although several studies focused on the oil yield and contents of extracts during fluidized bed gasification as well as the kinetics of combustion [9–11], there are no available studies on the behavior and sintering of Jordanian oil shale ash at fluidized bed combustion.

This work aims at studying the sintering behavior of Jordanian oil shale from a well-known deposit, El-Lajjun. Special emphasis will be placed on the measurement of the sintering temperature of Jordanian oil shale ash.

2. Experimental

2.1. Materials

Oil shale samples were collected from a recently mined surface outcrop of El-Lajjun oil shale deposit. Table 1 presents the proximate analysis of the oil shale ash used in this study while Table 2 presents an X-Ray Fluorescence (XRF) analysis of the collected oil shale sample. The major minerals present in the as received sample are calcite, quartz, tridymite, apatite and traces of some clay minerals (see Fig. 1A).

Table 1. Proximate analysis of El-Lajjun oil shale sample used in the study

Property	Proportions, wt%
Moisture	1.1
Volatile matter	44.0
Ash	54.5
Fixed carbon	0.4

Table 2. XRF analysis of El-Lajjun oil shale ash

	Raw oil shale*	Ash 550	Ash 650	Ash 750	Ash 850	Ash 950
	Wt%					
Na_2O	0.28	0.33	0.30	0.28	0.31	0.31
MgO	0.32	0.51	0.59	0.59	0.62	0.59
Al_2O_3	2.60	4.09	4.54	4.24	4.32	4.26
SiO_2	30.61	42.96	41.11	41.68	41.99	43.33
P_2O_5	2.13	3.49	3.46	3.50	3.56	3.58
SO_3	8.21	8.72	6.86	7.03	6.34	5.80
Cl	0.13	0.13	0.17	0.16	0.10	0.06
K_2O	0.48	0.75	0.78	0.75	0.75	0.71
CaO	40.45	36.01	39.00	38.66	38.84	38.13
TiO_2	0.16	0.24	0.26	0.25	0.24	0.25
V_2O_5	0.03	0.11	0.12	–	–	0.07
Cr_2O_3	0.07	2.27	2.38	0.11	0.11	0.11
Fe_2O_3	1.36	0.04	0.05	2.34	2.39	2.37
NiO	0.03	0.03	0.03	0.05	0.05	0.05
CuO	0.02	0.13	0.14	0.03	0.03	0.03
ZnO	0.08	0.01	0.01	0.15	0.15	0.14
SrO	0.10	0.16	0.16	0.16	0.17	0.16
ZrO_2	0.0029	0.0019	0.0046	0.0036	0.0044	0.0041
MoO_3	0.0209	0.0328	0.0345	0.0338	0.0337	0.0332

* Assuming that 17% of oil is present as matrix.

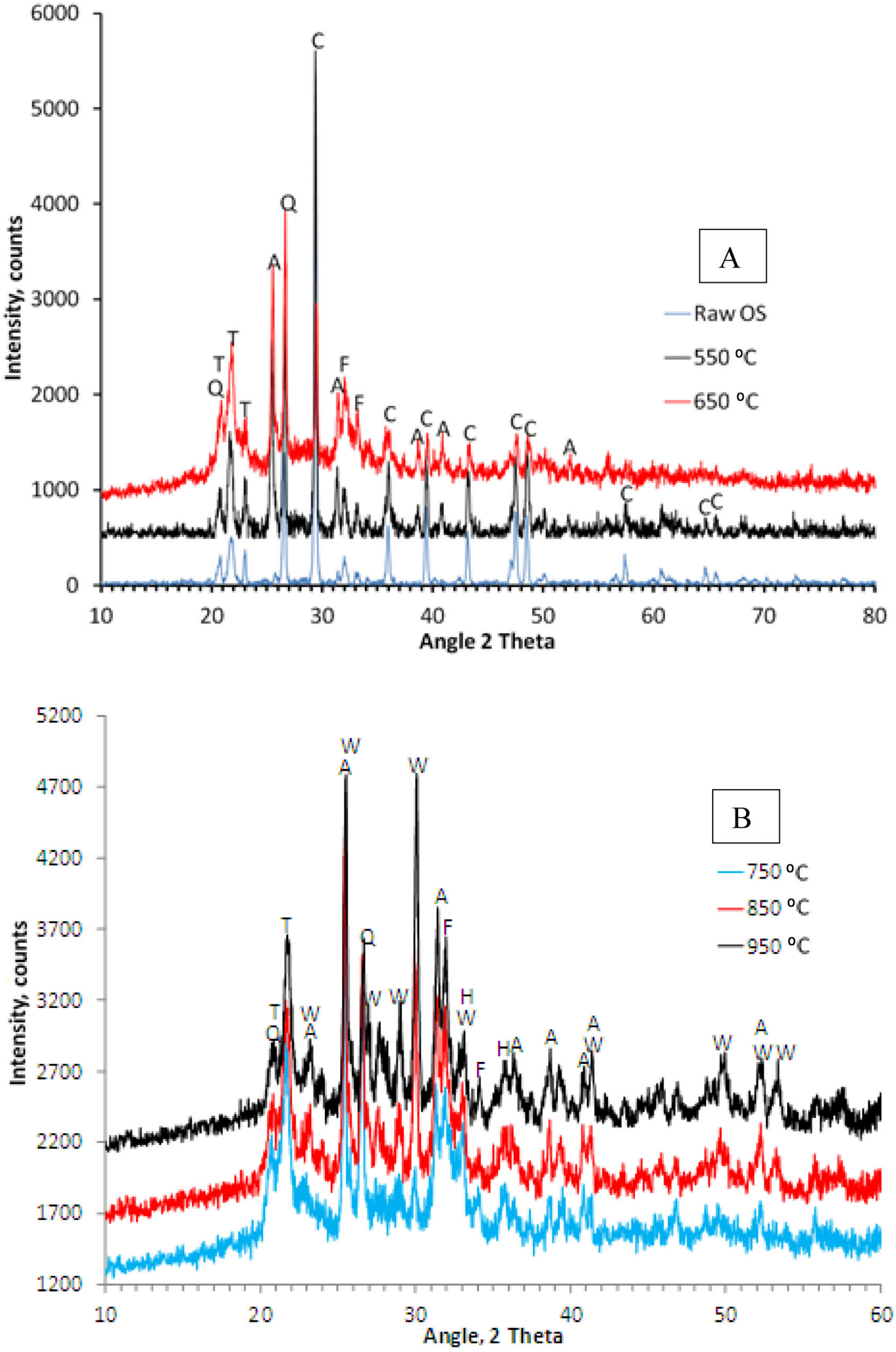

Fig. 1. XRD patterns of raw oil shale and oil shale ash obtained at different combustion temperatures (A – for raw oil shale, ash obtained at 550 and 650 °C; B – for oil shale ash obtained at 750, 850 and 950 °C).

2.2. Experimental procedure

Oil shale samples were crushed and sieved to 2 fractions: < 106 µm and 106–250 µm. Samples of each size fraction were combusted in air for 24 hours at different combustion temperatures ranging from 650 °C to 950 °C in a muffle furnace covering the range of temperatures encountered in fluidised bed combustion systems. The heating rate used for these combustion runs was 10 °C/min. The long residence time of combustion was chosen in order simulate the behaviour of ash deposits on surfaces such as heat exchanger tubes of the fluidised bed combustion system at different temperatures. These deposits may stay long enough to reach the equilibrium state. Some selected samples were analysed using SEM to verify the phenomenon of sintering. In addition, BET surface area for oil shale samples was measured after combustion at different temperatures to identify the temperature at which the reduction of the surface area occurs. The reduction in the surface area of ash samples corresponds to the sintering phenomenon. Differential Thermal Analysis (DTA) for the oil shale samples was also performed in order to understand the behaviour of the ash at different temperatures.

2.3. Pressure drop sintering technique

The pressure drop technique for the measurement of the sintering temperature was developed earlier and verified by Al-Otoom et al. in 2000 [12]. The technique consists in the measurement of pressure drop across a pellet of ash formed inside an alumina tube while feeding air to this tube at a constant flow rate and during heating in a tubular furnace. Figure 2 shows a schematic diagram of the pressure drop sintering technique. The sintering temperature obtained by this technique corresponds to the temperature at

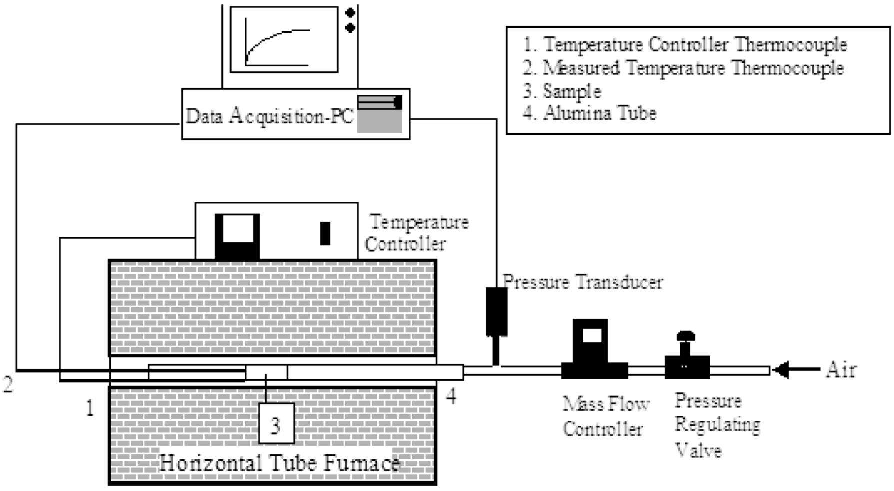

Fig. 2. Schematic diagram of the set-up for the pressure drop sintering technique.

which a maximum pressure drop is achieved, since after sintering the pellet starts to shrink allowing new and easier pathways for air to pass through.

The pressure drop sintering technique measures the pressure drop across the ash pellet, which initially reflects the degree of packing of the particles, which is a function of the open pores inside the pellet, as well as the velocity and viscosity of the air passing through the pellet. As the temperature of the pellet increases, the pressure drop increases due to the increase in the viscosity of the air with temperature while maintaining a constant velocity. The velocity is maintained at a constant value by using a mass flow controller, which provides a constant volumetric flow rate of 15 ml/min over the entire experiment. According to Darcy's law [13], the rate of flow is directly proportional to the pressure gradient and inversely proportional to the viscosity, μ, of the gas:

$$\frac{\Delta P}{L} = \frac{u\mu}{B_0}, \tag{2}$$

where ΔP is the pressure drop across a sample of length L, u is the velocity, and B_0 is the permeability coefficient. As this equation is only valid for a viscous flow, the flow rate used in the pressure drop sintering technique is very low (15 ml/min) and the corresponding Reynolds number is smaller than 0.1.

The sintering temperature from the pressure drop experiment is designated as the point at which the pressure drop reaches a maximum. When sintering occurs, the pellet starts to shrink, and thus is pulled away from the wall of the alumina tube, resulting in the formation of new pathways for the passage of air. As a result, the pressure drop starts to decrease.

3. Results and discussion

Figure 1 shows the results of X-Ray Diffraction (XRD) analysis of raw oil shale sample and ash samples obtained after combustion at different temperatures. From Figure 1A it can be seen that raw oil shale sample contains calcite, quartz, apatite and tridymite (SiO_2) as major phases. Detailed analysis shows the presence of kaolinite and traces of pyrite, which are contained mainly in the kerogen capsules as was confirmed in a previous study by SEM analysis [12]. After combustion at a temperature of 550 °C anhydrite ($CaSO_4$) appeared as a new phase with increasing intensity as the combustion temperature increased. At a temperature of 650 °C the intensity of calcite XRD peaks decreased considerably while the intensity of anhydrite peaks increased. The XRD pattern of oil shale ash obtained at a combustion temperature of 750 °C (see Fig. 1B) shows a complete disappearance of calcite and appearance of new peaks related to wollastonite ($CaSiO_3$), the intensity of which increases with increasing temperature. The CaO formed as a result of decomposition of calcite seems to be amorphous although it could be that some crystallization process occurs as the combustion temperature increases (peaks at 32.2, 37.35 and 53.85° [15]. Furthermore, at 33.2 and 35.7° one could also identify hematite peaks which resulted from the oxidation of pyrite occurring at about 530 °C.

It was shown in a previous study [13] that the major inorganic loss of El-Lajjun oil shale occurs in the temperature region between 650 °C and 850 °C depending on heating rate. This loss is related to calcite decomposition. An example of the thermogravimetric analysis (TGA) non-isothermal profile of El-Lajun oil shale at a heating rate of 3 °C/min is shown in Figure 3A. The derivative weight loss profile shows a peak at a temperature of 695 °C. This is consistent with the results of XRD analysis discussed above.

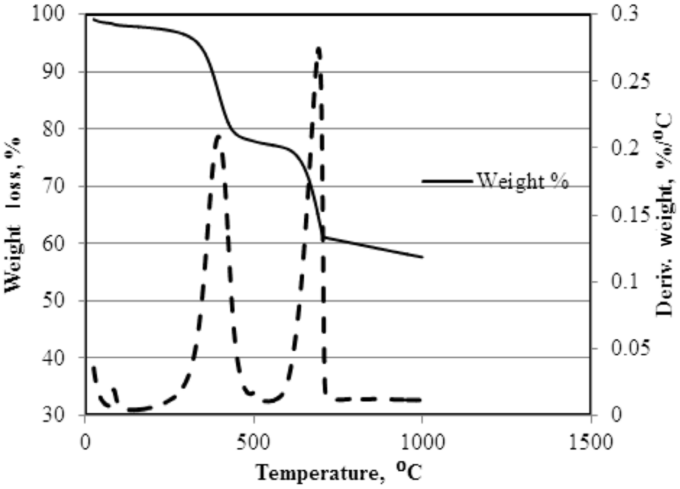

Fig. 3A. TGA and DTG curves of oil shale at a heating rate of 3°C/min.

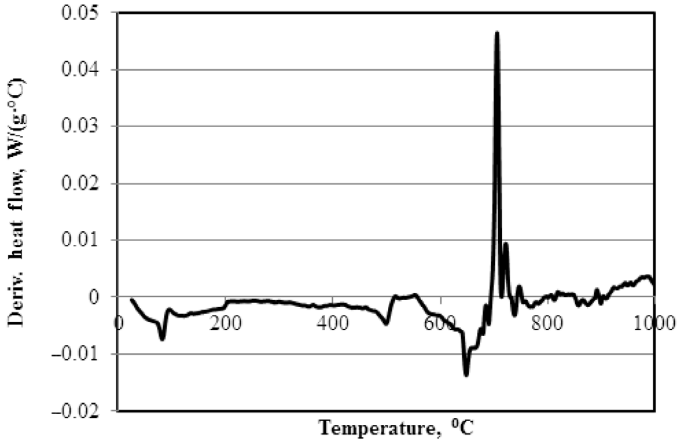

Fig. 3B. DTA analysis of the studied oil shale.

Initially, changes of the surface area of oil shale ash as a function of combustion (ashing) temperature were measured. The N_2 BET surface area of oil shale ash combusted at 550 °C increased to about 2.5 times that of the raw oil shale sample (Fig. 4), which could be related mainly to opening new pores as a result of the complete devolatilisation combustion of organic matter present in oil shale. A further increase of combustion temperature has resulted in a decrease of the surface area reaching values below that of raw sample at a temperature of 950 °C. This suggests that sintering of oil shale ash may have started beyond 600 °C, causing a significant reduction in surface area above this temperature. These results have provided a basis for further experimentation. This basis depends on measurement of the sintering temperature for oil shale combusted at different temperatures to build a relationship between the combustion temperature and the sintering temperature.

Sintering temperature measurements were carried out for oil shale combusted at different temperatures ranging from 650 °C to 950 °C, covering all possible temperature ranges inside the fluidized bed combustors. Triplicates of measurements were made at each combustion temperature in order to verify the repeatability of these measurements. Figure 5A shows the results obtained for oil shale ash combusted at 850 °C. The difference in the particle size of the studied particle size range did not show any variation in the sintering temperature since the chemical composition of these size fractions was identical. Figure 5B shows the relationship between the sintering temperature and the combustion (ashing) temperature of oil shale ash. It is clear from this figure that if the combustion temperature of the oil shale ash is below 800 °C, the sintering temperatures are between 700 °C and 750 °C. This can be explained by the sintering of limestone which exists in

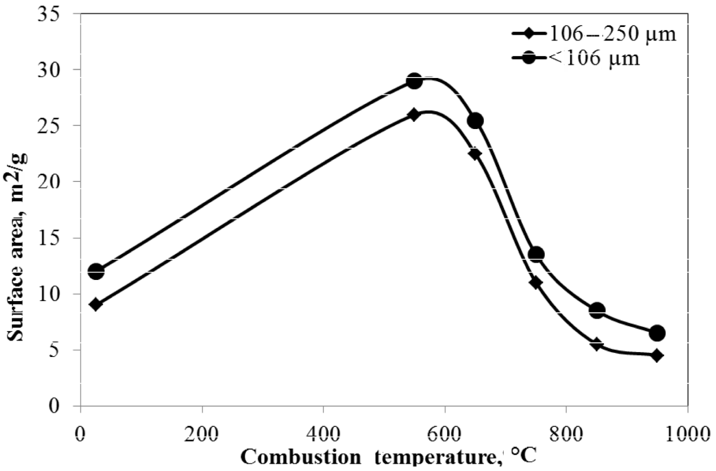

Fig. 4. N_2 BET surface area changes with combustion temperature for two particle size distributions of oil shale ash.

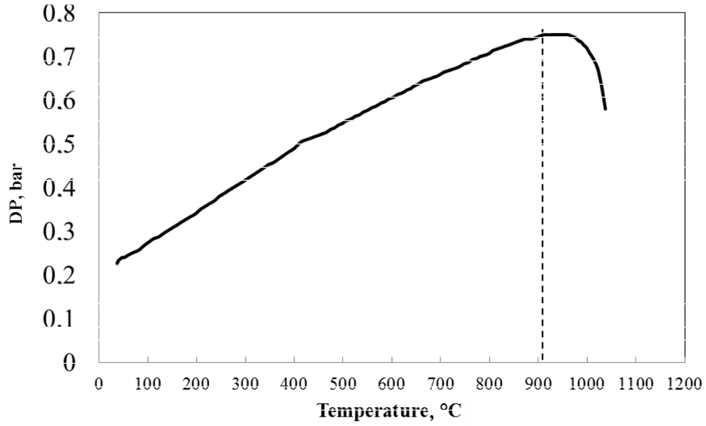

Fig. 5A. Results of pressure drop experiments for oil shale ash combusted at 850 °C (< 106 µm).

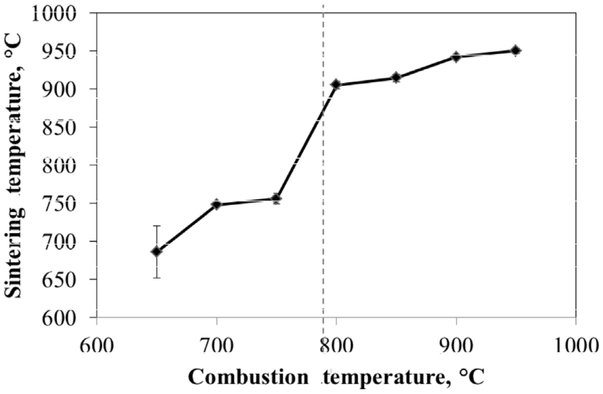

Fig. 5B. The sintering temperature of oil shale ash as a function of the ashing temperature.

abundance in the oil shale ash. It was shown earlier [14] that limestone sinters under atmospheric conditions before any significant decomposition, calcination or reaction occurs and that limestone shows a significant sintering at 750 °C. In addition, it was found that anhydride, which is also present in the studied oil shale samples, sinters at around 700 °C, too. For verification purposes, DTA was performed for the studied oil shale at a heating rate of 3 °C/min. Figure 3B shows the results of this analysis; at a temperature of about 695 °C there is a major endothermic peak which is related to the decomposition of calcite, followed by another smaller exothermic peak at a temperature of about 723 °C. Zhu et al. [15] reported that the molar enthalpy of wollastonite formation is –89.6 kJ. Therefore, the exothermic peak at 723 °C could be assigned to the formation of wollastonite, which should have formed in the temperature region between 695 °C and 750 °C based on the TGA and XRD pattern of the sample combusted at 750 °C. On the other hand, if the combustion temperature is above 800 °C, the sintering temperatures are between 900 °C and 950 °C. When explaining the second region of sintering in Figure 5B, the authors believed this to be the result of sintering of wollastonite, which was earlier found by Ma et al. to sinter at temperatures above 900 °C [16]. Wollastonite was also found earlier to cause agglomeration in fluidised bed combustion systems [17].

SEM images were taken for ash samples combusted at different combustion temperatures Figure 6A shows the sintering of limestone in oil shale ash at 750 °C, while Figure 6B depicts the sintering of wollastonite in the oil shale ash at 950 °C.

The findings in this study reveal that if the operating temperature of the FBC system is between 800 °C and 900 °C, then the Jordanian oil shale might not face any operational problems related to agglomeration, defluidization, or formation of strong deposits on heat exchanger tubes. Therefore, it is believed that this oil shale is suitable for utilization in the FB technology.

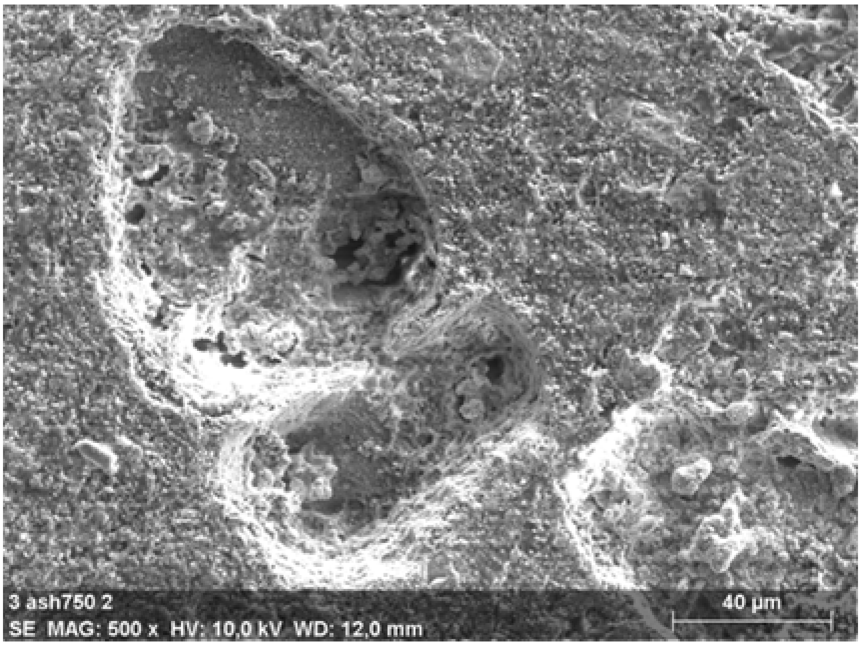

Fig. 6A. SEM image for ash combusted at 750 °C.

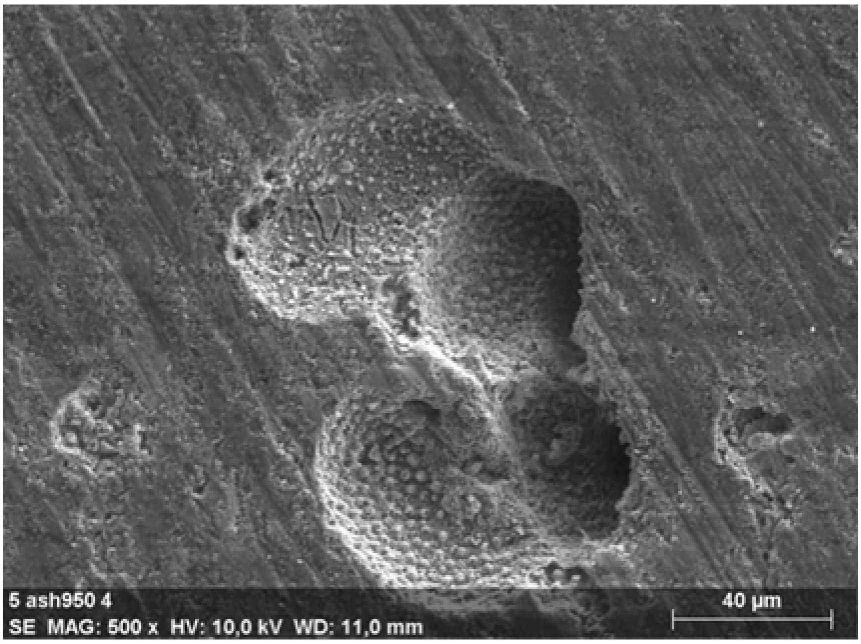

Fig. 6B. SEM image for ash combusted at 950 °C.

4. Conclusions

The mineral behavior of Jordanian El-Lajjun oil shale under the conditions of fluidized bed combustion systems was investigated. The mineral thermal transformation was dominated by the formation of wollastonite by the solid state reaction of CaO and SiO_2 at temperatures higher than 750 °C. Two regions of sintering were found: a low temperature sintering region and a high sintering temperature region. The low sintering temperature region starts at around 700 °C and is believed to be due to the sintering of limestone. The high sintering temperature region, which starts at 900 °C, is thought to be due to the sintering of the wollastonite formed. The authors are of the opinion that Jordanian oil shale would pose minimal operational problems related to sintering and agglomeration if the operating temperature is between 800 °C and 900 °C.

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