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# Utilization of pyrolytic wastewater in oil shale fired CFBC boiler

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# ABSTRACT

The current paper presents the results of incineration of pyrolytic wastewater (WW) in an oil shale fired 250 MW thermal (MW<sub>th</sub>) circulating fluidized bed combustion (CFBC) boiler. The measurements in the industrial-scale oil shale fired CFBC unit show that WW incineration did not cause the plant to exceed the gaseous pollutant or particulate matter (PM) emission limits set for large combustion plants. The data obtained is compared to previous results from a pilot-scale 60 kW<sub>th</sub> CFB combustor. In pulverized combustion (PC) units, incineration of pyrolytic WW was carried out a long time ago as it reduced SO<sub>2</sub> emissions, a similar result was achieved in a CFBC unit; however, a high nitrogen content in WW results in increased NO<sub>x</sub> emissions. From the practical point of view, pyrolytic WW incineration (ca 13 t/h) increases fuel (oil shale) consumption by up to 6% for the same thermal output, which consequently reduces a unit's efficiency.

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## 1. Introduction

Global Energy demands are increasing and according to International Energy Agency (IEA) data, combustion with conventional fuels will still be needed to meet this energy demand (Table 1). Fuel combustion (for heat and power generation) remains the most significant source of GHG emissions, of which CO<sub>2</sub> emissions constitute about 65% (Lee et al., 2017).

Estonia has had long-term experience with oil shale. It is used for power generation (via combustion) and for shale oil production (via pyrolysis) as shown in Fig. 1. For power production, old outdated pulverized combustion (PC) combustors are still used together with new, more efficient, and environmentally friendly CFB combustors. Moving to CFB units has helped to reduce the carbon footprint in the oil shale power sector which is a problem experienced throughout the world (Klemeš et al., 2017).

On a national level, shale oil production is seen as the most promising option for oil shale utilization (Anon., 2016). Although shale oil production is seen as the superior option, its production is also associated with the generation of pyrolytic WW, which contains PAHs, ammonia, sulfates etc. (Maaten et al., 2017) and hence poses a considerable environmental hazard. Under the current annual shale oil production capacity (around 1 Mt), about

\* Corresponding author. E-mail address: alar.konist@taltech.ee (A. Konist). 0.10–0.15 Mt of pyrolytic WW must be disposed of annually. Currently, there is no economically feasible solution for purification of this WW. Moreover, only limited success has been achieved in the treatment of pyrolytic WW under laboratory conditions using various WW purification processes (Klein et al., 2017). Therefore, currently its disposal is carried out by incineration in PC units. This cannot be regarded as a sustainable option because under gov-ernment policy, by the end of 2023 all such PC units must be permanently closed down. The problem is even more challenging, given that according to the "Estonian National Development Plan for the Use of Oil Shale" (Anon., 2016) pyrolytic WW generation is expected to increase by 5–6 times.

Under one possible solution, it is proposed that WW incineration could be carried out in the new CFBC units. An obvious advantage of this option is that it can be easily realized without any additional investments. Although incineration of wastewater containing recalcitrant compounds is common in petroleum, and pulp and paper industries (Ji et al., 2016), limited literature is available on this topic. It is generally agreed that CFBC units are the best choice for incineration tasks allowing simple and controlled waste elimination (Mu et al., 2012). These general conclusions were validated by incineration of oil shale pyrolytic WW in a pilot-scale 60 kW<sub>th</sub> CFB combustor (Konist et al., 2018). As shown WW injection did not affect the oil shale combustion efficiency and volatile organic compounds (VOC) and SO<sub>2</sub> emissions were unchanged.

An important issue related to the incineration of fuels or (py-rolytic) WW is  $NO_x$  emissions, which depend primarily on the





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#### Table 1

World total primary energy supply (TPES) by source (OECD/IEA, 2019).

	Coal	Natural gas	Nuclear	Hydro	Geothermal, solar, etc.	Biofuels and waste	Oil	SUM
World TPES in 2016 (Mtoe)	3731	3035	680	349	226	1349	4390	13,760
Increase (%, basis 1990)	68.1	82.5	29.3	89.7	517.5	48.4	35.7	56.9



Fig. 1. Oil shale utilization routes and process streams.

nitrogen content in fuel, but also on the combustion temperature and which may need to be controlled by secondary measures to meet environmental limits (Yang et al., 2016). Another issue for incineration of high humidity fuels in industrial scale boilers, is that CO emissions could significantly increase due to poor combustion (Tsai et al., 2002).

Given the results from pilot-scale pyrolytic WW incineration tests (Konist et al., 2018), further experiments on industrial scale oil shale fired 250 MW<sub>th</sub> CFB boiler were planned. This was anticipated to provide a unique set of data to compare the performance of pilot-scale 60 kW<sub>th</sub> and industrial scale 250 MW<sub>th</sub> CFBC units. In any case, the emission of CO and other gaseous pollutants, as well as the particulate matter from industrial scale unit under normal operational conditions must be known. The extent of fuel consumption increase must be determined as it directly affects process efficiency, pollutants emissions and the environmental impact of oil shale industry.

# 2. Materials and methods

# 2.1. Test plan

The test plan included normal CFBC boiler operation (so-called reference tests) at nominal (100%) load, meaning only oil shale was fired, followed by pyrolytic WW incineration tests at nominal (100%) and partial (60%) loads, meaning the planned oil shale mass flow was approximately 30 kg/s and 20 kg/s, respectively. Before emission measurements, the boiler was allowed to reach steady-state operation (at least 6 h). Each test was planned to last for at least 3 h and the test plan is shown in Table 2. The flow rate of pyrolytic WW was nominally set as 13 t/h.

# 2.2. Wastewater and oil shale

The pyrolytic WW samples were taken from the sampling point before boilers. The WW was a mixture of pyrolytic water from the Enefit-140 (Golubev, 2003) and Enefit-280 (Neshumayev et al., 2019) shale oil plants. In the Enefit-140 plant on average WW production was about 8 t/h. While, the average flow rate of pyrolytic WW from Enefit-280 plant was around 5 t/h. The results of the analysis of the WW from two samples is given in Table 3. The two samples were taken during test #2 and #3 and the results show that pyrolytic WW composition is comparable to previous data from the Enefit-140 plant (Maaten et al., 2018).

Data on the daily average oil shale samples is given in Table 4. The oil shale sample can be characterized as average with a water content of 10.5 wt % and a lower heating value (LHV) around 8 MJ/kg.

# 2.3. The CFBC test facility

Incineration tests were carried out in a 250 MW<sub>th</sub> CFBC boiler that is part of a 215 MW<sub>e</sub> power unit at the Eesti Power plant. The unit itself has two CFBC boilers, which were commissioned in 2004 by Foster Wheeler Energia Oy (Sumitomo SHI FW) (Hotta et al., 2005). The thermal efficiency of the oil shale fed CFB boiler is in the range of 88–90% and the oil shale used has the fraction size below 20 mm and LHV starting from around 7 MJ/kg. At nominal load (215 MW<sub>e</sub>) the power unit consumes about 60 kg/s of oil shale.

## 2.4. Ash sampling and ash analysis

Possible ash sampling points are shown in Fig. 2. For the analysis boiler bottom ash sample (port 1, Fig. 2) and electrostatic precipitator (ESP) ashes from field 1 to 4 (ports 5 to 8, Fig. 2) were taken. Generally, boiler bottom ash and ESP field 1 ash flows form approximately 35% and 45% of the total ash flow, respectively (Plamus et al., 2011). All the ash samples were stored in airtight containers. The chemical compositions of the ash samples was determined via wavelength-dispersive X-ray fluorescence spectroscopy (WD-XRF, Rigaku ZSX Primus II) and the Loss of ignition (LOI) was measured at 920 °C.

#### Table 2

Test plan	for p	yrolytic	WW	incineration	tests and	reference	tests.
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Test #	Description	Duration, hours	MWe	Pyrolytic water flow rate, t/h
1	Stabilization, day 1	6	215 (100%)	_
	Reference test, day 1 and day 2	>3	215 (100%)	_
2	Stabilization, day 2 and day 3	12	215 (100%)	13
	WW incineration at nominal load, day 3	>3	215 (100%)	13
3	Stabilization, day 3	6	172 (60%)	13
	WW incineration at partial load, day 3	>3	172 (60%)	13

## Table 3

Characteristics of pyrolytic wastewater and oil shale.

Parameter	Sample 1 (test #2)	Sample 2 (test #3)
Chemical Oxygen Demand, mgO <sub>2</sub> /L	42,470	41,052
Total Organic Carbon, mg/L	9250	8450
Phenol Index, mg/L	650	800
Petrochemicals (C10–C40), mg/L	2840	2440
рН	10.4	12.7
Total Kjeldahl Nitrogen, mg/L	1600	1500
Total Sulfur, mg/L	8200	9000
Total Suspended Solids, mg/L	65	246
Total Phosphorus, mg/L	<2	<2
Conductivity, mS	10.4	17.7
Sulfides, mg/L	71.7	35.8

procedure is described in detail elsewhere (Parve et al., 2011). Finally, the flue gas flow rate was measured periodically (in the beginning and at the end of each test) and the temperature was measured continuously.

# 3. Results and discussion

# 3.1. Boiler and power unit parameters

The test plan is given in Table 2, and the actual parameters during tests are given in Table 5 (see also Fig. 3). However, the mass flow rate of pyrolytic WW during stabilization phase before test #2

## Table 4

Proximate and ultimate analysis of daily average oil shale samples.

Test #	Oil shale sample	W <sup>ar</sup> , wt. %	LHV, MJ/kg	$(\textbf{CO}_2)_{m}^{ar}\text{, wt. }\%$	A <sup>ar</sup> , wt. %	C <sub>elem</sub> , wt. %	N <sub>elem</sub> , wt. %	S <sub>elem</sub> , wt. %	H <sub>elem</sub> , wt. %
1	Day 1	10.5	8.31	19.95	45.99	27.90	0.07	1.43	2.72
1	Day 2	10.3	7.93	20.95	46.43	27.28	0.06	1.41	2.72
2 and 3	Day 3	10.5	8.07	20.65	46.32	27.34	0.06	1.43	2.76

ar – as received base.



Fig. 2. The conceptual scheme for the 250  $\mathsf{MW}_{\mathsf{th}}$  CFBC boiler with ash sampling ports.

# 2.5. Flue gas analysis

During the tests the analysis of flue gas was carried out continuously and flue gas composition (including flue gas moisture) was determined using a Gasmet DX4000 FTIR type analyzer. Sampling ports located on a horizontal gas pass after ESPs. The same ports were used for isokinetic fly ash sampling to determine the emitted particle concentration in flue gases (PM-sum) and the sampling time was 60 min per sample. The exact PM-sum sampling was reduced to save WW for main tests, as shale oil production capacity in Enefit-140 and 280 plants was lower than usual.

The data presented shows the effect of injected WW on the boiler parameters and thermal output of the CFBC boiler. The power unit load, which is shown in Fig. 3 depends on the operation of two CFBC boilers as described previously in the section of materials and methods. Therefore, in Fig. 3 outside the test periods there is no direct interdependence between fuel mass flow rate and unit load.

An important aspect when considering WW incineration is fuel

Table 5

3

Stabilization, day 3

WW incineration at partial load, day 3

leasured o	easured oil shale mass flow, WW mass flow and unit electrical power during tests and stabilization regimes.										
Test #	Description	Oil shale mass flow to the CFB, kg/s	Electrical power, MW <sub>e</sub>	Pyrolytic water flow rate, t/h							
1	Stabilization, day 1	28.36	215.6 (100%)	_							
	Reference test, day 1 and day 2	29.72	215.6 (100%)	_							
2	Stabilization, day 2 and day 3	31.38	215.1 (100%)	9.20							
	WW incineration at nominal load, day 3	31.46	215.1 (100%)	12.85							

24.42

24.42





Fig. 3. CFB boiler and power unit parameters obtained from plant data acquisition system.

consumption. Water has a high latent heat of vaporization, thus from an energetic point of view, WW may be regarded as fuel moisture. With this assumption, the effective fuel moisture content during test #2 and #3 is calculated to be 19.5 and 22 wt % which is a two-fold increase compared to reference test (test #1). The corresponding calculated values of LHV (assuming the heat of vaporization of water to be 2.25 MJ/kg) are 7.02 MJ/kg and 6.75 MJ/kg, respectively. As a result, to maintain thermal output during WW incineration tests more fuel must be fed to the boiler. In Table 5 the real (according to the plant DCS system) average oil shale mass flow rate during different tests is given. At full load WW incineration increased oil shale consumption by approximately 6%. In addition, the WW injection resulted in lowered boiler temperatures as compared to reference test (Table 6 and Fig. 4). However, this had negligible effect on the emissions. Generally, a similar temperature reduction was observed in the pilot-scale unit when pyrolytic WW incineration was tested (Konist et al., 2018).

## 3.2. Ash properties and the effect of water content

The estimated water content equivalent to 20 wt % water/ moisture content of fuel is similar to that studied for example by Suksankraisorn et al. (2003). On a laboratory scale unit, they observed a significant decrease in combustion efficiency after fuel moisture content was further increased. By contrast, in the Emile Huchet power plant 125 MWe unit in France it has been demonstrated that in a CFB boiler coal slurry with moisture content of approximately 33 wt % and LHV of 10.5 MJ/kg can be efficiently

combusted (Gauvillé et al., 2012). This efficiency is highlighted by the resulting residual (or unburnt) carbon content in bottom and fly ash, which are below 0.4% and 6%, respectively. A high carbon burnout efficiency (close to 100%) is common in CFBC units (especially for high volatile coals), although sometimes problems have been experienced (Xiao et al., 2005). The highest organic carbon content in oil shale ashes measured in the framework of the current study was below 0.6% in boiler bottom ash during normal operation at nominal load (test #1). The respective values in bottom ashes taken during WW incineration at nominal and partial load were 0.4%. None of the fly ash samples taken from four electrostatic precipitators fields contained measurable amount of residual organic carbon.

173.0 (61%)

173.0 (61%)

12 87

12 92

The chemical composition of ashes (Table 7) is primarily determined by the composition of the fuel although also several other factors like the size of the ash particles and combustion conditions (temperature, excess air) have an effect on it. There are obvious differences between the bottom and ESP ashes, however, the WW incineration itself, had minor effect on the chemical composition of ashes. Most notably, compared to nominal load conditions (test #1 and #2), bottom ash from WW incineration at partial load (test #3) had approximately 2 wt% higher mineral CO2 and 2 wt% lower free lime contents indicating reduced extent of decomposition of oil shale mineral matter (carbonates). A decrease of Ca and enrichment in Si and metals content in finer ash particles is also evident. Compared to the PC coal fly ashes from European power plants (Moreno et al., 2005), oil shale ashes are generally Carich, and poor in Al and Si. A high residual CaCO3 content in oil shale

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Test #	Description	Temperature, °C			
		Dense bed	Furnace	Furnace exit	Separator entrance
1	Reference test	785	788	836	831
2	WW incineration at nominal load (100%)	772	773	825	824
3	WW incineration at nominal load (61%)	731	736	763	774



Fig. 4. Changes in temperatures in the boiler during tests.

 Table 7

 Chemical composition and LOI values [wt. %] of ash samples.

Test #	Sampling port #	(CO <sub>2</sub> ) <sub>mineral</sub>	Corg	$SO_3$	CaO	CaO <sub>free</sub>	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	LOI <sub>920°C</sub>
1	1	18.7	0.6	6.2	54.1	14.9	9.7	3.2	2.8	6.1	1.0	0.1	20.2
	5	3.3	n.d.	4.2	33.0	14.9	34.0	10.8	4.6	5.2	4.5	0.2	3.8
	6	3.2	n.d.	5.7	32.5	14.8	33.1	11.0	4.6	5.5	4.5	0.2	3.9
	7	4.1	n.d.	6.1	32.4	10.1	31.1	10.4	5.1	5.9	4.2	0.1	6.0
	8	4.6	0.1	9.0	34.1	9.1	27.2	9.4	4.9	6.7	3.6	0.1	8.0
2	1	17.5	0.4	7.4	54.4	17.1	9.5	3.1	3.0	6.7	1.0	0.1	18.8
	5	3.9	n.d.	4.0	32.1	13.9	34.0	10.8	4.7	5.5	4.4	0.5	4.4
	6	3.8	n.d.	5.3	32.2	15.1	33.6	10.9	4.6	5.7	4.4	0.5	4.4
	7	3.2	n.d.	5.7	33.3	13.2	31.2	10.6	4.9	6.4	4.1	0.3	4.6
	8	5.8	n.d.	9.9	35.8	7.0	26.9	9.4	5.0	7.0	3.4	0.1	9.5
3	1	21.1	0.4	6.0	53.7	13.0	8.8	2.9	2.9	5.4	0.9	0.1	22.0
	5	5.2	n.d.	4.5	30.6	12.6	36.3	11.6	4.9	4.9	4.7	0.7	5.8
	6	5.6	n.d.	4.5	29.6	12.0	37.3	11.9	4.9	4.9	5.0	0.6	6.2
	7	5.0	n.d.	5.3	30.1	11.4	35.3	11.6	5.0	5.5	4.8	0.5	9.5
	8	4.8	n.d.	10.4	36.5	5.8	26.0	9.3	5.1	7.1	3.2	0.1	8.1

\*n.d. - not detected.

ashes (especially that of bottom ashes) is the reason the LOI values are high.

### 3.3. Gaseous pollutants

The combustion of oil shale in CFBC unit is generally much cleaner compared to that from a PC. The advantage of CFBC technology results from its various characteristics, and in particular its normally lower combustion temperatures (<850 °C, Table 6). As a result, air nitrogen oxidation is negligible resulting in approximately 50% lower NO<sub>x</sub> emissions from oil shale CFBC units compared to PC units. This low temperature also offers a reduction of the CO<sub>2</sub> emissions since the extent of the mineral matter (carbonates) decomposition of oil shale is in the range of 70% while in PC boilers it is almost complete (ca. 97%) (Hotta et al., 2005). As a result,  $CO_2$  emissions are lowered by 25% (based on average kg  $CO_2$ / kWh data). From, the ash analysis data, it could be concluded that WW incineration at partial loading further reduced the extent of carbonate decomposition. Any CaO formed effectively binds SO<sub>2</sub> at these combustor temperatures, meaning the SO<sub>2</sub> emissions are also low. SO<sub>2</sub> emissions from CFB combustor are reduced by >95% compared to a PC (Konist et al., 2013). In addition, due to extensive heat and mass transfer in CFBC unit, complete fuel carbon burnout (represented by a low concentration of CO and VOC in the flue gases) is achieved.

The average concentrations of gaseous pollutants are presented in Table 8 while trends during tests are shown in Fig. 5. NO<sub>x</sub> in flue gases was increased by 27% (36 mg/Nm<sup>3</sup>). This increase is caused by addition of WW, which contains substantial amount of nitrogen (Table 3).  $NO_x$  average concentrations in flue gases for test #2 and #3 were essentially the same despite the fact that the amount of WW pumped to combustor per 1 kg of oil shale was greater in test #3 (0.113 kg<sub>WW</sub>/kg<sub>oil shale</sub> and 0.147 kg<sub>WW</sub>/kg<sub>oil shale</sub>, respectively). This is possibly caused by the changes in WW composition (Table 3). A point worth noting is that in previous pilot-scale WW incineration tests increases in NO<sub>x</sub> concentration compared to reference test was approximately two fold higher (76 mg/Nm<sup>3</sup>) as WW to oil shale ratio was also higher (0.19 kg<sub>WW</sub>/kg<sub>oil shale</sub>) (Konist et al., 2018). The measured increase in NOx concentration in the flue gases does not limit incineration of up to 13 t/h of pyrolytic wastewater in CFB combustors as even at partial load at highest WW to oil shale ratio the concentration remained below the limit of 200 mg/Nm<sup>3</sup> (expressed at 6%  $O_2$  in dry gases) set for large combustion plants by the so-called large combustion plant (LCP) directive ("Directive, 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on Industrial Emissions," 2010).

The CO content in the flue gas is relatively low and stable during all tests (as depicted in Fig. 5). However, at the partial load CO was

Table 8	
Average composition of flue gas measured during reference (test #1	) and incineration tests (test #2 and #3).

Test #	Concent	Concentration, mg/Nm <sup>3</sup> , 6% O <sub>2</sub> , dry										Concentration,vol. %, dry		
	со	$NO_x$ as $NO_2$	SO <sub>2</sub>	HCl	CH <sub>4</sub>	$C_2H_6$	$C_3H_8$	$C_2H_4$	TOC as CH <sub>4</sub>	H <sub>2</sub> O	CO <sub>2</sub>	02		
1	40.6	136.9	44.1	0.1	<1.6*	<3.0*	<4.4*	<2.8*	<5*	11.6	14.0	4.7		
2	33.1	173.9	7.2	7.3	<1.6*	<3.0*	<4.4*	<2.8*	<5*	16.4	14.8	4.9		
3	69.8	172.2	9.7	4.8	<1.6*	<3.0*	<4.4*	<2.8*	<5*	16.3	14.2	5.7		

\*value below detection limit.



**Fig. 5.** Trends in concentrations of gaseous pollutants during reference test (day 1 and 2), pyrolytic wastewater incineration test at boiler full load (day 3), and partial load (day 3). Solid line – NO<sub>x</sub> concentration; dashed line – SO<sub>2</sub> concentration; dotted line – CO concentration.

substantially increased. A general increase was also accompanied with increased fluctuations in CO concentrations, indicating reduced combustion efficiency. This trend is possibly related to lowered temperatures in the combustion chamber (Fig. 4). The VOC concentrations remained below detection limit. While the SO<sub>2</sub> concentration in flue gases during pyrolytic wastewater injection (tests #2 and #3) was below 20 mg/Nm<sup>3</sup> which is common in case of Kukersite oil shale combustion in CFBC boilers (Pihu et al., 2017). Furthermore, when the humidity is increased, SO<sub>2</sub> removal is enhanced as the capture of SO<sub>2</sub> by CaO is increased (Pandey et al., 2005). Similar preliminary tests performed in the pilot-scale CFB unit have given effectively identical results.

The lower SO<sub>2</sub> emissions from oil shale fired CFBC units is a significant advantage of oil shale as a fuel compared to coal. Owing to the high content of CaCO<sub>3</sub> in oil shale, a favorable Ca to S molar ratio in the furnace is naturally achieved. Despite the higher S content in oil shale (and additional S in pyrolytic WW) as compared for example to coal slurry combusted in the Emil Huchet CFBC unit, the SO<sub>2</sub> emissions were very low. As highlighted by Gauvillé et al. (2012) to achieve SO<sub>2</sub> emissions in the range of 140 mg/Nm<sup>3</sup> (at 6% O<sub>2</sub>) in the combustion of coal slurry in CFBC unit, lime injection to the furnace is essential (Ca to S molar ratio 1.7 to 1.8).

## 3.4. Emission of solid particles

Solid particulate matter (PM) emitted with the flue gases present serious health risk (WHO, 2006). The harmfulness of the fine PM (especially respirable PM) is caused by its small size and chemical (and mineralogical) composition (Brown et al., 2013). The fine PM (PM2.5) is known to be respirable, and is also able to penetrate the circulatory system and is therefore also associated with the mutagenic and carcinogenic activity related to PAHs and transition metals (Lighty et al., 2000). The most dramatic results of the direct health effect of PM (more precisely condensable PM) was seen during/after the event known as the Great Smog of London in 1952 (Wang et al., 2016). An additional problem is that elevated PM concentrations cause reduced visibility and haze formation and this is becoming increasingly unacceptable to the public.

The results of PM measurements are presented in Table 9. As can be seen, the injection of WW, which increases flue gas humidity, reduces PM concentration. At partial load PM concentration is further reduced possibly due to decreased flue gas flow rate. Under the reference test conditions emission limit value of 30 mg/Nm<sup>3</sup> for dust set by LCP directive ("Directive, 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on Industrial Emissions," 2010) was met, hence it appears that WW injection is definitely worth considering when further PM removal is desired or required.

## 4. Conclusions

Incineration of pyrolytic WW from shale oil production process was carried out on a full-scale oil shale fired 250 MW<sub>th</sub> CFB boiler at two loads and at WW flow rates of 12.9 t/h (0.113 kg<sub>WW</sub>/kg<sub>oil shale</sub>)

Table 9
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Concentration of	particulate	matter in	flue gas	after	ESP.
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Test #	Average PM-sum concentration, mg/Nm <sup>3</sup> , 6% O <sub>2</sub> , dry	Flue gas volumetric flow rate, Nm <sup>3</sup> /s, dry	Flue gas humidity, vol. %	Flue gas temperature, °C
1	19.9	104.9	11.6	188.4
2	9.4	118.7	16.4	193.2
3	6.5	95.3	16.3	194.4

and 0.147 kg<sub>WW</sub>/kg<sub>oil shale</sub>). The results for gaseous emissions are similar to those obtained from pilot-scale WW incineration tests. Namely, the NO<sub>x</sub> concentrations increased proportionally to the injected WW and combusted oil shale ratio as nitrogen is found in both WW and oil shale. Compared to the reference test, WW incineration increased NOx emissions by 27%. The SO<sub>2</sub> concentration in the flue gas was not increased due to the natural high Ca to S molar ratio of the oil shale. However, the CO concentration did increase at combustor partial load due to reduced temperatures (approximately 50 °C compared to the reference test). It is common that after the ESP the measured PM emissions from oil shale fired CFB combustor are below 20 mg/Nm<sup>3</sup>. The pyrolytic WW incineration test showed that the PM concentration was reduced by approximately three times compared to the reference test as the flue gas humidity was increased.

Thus, based solely on emissions measurement results, incineration of pyrolytic WW is an option and does not cause the concentrations of gaseous pollutants or PM in flue gas to exceed those set in the LCP directive. However, the downside of WW injection is increased fuel consumption, which the makes justification of WW incineration more difficult, as for example, is the case of PC units where WW injection has a significant positive effect on SO<sub>2</sub> emissions.

# References

- Anon, 2016. National Development Plan for the Use of Oil Shale 2016-2030. Tallinn, Estonia. https://www.envir.ee/sites/default/files/2016\_2030ak\_ingl.pdf.
- Brown, J.S., Gordon, T., Price, O., Asgharian, B., 2013. Thoracic and respirable particle definitions for human health risk assessment. Part. Fibre Toxicol 10, 12. https:// doi.org/10.1186/1743-8977-10-12.
- Directive 2010/75/EU of the, 2010. European parliament and of the Council of 24 november 2010 on industrial emissions. Off. J. Eur. Union 17–119. https://doi.org/10.3000/17252555.L\_2010.334.eng.
- Gauvillé, P., Foucher, J.-C., Moreau, D., 2012. Achievable combustion efficiency with Alstom CFB boilers for burning discarded coal. J. South. African Inst. Min. Metall. 112, 437–447.
- Golubev, N., 2003. Solid heat carrier technology for oil shale retorting. Oil Shale 20, 324–332.
- Hotta, A., Parkkonen, R., Hiltunen, M., Arro, H., Loosaar, J., Parve, T., Pihu, T., Prikk, A., Tiikma, T., 2005. Experience of Estonian oil shale combustion based on CFB technology at narva power plants. Oil Shale 22, 381–397.
- Ji, X., Bie, R., Chen, P., Gu, W., 2016. Reed black liquor combustion in fluidized bed for direct causticization with limestone as bed. Material. Energy & Fuels 30, 5791–5798. https://doi.org/10.1021/acs.energyfuels.6b00847.
- Klein, K., Kattel, E., Goi, A., Kivi, A., Dulova, N., Saluste, A., Zekker, I., Trapido, M., Tenno, T., 2017. Combined treatment of pyrogenic wastewater from oil shale retorting. Oil Shale 34, 82–96. https://doi.org/10.3176/oil.2017.1.06.
- Klemeš, J.J., Liu, X., Varbanov, P.S., 2017. Virtual greenhouse gas and water footprints reduction: emissions, effluents and water flows embodied in international trade. Chem. Eng. Trans. 56. https://doi.org/10.3303/CET1756010.
- Konist, A., Järvik, O., Pihu, T., Neshumayev, D., 2018. Combustion as a possible solution to pyrolytic wastewater utilization. Chem. Eng. Trans. 70, 859–864. https://doi.org/10.3303/CET1870144.
- Konist, A., Pihu, T., Neshumayev, D., Siirde, A., 2013. Oil shale pulverized firing: boiler efficiency, ash balance and flue gas composition. Oil Shale 30, 6–18. https://doi.org/10.3176/oil.2013.1.02.

- Lee, C.T., Hashim, H., Ho, C.S., Fan, Y. Van, Klemeš, J.J., 2017. Sustaining the lowcarbon emission development in Asia and beyond: sustainable energy, water, transportation and low-carbon emission technology. J. Clean. Prod. 146, 1–13. https://doi.org/10.1016/J.JCLEPRO.2016.11.144.
- Lighty, J.S., Veranth, J.M., Sarofim, A.F., 2000. Combustion aerosols: factors governing their size and composition and implications to human health. J. Air Waste Manag. Assoc. 50, 1565–1618. https://doi.org/10.1080/10473289.2000. 10464197.
- Maaten, B., Järvik, O., Loo, L., Konist, A., Siirde, A., 2018. Characterization of the pyrolytic water from shale oil industry. Oil Shale 35, 365–374. https://doi.org/ 10.3176/oil.2018.4.06.
- Maaten, B., Järvik, O., Loo, L., Konist, A., Siirde, A., 2017. Characterization of the pyrolytic water from shale oil industry. In: The Eighth Jordan International Chemical Engineering Conference.
- Moreno, N., Querol, X., Andrés, J.M., Stanton, K., Towler, M., Nugteren, H., Janssen-Jurkovicová, M., Jones, R., 2005. Physico-chemical characteristics of European pulverized coal combustion fly ashes. Fuel 84, 1351–1363. https://doi.org/10. 1016/J.FUEL.2004.06.038.
- Mu, L., Zhao, L., Liu, L., Yin, H., 2012. Elemental distribution and mineralogical composition of ash deposits in a large-scale wastewater incineration plant: a case study. Ind. Eng. Chem. Res. 51, 8684–8694. https://doi.org/10.1021/ ie301074m.
- Neshumayev, D., Pihu, T., Siirde, A., Järvik, O., Konist, A., 2019. Solid heat carrier oil shale retorting technology with integrated CFB technology. Oil Shale 36, 99–113. https://doi.org/10.3176/oil.2019.2S.02.
- OECD/IEA, 2019. Statistics | world total primary energy supply (TPES) by source (chart) [WWW document]. URL https://www.iea.org//statistics/? country=WORLD&year=2016&category=Key indicators&indicator= TPESbySource&mode=chart&categoryBrowse=false&dataTable=BALANCES& showDataTable=false. accessed 1.7.19.
- Pandey, R.A., Biswas, R., Chakrabarti, T., Devotta, S., 2005. Flue gas desulfurization: physicochemical and biotechnological approaches. Crit. Rev. Environ. Sci. Technol. 35, 571–622. https://doi.org/10.1080/10643380500326374.
- Parve, T., Loosaar, J., Mahhov, M., Konist, A., 2011. Emission of fine particulates from oil shale fired large boilers. Oil Shale 28, 152–161. https://doi.org/10.3176/oil. 2011.1S.07.
- Pihu, T., Konist, A., Neshumayev, D., Loo, L., Molodtsov, A., Valtsev, A., 2017. Fullscale tests on the Co-firing of peat and oil shale in an oil shale fired circulating fluidized bed boiler. Oil Shale 34, 250. https://doi.org/10.3176/oil.2017.3.04.
- Plamus, K., Soosaar, S., Ots, A., Neshumayev, D., 2011. Firing Estonian oil shale of higher quality in CFB boilers - environmental and economic impact. Oil Shale 28, 113. https://doi.org/10.3176/oil.2011.1S.04.
- Suksankraisorn, K., Patumsawad, S., Fungtammasan, B., 2003. Combustion studies of high moisture content waste in a fluidised bed. Waste Manag. 23, 433–439. https://doi.org/10.1016/S0956-053X(03)00060-6.
- Tsai, M.-Y., Wu, K.-T., Huang, C.-C., Lee, H.-T., 2002. Co-firing of paper mill sludge and coal in an industrial circulating fluidized bed boiler. Waste Manag. 22, 439–442. https://doi.org/10.1016/S0956-053X(02)00027-2.
- Wang, G., Zhang, R., Gomez, M.E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P.S., Duce, R.A., Kolb, C.E., Molina, M.J., 2016. Persistent sulfate formation from London Fog to Chinese haze. Proc. Natl. Acad. Sci. U.S.A. 113, 13630–13635. https://doi.org/10. 1073/pnas.1616540113.
- WHO, 2006. Health Risks of Particulate Matter from Long-Range Transboundary Air Pollution. WHO Regional Office for Europe, Copenhagen (Copenhagen).
- Xiao, X., Yang, H., Zhang, H., Lu, J., Yue, G., 2005. Research on carbon content in fly ash from circulating fluidized bed boilers. Energy Fuels 19, 1520–1525. https:// doi.org/10.1021/EF049678G.
- Yang, M., Jianguo, L., Chao, F., Sha, W., Jiang, X., 2016. The experimental study on the incineration of the acrylonitrile effluent in the CFB boiler burning oil shale. Oil Shale 33, 58–68. https://doi.org/10.3176/oil.2016.1.05.