

Title Particulate emissions from large-scale
 medium-speed diesel engines: 2. Chemical
 composition

Author(s) Sarvi, A.; Lyyränen, Jussi; Jokiniemi, Jorma;
 Zevenhoven, R.

Citation Fuel Processing Technology
 vol. 92(2011):10, pp. 2116-2122

Date 2011

URL <http://dx.doi.org/10.1016/j.fuproc.2011.06.021>

Rights Copyright © (2011) Elsevier.
 Reprinted from Fuel Processing Technology.
 This article may be downloaded for
 personal use only

VTT
<http://www.vtt.fi>
P.O. box 1000
FI-02044 VTT
Finland

By using VTT Digital Open Access Repository you are bound by the following Terms & Conditions.

I have read and I understand the following statement:

This document is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of this document is not permitted, except duplication for research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered for sale.

Particulate emissions from large-scale medium-speed diesel engines: 2. Chemical composition

Arto Sarvi¹, Jussi Lyyränen², Jorma Jokiniemi^{2,3}, Ron Zevenhoven^{1*}

¹Åbo Akademi University, Thermal and Flow Engineering Laboratory, Biskopsgatan 8, FI-20500 Åbo/Turku, Finland

²VTT Technical Research Centre of Finland, P.O. Box 1602, FI-02044 Espoo, Finland

³University of Kuopio, Department of Environmental Sciences, Fine Particle and Aerosol Technology Laboratory, P.O. Box 1627, FI-70211 Kuopio, Finland

* Corresponding author, e-mail: ron.zevenhoven@abo.fi tel. +358 2 215 3223 fax. +358 2 215 4792

Highlights

- Chemical composition data is given for PM sampled from large-scale diesel engine exhaust
- Important differences for different fuel (LFO vs. HFO) and varying engine load were found
- Sulphur and metallic matter content of fuel and lubricant oil affect PM emissions
- Different elements end up in different size fractions

Particulate emissions from large-scale medium-speed diesel engines:

2. Chemical composition

Arto Sarvi¹, Jussi Lyyränen², Jorma Jokiniemi^{2,3}, Ron Zevenhoven^{1*}

¹Åbo Akademi University, Thermal and Flow Engineering Laboratory, Biskopsgatan 8, FI-20500 Åbo/Turku, Finland

²VTT Technical Research Centre of Finland, P.O. Box 1000, FI-02044 Espoo, Finland

³University of Eastern Finland, Department of Environmental Sciences, Fine Particle and Aerosol Technology Laboratory, P.O. Box 1627, FI-70211 Kuopio, Finland

* Corresponding author, e-mail: ron.zevenhoven@abo.fi tel. +358 2 215 3223 fax. +358 2 215 4792

ABSTRACT

The effect of diesel fuel and operation mode on diesel particulate matter (PM) emissions was studied using a combination of a gravimetric impactor (DGI) and SEM/EDX analysis of PM particles from 0.005 to 2.5µm aerodynamic size. Tests were made with heavy fuel oil (HFO) and light fuel oil (LFO) with medium speed (500 rpm), turbo-charged, power per cylinder ~ 1 MW, multivariable large-scale diesel engines. Diesel PM was sampled from diluted and cooled exhaust gases. The sampled PM was found to be primarily made of carbon and sulphur derived from the fuel and lube oil but contain several other chemical species as well. In this paper the submicron particle size range (0.2-0.5 µm and 0.5-1.0 µm) is discussed. The EDX analysis gave reasonably accurate quantitative results featuring the important elements present in the samples, namely, C, O, Mg, Si, S, Cl, Ca, V, Fe, Ni, Zn (and Al). The results indicate that the finest particles originate primarily from the fuel while the somewhat larger particles contain also significant amounts of elements derived from the lubrication oil. As expected, the concentrations of sulphur and certain metallic elements such as V, Ni, Ca, Zn, Fe, Mg are significantly higher in diesel PM from HFO firing than for LFO firing.

Keywords: *Particulates, chemical composition, fuels, diesel, SEM/EDX*

1. INTRODUCTION

Diesel engines find wide applications in on-road and off-road vehicles, where the benefit of higher fuel efficiency than gasoline-fired engines results in lower emissions of carbon dioxide. Besides these small (< 1 MW) machines, large (>> 1 MW) multivariable (with respect to fuel type, generator vs. propulsion operation mode, number of cylinders, L vs. V arrangement) diesel engines find increasing markets for marine applications and as electric power generation units at locations outside the range of the power grid. For large and small units alike it is an ongoing challenge to comply with increasingly stringent regulations on emissions, with nitrogen oxides (NO_x) and diesel particulate matter (diesel PM) being the most important (and urgent). Optimization of the diesel engine combustion process has already resulted in significantly reduced particle emissions [1], but the literature states almost exclusively that the exhaust control methods applied to small engines are less suitable for large, turbo-charged and air-cooled engines. Having recently reported on how emissions of NO_x, CO, HC (hydrocarbons), soot and PM from a large-scale turbo-charged diesel engine vary with load, fuel type and operation mode (propulsion vs. generator) [2], we focus here on a detailed characterization of the PM material.

Diesel PM particles are described typically by their physical characteristics like particle size, and chemical composition, and several reviews addressed the details of diesel PM sampling and characterization methods [e.g., 3,4]. Especially when using light fuel oils (LFO) the solid fraction (SOL) of diesel particulates is composed primarily of elemental carbon, C, as confirmed by our work presented here. This carbon is the finely dispersed carbon black or “soot” responsible for black smoke (FSN) emissions [5]. Sakurai et al. [6] showed that unburned fuel contributes to most of the mass of the PM particles in the accumulation mode (50-200 nm).

Sulphuric acid in the diesel exhaust is derived from sulphur in the fuel oil, especially for heavy fuel oil (HFO) [7,8,9]. For HFO the relative fuel sulphur content is approximately ten times higher than for LFO (in this work: 8300 ppm versus 1000 ppm). Switching from HFO to LFO can reduce diesel PM emissions by over 50% (by mass) as we presented earlier [10]. Engine lubricating oil additives influence diesel PM formation and emissions also, because during combustion, a small amount of lubricating oil is burnt as well. Hydrocarbons adsorbed on the surface of carbon particles and/or present in the form of the fine droplets form the soluble organic

fraction (SOF) of diesel particulates. At the temperatures of the diesel exhaust, most of the SOF compounds exist as vapors at higher engine loads when temperatures are relatively high [11].

Another source of solid material in diesel exhaust are metal ash compounds derived from lubricating oil additives and from mechanical wear of the engine. Nucleation of volatile ash constituents is believed to take place during expansion stroke in the engine cylinder and subsequently these ash nuclei can agglomerate to form accumulation mode particles, size 0.2-1.0 μm [12,13]. Depending on the fuel and lube oil used, diesel exhaust ash typically contains a mixture of the following components; Ca, Zn, Mg, Fe, Cu, Cr, Al. Sulphates and phosphates, oxides of calcium, zinc, magnesium and other metals are formed in the engine combustion chamber from the burning of the additives (detergents, dispersants and anti-wear) in the engine lube oil [14].

Although the fundamental particle formation processes during combustion of HFO is similar to LFO, there are distinct differences between the two fuel types. Typical fuel oils contain Fe, Ni, V, and Zn, in addition to Al, Ca, Mg, Si, and Na. Transition metal (Fe) and alkaline-earth metals (Ca, Mg) may be added for the suppression of PM formation [15,16]. The use of calcium carbonate and calcium sulphate in the fuel oil for preventing the accumulation of deposits was reported recently [17]. Likely sources for iron (Fe) are wearing of the exhaust manifold, abrasion of the engine block and fuel oil [18]. One of the engine oil additives, zinc (Zn), which functions as an anti-wear agent, is another likely source for ash in diesel particles [19]. The composition of various (truck engine) diesel particulate ash analysis for oxides of Ca, Zn, Mg revealed the presence of Zn-Mg compounds and CaSO_4 , which agglomerates to particles of 0.1 - 0.5 μm in size [20].

A recent study on diesel engine emissions (from a 6.6 litre DI turbo-charged truck engine), covering twenty elements, reported a 95% release of diesel fuel inorganic elements with exhaust PM [14]. While the concentrations of diesel PM in exhaust gases were found to decrease with engine load (speed, Bmep), the concentration of metallic and other inorganic elements in the PM showed the opposite trend.

In this paper we study the relation between diesel PM composition and particle size and how this depends on engine load, fuel type and lubricating oil. The aim of the work was to characterize the PM as it is emitted from the exhaust pipe. It is well known that the majority of particles in the diesel engine emissions is in the $\text{PM}_{2.5}$

(diameter $d_p < 2.5 \mu\text{m}$) size class. However, a large amount of the particles is already found in the $\text{PM}_{1.0}$ (diameter $d_p < 1.0 \mu\text{m}$) size class, as we show in [21], reporting that in many tests most PM mass was found in the size range $0.2 - 1.0 \mu\text{m}$. In this study we therefore focus on experimental data on fine particles ($d_p < 1 \mu\text{m}$) that were sampled from the exhaust of a large-scale diesel engine with a traditional gravimetric impactor (DGI) method. While part 1 of this paper [19] deals with the particle size distributions, this paper covers the chemical analysis of the two $\text{PM}_{1.0}$ size fractions ($0.2\text{-}0.5 \mu\text{m}$ and $0.5\text{-}1.0 \mu\text{m}$) for tests with HFO and LFO fuel with 50% and 100% load for generator mode (constant speed). The PM characterization is based on chemical analysis of the various size fractions sampled with the DGI by using SEM/EDX (energy-dispersive X-ray spectroscopy analysis conducted by means of SEM, which allows to determine the chemical composition of a specimen) methods mentioned in [4], focusing on carbonaceous compounds, sulphur and other species.

2. EXPERIMENTAL METHODS

2.1 *The engine and test conditions*

The test engines used were turbo-charged, after-cooled and trimmed 6-18 cylinder diesel engines with power output ~ 1 MW per cylinder. About 300 different engines of both L and V type were tested. No effect was found of the size (i.e. number of cylinders) or type (L or V) of the engines used. All engines were new when tested and had the same power output per cylinder. Engine tests were carried out according to MARPOL 73/78 [22] and ISO 3046-1 [23] test conditions. The temperature of the fuel entering the fuel pump was for $\sim 120 \text{ }^\circ\text{C}$ for HFO and $\sim 60 \text{ }^\circ\text{C}$, for LFO and injection pressure ~ 130 MPa. Results will be given below for generator mode (constant speed ~ 500 rpm, typical for electric power generation) only. More detail on the engines and engine operation is given in Part 1 of this paper [21].

2.2 *Test fuels and lubricating oil*

Two diesel fuels, heavy fuel oil (HFO) and light fuel oil (LFO), with different sulphur contents were selected to evaluate the effect of sulphur and several other elements on the exhaust PM particles. The properties of the fuel oils and the chemical composition

of the fuel oils and the lubrication oil are given in Table 1 and 2, respectively. Diesel fuels sulphur was determined by ASTM method D4294.

2.3 PM measurement and SEM/EDX analysis

A gravimetric impactor (DGI) [24] was used to measure PM_{2.5} particles. The lowest stage of the impactor has a 50 % aerodynamic cut point¹ of 0.2 μm . A four-stage (stages 2,3,4 and 5) impactor DGI as used in this study classifies particles into four size fractions with 50 % collection efficiency for aerodynamic (d_{p50}) cut-points of 2.5, 1.0, 0.5, 0.2 μm plus a back-up filter (stage 1) for particles smaller than $d_p > 0.2 \mu\text{m}$, down to $\sim 0.005 \mu\text{m}$. The diesel PM does not change once the exhaust gases enter the dilution unit before the impactor [2,7] where it is mixed with air, and cooled to below 50 $^{\circ}\text{C}$ [25]. See also Fig. 1 - more detail on the sampling is given in part 1 of this paper [21].

As discussed in part 1 of this paper, [21], PM emissions are measured by weighing the total mass of material collected on the sampling substrates. As a consequence, the sulphuric acid, sulphate salts, and condensed water are all part of the condensed material that forms the PM [26]. Hydrocarbons (HC), which are derived from lube oil and unburned fuel, condense or adsorb onto the surface of carbon particles forming the organic portion of diesel PM (SOF). (Some contribution of combustion products CO₂ and H₂O via the Boudouard reaction and gasification reactions may be possible.) Sulphate particulates (SO₄) are composed primarily of hydrated sulphuric acid, and are mostly liquid [27].

The back-up filter (\varnothing 70 mm) after the impaction stages collects all particles typically smaller than 0.2 μm (these particles could not be separated and analysed). All $d_p > 0.2 \mu\text{m}$ particles were collected on aluminium substrates ($d = 47 \text{ mm}$) placed on top of the four impactor collection plates, allowing for easy and reliable mass size distribution as well as total mass concentration measurement and eventually chemical elemental SEM/EDX analysis (LEO Electron Microscopy Ltd / Thermo-Noran Vantage – see [28]) for each size fraction. No grease was used on the impactor plates. Sampling rate

¹ *I.e.* the aerodynamic diameter for which 50% of the PM passes this stage while 50 is trapped on the impactor disc. Smaller particles are removed less effectively, larger particles more effectively.

was constant at 1 liter/s for all measurements and dilution ratio (DR) was seven (7) [23]. (While this is not an industry standard it is widely used in practice. Dilution ratio (DR) and especially dilution temperature determine VOC behaviour, i.e. whether it stays in gas phase, condenses or evaporates. It is very sensitive for all parameters and thus difficult to control. The easiest, most reliable and repeatable measurement is for solid PM (black carbon) which is done by heating the dilution system and having a high enough dilution ratio. A 1:7 DR is typically just enough to prevent condensation if thermal treatment (heating) is applied for dilution as well [29].) Total particle mass of the substrates and the filter was determined by weighing in a humidity-controlled room before and after sampling [30].

For clarity, we only present and compare results for the size classes 0.2-0.5 μm (stage 2 = last stage before filter) and 0.5-1.0 μm (stage 3), because the number of particles in samples with $d_{p50} > 1.0 \mu\text{m}$ was much smaller. In the discussion below, “0.2 μm ” refers to the 0.2 μm impactor disc that collects PM from 0.2 to 0.5 μm while 0.5 μm refers to the disc that collects 0.5 to 1.0 μm .

2.4 *Experimental and measurement error analysis*

A total of 137 PM measurements were made with each test repeated four or more times. More detail on the statistics and of the PM concentration measurements is given in part 1 of this paper [20]. For the SEM/EDX elemental analysis data, the relative errors were found to depend on the amounts (as wt. %) of the species detected: for levels measured at $> 50\%$ -wt, the relative error was $< 2\%$, for 10% - 50% -wt: $< 10\%$, for 2% - 10% -wt: $< 25\%$, for 0.5% - 2% -wt: $> 25\%$, for $< 0.5\%$ -wt: $> 100\%$ relative error. More detail is given elsewhere [31]; see also [32] where SEM/EDX is compared to ICP/MS.

3. RESULTS and DISCUSSION

Already several decades ago exhaust particles were observed to be made up of several species such as partially oxidized compounds from fuel and lubrication oil [30,33]. As we reported earlier [21], the particle mass of HFO mode exhaust particles increases rapidly under the d_{p50} size 0.5 μm , while for LFO the emitted PM mass is less dependent on particle size (d_{p50} 0.2 to 2.5 μm) [20]. Therefore, it was not a surprise that the difference between PM from LFO versus HFO could to a significant extent be

related to sulphate. It was also expected that much of the HFO-derived exhaust particles will be apportioned to calcium sulphate or calcium phosphate based on the fuel and lubricating oil element analysis (Table 2).

SEM/EDX elemental analysis for particles sampled from the engine exhaust for HFO and LFO diesel fuels during generator mode operation using a gravimetric impactor are presented in Figs. 2-13 for twelve elements C, O, Mg, Si, S, Cl, Ca, V, Fe, Ni, Zn and Al for 50% and 100% engine load for two PM size ranges 0.2-0.5 μm (d_{p50}). For the latter element the results presented should be interpreted with caution since the impactor substrates were made of aluminium. The Al analyses for EDX seem somewhat high for Al to originate only from fuel and lube oil but nonetheless clearly distinguishable trends are shown. Although the specific fuel consumption (SFC) varied by about 3-10 % for the results shown here, the overall diesel PM emission concentrations clearly increase with the sulphur and metallic species content of the fuel, as shown by the data given in part 1 [21] of this paper. (See also Table 3.)

Also the higher aromaticity of HFO compared to LFO may have an effect: increased levels of aromatics in fuel may result in more smoke or PM, via a lower cetane number as we discussed earlier while also considering HC emissions [10]. However, comparison of LFO and HFO shows a much higher and metallic species content for HFO, and our work reported here shows significantly higher sulphur and metallic content in PM from HFO compared to LFO at the expense of carbon content. Moreover, in [34] it is stated that “most studies indicate that the aromatics content has no influence on HC, CO or PM”, adding that for older engines some effect of polyaromatics versus total aromatics was found. The tests reported here are done on (new) engines from after year 2000.

When comparing the elemental concentrations for 50 and 100% load, different elemental concentrations can be seen for the two particle sizes classes considered here. Since oxygen can be present as either metal oxides or sulphates there is not a perfect correlation between Ca – and S – content of the PM.

In the Supplementary material, SEM/EDX analysis results for four samples are given for 100% load, 0.2-0.5 μm and for 50% load, 0.5-1 μm , for LFO and HFO fuels, generator mode (constant speed).

Carbon content (Fig. 2) in the diesel PM is somewhat lower for HFO than for LFO for most tests but is found to be significantly lower (approx. half of the LFO C-content) for the finest particles (0.2 μm) for 100% load. For LFO the PM carbon is roughly

constant (approx. 80 % by weight) for the total load range. It seems that burnout (defined as consumption of combustible components, here primarily carbon) is better with HFO (partly because the fuel injection nozzle was optimised (“matched”) for this fuel [35]). Simply the presence of significant amounts of other species brings down the percentage of carbon. It has been reported that the burnout and particle formation mechanisms are different depending on the metal species, pointing at catalytic effects [36]. In addition, the C content at 100 % load is lower at 0.2 than at 0.5 μm fraction, which also indicates that metallic species improve the C burnout and thus decrease the relative amount of carbon in PM. This is also evident when looking at e.g. Fe and Ni to be discussed below: their content is higher in the 0.2-0.5 μm fraction than in the 0.5-1 μm fraction.

Showing an opposite trend with respect to carbon, the oxygen content (Fig. 3) in the PM is for all cases lower for LFO than for HFO (with the most significant difference, more than half, found at 100 % load for 0.2 μm size fraction). This suggests better combustion and/or fewer binding into metal oxides. The large oxygen content in the fine fraction for HFO at full load appears to correspond to oxidized metallic species and sulphur. A general trend is seen in the figures: the amount of O for HFO is decreasing from 0.2-0.5 to the 0.5-1.0 μm fractions as are the amounts of V, Fe and Ni. These are elements originating from the fuel oil, in contrary to Zn, Mg, Ca and Al that originate mainly from lube oil and other sources.

Magnesium (Fig. 4) comes primarily from lubricating oil, where its content is approximately 30 ppmw. HFO gives more Mg for all PM samples than LFO, but the difference between HFO and LFO is small in the 0.2-0.5 μm size fraction, being more pronounced for the 0.5-1.0 μm fraction. The presence of Mg in PM is not solely due to an evaporation/condensation mechanism but more a result of aggregated PM released from the combustion chamber walls and crevices. The same appears to hold for silicon (Fig. 5) which comes primarily from lubricating oil or as catalytic cracking remains in the fuel oil as well, with a content of approximately 20 ppmw in the LBO (see Table 2). A much larger Si content is found in HFO PM than in LFO PM for the larger PM fraction, but without a significant difference for the fine fraction. With higher load more Si in PM is emitted: due to a somewhat higher combustion pressure somewhat more lube oil is burnt and PM increases [6]. Si may also partly originate from the remains of the catalyst applied in the catalytic cracking processes to produce the different fuel oil fractions.

The sulphur in the fuel (Fig. 6) is oxidized to SO_2 and partly SO_3 and contributes to the total PM emission as sulphates. As discussed in our earlier work [2,10], there is no evidence that sulphur influences the carbonaceous fraction of PM or smoke. Interestingly, small PM particles from HFO firing contain more sulphur than for LFO firing, while for LFO the PM sulphur content is roughly independent on PM size or engine load. The trend is identical for that of oxygen (Fig. 2), indicating that sulphur is primarily present as oxides, most probably as condensed sulphates, i.e. sulphuric acid, sodium sulphate, etc. (Because of the low collection temperature maximum 50°C , and low dilution ratio ($\text{DR} = 7$) at these conditions, condensation of sulphuric acid is unavoidable.)

The largest fraction of vanadium (Fig. 7) occurs in crude oils, as here in HFO at about 18 ppm and in LFO at less than 1 ppm. Here the element follows also the trends of oxygen and sulphur, apparently being present as vanadium pentoxide V_2O_5 , which is known to catalyze the SO_2 to SO_3 oxidation reaction with a risk for increased corrosion [6]. It also seems that V in the case of LFO originates mainly from re-entrained particles or lube oil or both, because it is mostly found on $0.5\ \mu\text{m}$ mode at 100 % load, and the amount of V clearly increases from the value at $0.5\ \mu\text{m}$ at 50 % load (increased in lube oil consumption due to more mechanical friction). In addition, the amount of V does not markedly change for LFO but clearly for HFO for $0.2\ \mu\text{m}$ - $0.5\ \mu\text{m}$ PM mode whatever the load is. For HFO the source for V is, obviously, primarily the fuel oil.

Iron (Fig. 8) is formed from fuel and lubricating oil in the combustion chamber and from metal oxide impurities resulting from the engine wear. Being more pronounced for HFO than for LFO, the iron content in PM at 100% load is higher than at 50% load. (See also discussion on carbon oxidation and the role of metals given above).

Nickel is present in fuel and lubricating oil. As shown in Fig. 9, HFO produced more Ni in all tests and especially for d_{p50} $0.2\text{-}0.5\ \mu\text{m}$ at 100% load; Ni shows the same behavior as V and S. (Again, see also discussion on carbon oxidation and the role of metals given above).

Only minor amounts of chlorine, i.e. below 1% by weight, were found (Fig. 10), being slightly higher for HFO firing in the finest fraction, being slightly lower for LFO for the larger size fraction. The concentration of chlorine in the fuels and lube oil must be very low since problems related to corrosion and to dioxins/furans formation must be avoided.

Calcium (Fig. 8) is a major component in lubricating oils, and oxides of Ca and maybe sulphates as well, are formed in the engine's combustion chamber. Similar to what was found for Mg and Si, according to our test results HFO produced PM with the highest concentrations of Ca especially at higher loads. Calcium oxides are a major part of diesel particulate ash, at about 25 wt- % of the oxides. The higher amount of Ca in the HFO case compared to LFO must come from the HFO fuel oil, which contains forty-two times more Ca than LFO. The emissions are practically identical for LFO and HFO at 50% load (presumably because the main source for Ca is the lube oil). A higher load gives a higher amount of fuel and higher combustion temperatures and as a result more lube oil is burned on the engine cylinder wall (at about 0.4-0.8 g/kWh). Thus at 100% load the Ca content is significantly higher for HFO, presumably as a result of a significantly increased temperature; which is not or much less the case for LFO [10].

Zinc (Fig. 12) must originate completely from lubricating oil since it is not present in the fuel. This element can be used as an indicator of lube oil contribution to PM [37]. While ash emission rate is proportional to the ash content of the lubricating oil (Table 2), also (Zn) in ash increases with concentration in the lubricating oil, with similar results for PM from LFO and HFO. Overall, Zn shows behaviour similar to calcium, also when it comes to increased temperature, which is also mainly derived from the lubrication oil.

Aluminium (Fig. 13), presumably present as oxide, results from engine wear and enters the combustion system with the lubrication oil. It is again noted that the DGI substrates are also made of Al so this element should be addressed with certain reservation. The results for Al indicate a clearly distinguishable trend, very similar to the more heavy metallic element Zn and to a lesser extend also V, showing however a much lower concentration in the finest size fraction. For the 0.5-1.0 μm size fraction the concentration of Al is quite high, at 5 – 15 wt-%. This suggests that Al may originate mainly from the surfaces of the combustion system or forms a portion of the inner core of the larger particles (originates e.g. from catalyst remains from catalytic cracking (CC) processes) [38].

In connection with the relatively high concentration of non-carbon species (oxidized sulphur and metals) found in the fine PM particles from HFO firing it is noted that the fine size fraction represents > 85% of the total PM mass at 50% load, and < 80% at

100% load. Also, at 50% load the average combustion temperature inside the engine cylinder is ~ 50°C lower for HFO than for LFO.

Finally, an attempt was made to calculate using a mass balance how much of a certain element as fed to the system with the fuel (which enters at around 60 g/s per cylinder at full load) was later found in the PM samples and how this was distributed over the size fractions. Unfortunately this did not give a reliable result because the samples analysed were very small compared to the total flue gas stream: only 0.004 % of the exhaust gas flow volume was sampled through the impactor and analysed. Nonetheless, the discussion given above was made possible by the fact that most of the elements considered are present in significant amounts in either the fuel or the lube oil but not in both.

4. CONCLUSIONS

This study (combined with its Part 1 [21]) shows that the diesel PM emissions from large-scale diesel engines strongly depend on the engine load, the sulphur and other elemental content of the fuel oil, and lubricating oil properties. Distinguishing and analyzing the fine PM_{1,0} particles with SEM/EDX analysis appears to be a very powerful method. The gravimetric impactor collection method used demonstrated its ability to measure and separate the particle size fractions of PM emissions for different test fuels and operating modes. The results demonstrated that the composition of the finer PM fraction is more sensitive to engine load and fuel type than the larger PM fraction. The sulphur content of the PM is proportional to that in the fuel sulphur but for HFO a significantly higher PM sulphur content was measured for the finest particles under full engine load compared to partial load.

It is possible to group the concentrations of PM for the twelve elements discussed here for the two fuels, size classes and engine load levels as follows:

- the carbon content is typically 75-80 wt-%, except for the finest PM fraction from HFO at 50% load, which shows much higher levels of (oxidized) sulphur and metallic species. LFO fuel gives higher PM C than HFO, for HFO increasing load gives a lower C content. More oxygen available at higher loads for carbon burn-out for HFO together with metallic species will boost the carbon burn-out. Adding metallic species to LFO may bring down the carbon in the resulting PM but increase the production of these particles.

- the sulphur and oxygen content follow the same trend which is opposite to carbon. HFO gives higher levels of S and O than LFO. Load hardly affects S and O for LFO but for HFO increased load gives increased S and O in the PM.
- Calcium (Ca), magnesium (Mg), silicon (Si) are derived from the lube oil and all show higher levels in PM for HFO than LFO. The higher levels are found in the larger particle fractions and with increasing engine load.
- Zinc (Zn), nickel (Ni), vanadium (V), and iron (Fe) are not present in LFO but are present in HFO and in the lube oil used. Their PM emission behaviour is similar to that of sulphur, showing significantly higher levels for PM from HFO, 50% and 100% load, the finest particles. Zn is mainly found in the large fraction 0.5 μm , originating mainly from the lube oil which is not exposed to the conditions (temperature and pressure) that the fuel species experience. Vanadium, nickel and iron are known to catalyse SO_2 oxidation to SO_3 which is a necessary step towards sulphuric acid formation.
- The concentrations of chlorine (Cl) are low, being < 0.1 wt-%, without a strong dependence on fuel type or operation
- Aluminium (Al) is found at significant concentration in the larger PM size fraction at much less in the finer particles, i.e. catalyst remains from CC processes. (Although amounts are clearly distinguishable this must be taken with some reservation since the impactor substrates are also made of Al.)

Overall, it can be stated that the elements from the lube oil are found in the larger, 0.5-1.0 μm PM size fraction, while the species present in the fuel make up most of the finer, 0.2-0.5 μm size fraction. As expected, the concentrations of sulphur and certain, Ca, Al, Zn, Fe, Mg metallic elements are significantly higher in PM from HFO firing than for LFO firing. This can be linked directly to the differences in fuel composition.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the technical support from Dekati Measurements Oy and the sample analysis contribution of Kurt Lundqvist and Clifford Ekholm at Åbo Akademi University.

Nomenclature

ASTM	American Society for Testing and Materials
Bmep	brake mean effective pressure
CC	catalytic cracking
CCAI	calculated carbon aromatic index
DGI	dekati gravimetric impactor
d_p	particle diameter
d_{p50}	aerodynamic 50% cut size particle diameter
PM	diesel particulate matter
DR	dilution ratio
EDX	energy dispersive x-ray spectroscopy
FBP	final boiling point
FSN	filter smoke number
Gen	generator mode
HC	hydrocarbon
HFO = hfo	heavy fuel oil
HHV	high heat value
ICP	inductive coupled plasma
IMO	international maritime organization
ISO	international standard organization
LBO	lubricate oil
LFO = lfo	light fuel oil
LHV	low heat value
MARPOL	maritime pollution
MS	mass spectroscopy
MW	megawatt
PM	particulate matter
ppmw	parts per million by weight = mg/kg
prop	propulsion mode
SEM	scanning electron microscope
SFC	specific fuel consumption
SOF	soluble organic fraction
SOI	start of injection

SOL	carbon material (solid phase)
TDC	top dead centre
VOC	volatile organic compounds
%-wt	weight percent

REFERENCES

- [1] Pagan J. Study of Particle Size Distribution Emitted by a Diesel Engines SAE Technical paper 1999-01-1141 (1999)
- [2] Sarvi A, Fogelholm C-J, Zevenhoven R. Emissions from large-scale medium-speed diesel engines: 1. Influence of engine operation mode. Fuel Proc. Technol. 89 (2008) 510-519 doi:10.1016/j.fuproc.2007.10.006
- [3] Burtscher H. Physical characterisation of particulate emissions from diesel engines: a review. Aerosol Sci. 36 (2005) 896-932
- [4] Maricq MM. Chemical characterisation of particulate emissions from diesel engines: a review. Aerosol Sci. 38 (2007) 1079-1118
- [5] AVL 415S Smoke meter.
https://www.avl.com/c/document_library/get_file?uuid=3b281792-57db-4654-87dc-e6592e8f4846&groupId=10138, accessed 1 sept. 2010
- [6] Sakurai H, Tobias HJ, Park K, Zarling D, Docherty S, Kittelson DB, McMurry PH, Ziemann PJ. On-line measurements of diesel nanoparticle composition and volatility. Atmos. Environm. 37 (2003) 1199-1210
- [7] Flagan, R.C., Seinfeld, J.H. Fundamentals of Air Pollution Engineering, Prentice-Hall, New Jersey, 1988.
- [8] Zevenhoven, R., Kilpinen, P. Control of pollutants from flue gases and fuel gases", 3rd Edition, Picaset, Espoo, Finland, 2004
- [9] Sippula, O., Hokkinen, J., Puustinen, H., Yli-Pirilä, P., Jokiniemi J. Comparison of particle emissions from small heavy fuel oil and wood fired boilers. Atmospheric Environment 43(32) (2009) 4855 - 4864.

- [10] Sarvi A, Fogelholm C-J, Zevenhoven R. Emissions from large-scale medium-speed diesel engines: 2. Influence of fuel type. *Fuel Proc. Technol.* 89 (2008) 520-527 doi:10.1016/j.fuproc.2007.10.005
- [11] www.dieselnet.com [accessed 08 Dec. 2007]
- [12] Lyyräinen J. Particle formation, deposition, and particle induced corrosion in large-scale medium speed diesel engines. PhD thesis. Helsinki University of Technology, Espoo, Finland, 2006; VTT Publication 598
- [13] Abdul-Khalek IS, Kittelson DB. The influence of dilution conditions on diesel exhaust particle size distribution measurements, SAE 1999-01-1142 (1999)
- [14] Wang Y-F, Huang K-L, Li C-T, Mi H-H, Luo J-H, Tsai P-J. Emissions of fuel metals content from a diesel engine. *Atmos. Environm.* 37 (2003) 4637 - 6643
- [15] Chartellieri WP, Tritthart P. Particulate analysis of light duty diesel engines (IDI and DI) with Particular reference to the lube oil particulate fraction; SAE Technical Paper No. 841395; 1984
- [16] Baumgard KJ, Johnson JH. The effect of the fuel and engine design on exhaust particle size distribution, SAE 960131 (1996)
- [17] Kasper A, Aufdenblatten S, Mohr M, Forss A, Matter U, Lutz T. Particulate emissions from a marine diesel engine, *J. Aerosol Sci. Suppl.*, 32 (S1) (2001) 79-80
- [18] Skillas G, Qian Z, Baltensperger U, Matter U, Burtscher H. The influence of additives on the size distribution and composition of particles produced by diesel engines. *Combust. kSci and Tech.* 154 (2000) 259-273
- [19] Nicholls JR. Corrosion and wear resistance of some novel and current diesel exhaust valve materials. *Mat. High Temp.* 12(1) (1994) 35-46
- [20] Perez JM, Williams RL. A Study of particulate extracts from heavy duty diesel engines run on steady state and transient cycles, SAE technical Paper Series. 892491 (1989)
- [21] Sarvi A, Lyyräinen J, Jokiniemi J, Zevenhoven R. Particulate emissions from large-scale medium-speed diesel engines. 1. Particle size distributions. *Fuel Processing Technology*, in press / available on-line: doi: 10.1016/j.fuproc.2011.04.031
- [22] International Maritime Organisation, Annex VI of MARPOL 73/78

Regulations for the Prevention of Air Pollution from Ships, IMO, MPG Books Ltd. UK 1998.

- [23] International Standard ISO 3046-1. Reciprocating Internal Combustion Engines – Performance, Part 1, Fourth edition 1995-12-01.
- [24] Dekati, 2001. DGI 1570: Gravimetric Impactor, Total mass concentration + size distribution measurement (2001); Dekati Measurements Ltd, Tampere, Finland <http://www.dekati.fi>
- [25] Kittelson DB. Engines and nanoparticles. A Review J Aerosol Sci. 29(5/6) (1998) 575-588
- [26] Hinds WC. Aerosol Technology, Second Edition, John Wiley & Sons, Inc. 1982
- [27] Baumgard KJ, Johansson JH. The Effect of Fuel and Engine Design on Diesel Exhaust Particle Size Distribution. SAE paper 960131 (1996)
- [28] www.findnano.fi/default/NanoCrmEquipment:UserView/id/1159 [accessed 29 May 2011]
- [29] personal communication with V. Niemelä, Dekati Oy, Finland, 15 April 2009
- [30] Kittelson DB. Diesel Aerosol Sampling Methodology –CRC E-43: Final Report, University of Minnesota, Report for the Coordinating Research Council, 19 August 2002.
- [31] Sarvi, A. Particulate and gaseous emissions from large-scale medium speed diesel engines. PhD (Eng) thesis, Åbo Akademi University, Turku Finland 2008.
- [32] Lyyränen J. Particle formation, deposition, and particle induced corrosion in large- scale medium speed diesel engines. PhD thesis, Helsinki University of Technology, Espoo, Finland, VTT Publication 598, 2006.
- [33] Heywood JB. Internal combustion engine fundamentals, McGraw-Hill; 1988
- [34] Majewski, A.W., Khair, M.K., “Diesel emissions and their control” SAE International, Warrendale (PA) 2006
- [35] Sarvi, A., Zevenhoven, R. Large-scale diesel engine control parameters. Energy 35 (2010) 1139-1145 doi:10.1016/j.energy.2009.06.007

- [36] Alkidas AC. Relationship between smoke measurements and particulate measurements, SAE Techn. Pap. Ser., N840412 (1984)

- [37] Okada, S, Kweon, KB, Stetter, JC, et al. Measurement of Trace Metal Composition in Diesel Engine Particulate and its Potential for Determining Oil Consumption: ICPMS and ATOFMS Measurements. SAE paper 2003-01-0076 (2003)

- [38] Readal, T.C., McKinney, Titmus, R.A. Hydrocarbon catalytic cracking process. US Patent 4,036,740, July 19, 1977 (1977)

Text for figures:

Fig. 1. Sampling system for PM measurement

Fig. 2 EDX analysis of C content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 3 EDX analysis of O content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 4 EDX analysis of Mg content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 5 EDX analysis of Si content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 6 EDX analysis of S content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 7 EDX analysis of V content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 8 EDX analysis of Fe content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 9 EDX analysis of Ni content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 10 EDX analysis of Cl content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 11 EDX analysis of Ca content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 12 EDX analysis of Zn content in the PM with HFO and LFO vs d_{p50} and Load

Fig. 13 EDX analysis of Al content in the PM with HFO and LFO vs d_{p50} and Load

Supplementary material, S1-S4

SEM/EDX analysis results for four samples are given for 100% load, 0.2-0.5 μm and for 50% load, 0.5-1 μm , for LFO and HFO fuels, generator mode (constant speed, ~ 500 rpm).

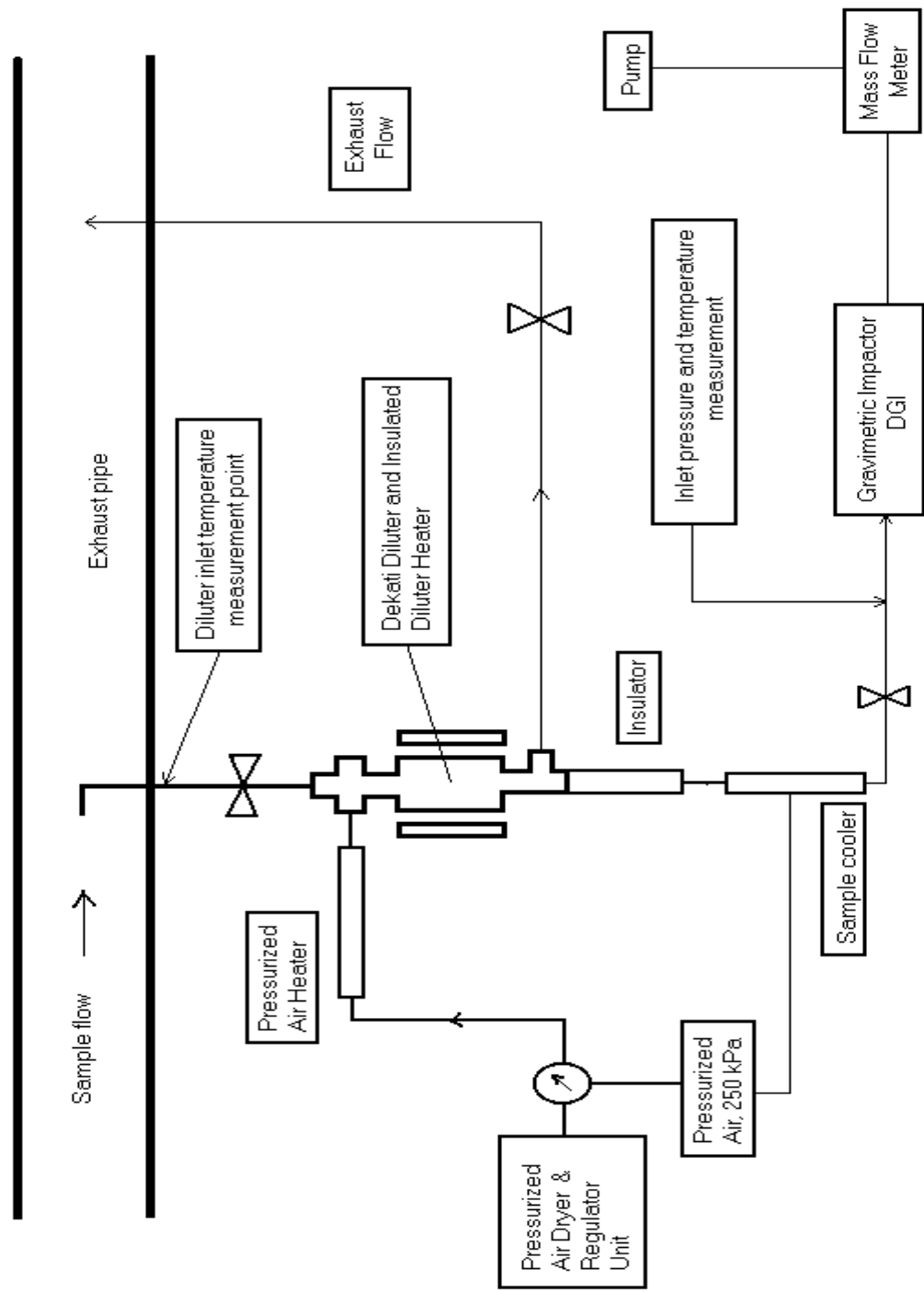


Fig. 1

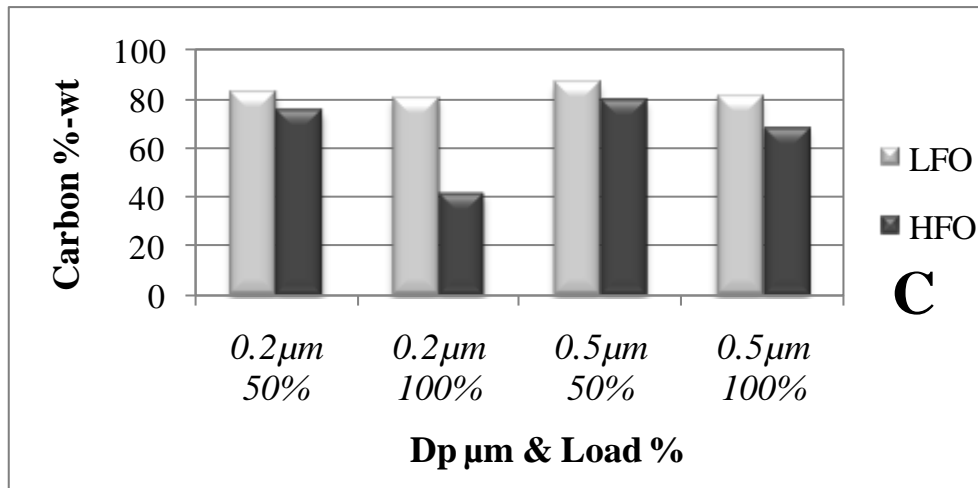


Fig. 2

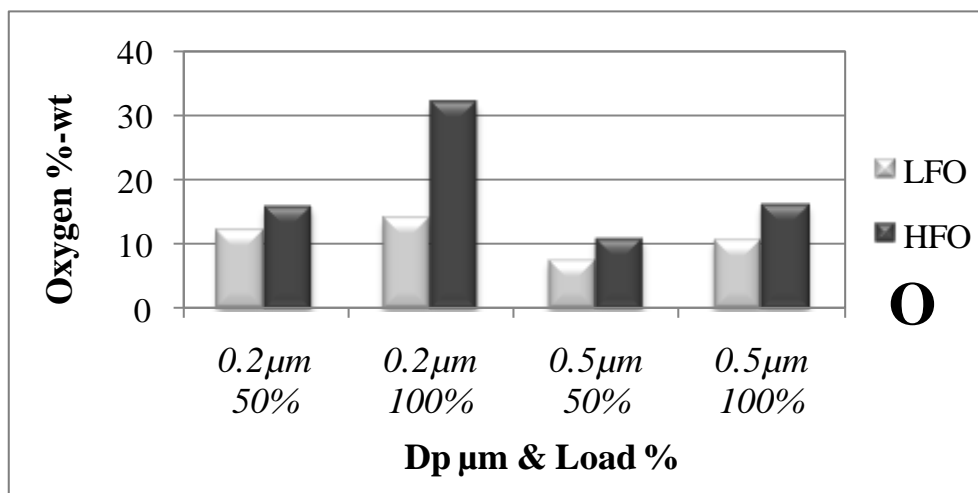


Fig. 3

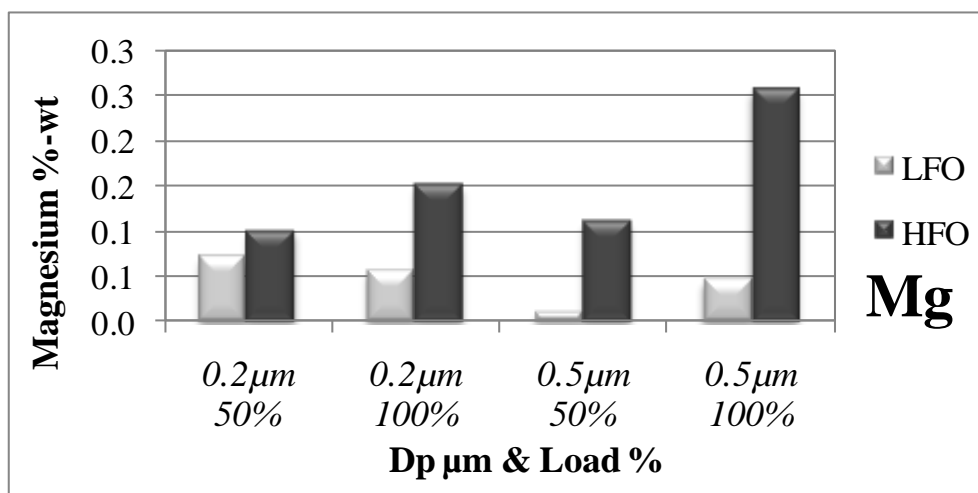


Fig. 4

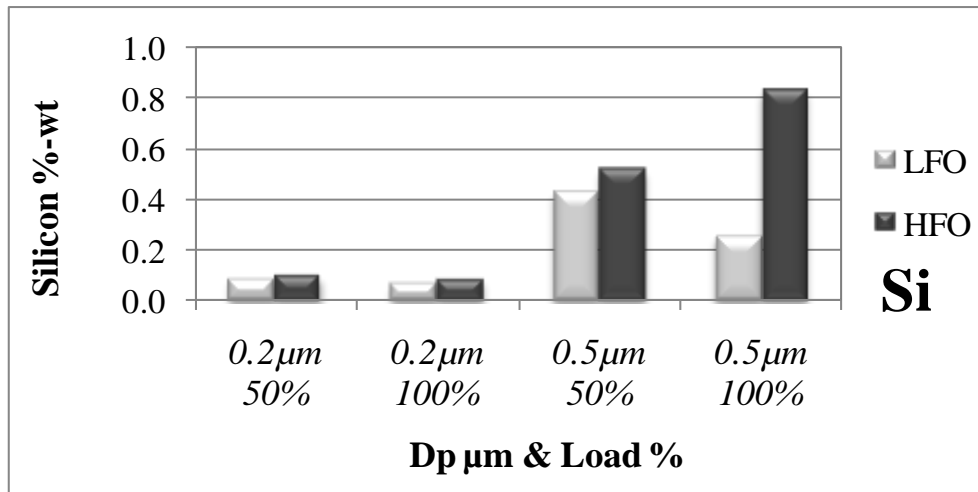


Fig. 5

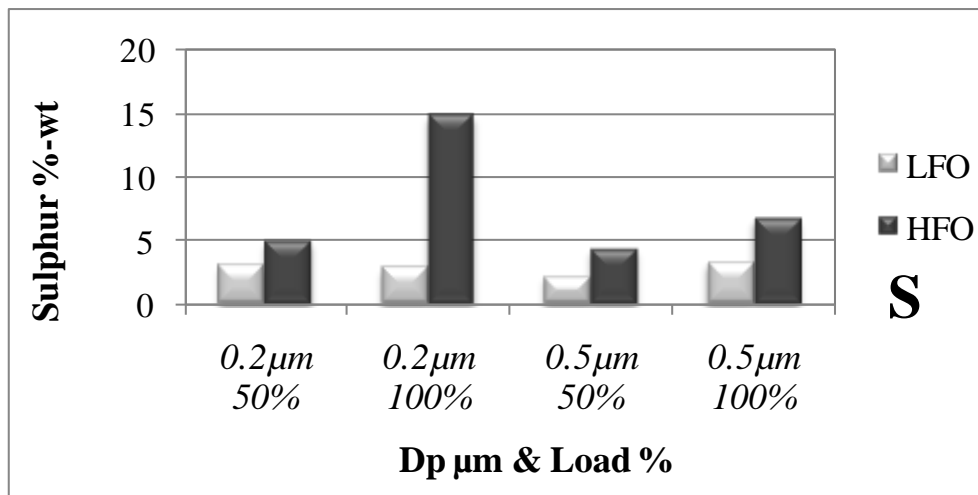


Fig. 6

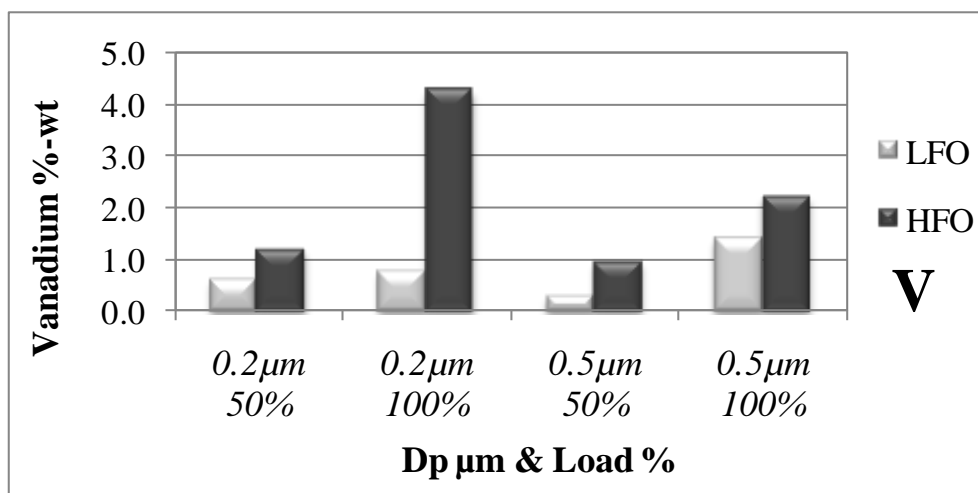


Fig. 7

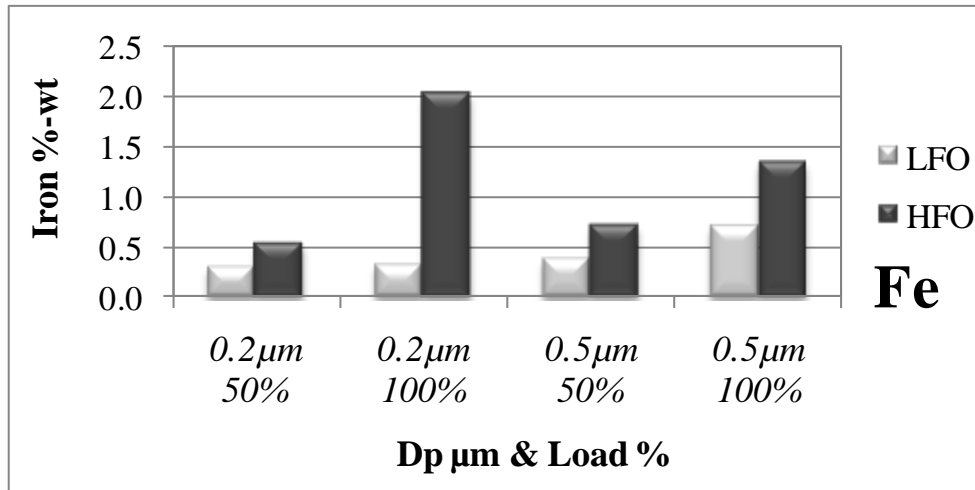


Fig. 8

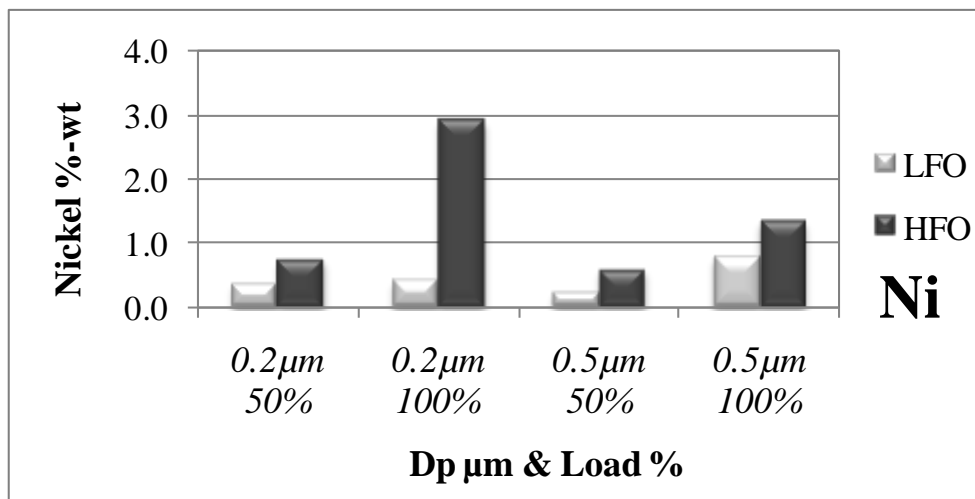


Fig. 9

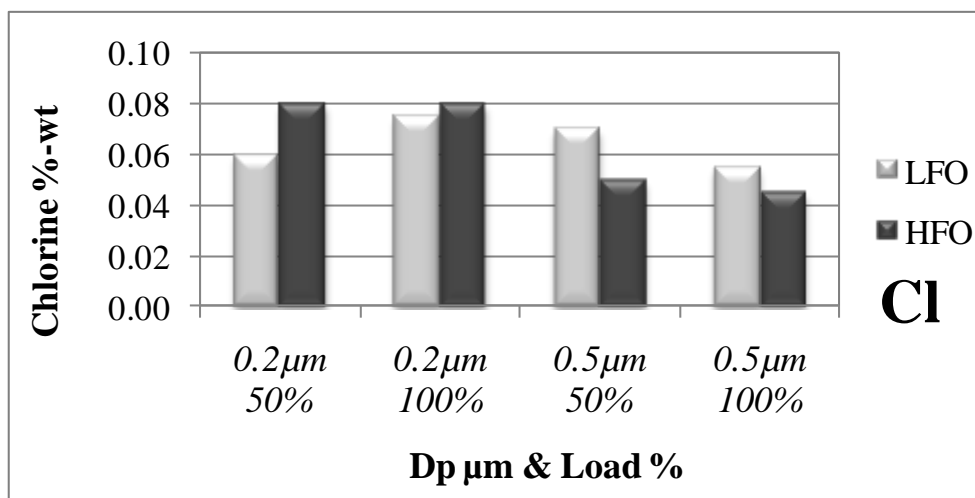


Fig. 10

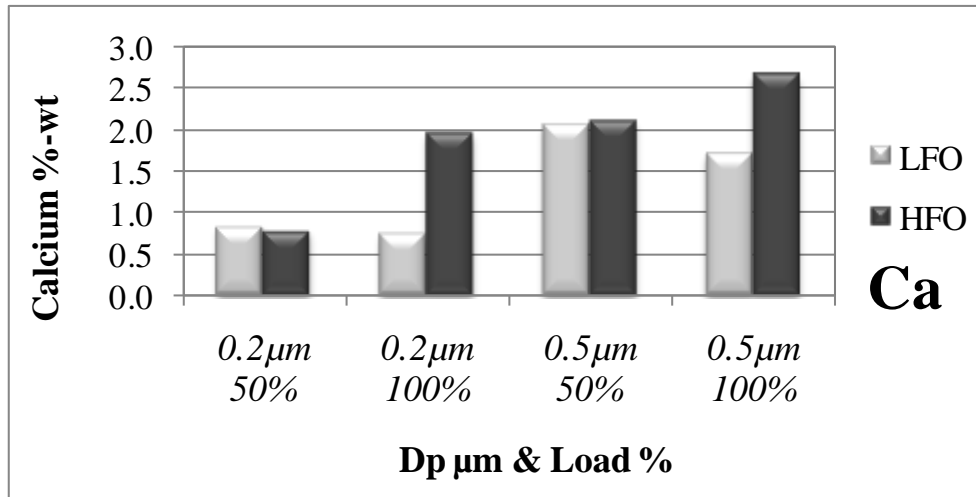


Fig. 11

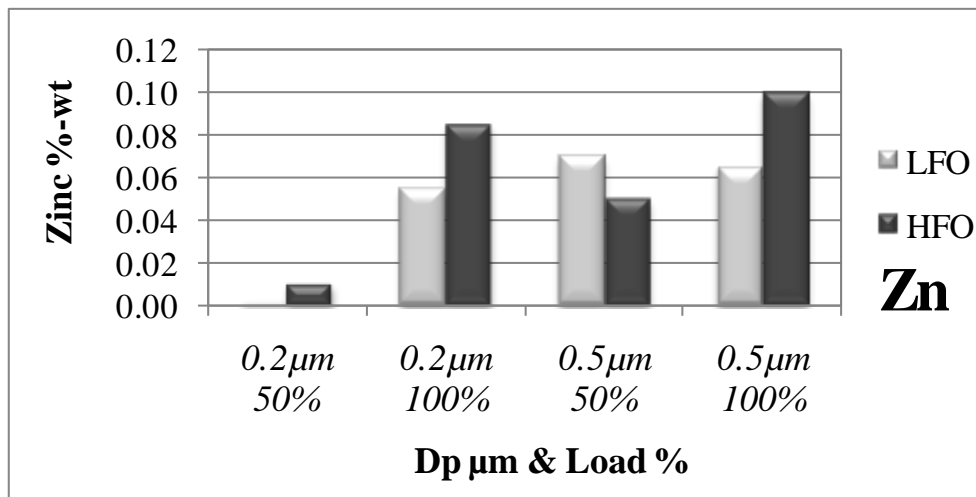


Fig. 12

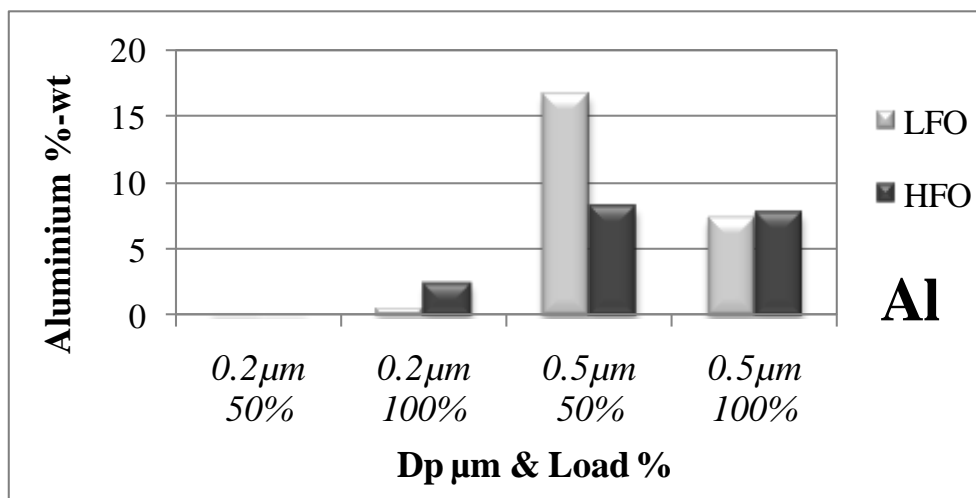


Fig. 13

Tables:**Table 1:** Test - Fuel properties

		<u>LFO</u>	<u>HFO</u>
Density (15 °C)	kg/m ³	834	940
Viscosity (80 °C)	mm ² /s	3.32	66.6
HHV	MJ/kg	45.5	43.2
LHV	MJ/kg	42.8	41.1
CCAI	-	809	822
Enthalpy of vaporization	kJ/kg	~287	~252
Stoich. air/fuel ratio	kg/kg	14.3	13.8
H/C ratio	(mol/mol)	1.96	2.06
Aromaticity	(vol %)	~ 14	~ 78
Cetane index	-	~ 50	~ 35
FBP	°C	~ 355	~ 577

Table 2: The element analysis of HFO, LFO and LBO

<u>Name (Symbol)</u>	Element ppm by weight:		
	<u>HFO</u>	<u>LFO</u>	<u>LBO</u>
Ash (-)	400	< 100	-
Aluminium (Al)	< 1	< 1	3
Calcium (Ca)	42	< 1	10 500
Carbon (C)	860 000	870 000	-
Chromium (Cr)	-	-	< 1
Copper (Cu)	-	-	5
Hydrogen (H)	110 000	130 000	-
Iron (Fe)	6	< 1	9
Lead (Pb)	-	-	2
Magnesium (Mg)	2	< 1	30
Molybdenum (Mo)	-	-	< 1
Nickel (Ni)	8	< 1	3
Nitrogen (N)	5000	200	-
Phosphor (P)	-	-	313
Silicon (Si)	< 1	< 1	20
Sodium (Na)	42	< 1	11
Sulphur (S)	8300	1000	-
Tin (Sn)	-	-	< 1
Vanadium (V)	18	< 1	320
Zinc (Zn)	-	-	< 1

Table 3: The total PM emissions (mg/Nm³) for the size fractions reported here

	<u>size range</u>	0.2-0.5 µm	0.2-0.5 µm	0.5-1.0 µm	0.5-1.0 µm
	<u>load</u>	<u>50%</u>	<u>100%</u>	<u>50%</u>	<u>100%</u>
<u>Fuel</u>					
LFO		1,46	1,08	2,11	1,66
HFO		5,33	8,40	3,77	3,02

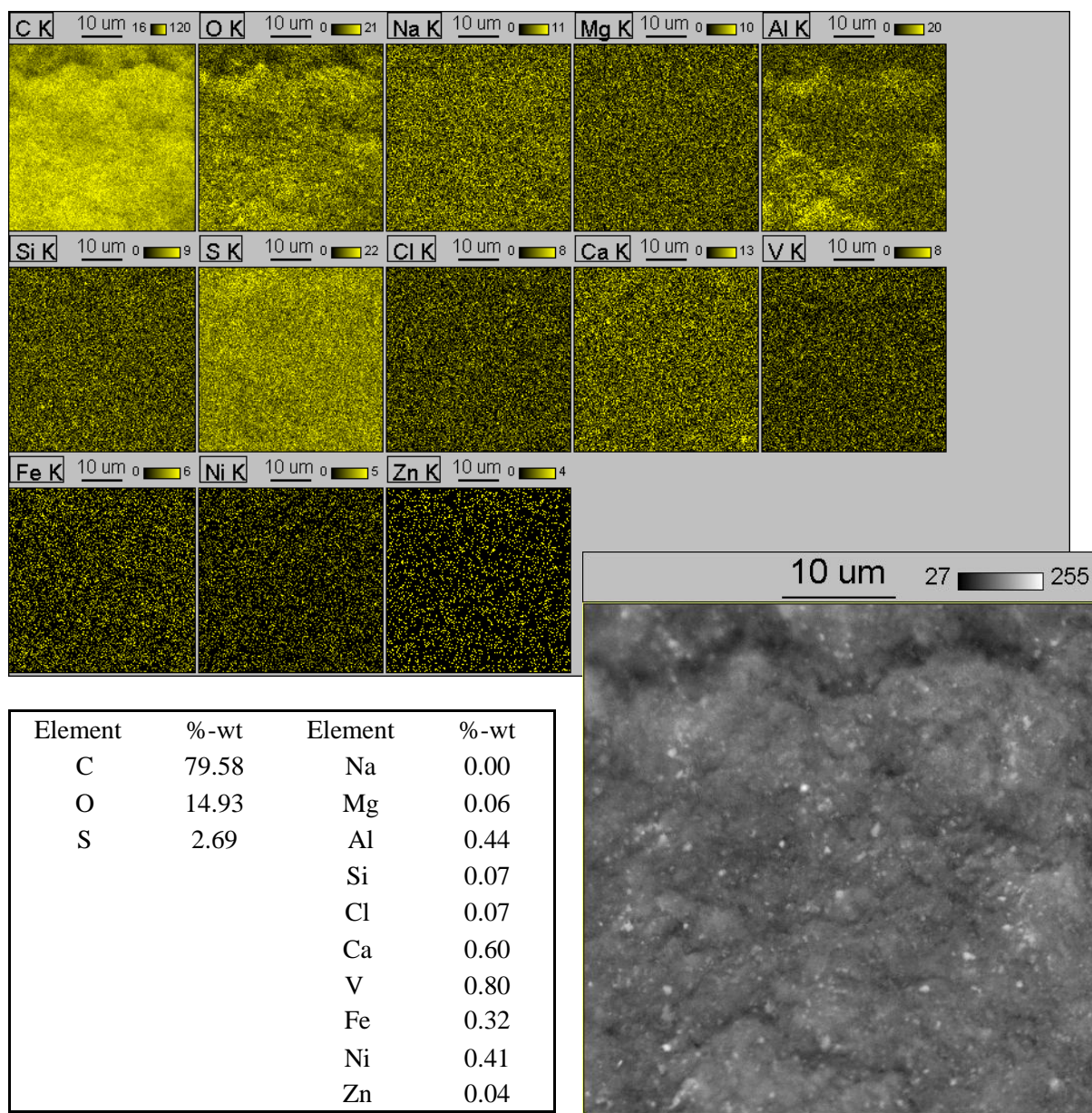


Fig. S1 SEM/EDX analysis for LFO d_p 0.2-0.5 μm ; load 100% (generator mode, \sim 500 rpm)

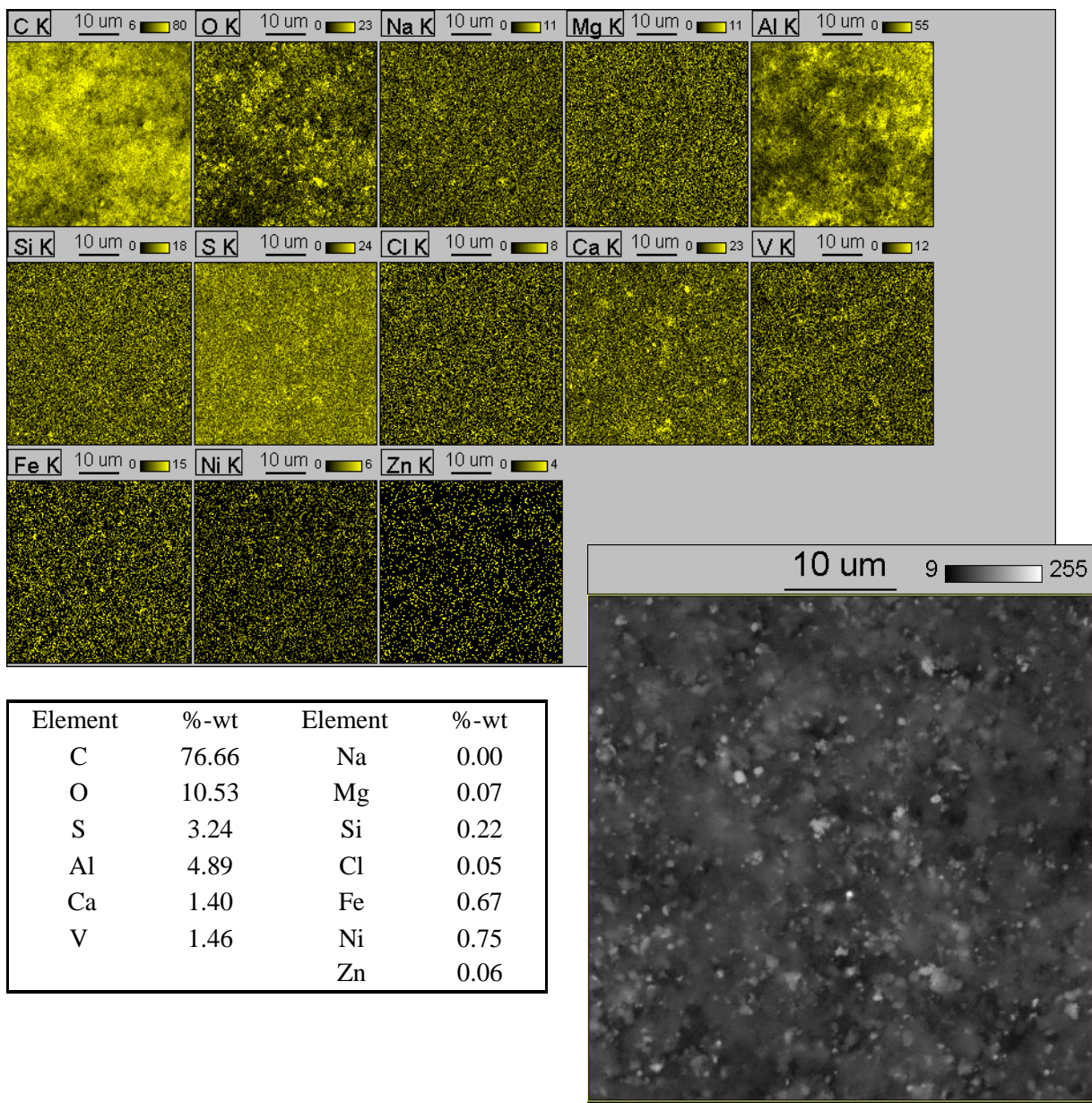


Fig. S2 SEM/EDX analysis for LFO d_p 0.5-1.0 μm ; load 50% (generator mode, \sim 500 rpm)

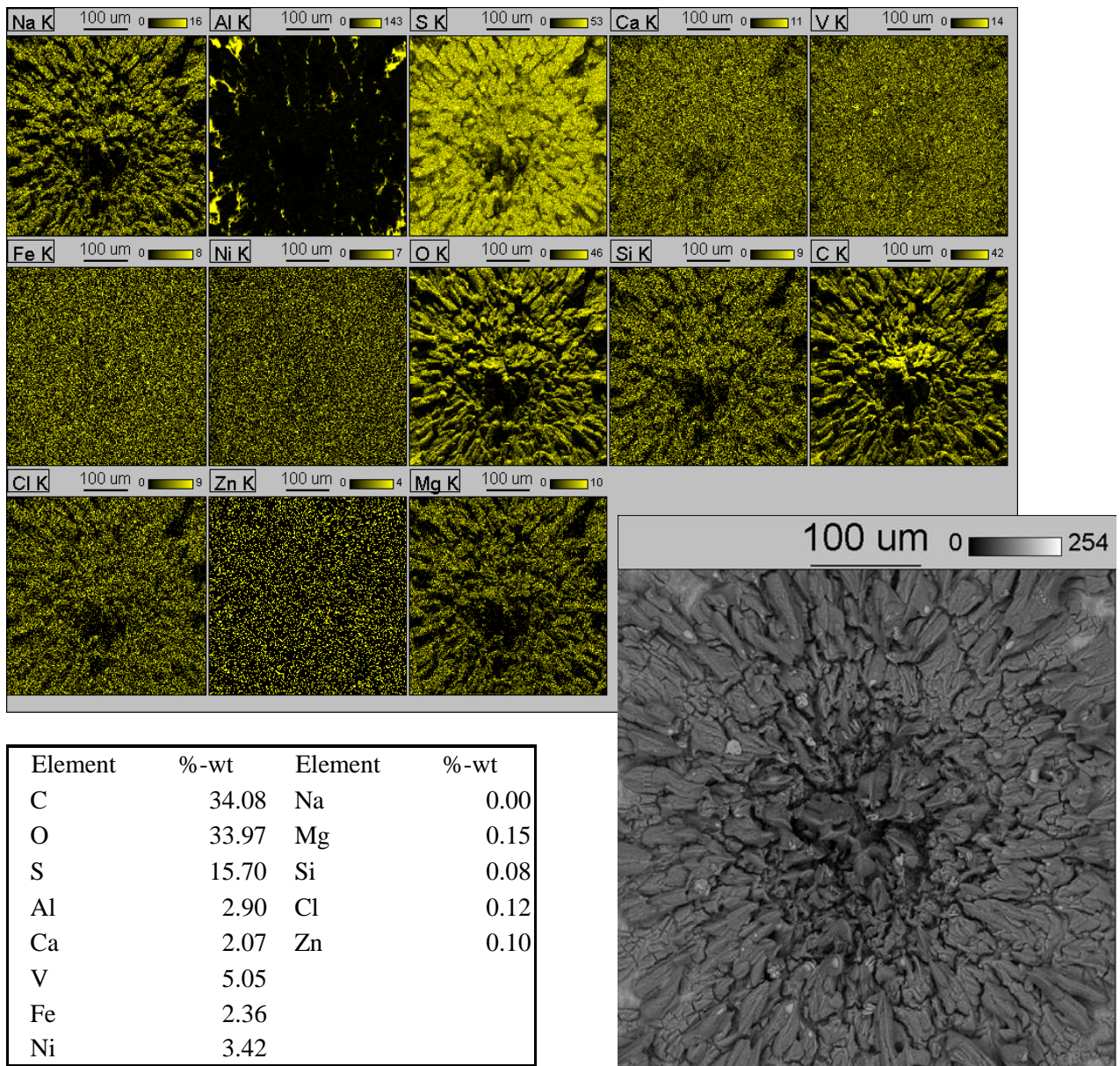


Fig. S3 SEM/EDX analysis for HFO d_p 0.2-0.5 μm ; load 100% (generator mode, ~ 500 rpm)

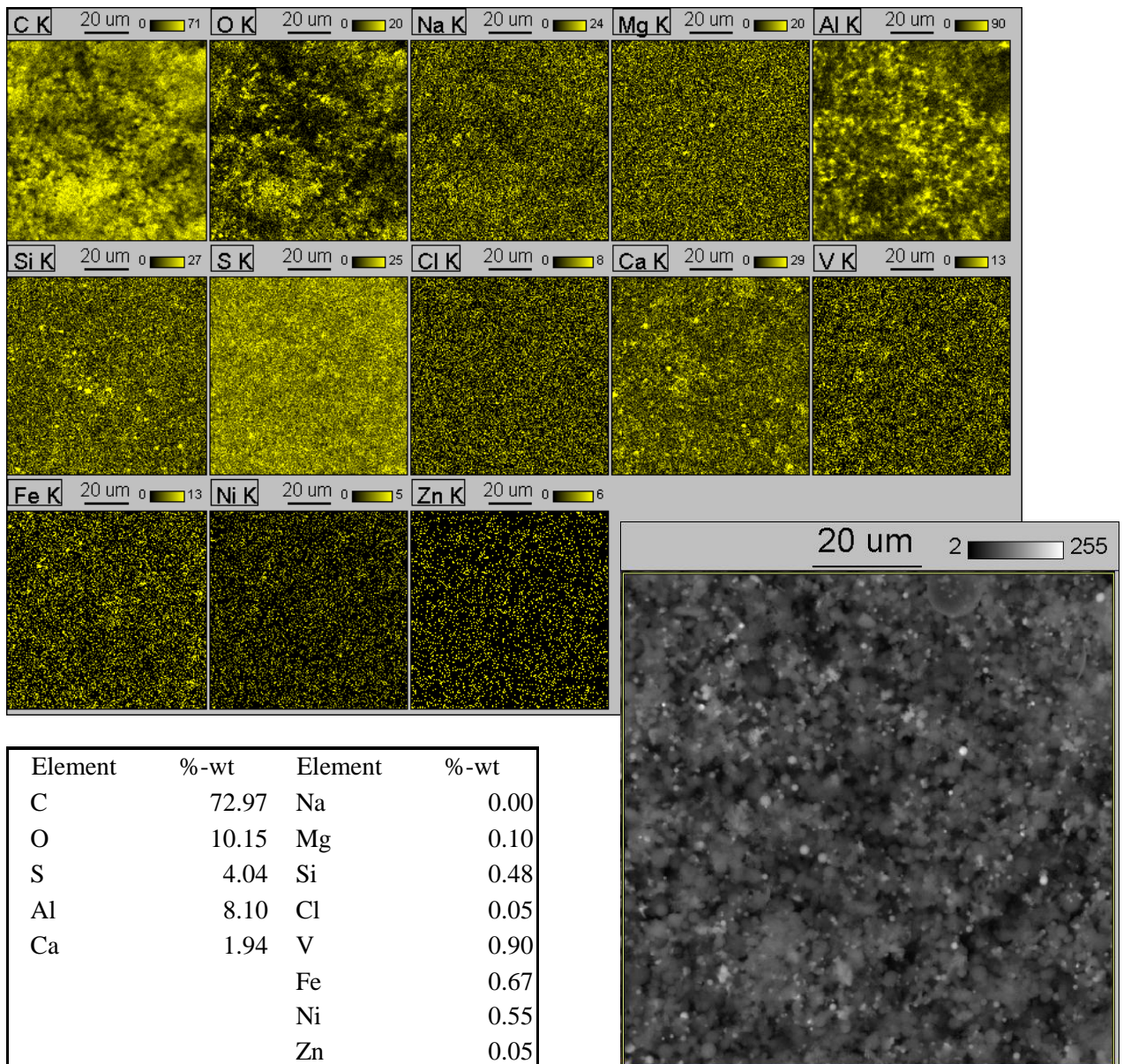


Fig. S4 SEM/EDX analysis for HFO d_p 0.5-1.0 μm ; load 50% (generator mode, ~ 500 rpm)