Institut für Energie- und Umwelttechnik e.V.
Bliersheimer Straße 58 - 60
47229 Duisburg
Approved testing laboratory according to TA Luft 5.4.8.10.3, 5.4.8.11.3
Recognised specialist waste management company

Report: ER3-15082018-001-E

Sample processing of cooling devices with Perlit filled full vacuum bodies (Perlit-VVK) of Liebherr Hausgeräte Ochsenhausen GmbH

Principal: Liebherr Hausgeräte Ochsenhausen GmbH; Ochsenhausen
Memminger Straße 77-79
88416 Ochsenhausen/Deutschland

Period of investigation: July / August 2018

Testing institution: Institut für Energie- und Umwelttechnik IUTA; Duisburg
Bliersheimer Straße 58 – 60
47229 Duisburg

Table of contents

1 Preamble

Vacuum insulation panels (VIP) have been installed in refrigerators for several years to increase their energy efficiency. These panels usually consist of an aluminium sheathing with a carrier core made of powder or fibres.

Liebherr has developed a new type of environmentally friendly full-vacuum technology based on Perlite-filled full vacuum bodies (Perlit-VVK). Liebherr would now like to test the migration of the carrier material into the material flows produced with a refrigerator recycling system and to investigate any changes in the morphology of the carrier material caused by the digestion and separation technologies.

For this purpose, Perlit-VVK from the pilot plant, which were manufactured for an IGN16 door, are to be processed in various trial batches within the framework of a practical test together with conventional household refrigeration appliances.

2 Principal

Liebherr Hausgeräte Ochsenhausen GmbH
Contact: Mr. Heisler
Tel.: +49 7352 / 928-4558
E-Mail: Thomas.Heisler@liebherr.com
Memminger Straße 77-79
88416 Ochsenhausen/Deutschland

3 Period of investigations

The investigations in the recycling plant took place on 31.07.2018 from 9:00 a.m. to 5.00 p.m.

The pilot plant and laboratory tests took place between 01.08.2018 and 31.08.2018.

4 Institution of investigation

Institut für Energie- und Umwelttechnik e.V.
Bliersheimer Straße 58 – 60
47229 Duisburg
Inspectors in the recycling plant:
Staatl. gepr. Techniker H.J. Prause
Dipl.-Ing. J. Schiemann
Inspectors in the laboratory:
Staatl. gepr. Techniker H.J. Prause
Staatl. gepr. Technikerin B. Schiemann

5 Place of investigation

Recycling plant:
Rekular GmbH (former Stena Technoworld GmbH)
Auf Schneeweid 19
55774 Baumholder

Laboratory:
Institut für Energie- und Umwelttechnik e.V.
Bliersheimer Straße 58 – 60
47229 Duisburg

6 Target

Liebherr wanted to use the tests to gain knowledge about the migration of the carrier material from the Perlit-VVK to the individual fractions produced in a refrigerator recycling plant and thus assess possible effects on the established recycling process. Furthermore, the possible effects of the recycling processes on the morphology of the carrier material were to be investigated.

To this end, used refrigeration appliances were to be treated in the normal operating mode of the recycling plant and gradually increasingly provided with a defined Perlit-VVK addition. The operating parameters, the processing conditions, possible dust emissions and other impairments of the recycling process should be observed, material discharges sampled and, if possible, described and assessed with regard to the whereabouts of the Perlit-VVK carrier material.

7 Boundary conditions of the investigations

For the investigations, individual defined, Perlit-VVK should be introduced into sufficiently large old cooling devices of the usual input of the plant in different mixing ratios and processed. The processing of Perlit-VVK has no effect on the treatment of the stage 1 therefore the investigations were limited to the treatment in the stage 2.

The processing of refrigerators with commercially available Perlit-VVK was already classified in previous tests at other recycling plants on behalf of Liebherr in cooperation with Miele and IUTA as problem-free for the typical aggregates of the stage 2.

Stena Technoworld Baumholder now: Rekular GmbH plant has agreed to carry out the trial processing. Old equipment from the B2C take-back system and from B2B is processed there. As there are already a few old appliances with commercially available Perlit-VVKs in the take-back system, these are already treated in the regular operation of the plant. There were no disturbances in the processes or anomalies in the product flows.

8 Description of the plant

The plant of the so-called stage 2 with a control throughput of approx. 60 units per hour essentially consists of an encapsulated two-stage comminution, various encapsulated or also open separation units, the respective discharge units of the different material flows produced and an exhaust air cleaning on the basis of direct cryo condensation. The device bodies are fed to a shredder combination (URT/Mewa) via an inclined belt. The shredding chamber is continuously sucked off. The shredder is supplied with nitrogen as required (as explosion protection).

The material is first separated with a zigzag air separator for the insulation foam, with overband magnets for ferrous metals and an eddy current separator for the separation of the non-ferrous metals aluminium and copper. The insulation foam fraction is degassed in a pelleting press (Salmatec). The controlled suctioned air volume of the encapsulated aggregates amounts to approx. 800 m^3/h. The process air is first treated via a condensation stage for the first separation of condensation water, dry dedusting system with cyclone and bag filter and a three-stage wet scrubbing system with spray towers. The conditioned process air is then fed into a cryo condensation plant (Herco Cryo-Condap 20-1000) and the propellants contained are condensed. The components that cannot be sufficiently liquefied are collected by molecular sieves and returned to the process air.

The plant is equipped with a continuous clean gas monitoring system (Fresenius) (measuring parameters R 11, R 12 and pentane).

9 Visual inspection and preparatory measurements

The plant was briefly inspected before starting the investigations. The entire operating sequence corresponded to the regular operation. The tests were carried out on the stage 2 aggregates.

Since the equipment feed between stage 1 and stage 2 offers sufficient space, it was possible to define a sufficiently dimensioned section for testing the equipment and adding the PERLIT-VVK.

Since the carrier material in the PERLIT-VVK was present in powder form, a measuring device was introduced into the process to assess the dust load. An optical particle counter from Palas, model Welas with a measuring range of 0.3 µm to 40 µm was used for the measurement. The measuring range corresponds to the specifications of the safety data sheet of the carrier material.

Figure 1: Particle measuring instrument

The particle measuring instrument can be used for the continuous measurement of dust in air and its aerosol distribution. The instrument uses the scattered light measurement of the individual particles. The measurement result can be classified and evaluated in different size channels (15 channels). The measured values are displayed as particle concentration in the unit particle/cm³.
First, a suitable measuring location for monitoring the process gas flow was agreed with both the plant operator and the customer. The section of the process gas flow after the "dry" dedusting before entering the scrubber was selected.
The measurement device was subjected to a functional test and calibration before being examined.
Then a measurement of the basic load was carried out in regular operation with the exclusive occurrence of PUR-containing dust emissions. The measured values should record the basic load.

Figure 2: Measuring location for particle measurement

The following diagram shows the basic load of the process gas flow with particles smaller than 40 µm after dry dedusting before entering the wet scrubber.

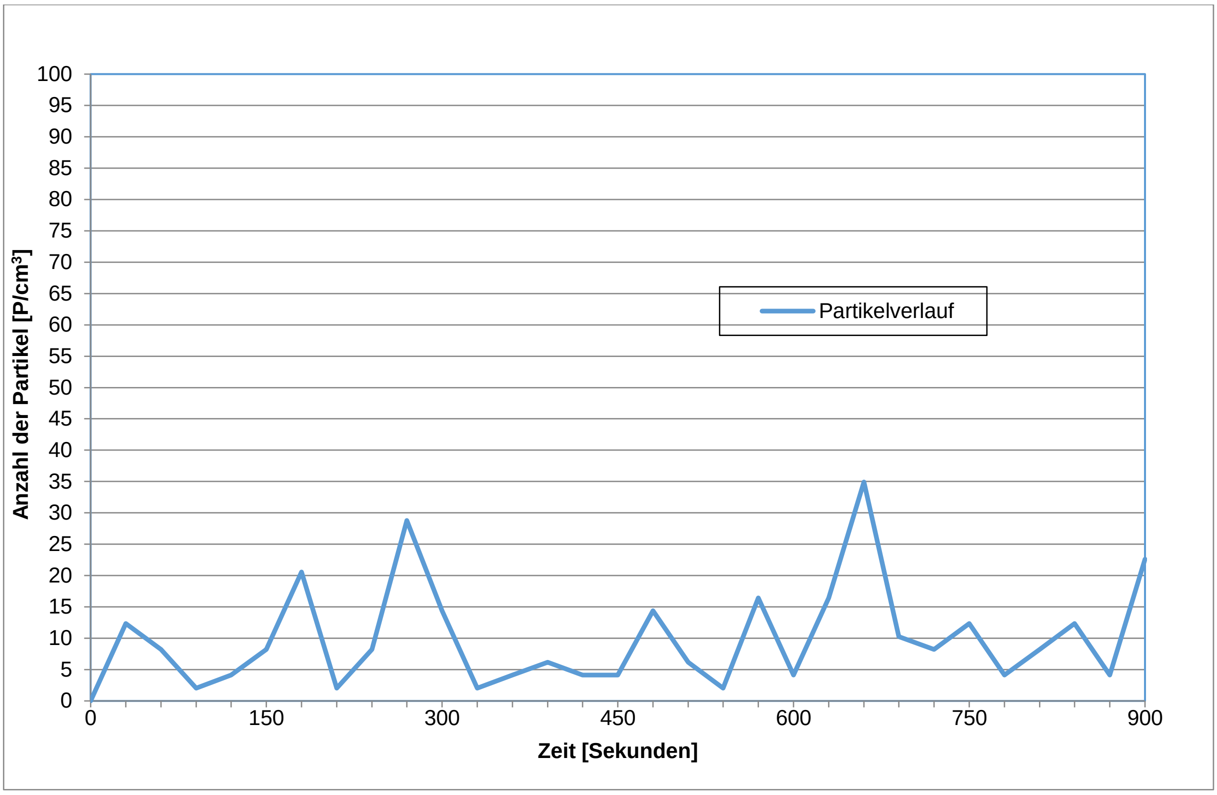

Diagram 1

The dust load of the process air behind the dry dedusting system is extremely low. The mean value of the number of particles in the measured period was 8 to 10 particles per cm³. The particle size distribution of the particles was between 0.5 µm and 6.5 µm.
(For comparison: rural areas have a particle count of approx. 2,000, urban areas more than 20,000 particles per cm³).

The dry dedusting system consisting of a cyclone and a bag filter with common industrial standard cleans the process air very well.

10 Effects of the Perlit-VVK on recovery

The Perlit-VVKs were manufactured by Liebherr in its own factory and delivered separately in advance.

The Perlit-VVKs had a size of 48 cm x 72 cm x 4.5 cm and a weight of 5.5 kg.

Figure 3: Liebherr Perlit-VVK

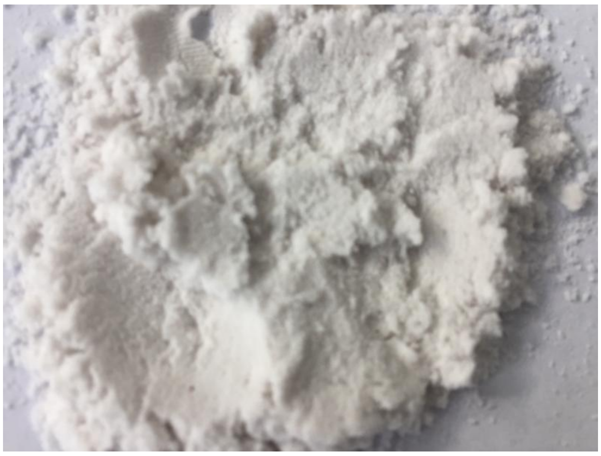

Figure 4: Perlit

In order to check the effects on the ongoing disposal operation, they should be added to the ongoing production in various batch proportions. Based on the experience of the already completed Perlit-VVK investigations, tests with the following batch proportions were planned:

- experiment A: Every 8th refrigerator with a Perlit-VVK
- experiment B: Every 6th refrigerator with a Perlit-VVK (skipped)
- experiment C: Every 4th refrigerator with a Perlit-VVK
- experiment D: Addition according to evaluation from A to C

The duration of each test was approx. one hour so that stable reproducible plant conditions were achieved.

A total of 80 cooling units, 10 of which were equipped with Perlit-VVK (12.5 %), were driven through the system and treated in test A. The cooling units were then placed in the Perlit-VVK (12.5 %) system. In test C, a total of 96 cooling units, 24 of which were equipped with Perlit-VVK (25 %), were treated in test D, 75 cooling units, 15 of which were equipped with Perlit-VVK (20 %).

A total of 251 cooling units and 49 Perlit-VVK were treated in the system during the trials.

Afterwards another 3 hours of cooling units with the Perlit-VVK mixing ratio of 20 % were driven through the plant. 215 cooling units and 43 Perlit-VVK were treated in the system.

10.1 Consideration of the process and the fractions applied

The recycling plant was initially equipped and operated for the conditioning of all plant aggregates without the addition of Perlit-VVK in regular operation.

With the start of the first experiment, the Perlit-VVKs were equally distributed and added to every 8th device. If possible, the Perlit-VVKs were placed inside the units and the doors or, in the case of chests, the lids were closed again in order to be as close as possible to a disposal situation with installed Perlit-VVKs.
The plant aggregates were regularly inspected during operation. The particle load was measured in the process air between dry dedusting and wet washing. After completion of the test, the initial fraction of the insulation material and the material discharge were sampled prior to the material separation of plastic and non-ferrous metals.

Both the shredding process and the separation processes showed no visually detectable deviations from normal operation. The tightness of the plant seemed to be unaffected and no additional emissions could be detected.


Figure 5 und 6: Output fractions after experiment A

On the left side you can see the mixed fraction of non-ferrous metals and plastics. On the right side you can see the fraction of the insulation foam material.

Both fractions did not seem to show any noticeable deviations from the fractions in normal operation. On closer inspection, individual fine grain fractions could be identified which could possibly have been obtained from Perlit-VVK.

The operation of the plant with this Perlit-VVK fraction in the input material flow was possible without impairments.
Due to the small effect on the process and the fractions at the first attempt, the dosing was immediately extended to every 4th unit. If possible, the Perlit-VVKs were placed inside the device, as before, and the doors or lids of the chests were closed again in order to be as close as possible to a disposal situation with installed Perlit-VVKs.
The system aggregates were regularly inspected during operation. Particle contamination was measured in the process air between dry dedusting and wet washing. After completion of the test, the initial fraction of the insulation material and the material discharge were sampled prior to the material separation of plastic and non-ferrous metals.

Both the comminution process and the separation processes showed no visually detectable deviations from normal operation. However, the temperature of the pelleting press rose sharply and the tightness of the press could not be maintained. Large amounts of dust escaped from the pelletizer.

Figure 7 und 8: output fractions after experiment C

On the left you can see the mixed fraction of non-ferrous metals and plastics. On the right you can see the fraction of the insulation foam material.

Both fractions showed conspicuous deviations from the fractions of normal operation. The insulation foam fraction contained almost no pellets, but consisted almost entirely of fine-grained material.

In addition, the escaped dust was sampled on the ground around the pelleting press.

Figure 9: sample dust from floor

This dust also appeared very fine-grained.

It was not possible to operate the plant with the PERLIT-VVK share of 25 % in the input material flow.

The escaped dust was removed by the operating personnel and the third attempt was started.

With the start of test D, the Perlit-VVKs were added equally to every 5th device (20 %). If possible, the Perlit-VVKs were placed inside the unit and the doors or, in the case of chests, the lids were closed again in order to be as close as possible to a disposal situation with installed Perlit-VVKs.
The plant aggregates were regularly inspected during operation. The particle load was measured in the process air between dry dedusting and wet washing. After completion of the test, the initial fraction of the insulation material and the material discharge were sampled prior to the material separation of plastic and ne metals.

Both the comminution process and the separation processes showed no visually detectable deviations from normal operation. The tightness of the plant seemed unaffected and no additional emissions could be detected.


Figure 10 and 11: Output fractions after experiment D

On the left you can see the mixed fraction of non-ferrous metals and plastics. On the right you can see the fraction of the insulation foam material.

The value fractions did not seem to show any noticeable deviations from the fractions in normal operation. On closer inspection, fine-grained fractions could be sighted that could possibly originate from Perlit-VVK. The insulation foam fraction contained fewer pellets than in normal operation.

The operation of the plant with this Perlit-VVK fraction in the input material flow was possible without impairments.

After completion of the three tests, the bag filter of the dry dedusting system was sampled and the mass of the dust quantity determined. A total mass of 6 kg of dust was weighed. With normal production without Perlit-VVK the dust quantity amounts to approx. 2 kg according to the data of the operator.

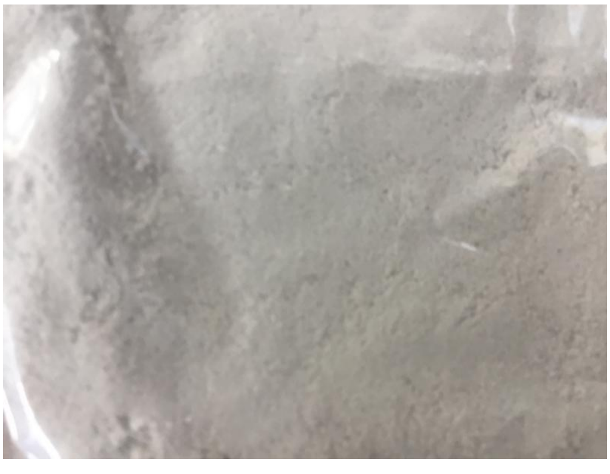

Figure 12: Sample bag filter dust

This dust appeared very fine-grained.

10.2 Consideration of process gas treatment

The following diagram shows as an example the dust load of the process gas flow after dry dedusting before entering the wet scrubber during the tests carried out.

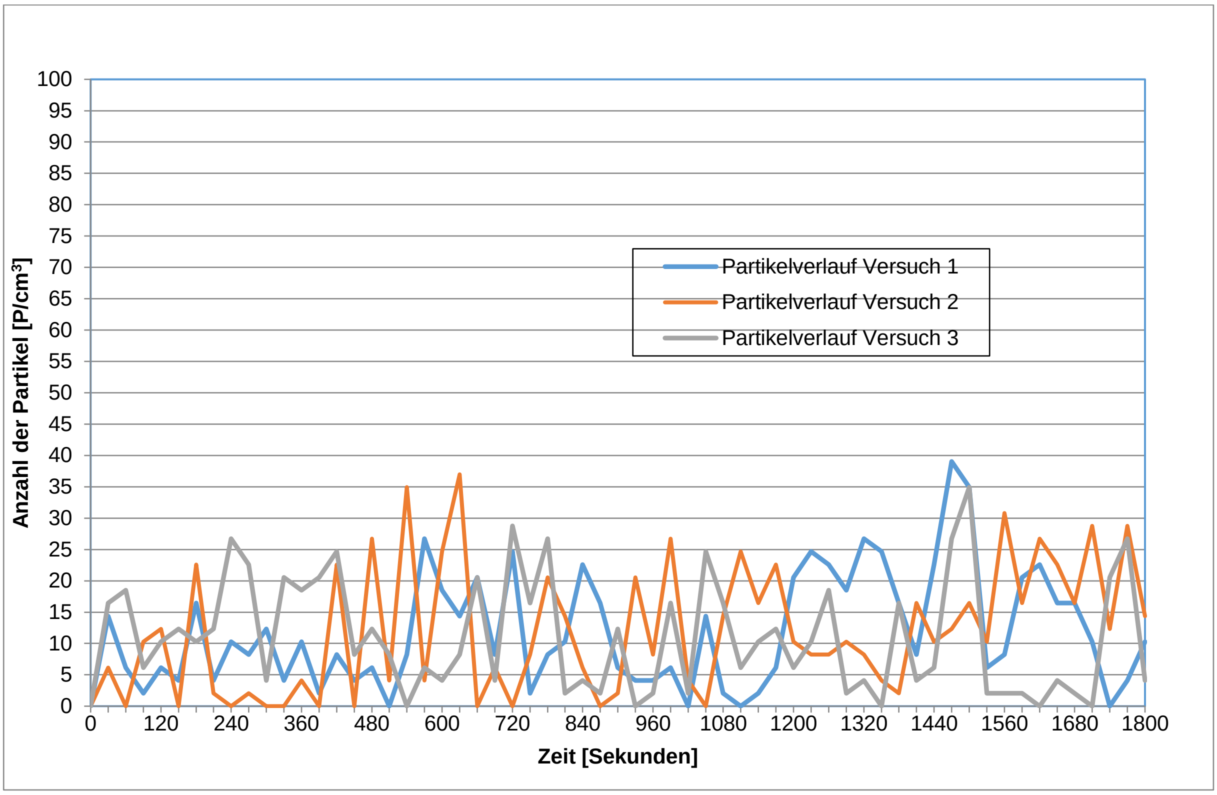

Diagram 2

The mean value of the number of particles in experiment 1 (A) was 11.8 particles/cm^3 in the measured period, 11.9 particles/cm^3 in experiment 2 (C) and 11.0 particles/cm^3 in experiment 3 (D). The particle size distribution of the particles in the three experiments was between 0.5 µm and 6.5 µm.

The particle load in the process air after dry dedusting during PERLIT-VVK processing is not significantly higher than in normal operation.

A dry dedusting system, as it is present in operation, is sufficient for the retention of the carrier material.

11 Effects of recycling on the morphology of Perlite

Six samples were taken from different parts of the plant and examined by scanning electron microscopy.

Figure 13: REM-samples

1. Original Perlit-material from VVK
2. Filter dust
3. Isolation material-output
4. Adhesions on plastic, ferrous, non-ferrous
5. Soil sample after leaving the pelletizer test C
6. Adhesions on non-ferrous after extraction

Three different magnifications 25x, 200x and 500x were selected for recognition and comparison of the structures.

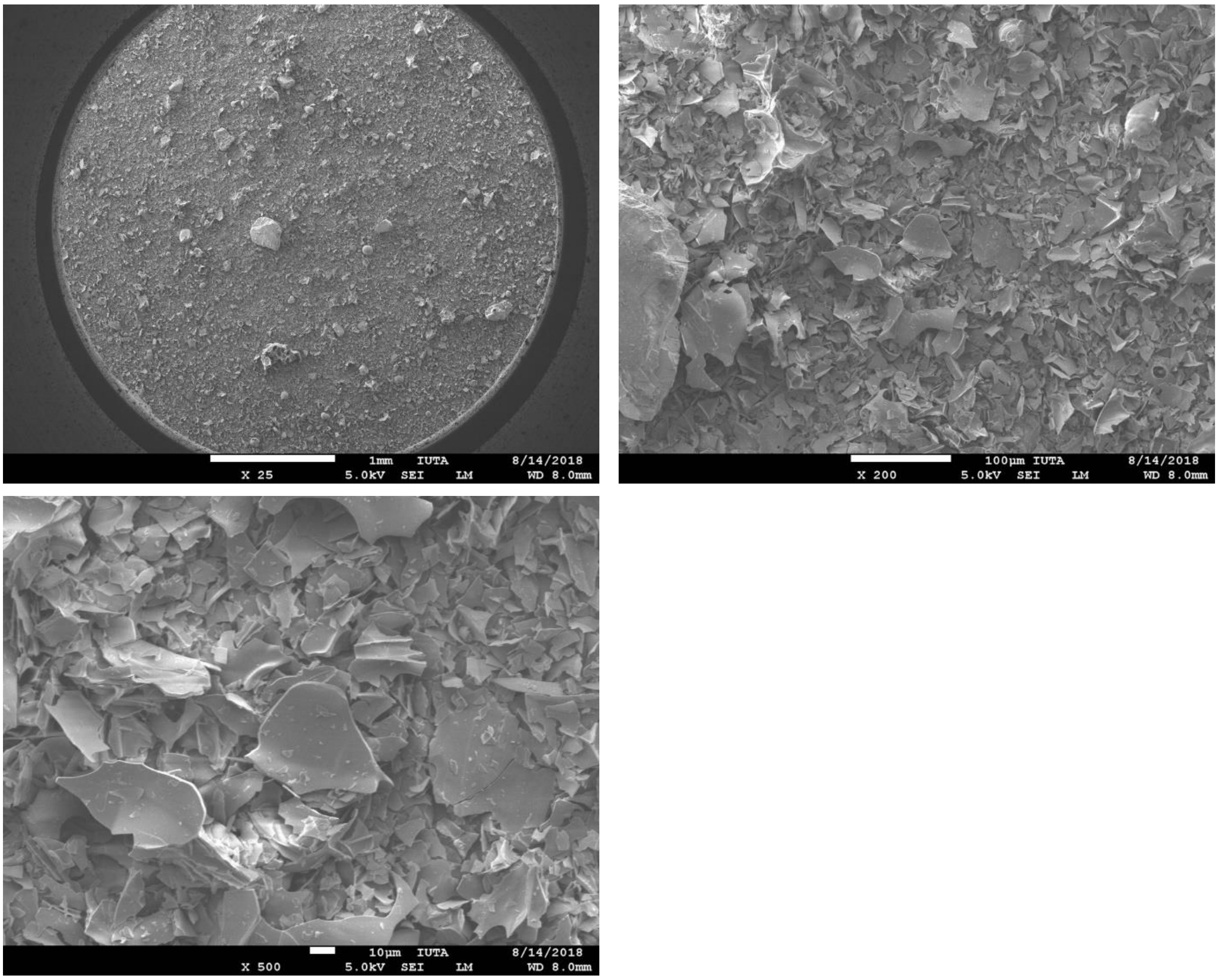

Figure 14: REM images (original material from Perlite VVK)

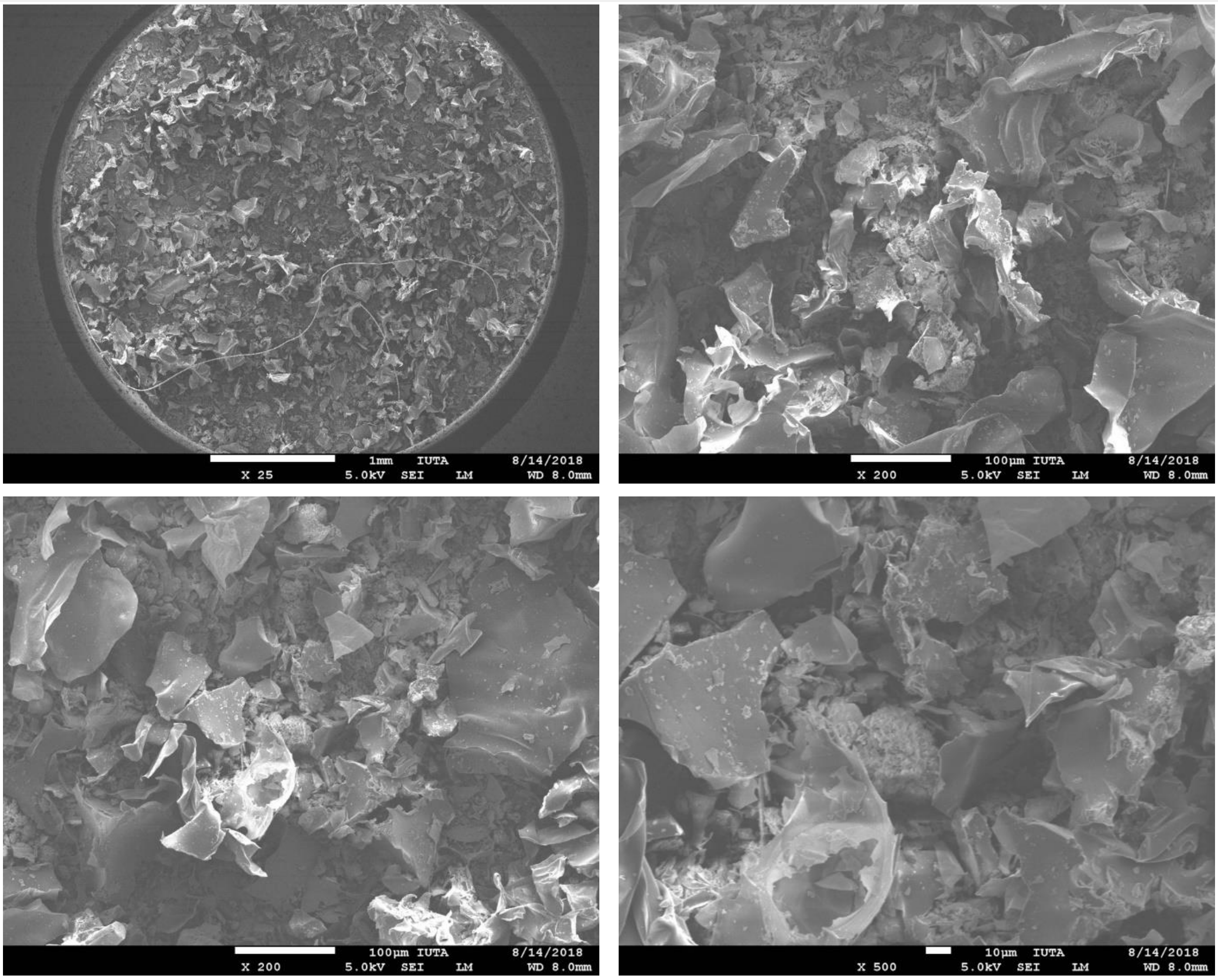

Figure 15: REM-pictures filter dust

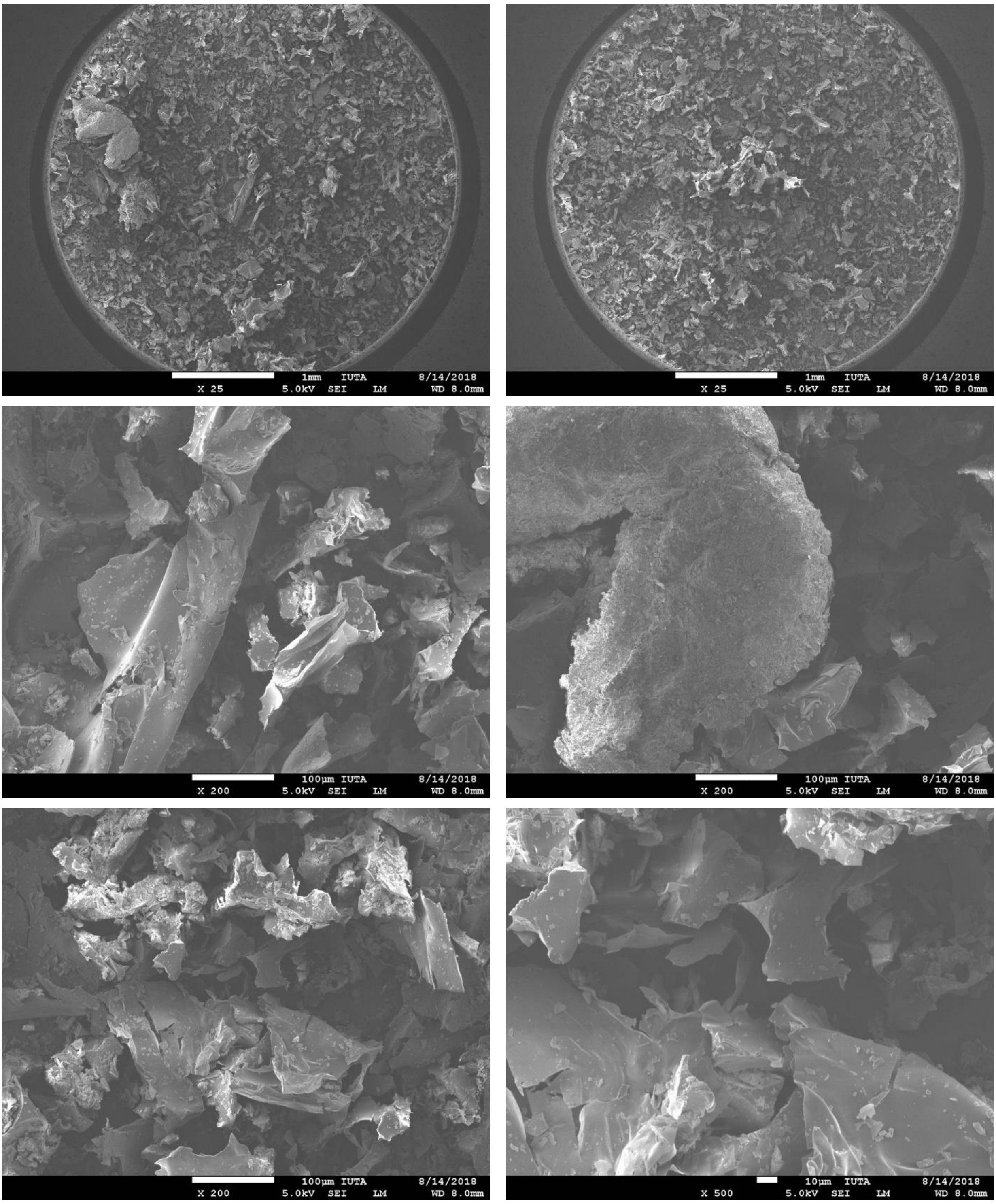

Figure 16: REM-pictures isolation material output

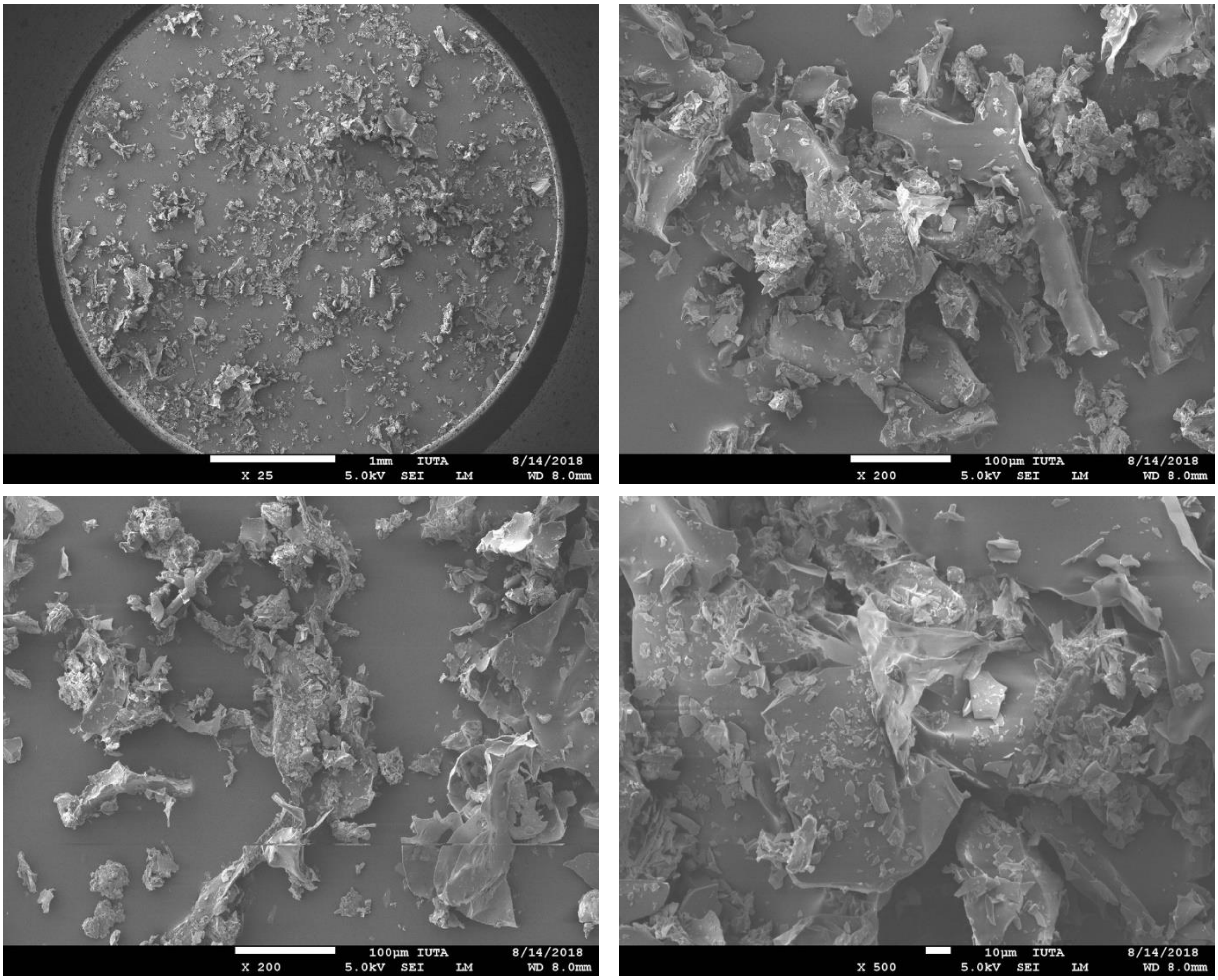

Figure 17: REM-pictures adhesions on plastics, ferrous and non-ferrous

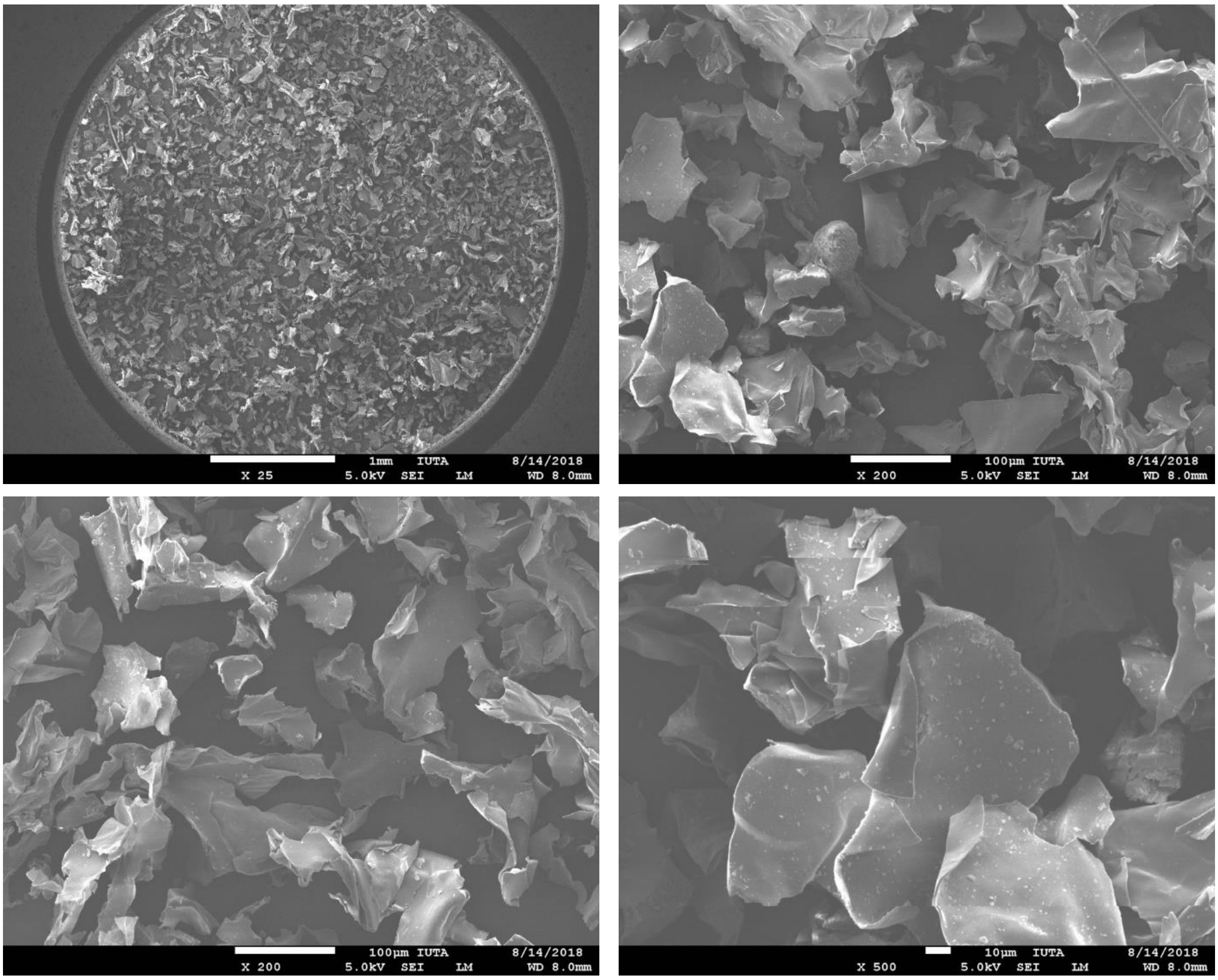

Figure18: REM-pictures sample dust from floor near pelletizer

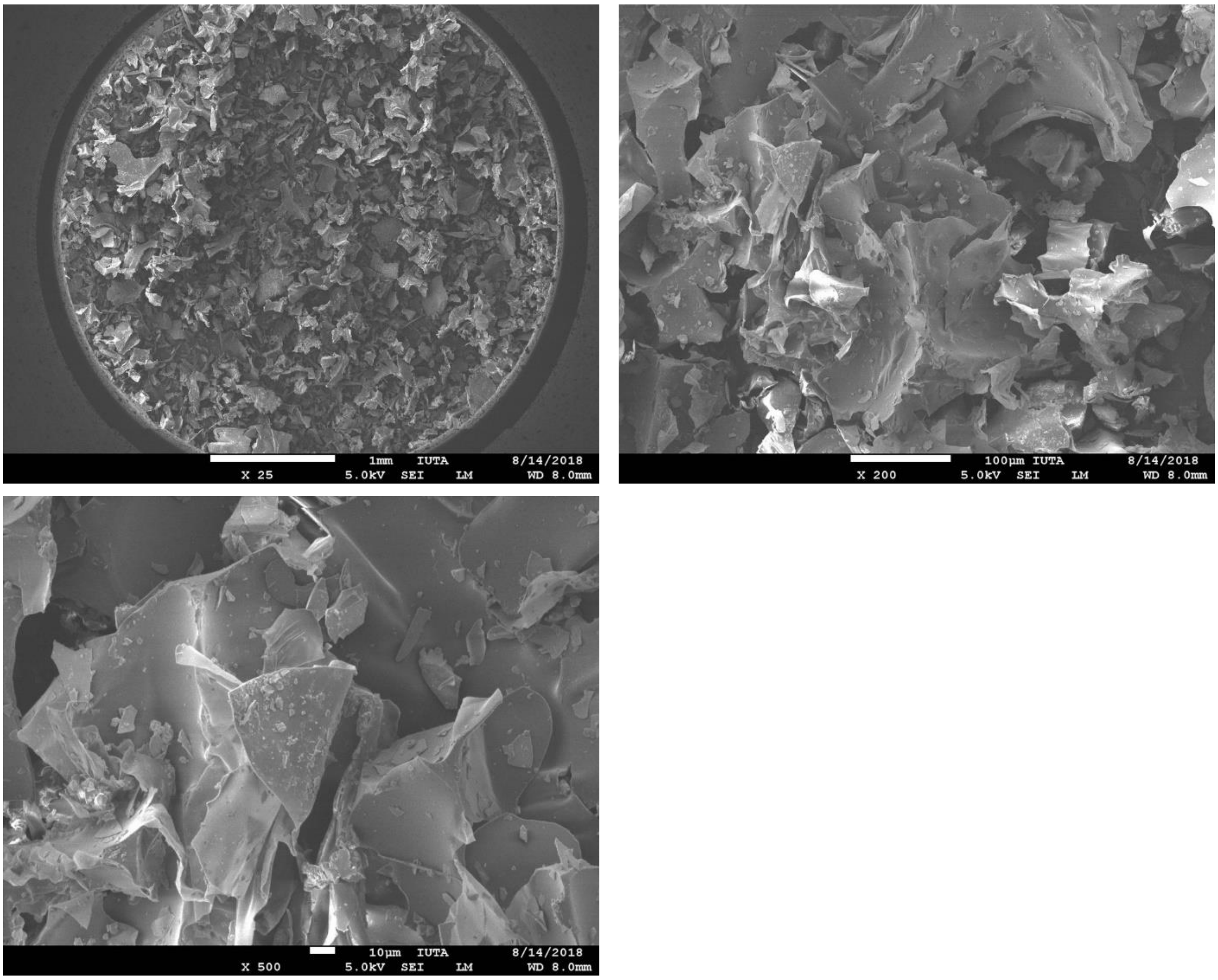

Figure 19: REM-pictures adhesions on non-ferrous

Figure 14 shows the morphology of the Perlite from the VVK, especially at 500x magnification. Clearly rounded platelets can be seen. Fibrous, pointed or elongated geometries are not present.

In all subsequent images with 200- and 500-fold magnification, it is clearly visible, independent of the material stream discharged, that the adhering particles from the pearlite retain their size, shape and other consistency and are discharged morphologically unchanged.

Neither agglomeration nor fragmentation of the particles takes place. Some particles are deformed without producing sharp edges or chipping.

12 Migration of the Perlite into the fractions

The visual examination of the fractions has shown that there is almost no migration of Perlite into the plastic-containing and metal-containing fractions. The change in the insulation foam fraction and the increase in the filter dust also indicate that the Perlite should be there.

An exemplary analytical confirmation can be performed by energy dispersive X-ray spectroscopy directly in the electron microscope or in a separate analytical instrument.

With EDX analysis, areas of a sample surface with a penetration depth in the µm range can be examined semi-quantitatively for elementary composition by means of a so-called fundamental parameter analysis. The detection range for the elements in the SEM for this method lies between beryllium and uranium. In order to capture a representative sample quantity, the measurement was performed as a so-called full area scan at 25x magnification. The excitation energy of 10 keV was chosen in order to optimally excite the elements to be detected to fluorescence. The element carbon, as a component of the sample carrier material (graphite), is also measured at locations with low sample coverage. The detected elements can mainly be assigned to the sample at locations with massive deposits or in so-called spot analyses.

For the analysis, which takes place in high vacuum, the material is glued onto a sample carrier and the immobile components of the sample are blown off with a bellows and then vaporized with a conductive material (here gold). This inevitably leads to gaps on the sample carrier where the carrier material (carbon) is exposed and is also detected. Spot analyses only cover selected areas of the sample. This allows the composition of individual particles to be analyzed.

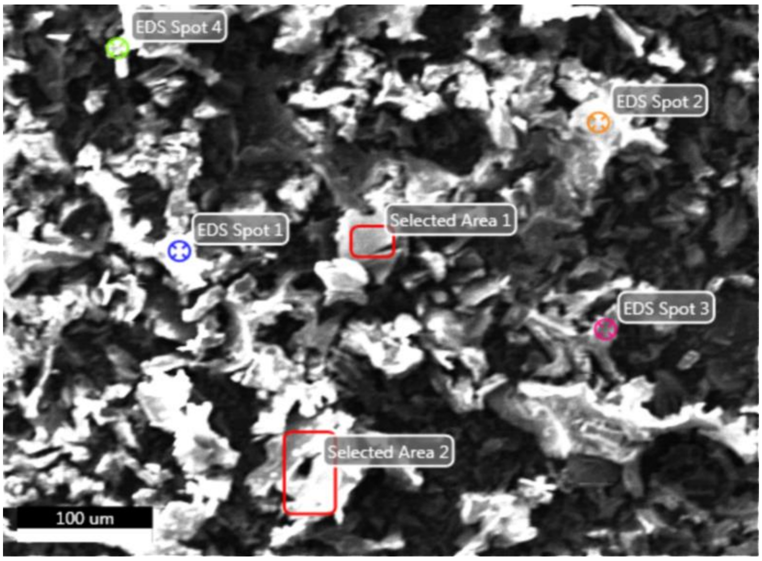

Figure 20: Sample of a spot analysis for the identification of individual particles

Alternatively, the entire sample area can be used for evaluation (Full Areas Scan). The samples of the individual fractions were evaluated with the help of the area analyses.

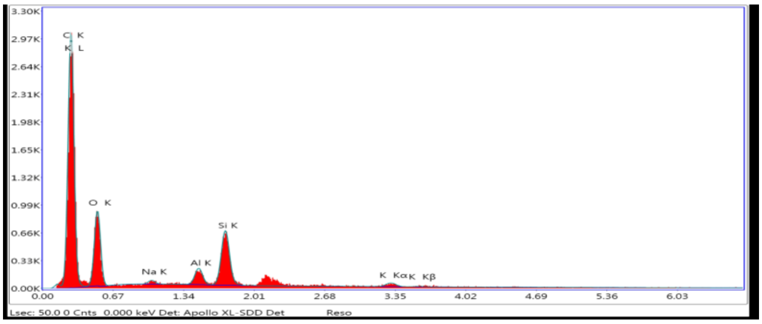

Figure21: X-ray fluorescence spectrum of a surface analysis

To identify the Perlit-VVK material, the focus was placed on the main components: Si; O; Al; Na and K. The surface area and thus the mass of the samples are relatively small.

However, the area covered and thus the mass of the samples covered are relatively small. The results in the table below can therefore only be evaluated semi-quantitatively.

Sample / elementconcentration [wt.-%]	C	O	Na	Al	Si	K
original Perlite from VVK	9,5	42,2	3,2	7,3	34,5	3,3
filter dust sample 1	60,8	22,5	0,7	2,3	11,8	1,9
isolation material sample 1	65,6	22,4	0,6	2,1	7,6	1,7
adhasions on plastic; ferrous; non ferrous sample 1	70,4	22,1	0,8	1,4	5,4	0,0
dust from floor sample 1	76,5	20,9	0,0	0,9	1,8	0,0
adhasions non ferrous sample 1	63,9	22,9	0,8	2	6,6	1,3

Table 1: Results from REM/EDX

With X-ray fluorescence analysis (XRF), samples with a larger volume can be examined for their elemental composition by means of a so-called fundamental parameter analysis. With this method, the detection range for the elements is from sodium to uranium.

The complete excitation range up to 50 keV was selected for the analyses. This analysis was also performed under vacuum.

The detection of the carrier material was carried out via the main component silicon.

In the case of bulk material samples with different grain sizes and different densities of the components, fines may be determined disproportionately, since the fines sediment downwards and thus to the analysis surface. This analysis method can therefore only be evaluated half-quantitatively in the present case.

sample /element-concentration [wt.-%]	**Na**	**Al**	**Si**	**K**	**Ca**	**Fe**	**Sonstige**
original Perlite from VVK	n.n.	n.n.	50,8	24,2	9,9	10,8	< 1 %: S; Ba; Ti; Mn; Cl; Ir
filter dust sample 2	n.n.	6,1	52,0	12,87	7,2	13,0	Cl: 3,1 Ti: 2,5 Zn: 2,4 Mn: < 1 S: <1
isolation material sample 2	n.n.	6,0	33,3	10,1	7,3	21,7	Ti: 8,7 Zn: 6,5 Cl: 4,9 S: 0,6 Mn: 0,3
dust from floor sample 2	n.n.	n.n.	14,1	2,0	27,1	28,9	Cl: 13,3 Ti: 7,1 Zn: 5,7 S 0,7 Cu: 0,3 Mn: 0,3

Table 2: Results from RFA

The analyses of the REM/EDX were primarily used to identify the carrier material in order to check for a possible change in morphology. The investigated partial samples were specially selected for this purpose. The additionally determined element concentrations refer to the selected sample area.

In XRF, the Perlite material is determined disproportionately for the above-mentioned reasons (grain size distribution).

A direct comparison of the results is therefore only possible to a limited extent.

In addition, both analysis methods provide only semi-quantitative results, but clearly confirm the visual impressions that the carrier material is mostly discharged with the insulation material fraction. The next larger fraction is in the dry dedusting discharge. The other fractions have little adhesion.

13 Summary of results

The processing of cooling units with Perlite Perlit-VVK could be carried out up to 20% of the total input without impairing the process or the fractions applied.

The processing of cooling units with Perlite Perlit-VVK with a share of 25% of the total input led to problems with one of the aggregates (pelleting press).

The established dry dedusting system was able to sufficiently separate the Perlite. An increase of the particle emission by the Perlit-VVK material compared to PUR was not found.

The Perlite was separated and discharged in the same way as the other insulation materials (PUR). After processing, it was mainly found in the insulation foam fraction and in the filter dust.
Only small traces were found in the other fractions.

The morphology of the Perlite was not changed by the processing of the refrigerators. In particular, no pointed or elongated structures were created.

Duisburg 08.10.2018

Dipl.-Ing. J. Schiemann staatl. gepr. Techniker H.J. Prause

staatl. gepr. Technikerin B. Schiemann

Supplement by Liebherr-Hausgeräte Ochsenhausen GmbH

Liebherr-Hausgeräte would like to thank those responsible at Stena Technoworld GmbH now: Rekular GmbH and the employees at the Baumholder location for their willingness to carry out the test.

We would also like to thank the IUTA for its constructive support during the test.

Copyright ©:

principal:
Liebherr Hausgeräte Ochsenhausen GmbH
Memminger Straße 77-79
88416 Ochsenhausen/Deutschland

author:
Institut für Energie- und Umwelttechnik IUTA
Bliersheimer Str. 58 – 60
47229 Duisburg

This report has been prepared in accordance with the „Grundsätzen für die Sicherung guter wissenschaftlicher Praxis an der Universität Duisburg–Essen“, Amtliche Mitteilung Jahrgang 2 Duisburg/Essen 10.08.2004 Seite 187 ff. Nr. 19 and is for information purposes only.