

# Investigation of metals content in the fine fraction of municipal waste from Alytus Regional Landfill

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This study presents the results of investigation of the fine waste fraction from the Alytus Regional Landfill. The fine fraction was analysed with the aim of characterization of the chemical elements content using scanning electron microscopy, coupled with energy-dispersive spectroscopy (EDS), SEM and X-ray diffraction (XRD) analysis. Quartz  $\text{SiO}_2$ , calcite  $\text{CaCO}_3$ , anhydrite  $\text{CaSO}_4$ , albite  $\text{NaAlSi}_3\text{O}_8$ , dolomite  $\text{CaMg}(\text{CO}_3)_2$ , microcline  $\text{KAlSi}_3\text{O}_8$ , periclase  $\text{MgO}$  and muscovite  $\text{KNa}(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}_{3.1}, \text{Al}_{0.9})\text{O}_{10}(\text{OH})_2$  minerals were identified. The quantity of C, O, Na, Mg, Al, Si, K, Ca, Fe, P, S, Cl and Ti chemical elements was determined and their percentage change after heating was calculated.

**Keywords:** fine fraction, landfill waste, SEM, EDS, XRD

## INTRODUCTION

Recently, the lack of resources and the deterioration of the quality of ores have led to new ways of extracting the necessary raw materials. This has led to attempts of finding new ways of recovering valuable resources. One of such ways is recovering resources from landfills. Besides the possibility of energy recovery from the combustible (mainly coarse) fraction there is also an opportunity to extract metals, mainly from the fine fraction of landfills. Recently there have been several studies of metals content in this fraction. It was found that the concentration of critical major elements and rare earth elements (REEs) is significantly lower than in mining and secondary resources mono-landfills (industrial dump) areas; the concentration of such elements as Fe, Al, Cu, Pb, Ni and some other might become of interest for extraction in more or less near future [2, 3, 10]. The fine fraction of waste (particle size ranging between <10 mm and <25.4 mm) is 40–70% (w/w) of mined landfill waste, and is typically considered

mainly soil containing varying amounts of landfilled materials [6, 8]. The fine fraction is the best source of metals in waste – [12] reported that 37–57% of heavy metals in the organic fraction of Municipal Solid Waste (MSW), including Cd, Cr, Cu, Hg, Ni, Pb and Zn, were concentrated in fine particles, which accounted for only 28% (m/m) of the total waste content. On the other hand, studies made on landfills with a high percentage of plastics and textiles show that under these conditions the fine materials are not the greatest fraction [11]. In [10] investigations of an open dump in Thailand, less than 18% of the material was smaller than 25 mm, while 69% had a size bigger than 50 mm.

The waste analysed in this article was obtained by drilling in the Alytus Regional Landfill [1].

In [5] using pyrometallurgical processes Zn and Mn recovery rates were 80.8–100% and 77.6–95.9%, respectively, while the Pb recovery rate was only 0.68–3.14%. It is worth mentioning [7] that despite larger initial capital investments, the production cost using pyrometallurgy is lower than using hydrometallurgy or electrometallurgy. That is why we decided to investigate changes of crystallographic structures

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and metal content after heating of the samples at 550°C and 850°C temperature.

## EXPERIMENTAL

### Fine fraction of municipal waste landfill

The morphological composition of landfills was investigated experimentally by the method of drilling (Alytus) or excavation (Torma). Investigations were made according to the Standard Test Method for Determination of the Composition of Unprocessed Municipal Solid Waste (D 5231 – 92). In Alytus, three drillings were conducted with a 15 cm drill in specified parts of the 1st section (which is operating from the year 2007 onwards. Later we will talk only about the 1st section) and waste samples were drawn every one meter between 1 and 10 meters in depth [4]. 285 kg was excavated in total. The waste was sorted into four size fractions of >80 mm, 80–40 mm, 40–20 mm, and <20 mm. The waste was classified into paper and cardboard, glass, textiles, soft plastics, hard plastics, medical and other non-combustible electronics, and fine fraction (<20 mm). The waste was dried at 105°C for two hours and then stored at room temperature in a desiccator. To get heated waste, it was heated using the muffle furnace SNOL 8.2/1100 at 550°C and 850°C temperature, respectively, for two hours, afterwards it was stored in a desiccator at room temperature.

The fine fraction of the municipal waste landfill was investigated in three cases:

- unburned;
- heated at 550°C temperature;
- heated at 850°C temperature.

A ZEISS EVO MA10 scanning electron microscope equipped with a Bruker XFlash 6/10 EDX detector was used for chemical composition measurements of the fine waste fraction from the Alytus Regional Landfill. The x-ray diffraction patterns of the fine waste fraction from the Alytus Regional Landfill were recorded with a DRON6 diffractometer in the Bragg–Brentano configuration. The CuK $\alpha$  wavelength radiation (tube voltage of 30 kV and current of 20 mA) filtered with a flat diffracted beam pyrolytic graphite monochromator was used. Data were collected over the diffraction range  $2\theta = 5\text{--}70^\circ$ , with a step of  $0.02^\circ$  and counting time of 1 s per step using a scintillation detector.

## RESULTS AND DISCUSSION

### Unburned fine fraction

X-ray diffraction analysis (XRD) was performed on unburned fine fraction samples taken from the landfill at 1, 2, 3, 5, 7 and 9 meters. The depths of 2, 5 and 9 m are characterized by minerals like quartz  $\text{SiO}_2$ , calcite  $\text{CaCO}_3$ , albite  $\text{NaAlSi}_3\text{O}_8$ , dolomite  $\text{CaMg}(\text{CO}_3)_2$  and microcline  $\text{KAlSi}_3\text{O}_8$ . At depths of 1, 3 and 7 m, muscovite  $\text{KNa}(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}_{3.1}, \text{Al}_{0.9})\text{O}_{10}(\text{OH})_2$  was also found (Fig. 1).

For the determination of the amount of main and trace elements in the fine fraction of waste, the EDS

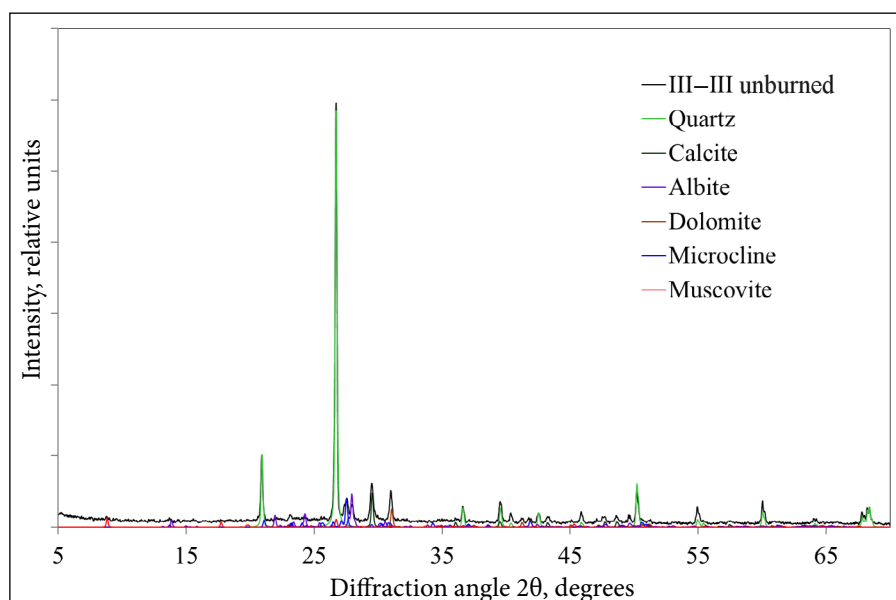


Fig. 1. XRD analysis of the unburned fine fraction at 3 m depth

analysis method was applied. In the unburned fine fraction, elements such as chlorine Cl, phosphorus P and titanium Ti have been identified in addition to the defined mineralogical modifications. This is true for all layers of the landfill at the depths of 1, 2, 3, 5, 7 and 9 m. The SEM micrograph shows that the unburned fine fraction is composed of different size crystals, the largest are around 20–60  $\mu\text{m}$  in size (Fig. 2). The EDS spectrum showed that the average amount of oxygen in all layers was 46.97 wt.%, followed by carbon with 22.71 wt.%, silicon accounted for 14.66 wt.%, and calcium 8.24 wt.% (Table).

The oxygen amount little changes between different layers. Carbon is varying from 26.21 wt.% in

the first layer, then as little as 19.34 wt.% in the 3rd layer, later increases and again decreases. The amount of silicon varies from 12.27 wt.% in the top layer to the maximum of 16.57 wt.% in the second layer. Calcium fluctuates a little, slowly decreasing from the top. By contraries, the amount of rest elements increases from top to bottom (Fig. 3).

#### Heated at 550°C temperature fine fraction

Quartz  $\text{SiO}_2$ , calcite  $\text{CaCO}_3$ , anhydrite  $\text{CaSO}_4$ , albite  $\text{NaAlSi}_3\text{O}_8$ , dolomite  $\text{CaMg}(\text{CO}_3)_2$ , microcline  $\text{KAlSi}_3\text{O}_8$  and muscovite  $\text{KNa}(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}_{3.1}\text{Al}_{0.9})\text{O}_{10}(\text{OH})_2$  were found in the heated at 550°C fine fraction (1, 2, 3 (Fig. 4), 7 and 9 m depths).

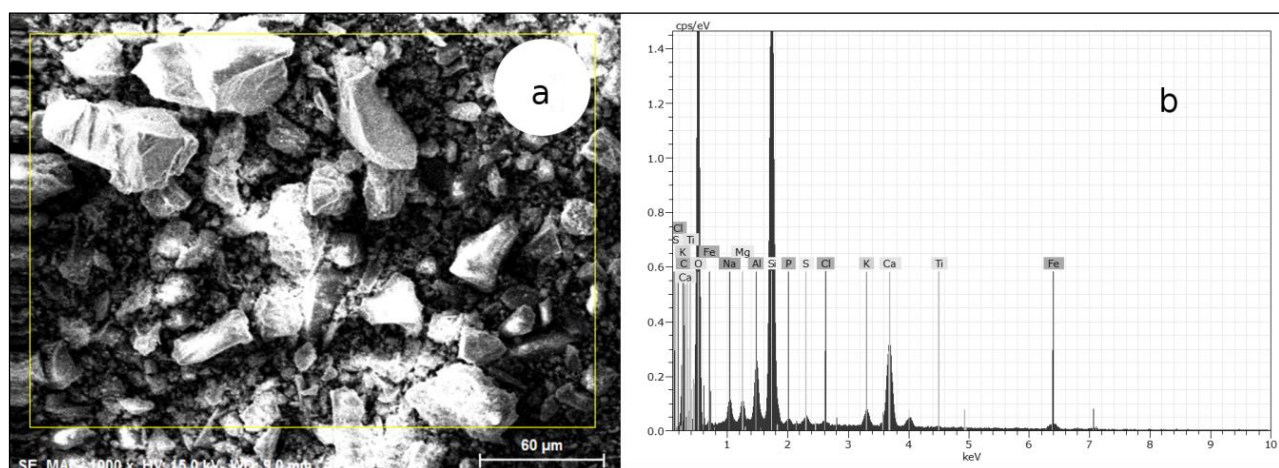
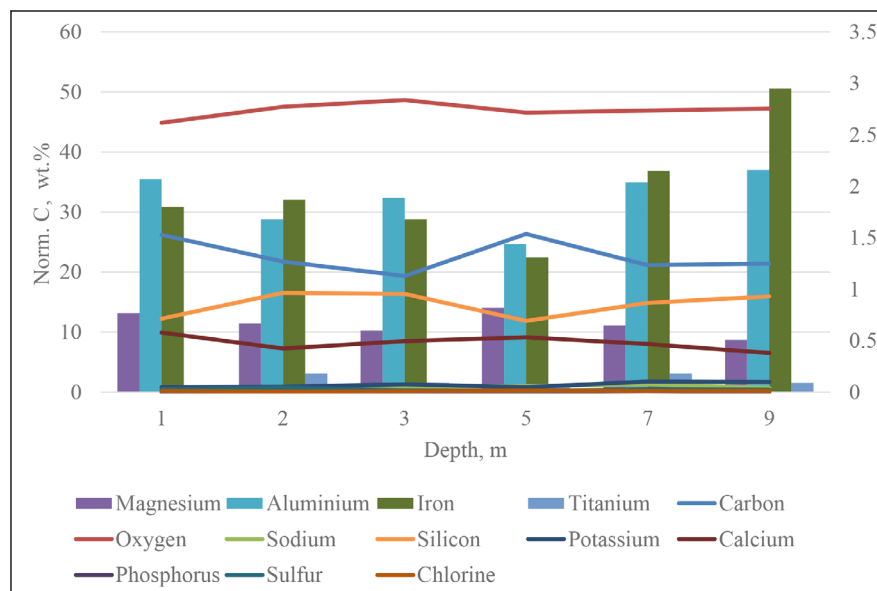


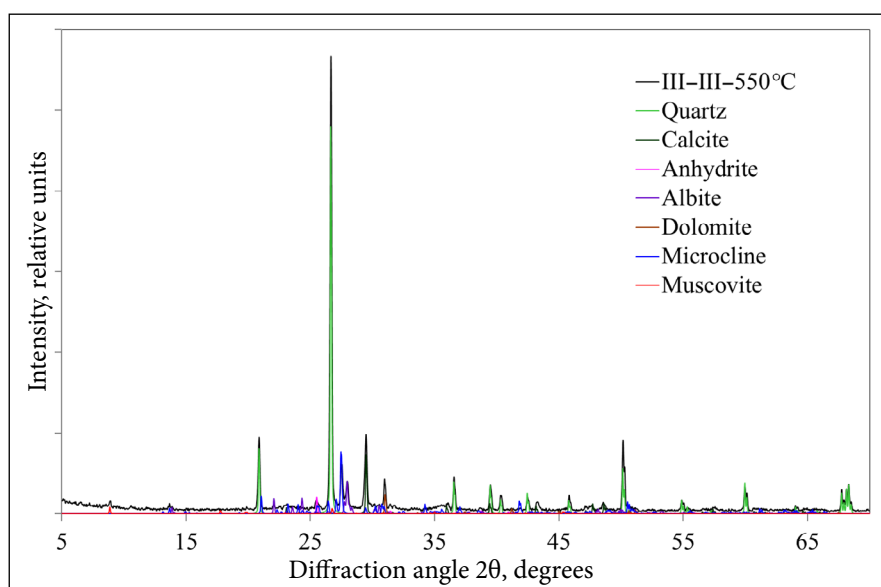
Fig. 2. Unburned fraction SEM under magnification of 1000 (a) and the EDS spectrum of the fine fraction (b) (3 m depth)

Table. Average amount of different elements in all landfill layers

	Unburned, average, %	550°C, average, %	850°C, average, %	% change, unburned → 550°C	% change, 550°C → 850°C	% change, unburned → 850°C
Carbon	22.71	7.20	3.06	-68%	-58%	-87%
Oxygen	46.97	47.46	46.38	1%	-2%	-1%
Sodium	0.85	0.88	1.26	4%	43%	49%
Magnesium	0.67	0.95	1.49	42%	57%	122%
Aluminum	1.88	2.59	3.26	38%	26%	73%
Silicon	14.66	18.63	21.06	27%	13%	44%
Potassium	1.24	2.06	1.71	67%	-17%	38%
Calcium	8.24	13.85	16.29	68%	18%	98%
Iron	1.96	3.92	3.42	100%	-13%	75%
Phosphorus	0.07	0.29	0.33	291%	16%	355%
Sulfur	0.46	1.31	0.98	188%	-25%	115%
Chlorine	0.20	0.46	0.39	134%	-15%	100%
Titanium	0.11	0.40	0.37	270%	-8%	242%



**Fig. 3.** Changes of the unburned fine fraction elemental composition in different landfill layers

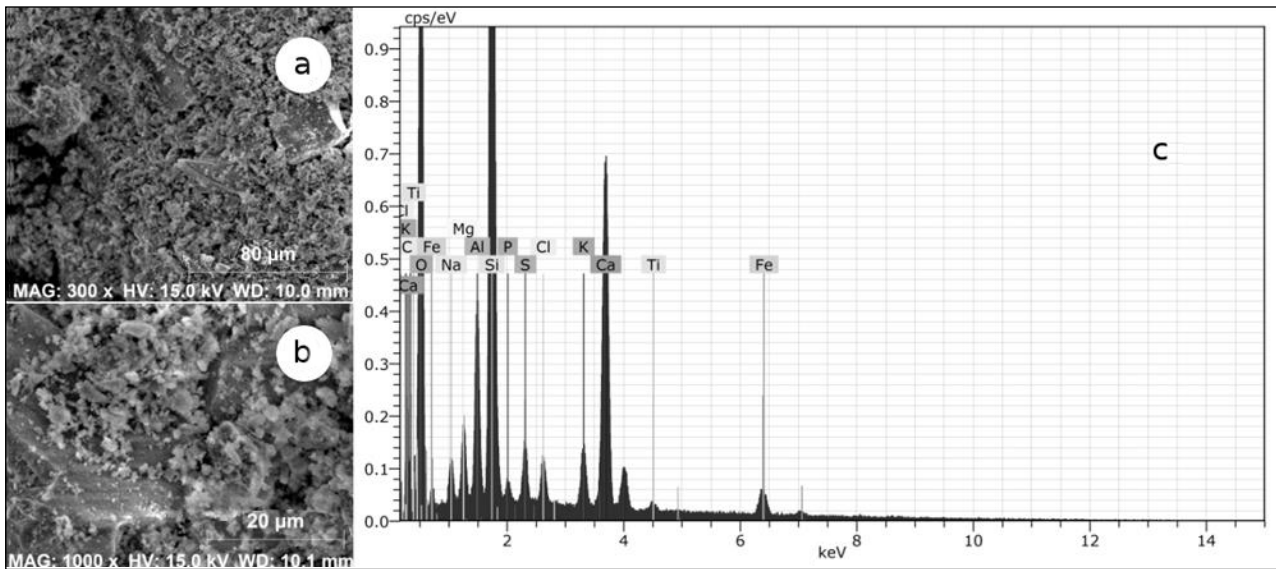


**Fig. 4.** XRD analysis of the heated at 550°C fine fraction from 3 m depth

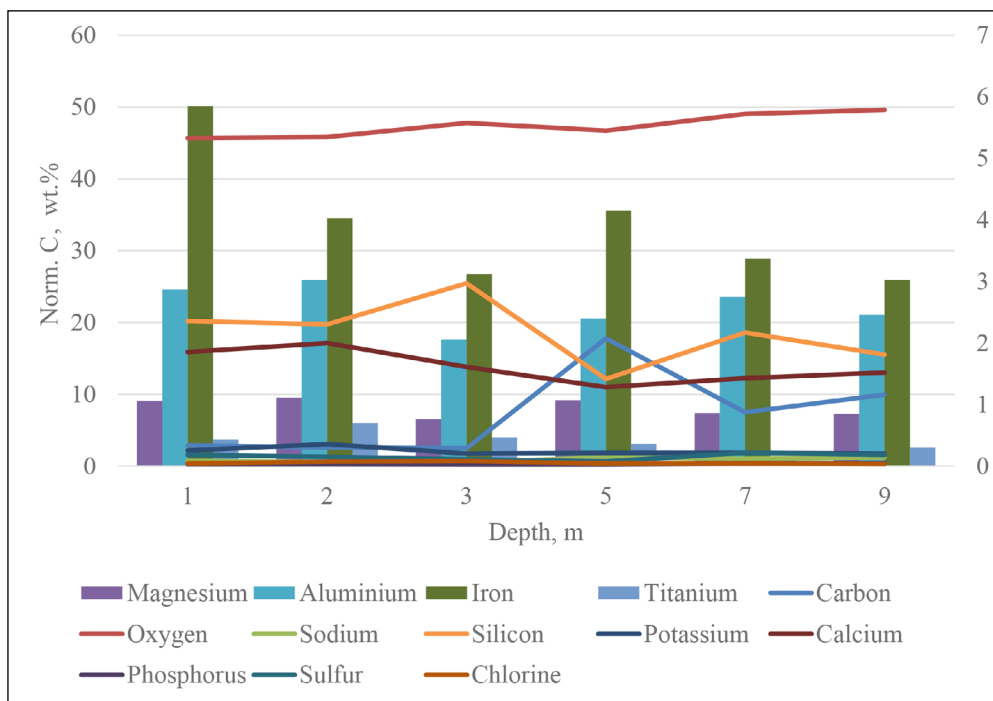
At a depth of 5 m, the same mineralogical modifications are typical, but periclase MgO is found instead of anhydrite. The SEM micrograph shows that the heated at 550°C fine fraction is composed of smaller crystals than unburned, this is mainly due to the fission of calcite and dolomite with the resulting formation of calcium and magnesium oxides (Fig. 5).

The elemental composition determined by the EDS method is showing a significant decrease of C (on average –68%) and an increase of all other elements in comparison with the composition of an unburned fraction (Fig. 5).

The oxygen amount is increasing from 44.21 at the top to 49.64 at the bottom layer. Little carbon was found in the top layers after heating (<3 wt.%), then it suddenly increases to 17.79 wt.% in the 5th layer, later again decreases to <10 wt.%. The amount of silicon increases in the beginning to the maximum of 25.47 wt.% in the third layer, later decreases to a minimum of 12.14 wt.% in the 5th layer. The amount of calcium is slowly decreasing from the top. By contraries, the amount of rest elements increases from top to bottom. There is a significant amount of iron, ~4–5 wt.% in different layers (Fig. 6).



**Fig. 5.** SEM under magnification of 300 (a), under magnification of 1000 (b), and the EDS spectrum of the fine fraction (c) (3 m depth) heated at 550°C

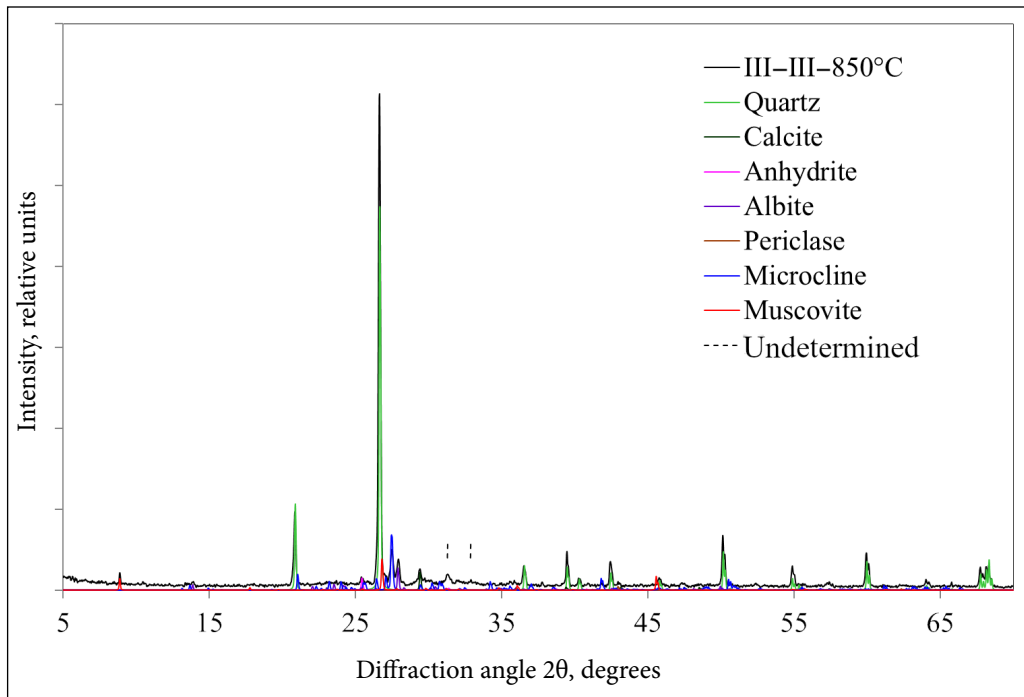


**Fig. 6.** Changes of the heated under 550°C fine fraction elemental composition in different landfill layers

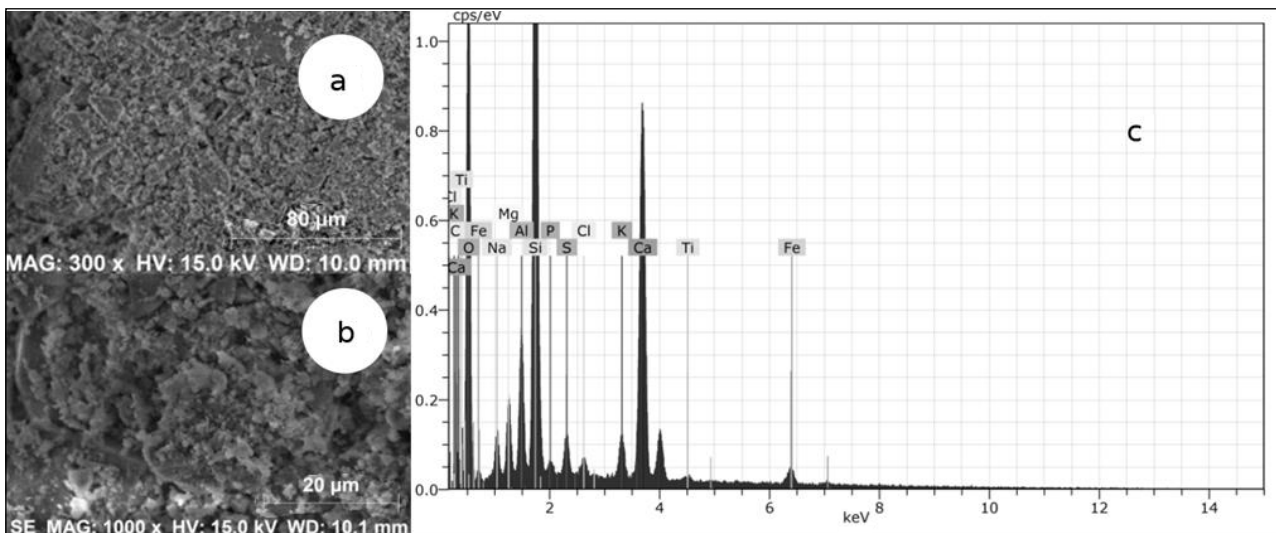
**Heated at 850°C temperature fine fraction**

The same waste samples were further heated at 850°C. Quartz SiO<sub>2</sub>, calcite CaCO<sub>3</sub>, anhydrite CaSO<sub>4</sub>, albite NaAlSi<sub>3</sub>O<sub>8</sub>, periclase MgO, microcline KAlSi<sub>3</sub>O<sub>8</sub> and muscovite KNa(Al, Mg, Fe)<sub>2</sub>(Si<sub>3.1</sub>Al<sub>0.9</sub>)O<sub>10</sub>(OH)<sub>2</sub> were found in the heated under 850°C fine fraction of the landfill (1, 2 and 3 m depths). At 5 and 7 m calcite CaCO<sub>3</sub> and periclase MgO were absent, at 9 m depth no muscovite was

found. Obviously, dolomite breaks down at this temperature and periclase MgO is formed (Fig. 7). The SEM micrograph shows that crystals of the heated at 850°C fine fraction are very similar to crystals of the heated at 550°C fine fraction, although the EDS analysis showed that carbonates were further decomposing, so a conclusion can be made that larger particles of carbonates are decomposing in the beginning (Fig. 8).



**Fig. 7.** XRD analysis of the heated at 850°C fine fraction from 3 m depth



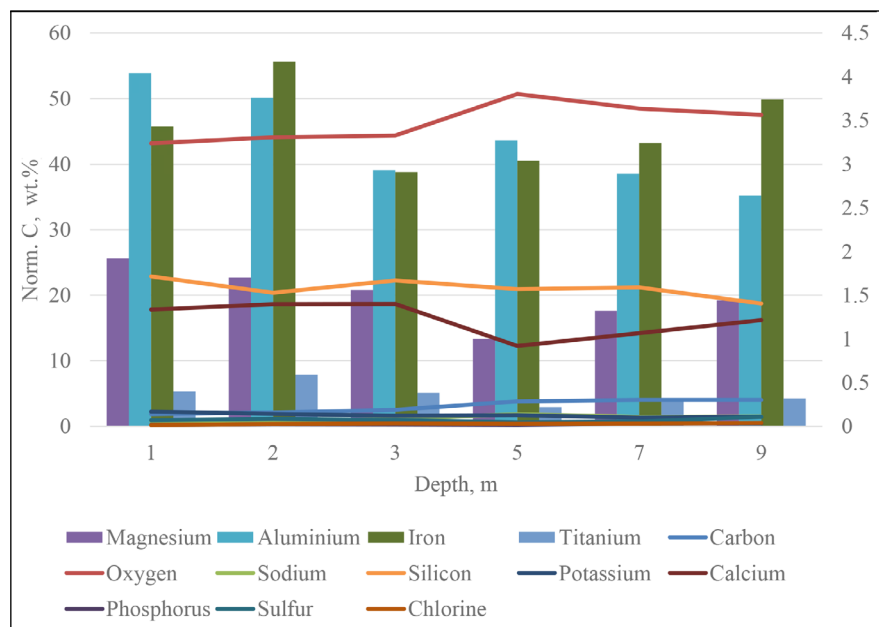
**Fig. 8.** SEM under magnification of 300 (a), under magnification of 1000 (b), and the EDS spectrum of the fine fraction (c) (3 m depth) heated at 850°C

The elemental composition determined by the EDS method is showing a significant decrease of C (on average –87%) and an increase of all other elements in comparison with the composition of an unburned fraction, with the exception of O, which virtually does not change (Fig. 8).

The oxygen amount is increasing from 43.18 wt.% at the top to 50.68 wt.% at the 5th layer and decreasing to 47.51 wt.%. The carbon amount

is low (<5 wt.% in all layers). The amount of silicon is ~20 wt.%. The amount of calcium is ~20 wt.% in the top layers, then decreases to 12.25 wt.% in the 5th layer and slightly increases at the bottom. The amount of rest elements generally increases from top to bottom (Fig. 9).

The average amounts of elements and their changes after thermal treatment are presented in the Table.



**Fig. 9.** Changes of the heated under 850°C fine fraction elemental composition in different landfill layers

## CONCLUSIONS

The mineralogical composition (by XRD method) and the preliminary elemental composition (by EDS method) of the fine fraction in the Alytus Regional Landfill were investigated. With respect to the fine fraction, these and other studies were performed on unburned material and burned at 550°C and 850°C.

The fine fraction of the landfill at depths of 2, 5 and 9 m is characterized by minerals such as quartz  $\text{SiO}_2$ , calcite  $\text{CaCO}_3$ , anhydrite  $\text{CaSO}_4$ , albite  $\text{NaAlSi}_3\text{O}_8$ , dolomite  $\text{CaMg}(\text{CO}_3)_2$  and microcline  $\text{KAlSi}_3\text{O}_8$ . In 1, 3 and 7 m depths, additionally muscovite  $\text{KNa}(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}_{3.1}\text{Al}_{0.9})\text{O}_{10}(\text{OH})_2$  is observed. By burning at 550°C and 850°C, dolomite decomposes, and the structure of periclase  $\text{MgO}$  is revealed.

The SEM analysis showed that after burning at 550°C the size of crystals significantly decreased. Change of the crystals size after burning at 850°C was not so big.

Using the EDS method, elements such as chlorine Cl, phosphorus P and titanium Ti were identified in the fine fraction of the landfill, in addition to the above-mentioned minerals.

Based on the results of the EDS analysis, the distribution of magnesium, aluminum, iron, titanium and others in the fine fraction was determined in

the landfill layers. It is not uniform and can only be explained by the change in the quantity of these elements in the waste removed in different years.

Compared to recent years (around 2008), there are little differences in the composition of different layers of landfills. As we can see that the quantities of precious metals are not high, the profitability of recovery requires a more detailed economic analysis.

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### **METALŲ KIEKIO TYRIMAS ALYTAUS REGIONINIO KOMUNALINIŲ ATLIEKŲ ŠĄVARTYNO SMULKIOJOJE FRAKCIJOJE**

#### *S a n t r a u k a*

Pateikiami Alytaus regioninio švartyno smulkiosios atliekų frakcijos tyrimo rezultatai. Smulkioji frakcija buvo analizuojama siekiant apibūdinti įvairių cheminių elementų kieki, naudojant skenuojančios elektroninės mikroskopijos metodą, energijos dispersijos spektroskopiją (EDS), SEM ir rentgeno difrakcijos (XRD) analizę. Aptikti šie mineralai: kvarcas  $\text{SiO}_2$ , kalcitas  $\text{CaCO}_3$ , anhidritas  $\text{CaSO}_4$ , albitas  $\text{NaAlSi}_3\text{O}_8$ , dolomitas  $\text{CaMg}(\text{CO}_3)_2$ , mikroklinas  $\text{KAlSi}_3\text{O}_8$ , periklazas ir muskovitas  $\text{KNa}(\text{Al}, \text{Mg}, \text{Fe})_2(\text{Si}_{3,1}, \text{Al}_{0,9})\text{O}_{10}(\text{OH})_2$ . Nustatytas C, O, Na, Mg, Al, Si, K, Ca, Fe, P, S, Cl, Ti cheminių elementų kiekis ir apskaičiuotas jų pokytis po kaitinimo.