Removal of Na$_2$SO$_4$ from a Filter Ash

Odstranjevanje Na$_2$SO$_4$ iz filtrskega prahu

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Abstract

In this paper, research on the possibilities of sodium sulphate (Na$_2$SO$_4$) separation from other substances in the filter ash sample is presented. The research material contains six components that differ in chemical composition and density. The possibilities of Na$_2$SO$_4$ separation using dry and wet methods were studied. The dry method was based on separation with a centrifugal air classifier at four cut size limits. The wet method was based on the dissolution of water-soluble components, filtration of insoluble components, and drying the products. The sulphur content of the individual products was determined using both methods. The aim of the research was to determine which method is more suitable for separation of the material in a way that most of the material would contain as little sulphur as possible and the rest of the material would contain concentrated sulphur. The wet method proved to be more successful. The product with mass fraction 33.1% of the total mass, obtained from the aqueous solution, contained 8.39% sulphur after filtration and drying. The water-insoluble component, with mass fraction 66.9% of the total mass, contained 0.56% sulphur. The dry method with the centrifugal air classifier proved to be less successful in comparison with the wet method. The particles containing Na$_2$SO$_4$ are very similar in size and density to the other components of the material, so the separation to the desired extent was not achieved.

Keywords: sulphur, centrifugal air classifier, filtration, filter ash, waste material.

Povzetek

V članku je predstavljena raziskava možnosti ločenja Na$_2$SO$_4$ od ostalih snovi v vzorcu filtrskega prahu. Preiskovan material vsebuje šest komponent, ki se med seboj razlikujejo po kemijski sestavi in gostoti. Preučevali smo možnost ločenja Na$_2$SO$_4$ s suhim in mokrim postopkom. Suh postopek je temeljil na ločevanju s centrifugalnim zračnim klasifikatorjem pri štirih mejah ločenja. Mokri postopek je temeljil na raztapljanju v vodi topnih komponent, filtraciji netopnih komponent in sušenju produktov. Po obeh izvedenih metodah smo določili vsebnost žvepla v posameznih produktih. Cilj raziskave je bilo ugotavljanje, s katero metodo doseči ločenje materiala tako, da bi večina materiala vsebovala čim manj žvepla, preostanek materiala pa bi vseboval koncentrirano žveplo. Kot bolj uspešna se je pokazala metoda z mokrim postopkom. Produkt z masnim deležem 33.1% od celote, pridobljen iz vodne raztopine, je po filtraciji in sušenju vseboval 8.39% žvepla. V vodi netopna frakcija, katere delež je bil 66.9% od celote, je vsebovala 0.56% žvepla. Suhi postopek z zračnim klasifikatorjem se je izkazal kot manj uspešen. Delci Na$_2$SO$_4$ so namreč po velikosti in gostoti dokaj podobni ostalim komponentam materiala, zato nismo dosegli ločenja v želenem obsegu.

Ključne besede: žveplo, centrifugalni zračni klasifikator, filtracija, filtrski prah, odpadne snovi.

Introduction

The construction industry in Slovenia is currently in expansion. Major repairs, reconstructions and renovations of residential, public and industrial buildings are underway. In connection with the increased number of buildings under construction, the production of construction materials is also increasing. Due to the demolition and reconstruction of buildings, the amount of construction waste is increasing, most of which have the potential of secondary use [1]. In the circular economy concept, waste is considered as raw material and could be reused in the production process. This avoids waste disposal and the associated environmental problems and reduces the need for new raw materials, in which sources are limited. The composition of construction waste has changed over the years. The construction waste whose use has spread in recent decades is increasing. Dry prefabricated materials such as gypsum boards and insulating materials which are the result of the energy efficiency concept and the introduction of new building materials and construction methods are included in this group.

In the European Union, 40.9 million tons of waste materials were generated in the field of construction and demolition in 2016, representing 36.4% of all waste, compared with 10.3% of industrial waste. The construction sector is thus the largest producer of waste in comparison with other economic sectors [2].

The European Commission Waste Directive also addresses waste hierarchy, which makes prevention of the top waste management priority, followed by preparation for reuse, recycling, recovery and landfill [3]. As a result, industrial companies are looking for new approaches to the waste management which are consistent with the environmental, social and economic sustainability [4].

As with most production processes, the production of building materials, whether using exclusively primary raw materials or adding secondary raw materials into the process, waste materials are produced as a by-product. Their quantity and composition depend on the type of technological process.

In the case of thermal treatment of materials, flue gases are mainly produced as by-products, carrying dusty ash particles with them. Mass fraction of heat treatment by-products may be significant in the intense production process. Products are frequently waste materials but can represent the potential for reuse in case of providing technological and environmental requirements. Some of these materials have one or more hazardous properties and may represent an environmental risk. If the material is characterised as hazardous waste, it represents a much higher cost to the waste producer or the payer to properly treat it than if the waste were considered to be a non-hazardous waste. Such materials may be prepared by mechanical and/or other processes to the extent that they are environmental friendly and reusable.

This study presents some methods for minimising sulphur content with mechanical processes in handling thermal treatment products, more specifically when handling filter ash containing a certain content of sulphur. By minimising the sulphur content, it is possible to achieve the removal of hazardous properties from waste which transforms waste from hazardous to non-hazardous type, thereby opening the possibilities of reuse or at least significantly reducing the cost of waste disposal.

Materials and Methods

The filter ash that is a subject of this research is a mixture of:
— Sodium bicarbonate ($NaHCO_3$),
— Sodium sulphate (Na_2SO_4),
— Coke,
— Limestone,
— Basalt (rock wool fibres),
— Ash.

In order to minimise the sulphur content of the filter ash, the aim of the research was to separate Na_2SO_4 from the other components or to concentrate sodium sulphate. One option was to perform the dry process separation using a centrifugal air classifier. Considering the fact that the research deals with the particulate matter, which was extracted from the flue gas by filters, it is logical that the maximum particle size in the sample taken was limited to about 50 μm. If the particles of the Na_2SO_4

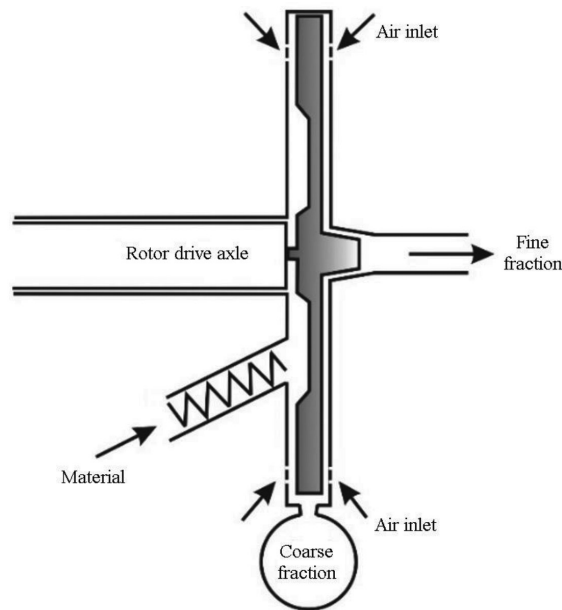**Figure 1.** *Principle of operation of the centrifugal air classifier.*

Table 1. *Density measurements with a pycnometer*

Test no.	Density (kg/m³)
1	2,445.8
2	2,579.5
3	2,539.5

$$F_c = \frac{4}{3} \cdot \pi \cdot r_p^3 \cdot \rho_p \cdot \frac{v^2}{r} \tag{1}$$

$$F_d = c_D \cdot \rho \cdot \pi \cdot r_p^2 \cdot \frac{v_a^2}{a} \tag{2}$$

$$F_g = m \cdot (\rho_p - \rho) \cdot g \tag{3}$$

component were present in a specific granulometric interval, there exists a possibility of separation with the centrifugal air classifier. Alternatively, a wet process could be performed in which the water-soluble Na_2SO_4 is separated from the other components by dissolving, filtration of insoluble components and drying the products.

A centrifugal air classifier is a device for separating particles according to their size and density. During the classification operation, the particles are under the influence of centrifugal force (F_c), drag force (F_d) and gravity (F_g) force. The centrifugal force field is generated by a rotor, which accelerates the particles towards the periphery of the classification zone where a coarse fraction is deposited. The air enters the classification zone tangentially, flows through the middle of the classification zone and removes finer particles on which the drag force of the air resistance is greater than the centrifugal force. The fine particles carried by the air stream are separated from the gas phase in the air cyclone. The material enters the classifier using a uniform dosing mechanism (dosing screw). The device principle is explained in Figure 1.

The definitions of the forces acting on particles are as follows [5]:

where r_p is particle radius, ρ_p is particle density, v is the peripheral velocity of the rotor, r is rotor radius, c_D is drag coefficient, ρ is the air density, m is mass of particle and g is gravitational constant.

The cut size of the classifier is the particle size limit at which the material is separated into a fine and coarse fractions. It depends on the rotor revolutions per minute (RPM), which creates the centrifugal field, and on the air volume flow through the classification zone. The required rotor RPM and the airflow for the selected cut size are determined from the diagram provided by the classifier manufacturer.

For the purpose of determining the operating conditions of the centrifugal air classifier, the sample density was measured using a pycnometer method. Since two components of the material ($NaHCO_3$ and Na_2SO_4) are water-soluble, in order to determine the density, we used isopropanol in which those components are insoluble or slightly soluble. First, we determined the density of isopropanol with a pycnometer (ρ = 784.8 kg/m³). Following this, we performed three measurements of sample density, which are presented in Table 1.

The calculated mean density of the sample was 2,521.6 kg/m³. In the next step, four different cut sizes were selected, namely 10, 20, 30 and 40 µm. For each cut size, the required rotor RPM and airflow quantity in accordance with

Table 2. *Determination of operating conditions for the centrifugal air classifier using the operating diagram of the classifier*

Cut size d_{TV} (mm)	RPM n (min⁻¹)	Airflow Q (m³/h)
10	8,900	46.1
20	5,200	49.8
30	4,100	50.9
40	3,500	51.5

Figure 2. *Sampling with a spoon [after 7].*
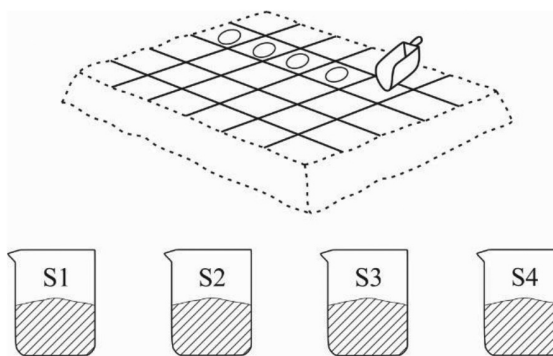
the operating diagram of the device were determined (Table 2).

Na_2SO_4 is soluble in water, so it is possible to remove it from insoluble components by mixing the material in water at the appropriate temperature, and then filtration process is used to remove the insoluble residue, which is followed by the elimination of water-soluble substances, including Na_2SO_4, for which drying or a reverse osmosis process may be used.

Of the components contained in the input material, $NaHCO_3$ is also soluble in water, whose solubility at 35°C is approximately 120 g/L. The solubility of sodium sulphate in the water rises to 32.4°C (497 g/L), and decreases slightly at higher temperatures [6].

Sampling of Material

The material was sampled with a spoon. It was poured on a flat surface; a rectangle 1–2 cm high was formed and 5 × 6 even squares were drawn into it. Next, we took a spoonful of material from each quadrant to get four samples with about 250 g each for classification purposes. Sampling is shown schematically in Figure 2. The sulphur content of the samples was measured with an X-ray fluorescence (XRF) spectrometer and $S = 3.38\%$ for the initial sample.

Results and Discussion

Removal of Sulphur from Filter Dust by a Dry Process with Classification

The classification of the sample was performed four times, for each cut size individually. After each classification, the weight of the material of the coarse and fine fraction was determined by weighing. The data are presented in Tables 3–6.

Classification of sample 1 at the cut size of 10 μm yielded 21.8% fine fraction and 78.2% coarse fraction. This means that by weight 21.8% of the particles are smaller than 10 μm and 78.2% are larger than 10 μm.

When classifying sample 2 at the cut size of 20 μm, we found that about half of the particles were smaller than 20 μm and half were larger than 20 μm.

Classification of sample 3 at the cut size of 30 μm yielded 75.1% fine and 24.9% coarse fraction.

When classifying sample 4 at the cut size of 40 μm, the share of the fine fraction was 78.3% and the share of the coarse fraction was 21.7%. The mean particle size of Na_2SO_4 can be, according to the sulphur content results, estimated to be around 20 μm. The most favourable result with air classification was obtained at a cut size of 10 μm, where the sulphur content in the fine fraction was 0.55%, but the mass share of the fine fraction was only 22.4% at this separation size. In all other cases, the sulphur content was not minimised.

The particles of the Na_2SO_4 component are quite dispersed in size and at the same time they are not significantly different in density from the other components in such a way that they can

Table 3. *Classification at a cut size of 10 µm*

Sample 1 (S1)	Mass (g)	Mass per cent (%)	Sulphur content (%)
	258.4	100.0	3.38
Fine fraction (1F)	56.3	21.8	0.55
Coarse fraction (1C)	202.1	78.2	4.19

Table 4. *Classification at a cut size of 20 µm*

Sample 2 (S2)	Mass (g)	Mass per cent (%)	Sulphur content (%)
	251.7	100.0	3.38
Fine fraction (2F)	128.9	51.2	3.30
Coarse fraction (2C)	122.8	48.8	3.44

Table 5. *Classification at a cut size of 30 µm*

Sample 3 (S3)	Mass (g)	Mass per cent (%)	Sulphur content (%)
	260.2	100.0	3.38
Fine fraction (3F)	195.4	75.1	3.71
Coarse fraction (3C)	64.8	24.9	2.32

Table 6. *Classification at a cut size of 40 µm*

Sample 4 (S4)	Mass (g)	Mass per cent (%)	Sulphur content (%)
	254.0	100.0	3.38
Fine fraction (4F)	198.8	78.3	3.49
Coarse fraction (4C)	55.2	21.7	2.81

be successfully separated from the other components by the air classifier.

Removal of Sulphur from Filter Dust by Wet Process

Approximately 100 g of sample was mixed with 800 mL of water. The suspension was stirred with a magnetic stirrer for 30 min, while it was heated to a temperature of about 35°C. The suspension was then poured into a Sartorius filtration cell equipped with a 0.2 µm aperture filter. The filtration was initially carried out at atmospheric pressure. The remaining fluid from the filtration cell was obtained using compressed air. The residue of the solid phase in the filtration cell (filter cake) was dried in an oven at 105°C until dry. The solution containing Na_2SO_4 was also processed to dryness in the oven. The process is schematically shown in Figure 3. After drying, both masses were determined. The weight of the filter cake of the water-insoluble solid phase was 72.5 g, while the mass in the water-soluble material was 35.9 g. The measured sulphur content of both samples is given in Table 7.

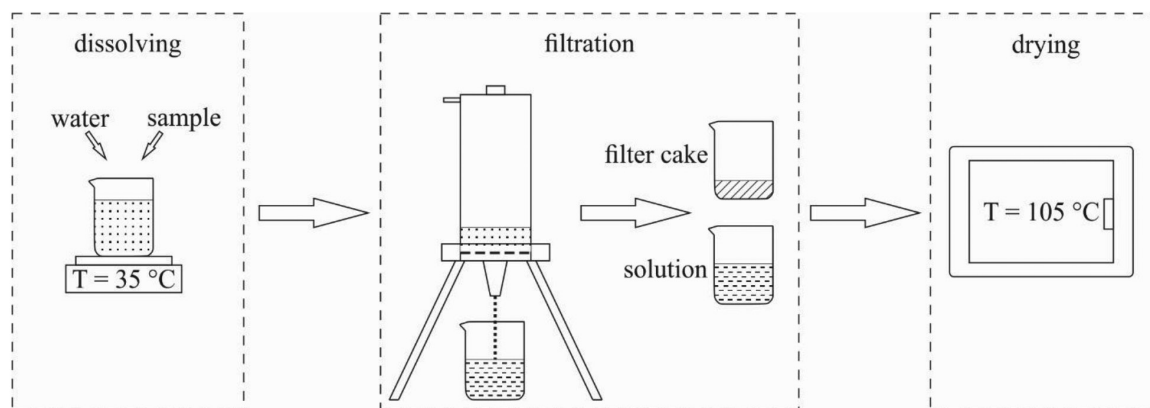Table 7 shows that the sulphur content of the insoluble material is 0.56%.

Figure 3. *Dissolution, filtration and drying of material.*

Table 7. *Results of an attempt to remove sulphur from filter ash by the wet procedure*

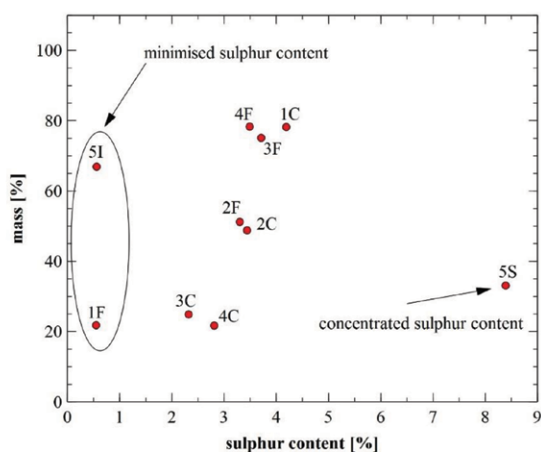| Sample 5 (S5)	Mass (g)	Mass per cent (%)	Sulphur content (%)
	108.4	100.0	3.38
Insoluble material (5I)	72.5	66.9	0.56
Soluble material (5S)	35.9	33.1	8.39

Figure 4. *Sulphur and mass content for different samples.*

In this case, it is the majority of the material (66.9%). Sulphur is concentrated in dissolved material, in which the sulphur content increased to 8.39%.

Figure 4 shows that only the 5I and 1F samples represent the minimisation of sulphur content, with the 5I sample having a much larger mass fraction than the 1F sample, which means that the separation using wet process is more optimal.

Conclusions

This article presents dry and wet methods of minimising the sulphur content in filter dust.

A dry method of sulphur minimisation would be a faster and more cost-effective method of sulphur removal in the industry but attempting to classify it at different cut sizes did not produce adequate results. With respect to the sulphur content, only a classification at the cut size of 10 µm would be appropriate, where the sulphur content in the fine fraction $S = 0.55\%$ was measured, but the share of this fraction was only 21.8%. The mass content of sulphur in the coarse fraction at this cut size was $S = 4.19\%$. In the case of all other cut sizes (20, 30 and 40 µm), the sulphur-containing particles are approximately evenly distributed between the fine and coarse fractions so that the sulphur content in both the fine and coarse fractions does not deviate significantly from the sulphur content of the starting sample.

Better results were obtained from the wet sulphur content minimisation process. In this part of the study, the sample was mixed with a sufficient amount of water, and the suspension was heated to the temperature necessary for

maximum solubility of sodium sulphate in water. The water-soluble material, together with the insoluble residue, was filtered on a 0.2 μm aperture filter and then dried, and the sulphur content in the insoluble and water-soluble material was measured. The insoluble material represented about two-third of the total sample and had a sulphur content of $S = 0.56\%$, while the measured sulphur content in the rest of the material was $S = 8.39\%$.

Considering that a lot of energy is consumed in drying the material, a suitable solution for the industrial removal of Na_2SO_4 would include mixing of water and material while heating at 35°C, separation of the solid and liquid phase by filtration, elimination of Na_2SO_4 from the liquid phase by reverse osmosis and drying of the products.

By using reverse osmosis, drying volumes and energy consumption would be greatly reduced.

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