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EXAMINATION OF THERMAL STABILITY OF WASTE ROCKWOOL AND AMMONIUM NITRATE MIXTURES

BADANIE STABILNOŚCI TERMICZNEJ MIESZANIN ODPADOWEJ WEŁNY MINERALNEJ I AZOTANU AMONU

Abstract: Results of research carried out on a waste rockwool and ammonium nitrate mixtures to examine the possibility of using them in fertilization of plants were presented. Reactions occurring between compounds were analyzed to determine the possibility of an uncontrolled exothermic decomposition of nitrogen fertilizer additive. Results obtained from the analysis of prepared mixtures in various proportions and separate samples of individual compounds were compared. Ammonium nitrate used in the research was supplied by one of the domestic fertilizers producer and waste rockwool was collected after a completed crop cycle of a tomato plant. Each sample was dried and ground before examination. Analysis was carried out using differential thermal analysis coupled with thermogravimetry and mass spectrometry (DTA-TG-MS). Obtained results indicate a possibility of use of rockwool mixed with ammonium nitrate in agriculture. However, it is important to choose optimal proportions of compounds to ensure the thermal stability of the mixture.

Keywords: ammonium nitrate, rockwool, thermal analysis, fertilizers, agriculture, decomposition

Introduction

Rockwool is obtained by melting basalts and dolomites. Rocks are being melted, stretched and rolled. A rockwool consists of amorphous fibers of thin diameter coated with binders and additives [1, 2]. Binders, such as phenol-formaldehyde resin, allow convenient shaping of the product. Impregnating oils and coating agents can be distinguished among other additives. The total organic content in the rockwool is about 2–4 wt %. This material is mainly used as an insulation or a hydroponic base for cultivation in gardening. It has a lot of advantages like a good stabilization of pH, temperature and moisture. In comparison to an organic base, rockwool shows lesser

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vulnerability to expansion of pathogens, which makes spreading of plant diseases less likely to happen [3]. Inert soil substitutes are usually replaced after each cultivation cycle due to deterioration of their physical properties after this time [4, 5]. However, it is sometimes being reused two or three times before wasting, which can influence quality of growing plants [6]. Rockwool is not an easy substance to dispose of. There are many ongoing researches aimed at viable recycling methods, because after a completed crop cycle, waste rockwool contains some amounts of residual nutrients [7]. Possibility of using a mixture of waste rockwool with a suitable amount of fertilizer is considered.

Ammonium nitrate is a chemical of a great practical importance. Among all nitrogen fertilizers, it is produced in the largest amounts [8]. Nitrogen contained in fertilizers is present in two forms – nitrate, which is assimilated immediately, and ammonium, that is retained in the ground and made available to plants after a prolonged period of time. The use of ammonium nitrate improves the quantity and quality of the crop and increases the weight of the above ground plant parts [9]. In order to ensure the optimal efficiency of fertilization, ammonium nitrate should be mixed with the soil. One of its drawbacks is the tendency to explosive decomposition, which is a real threat that must be strictly controlled [10]. Due to its properties, it is commonly used as an explosive material for miners in form of porous granules soaked in fuel oil. Before using any mixtures of ammonium nitrate with other components, for safety reasons, the influence of these additives on the thermal stability of the fertilizer must be examined [11, 12].

Thermal analysis allows to determine the temperature range of physical or chemical changes, which are associated with thermal effects in tested materials. This allows to assess in which temperatures it is safe to store such materials without any risk of occurrence of unwanted processes [13]. Additionally, thermal analysis demonstrates how examined materials change their thermal properties, depending on the mass ratio of the individual components in the test samples [14].

Materials and methods

The present study uses ammonium nitrate of fertilizer grade, supplied by one of the domestic producers of nitrogen fertilizers. The rockwool was collected after a completed one-year crop cycle of tomatoes, air-dried and ground on a sieve of 0.4 mm diameter. An analysis of 100 mg (± 0.5 mg) samples was performed. Samples consisted of 20 mg of ammonium nitrate and 80 mg of rockwool (sample WM80AN20) and in reverse ratios (sample WM20AN80). Prior to measurement, the mixtures were thoroughly triturated in a mortar in order to homogenize their composition.

The measurements were performed using differential thermal analysis and thermogravimetry coupled with mass spectrometry (DTA-TG-MS). Thermal analyzer STA 449 F3 with thermobalance and a mass spectrometer QMS 403 C, Netzsch were used. The samples were tested in crucibles of 0.3 cm^3 capacity made of alumina.

The measurements consisted of several consecutive steps. The first one was heating the empty crucible in order to remove any possible impurities, then a correction conducted to compensate for thermal effects associated with the characteristics of the crucible. Afterwards, the crucible with the sample was heated to selected temperature at a rate of 5 ^{o}C/min in the atmosphere of synthetic air with a total flow of 60 cm^3/min. Before each correction and measurement, a proper evacuation of gas from the furnace chamber was performed and followed by filling it with a synthetic air. This sequence was repeated three times before each measurement.

For comparison purposes, samples of 100 mg (± 0.5 mg) ammonium nitrate and 100 mg (± 0.5 mg) waste rockwool were examined according to the same methodology. Results were analyzed using software supplied by the manufacturer of the measuring equipment.

Results and discussion

The aim of this study was to investigate the possibility of reusing in a fertilization the waste rockwool derived from tomatoes cultivation. Thermal properties of mixtures of ammonium nitrate with waste rockwool were examined. Ammonium nitrate, the compound used in fertilizing to provide plants with necessary nitrogen, may undergo a rapid decomposition in contact with various organic compounds [15]. In order to avoid undesired exothermic reactions, it was necessary to investigate the influence of binders contained in a rockwool on the decomposition of ammonium nitrate.

Fig. 1 shows the result of thermal analysis of waste rockwool sample, while Fig. 2 shows the result of measurement carried out for ammonium nitrate. Both analyzes were

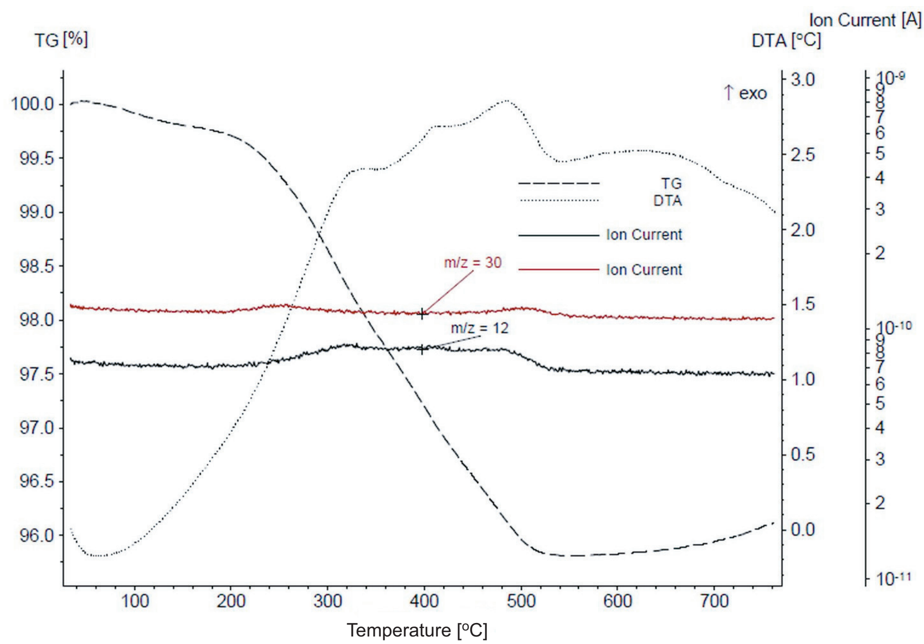

Fig. 1. DTA-TG-MS results for a 100 mg sample of a waste rockwool

performed in order to determine the optimal temperature range for the examination of selected mixtures (WM80AN20 and WM20AN80).

The first step of weight loss of a rockwool sample observed in the range of 50–200 °C is associated with vaporization of water and did not exceed 0.2 % of the total mass. Another weight loss was observed over 230 °C and was accompanied with an exothermic effect caused by an oxidation of organic binder. The observed weight loss due to burnout of the binder is typical for organic compounds content in rockwool which is ca. 4 % of the total mass. MS signal for carbon dioxide (*m/z* = 12) and the DTA signal clearly indicate the combustion of the binder with heat generation, while no changes in signal for nitrogen oxides (*m/z* = 30) show that there are no significant amounts of nitrogen compounds present in examined sample. The decomposition ends at a temperature slightly above 500 °C. The mass gain over 650 °C is related to the oxidation of the silicate groups in the rockwool [16]. Above this temperature there are no relevant reactions occurring [17].

Examined sample of ammonium nitrate showed no significant deviations from thermal properties of this compound reported in the literature [9]. Endothermic phase transitions typical for ammonium nitrate can be observed on the DTA curve shown in Fig. 2. Afterwards, the exothermic decomposition of the test sample occurs in the temperature range from 230 °C to 300 °C. MS signal for carbon dioxide shows that there were no organic impurities in ammonium nitrate, while signal *m/z* = 30 confirms the evolution of significant amounts of nitrogen oxides due to the decomposition of fertilizer.

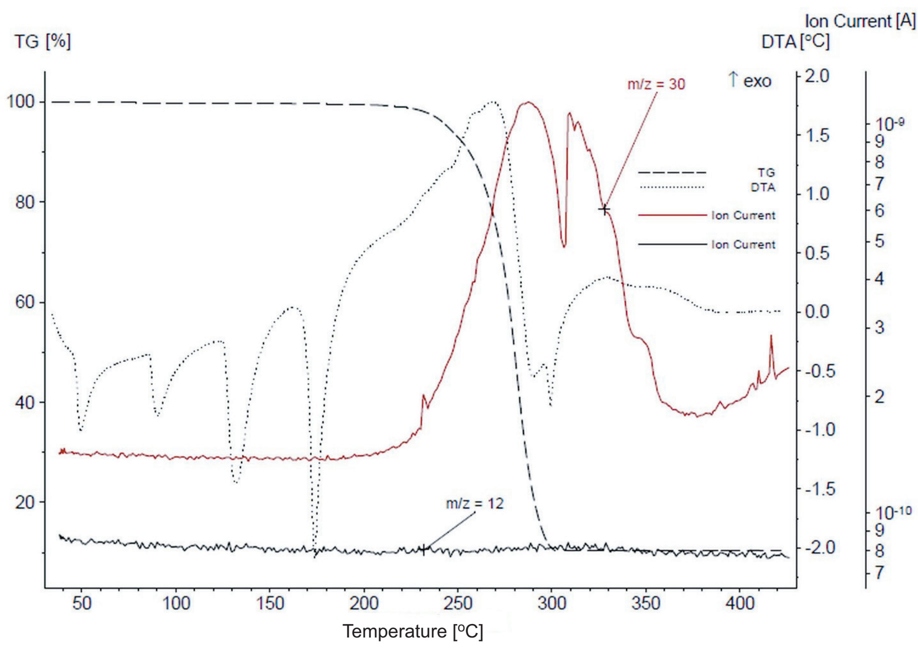

Fig. 2. DTA-TG-MS results for a 100 mg sample of a fertilizer grade ammonium nitrate

Results of thermal analysis of tested mixtures of ammonium nitrate and rockwool in two different proportions are presented in Fig. 3 and Fig. 4. The range of temperature in those measurements was chosen based on previous analyzes. Thermal analysis of tested samples revealed that their exothermic decomposition occurs more rapidly and in lower temperature than decomposition of pure components. Exothermic decomposition began in 205.7 ^{o}C and lasted until around 500 ^{o}C for the WM80AN20 sample. It is possible to distinguish two stages of exothermic decomposition of the studied mixtures. The decomposition of ammonium nitrate with a part of organic binder, that lasted up to about 270 ^{o}C, was the first stage. The second one, occurring over 400 ^{o}C, was accompanied with burning of the residual organic binder contained in a rockwool. Compared to pure components, the examined sample showed reduced thermal stability. It proves that ammonium nitrate interacts with organic compounds from rockwool, which is also evidenced by simultaneous evolution of carbon dioxide and nitrogen oxides.

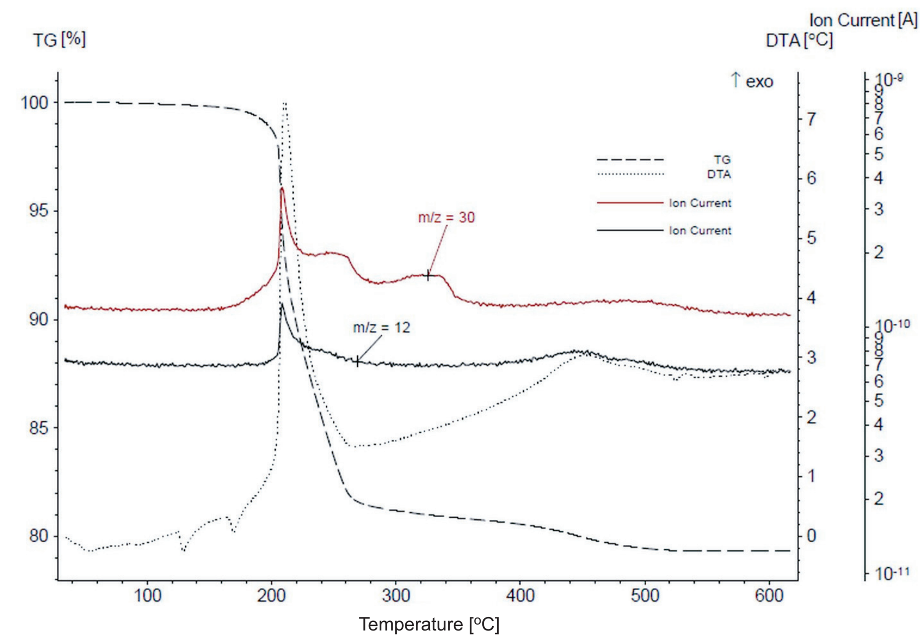

Fig. 3. DTA-TG-MS results for a 100 mg WM80AN20 sample

In sample WM20AN80, the decomposition began in 204.3 ^{o}C and observed reactions occurred in temperature ranges similar to WM80AN20 sample. However, it was possible to notice a dominance of decomposition of ammonium nitrate over processes related to organic binder. The rate of the heat generation in that sample was also lower. This effect may be associated with a smaller amount of an organic binder in the sample, not high enough to cause as strong exothermic reaction with ammonium nitrate as in the case of WM80AN20.

MS signal for carbon (*m/z* = 12), originating from carbon dioxide generated from the decomposition of an organic binder, and signal for nitrogen oxides (*m/z* = 30), from the decomposition of ammonium nitrate, were qualitatively similar and occurred at approximately the same temperature range for both tested mixtures. It can be noted that above 200 °C there are present both nitrogen oxides and carbon dioxide in exothermic reaction products. This is a confirmation of the simultaneous decomposition of ammonium nitrate and an organic binder contained in the rockwool. It may have an adverse influence on thermal stability of mixtures. Intensity of an exothermic reaction depends on proportions of components in examined samples.

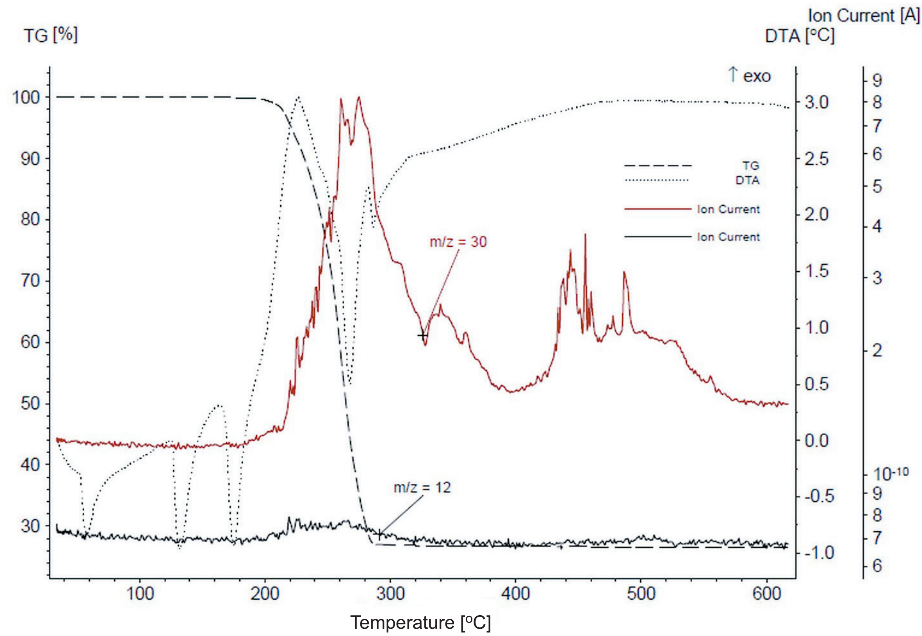

Fig. 4. DTA-TG-MS results for a 100 mg WM20AN80 sample

Table 1 presents temperatures of phase transitions and exotherm maximum in examined samples. Mixtures of ammonium nitrate and rockwool were melting in a slightly lower temperature than pure ammonium nitrate. The maximum rate of their exothermic decomposition was also reached earlier. Exotherm maximum for WM80AN20 sample was at 210.6 °C, which is the lowest temperature among all examined samples.

Table 1

Results of thermal analysis of samples containing ammonium nitrate

Sample	Temperature of phase transitions [°C]				Exotherm maximum [°C]
	IV → III	III → II	II → I	Melting	
Ammonium nitrate	46.8	86.5	126.0	169.8	268.2
WM80AN20	—	—	125.9	166.4	210.6
WM20AN80	53.2	—	126.3	168.3	226.4

Conclusions

Based on performed research, it can be concluded that the interactions between ammonium nitrate and organic binder contained in an inert rockwool result in a higher intensity and lower temperature of the beginning of thermal decomposition of ammonium nitrate. The observed exothermic reactions in studied mixtures occur at a lower temperature than decompositions of individual components, which shows a clear synergetic effect. It is possible that ammonium nitrate, as a strong oxidant, causes burning of an organic binder at temperature above 200 ^{o}C. This fact may reduce the safety during improper usage and storage of this type of mixtures. However, the possibility of safe usage of mixtures with different mass proportions cannot be excluded, which is a basis for a further research. This means that the selection of appropriate proportions of such mixtures cannot be based solely on the needs of plants for nutrients contained in fertilizers. Safety issues associated with destabilizing effects of rockwool's binder on ammonium nitrate should also be taken under consideration.

Acknowledgements

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BADANIE STABILNOŚCI TERMICZNEJ MIESZANIN ODPADOWEJ WEŁNY MINERALNEJ I AZOTANU AMONU

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Abstrakt: Przedstawiono wyniki badań przeprowadzonych dla mieszanin odpadowej wełny mineralnej z azotanem(V) amonu w celu przeanalizowania możliwości zastosowania ich w nawożeniu. Zbadano zachodzące w mieszaninach przemiany fizykochemiczne, co umożliwiło określenie ryzyka zajścia gwałtownego egzotermicznego rozkładu azotowego komponentu mieszanki. Porównane zostały wyniki uzyskane z analiz mieszanin azotanu(V) amonu z odpadową wełną mineralną w różnych proporcjach masowych oraz oddzielnych próbek poszczególnych składników. Stosowany azotan(V) amonu pochodził od krajowego producenta nawozów, natomiast wełna mineralna została uzyskana po jednorocznym cyklu uprawy pomidora. Do przeprowadzenia analizy zachodzących w badanym układzie przemian zastosowano różnicową analizę termiczną sprzężoną z termograwimetrią i spektrometrią mas (DTA-TG-MS). Uzyskane wyniki wskazują na możliwość wykorzystania odpadowej wełny mineralnej w mieszance z azotanem(V) amonu w rolnictwie. Należy jednak odpowiednio dobrać skład mieszaniny, biorąc pod uwagę jej stabilność termiczną.

Słowa kluczowe: azotan amonu, wełna mineralna, analiza termiczna, nawozy, rolnictwo, rozkład