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AGH
AKADEMIA GÓRNICZO-HUTNICZA
IM. STANISŁAWA STASZICA W KRAKOWIE

Wydział Górnictwa i Geoinżynierii

Study:

# "Testing of rock salt samples to confirm that the use of explosive materials for excavating salt rocks in a mine has no effect on the quality of the final product – rock salt for human and animal consumption"

Requesting entity: Kopalnia Soli „Kłodawa" S.A. (Kłodawa Salt Mine)

Researchers:

[redacted]

[redacted]

## 1. Introduction

This study was prepared at the request of Kopalnia Soli "Kłodawa" S.A. (Kłodawa Salt Mine) to confirm that the use of explosive materials for excavation salt rocks in a mine has no effect on the quality of the final product – rock salt for human and animal consumption (salt for food use and feed salt).

In many countries this resource is obtained by blasting [1], which is based on using explosives. The types of explosives used at a salt mine include Ammonite explosives based on ammonium-nitrate ($NH_4NO_3$). The legal system regulates the marketing of explosives for civil use in Poland and EU Member States [2], specifying the conditions that need to be fulfilled.

Mining regulations in Poland allow the presence of oxides in post-detonation reaction products at underground mining facilities. The amounts in question may be as follows: CO = max. 0.135%, $NO_x$ = max. 0.080%. When the use of explosives is permitted in underground mining, the only limiting factor involves the said oxides.

Gas products generated during the detonation of civil-use explosives used in underground pits may contain only such amounts of carbon oxide (CO), nitrogen oxides (NOx), other gases, vapours or solids that do not have an adverse effect on health [3].

An important indicator determining the quality and volume of the combustion products of explosives is oxygen balance [4, 5]. It defines the oxygen content in an explosive in relation to the amount of oxygen theoretically required for the full oxidation of the flammable elements contained in it (carbon to $CO_2$, hydrogen to $H_2O$, etc.). The fundamental assumption made in the design process of explosives used for industrial purposes is a zero oxygen balance.

Ammonites have a positive oxygen balance, which is 1.8% and 2.9% respectively (Ammonite H2E, Ammonite H3E), which can lead to the formation of nitrogen oxides in post-detonation reaction gases.

Blasting conditions have a significant effect on the formation of toxic gases. Ammonite explosions showed [6] a highly diversified oxide content, which depended heavily on the conditions – they ranged from 1.1. to 22.8 $dm^3/kg$ of explosives.

## 2. Study methodology

### 2.1. Specification of samples

The tests were conducted on 5 samples of non-iodised rock salt with the following grain sizes:

- 1N type: grains over 1 mm – 20% max.
  grains below 1 mm – 80% min.
- 0J type: grains over 1.5 mm – 0% max.
  grains over 1.0 mm – 10% max.
  grains below 0.2 mm – 150% min.

Salt from the drill core in undisturbed rocks which could not be affected by excavtion with explosives was used as the standard material.

The samples were taken from the heading, level 750, opening - field 2, distance – 54 m from KS 37.

The analyses were carried out on samples of 0J type – easy to prepare for analysis (due to smaller fragmentation no additional grinding and filtering of solutions for pollution removal were required).

### 2.2. Chemical analyses

The purpose of the chemical analyses of salt samples was to determine the content of identifiable nitrogen ion forms: ammonium $NH_4^+$, nitrate $NO_3^-$ or nitrite $NO_2^-$.

The following instrumental methods were used:

- spectrophotometry at the Laboratory of the Department of Hydrogeology and Engineering Geology, Faculty of Geology, Geophysics and Environmental Protection of the University of Science and Technology in Kraków and
- ion exchange chromatography at the Laboratory of Industrial Gases and Coal Derived Products of the Institute for Chemical Processing of Coal in Zabrze.

Spectrophotometry serves to find the values of the said ions in water and was used to determine the ammonium ion $nH_4^+$ and nitrate ion $NO_3^-$. For the ammonium ion it was carried out using a Slandi LF205 photometer and for the nitrate ion using a HACH DR2800 photometer.

Ion exchange chromatography employed a Dionex ICS 5000 system. Separation column: Ion Pack AS 25. Eluent 25mM KOH. Conductivity detection with suppression. Ion exchange chromatography is currently the most important method of determining ions in water and wastewater. It is a reference method for determining selected inorganic anions and cations in waters, and the International Organization for Standardization (ISO) followed by the Polish Committee for Standardization published a number of standardised methods regarding the determination of ions in water, wastewater and air [11].

## 3. Results and discussion

### 3.1. Spectrophotometry

The tests were conducted on an 0J salt sample, 40 g of which was dissolved in 150 ml of deionised water. The following ion contents were obtained:

$NO_3^-$ 4.0 mg/kg, i.e. 0.0004%

$NH_4^+$ 6.1 mg/kg, i.e. 0.00061%.

The standard material (baseline salt sample) was determined by dissolving 26 g of salt in 100 ml of deionised water. The contents of the respective ions were as follows:

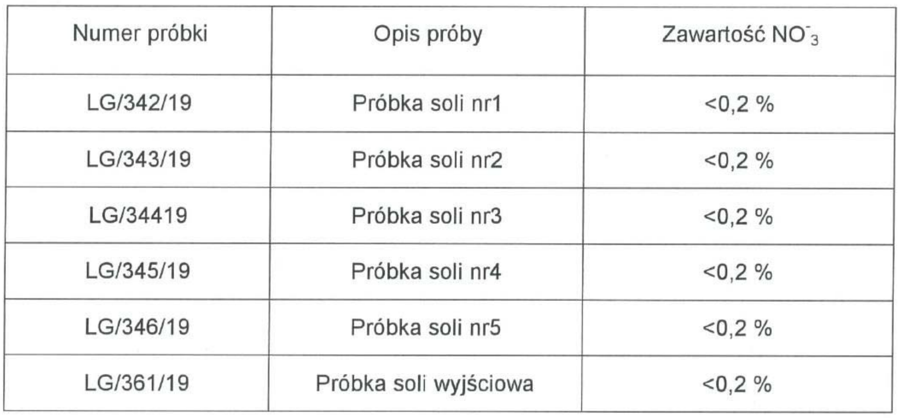
$NO_3^-$ <2 mg/kg, i.e. < 0.0002%

$NH_4^+$ 4.2 mg/kg, i.e. 0.00042%.

### 3.2. Chromatography

The tests were conducted on 6 samples – 5 0J salt samples and the standard material. All samples were prepared for analysis as required in this type of tests. After placing in the column, with a selected eluent, the retention time was recorded, which should be followed by a peak of $NO_3^-$ nitrate ions. Calculating the surface area covered by the ion peak is followed by calculating the quantity of the determined ion.
The final results obtained for individual samples are listed in Table 1.
The expanded uncertainty of measurement is determined for k=2 and confidence level of about 0.95.

Table 1 Analysis results



| Numer próbki | Opis próby | Zawartość $NO^-_3$ |
|---|---|---|
| LG/342/19 | Próbka soli nr1 | <0,2 % |
| LG/343/19 | Próbka soli nr2 | <0,2 % |
| LG/34419 | Próbka soli nr3 | <0,2 % |
| LG/345/19 | Próbka soli nr4 | <0,2 % |
| LG/346/19 | Próbka soli nr5 | <0,2 % |
| LG/361/19 | Próbka soli wyjściowa | <0,2 % |

*[Numer próbki – Sample No.*
*Opis próby – Sample description*
*Zawartość $NO^-_3$ - $NO^-_3$ content*
*Próbka soli nr... – Salt sample No.*
*Próbka soli wyjściowa – Baseline salt sample]*

The analysed samples demonstrated minimum signal for a retention time adequate for a given ion, which is less than 0.2% after conversion. Such results were obtained for every analysed sample.

A sample of the baseline salt also contained less than 0.2% nitrate ions, i.e. the same amount as the remaining samples.

## 4. Summary

The tests carried out on the supplied salt rock samples involved the determination of $NO_3^-$ nitrate ions using highly accurate instrumental methods. Ion chromatography is the most popular instrumental method of determining anions and cations used in most laboratories worldwide [8].

The greatest advantage of this method is the low detection limit, which guarantees the determination of the smallest concentration amount of a given substance.

For the analysed salt, the results confirmed that the standard material contained the same amount of nitrate ions (sampled prior to using explosives) as any of the samples taken after using explosives.

This provides unambiguous evidence that the use of explosives has no effect on the quality of the final product. It should be noted that the explosive used, Ammonite, has a variable content of nitrogen oxides in post-detonation reaction gases (depending on explosion conditions). Despite this, their presence is not detected in the salt rock being excavated.

## 5. Conclusions

1. The use of an ammonium-nitrate explosive, i.e. Ammonite, does not trigger the presence of environmentally harmful post-detonation reaction gases, provided that blasting is performed correctly. The excavated salt rock is free of these gases.
2. The detonation velocity of such explosives is 2,500 m/s (in accordance with the material safety data sheet provided by the manufacturer), so they can be classified as weak. It is nearly half the detonation velocity of Dynamite or emulsion explosives. The seismic events triggered during blasting will not be perceptible on the surface.

## 6. References

[1] Poborska-Młyna określenia najmniejszej ilości lub najmniejszego stężenia substancji orska K.: Współczesne techniki eksploatacji soli kamiennej w kopalniach podziemnych, Przegląd Górniczy Nr 12, 140-146, 2015.

[2] Dyrektywa Rady 93/15/WE (dyrektywa w sprawie materiałów wybuchowych przeznaczonych do użytku cywilnego).

[3] Czajka B., Sałaciński T., Wachowski L., Maranda A.: Materiały wysokoenergetyczne (MW) – Innowacje w aspektach środowiska przyrodniczego, Materiały Wysokoenergetyczne / High Energy Materials, 9, 40-55, 2017.

[4] Fickett W., Davis W.C.: Detonation, Berkeley-Los Angeles-London, University of California Press 1962.

[5] Politzer P., Murray Jane S.: The role of products composition in determining detonation velocity and detonation pressure. Cent. Eur. J. Energ. Mater. 11 (4): 459-474, 2014.

[6] Maranda A., Gołąbek B., Kasperski J.: Wpływ stosowania materiałów wybuchowych na stopień zanieczyszczenia środowiska. WARSZTATY 2003 z cyklu „Zagrożenia naturalne w górnictwie”. Mat. Symp. 427-433, 2003.
[7] Michalski R.: Chromatografia jonowa, jako referencyjna metoda oznaczania nieorganicznych jonów w wodach i ściekach, LAB, 2, 30-35, 2006.
[8] Michalski R.: Chromatografia jonowa. Podstawy i zastosowania. WNT, Warszawa 2005.