Metallurgy and Foundry Engineering – Vol. 42, 2016, No. 4, pp. 203–211
http://dx.doi.org/10.7494/mafe.2016.42.4.203

**Beata Grabowska, Żaneta Kurleto-Kozioł, Łukasz Szymański, Karolina Kaczmarska, Artur Bobrowski**

# Detection of nitrates(V) and sulfates(VI) by UV-Vis spectrophotometry method in used green sand bonded by bentonite with modified starch addition

# Oznaczanie azotanów(V) i siarczanów(VI) metodą spektrofotometrii UV-Vis w zużytej masie formierskiej wiązanej bentonitem z dodatkiem modyfikatu skrobiowego

**Abstract**
The research results (SEM, UV-Vis) that contain a part of the work connected with determining the influence of a modified starch addition on the physical and chemical property changes of green sands (including the emission levels of harmful substances from the used molding sands formed as a result of the liquid metal pouring of molds) are presented in this paper. A surface analysis (SEM) was performed for the fresh molding sands and used molding sands with and without modified starch samples. On the bases of the received microscopic images, the impact of the temperature factor on the morphology of the molding sand samples after the liquid metal pouring process are assessed. In the second part of the performed work on the UV-Vis research, eluates from two used molding sands (green sand [sand number 1] and green sand with the addition of a modified starch [sand number 2]) were tested for nitrate and sulfate content. In order to determine whether the level of nitrate and sulfate elusion from the used molding sands is permissible, the received results were compared with the Minister of Environment's regulations concerning the requirements of surface waters used for supplying the population with potable water.

**Keywords:** used molding sands, green sand, starch additions, elution, spectrophotometry UV-Vis

**Beata Grabowska Ph.D., Żaneta Kurleto-Kozioł M.Sc. Eng., Łukasz Szymański M.Sc. Eng., Karolina Kaczmarska M.Sc. Eng., Artur Bobrowski Ph.D.:** AGH University of Science and Technology, Faculty of Foundry Engineering, Krakow, Poland; beata.grabowska@agh.edu.pl

**Streszczenie**
W artykule przedstawiono wyniki badań (SEM, UV-Vis), wchodzących w zakres prac związanych z określeniem wpływu dodatku modyfikatu skrobiowego na zmianę właściwości fizycznych i chemicznych mas wiązanych bentonitem, w tym na poziom wydzielania substancji szkodliwych ze zużytych mas powstałych w procesie zalewania formy ciekłym metalem. Analizę powierzchniową (SEM) przeprowadzono dla próbek klasycznych mas świeżych i zużytych bez dodatku i z dodatkiem modyfikatu skrobiowego. Na podstawie otrzymanych zdjęć mikroskopowych oceniono wpływ czynnika temperatury na morfologię próbek masy po procesie zalewania formy ciekłym metalem. W drugiej części wykonanych prac badaniom UV-Vis na zawartość azotanów(V) i siarczanów(VI) poddano eluaty przygotowane z udziałem dwóch mas zużytych, tj.: klasycznej masy formierskiej (masa I) oraz klasycznej masy formierskiej z dodatkiem modyfikatu skrobiowego (masa II). W celu określenia poziomu wymywalności azotanów(V) i siarczanów(VI) ze zużytych mas otrzymane wyniki porównano z obowiązującym Rozporządzeniem Ministra Środowiska z dnia 27 listopada 2002 r. w sprawie wymagań, jakim powinny odpowiadać wody powierzchniowe wykorzystywane do zaopatrzenia ludności w wodę przeznaczoną do spożycia.

**Słowa kluczowe:** zużyte masy, klasyczna masa formierska, dodatki skrobiowe, wymywalność, spektrofotometria UV-Vis

## 1. Introduction

The research carried out for molding and core sands along with their binders was aimed at developing new binding materials or modifications of well-known ones for limiting their addition, improving the technological properties of molding sands, and reducing their harmfulness to the environment [1–3]. This topic is of high importance, as molding materials pose an essential factor of a foundry's harmfulness to the environment [2]. In the Laboratory of Environmental Protection of the Foundry Engineering Department at AGH, works concerning this scope have been carried out. They concern not only the implementation of new polymeric materials as components of molding and core sands but also their physicochemical and ecological properties [4, 5]. The problem of developing technological processes suitable for used molding sands (treated as waste) is also considered.

Knowledge of waste ingredients and their physicochemical properties help us decide on the method of waste utilization. The best way is to recycle the waste. Further uses of used molding sands in mold technology (bentonite refresh process) or in another industrial branch is valuable while considering the economics [6, 7]. However, not all waste materials can be used in this same way; often, the preparation process for further use is uneconomical. Therefore, the waste (including used molding sands remaining after the liquid metal pouring process) are often sent to rubbish dumps. However, stored wastes have different levels of toxicity; over a long time perspective, this could have a negative impact on the local environment (mainly regarding ground waters). Therefore, the analytical characteristics of wastes sent directly to rubbish dumps were determined, paying special attention to the elution of harmful substances such as nitrates, sulfates, chlorides, cyanides, and heavy metals (among other things) [8, 9].

It should be noticed that the technological harmfulness of molding or core sands is not only related to the types and amounts of substances emitted into the air during the molding sand or liquid metal pouring processes; it also depends on the content of harmful substances in the used sands (after mold accomplishments). The amounts of harmful substances in the used sands or output wasted sands that could be washed into the environment make us consider the possibility of reusing these sands. They could also be used to evaluate the conditions for the safe storage of used molding sands. Therefore, estimating the harmfulness of core or molding sands to the environment should include not only the emission of harmful substances into the atmosphere but also the elution of these substances into the environment [10, 11].

The selected results of investigations on the physicochemical properties of used molding sands and their harmfulness gradations are shown in this paper. Spectrophotometric descriptions of the nitrates and sulfates found in the received eluate during elution tests of used green sands with and without the addition of modified starch were performed. Additionally, the pH values and electrolytic conductivity of these two types of used sands were measured. The received results were compared with the maximum acceptable concentrations specified in the effective legal regulations concerning the requirements that surface waters used to supply the population with potable water should fulfill.

## 2. Materials

### 2.1. Materials used for preparation of molding sands

The materials used in this study are as follows:

- silica sand (BK D 0.16–0.32 MM, Sibelco Europe),
- activated bentonite (Bentonite Specjal, ZGM "Zębiec"),
- modified starch in the form of Polvitex® Z by Xenon Industry; this is a polymeric material based on etherified starch with the presence of sodium; this modification is characterized by fast and easy swelling as well as good solubility; the main physicochemical properties of this modified starch are as follows: pH level of 5% solution: 9.5–12.5; residue on sieve of 2 mm side square mesh: 0.5%; humidity: 3–8% [12],
- distilled water by POCH.

### 2.2. Reagents included in spectrophotometry UV-Vis test

Reagents used in spectrophotometry UV-Vis test are:

- distillated water POCH,
- Sulfa Ver 4 agent – sulfate reagent pk/100 for 10 ml sample, by HACH, toxic,
- Nitra Ver 5 agent – nitrate reagent pk/100 for 10 ml sample, by HACH, toxic and hazardous to the environment.

# 3. Methodology

## 3.1. Preparation of molding sand mixtures

Two molding sands were prepared in a laboratory roller mixer (LM-1 type).

All dry ingredients were mixed for three minutes with the addition of water in the mixer. After this, the molding sands were sieved and protected against drying in an Aulich container.

The relative air humidity in the laboratory during measurements was within a range of 35–48%, and the temperature was 23–25°C.

## 3.2. Pouring process

Molds imitating type Y ingots (12.7 mm) (prepared in accordance with ASTM a395) are prepared from molding sands.

The mold poured with liquid iron had the following composition: 2.84% C, 1.52% Si, 0.149% Mn, 0.039% P, 0.0169% S, 0.0360% Cr, 0.0414% Ni, 0.0092% V, <0.0003% Al, 0.124% Cu, 0.009% Ti, 0.00709% Sn, <0.00140% Nb. The pouring temperature was about 1420°C.

## 3.3. Equipment

Equipment used to carry out test:

- vortex mixer type 358 S,
- laboratory centrifuge DANLAB MPW-350,
- laboratory vacuum filtering kit with vacuum pump, 4EKF56CX-4 type, ABM industry,
- microcomputer CP-251, pH-meter with automatic temperature compensation system Elmetron industry, equipped with combined pH electrode OSH 10-00 type,
- microcomputer CC-315, electrical conductivity meter with automatic and manual temperature compensation Elmetron industry, equipped with glass electrode Euro Sensor EPS-2-ZE,
- VIS ODYSSEY DR/2500 spectrophotometer with automated wave length calibration (Hach industry). Range of wave length: 365–880 nm; resolution: 1 nm.

## 3.4. Elution process

Research of the elution was prepared in agreement with the existing procedure [13].

At the beginning, used molding sand (around 1 kg) was sifted by a woven sieve with square mesh number 10. Then, 100 g of the sample was weighted out, put in a flask, and overflowed by 1 liter of distillated water so as to keep a 1:10 ratio. Later, the flask with the solution was mixed in a vortex mixer for six hours. After this time, the device was switched off, and the flask with the sample was set aside for 18 hours. After this time, the received eluate was overflowed to four plastic containers and was set for five minutes in a laboratory centrifuge at 2500 rpm.

### 3.5. Microscopic studies

The microscopic examinations were conducted using a NOVA Nano SEM 200 ultra-high resolution scanning electron microscope (by the FEI EUROPE COMPANY) cooperating with the EDAX EDS company's analyzer.

### 3.6. Spectrophotometry UV-Vis tests

To make the spectrophotometric descriptions, the VIS ODYSSEY DR/2500 spectrophotometer with automated wave-length calibration of the Hach industry was used. Range of wave length: 365–880 nm; resolution: 1 nm.

**Nitrate detection**

A round measuring tray was filled by the tested sample (10 ml). Then, the packed Nitra Ver 5 reagent was added to the tray. After closing the measuring tray, the content was mixed for one minute. After one minute of mixing, five minutes of reaction time were allowed; at this moment, the measuring tray was put aside. A spectrophotometric measurement was carried out for the tested sample as Sample 0.

**Sulfate detection**

A round measuring tray was filled by the tested sample (10 ml). Then, the packed Sulfa Ver 4 reagent was added to the tray, and the mixture was mixed by a rotating motion. After mixing and closing the measuring tray, five minutes of reaction time occurred. A spectrophotometric measurement was carried out for the tested sample as Sample 0.

## 4. Results and discussion

The molds were made from green sands with and without the addition of the starch material; then, the pouring process by liquid metal was performed (Fig. 1).

a) b)

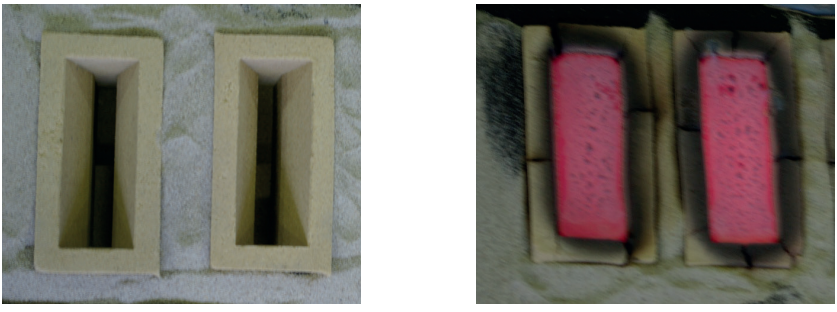

*Fig. 1. Mold: a) before liquid metal pouring; b) after liquid metal pouring*

The morphologies of the green sands without the addition of starch are shown in Figure 2. In the results of the pouring by liquid metal, a violation of the binding bridges in the binding materials (metallic matrix) takes place (Fig. 2b). Permanent changes in the bentonite structure occur, which are revealing by the loss of its adsorptive and binding properties.

a) b)

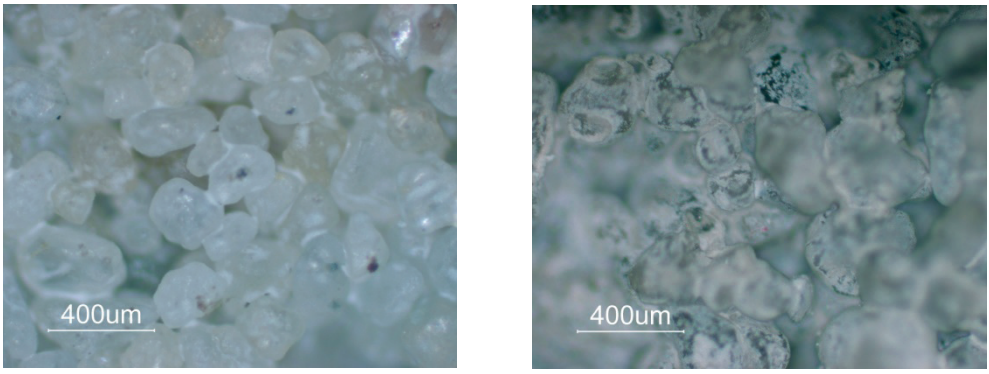


*Fig. 2. Morphology of green sand surface I: a) before liquid metal pouring; b) after liquid metal pouring*

The morphology of the green sand with the addition of modified starch is shown in Figure 3. After the liquid metal pouring of the mold, the molding sand behaves like the green sand without any additions. Due to the high temperature, the Bentonite loses its binding properties. Additional organic additions in the form of modified starch are thermally fully degraded. On the surface of the grain metallic matrix, some carbonized places appear (Figure 3b – in darkest places – shows this effect).

a) b)

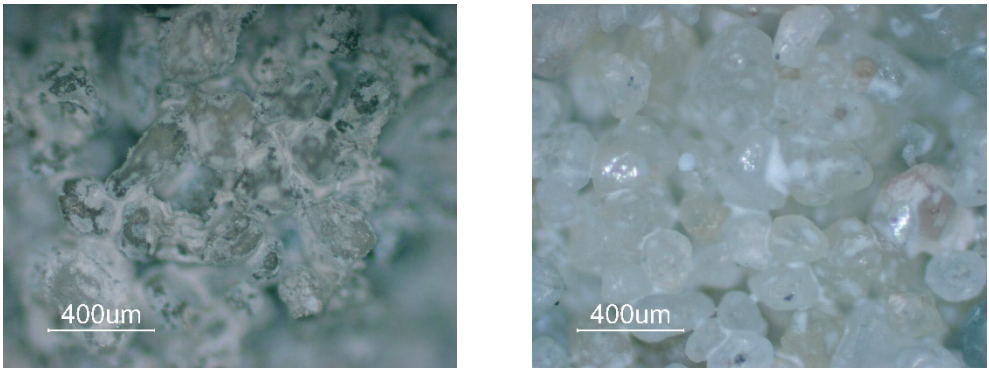


*Fig. 3. Morphology of green sand surface II: a) before liquid metal pouring; b) after liquid metal pouring*

In the second part of this research, the used molding sands were tested for elution. In the received samples, nitrates and sulfates were detected. Additional pH and electrical conductivity measurements were performed by the conductometry method (Tab. 1). For comparisons, the concentration values (acceptable by existing legal regulations concerning surface water) are given in Table 1 as well as in Figures 4 and 5 [14].

*Table 1. Comparison of results of electrical conductivity and pH*

| Name of sample | Color | Electrical conductivity [mS] | pH |
|---|---|---|---|
| Green sand | brown | 0.296 | 9.65 |
| Green sand with Polvitex Z | brown | 0.577 | 10.19 |
| Data from regulations [14] | – | 1 | 6.5–8.5 |

The received results of the electrical conductivity of both molding sands described in this paper remain within the permitted range. However, the modified starch addition caused an electrical conductivity that was two times greater as compared to the molding sand without such an addition. This is the result of the fact that the modified starch contains polar groups.

The received results of the pH values indicate the high alkalinity of the used molding sands. This is the result of the presence of sodium atoms, both in the bentonite and the modified starch.

Figure 4 shows a comparison between the results being within the range of the nitrate concentration detection. Both molding sands show low levels of nitrate elutions. These results are very similar, as the concentration of nitrates in the green sand is 4.2 mg/l, while it is 4.75 mg/l in the green sand with the addition of Polvitex Z (acceptable limit = 50 mg/l).

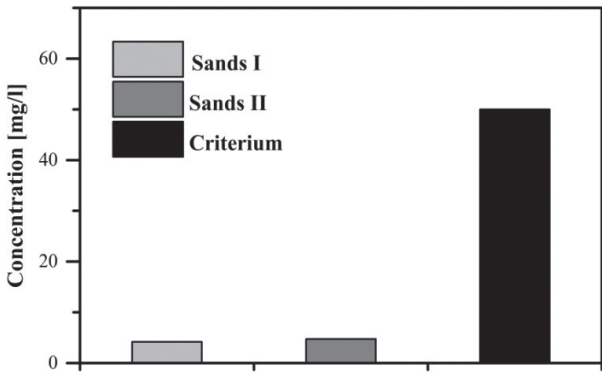


*Fig. 4. Comparison of nitrate(V) concentration results*

The results of the elution tests in the range of the sulfate concentration detection are placed in Figure 5. The values shown in the chart indicate the low elution of sulfates for both molding sands used. In the case of the green sand without the modified starch addition, the nitrate concentration value is equal to 30 mg/l, while the sand with modified starch shows a little lower value equal to 27 mg/l (acceptable limit = 250 mg/l).

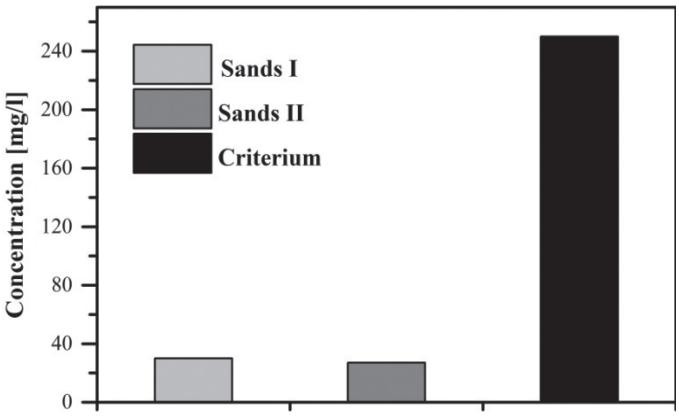


*Fig. 5. Comparison of sulfate(VI) concentration results*

## 5. Conclusion

On the basis of the performed research, we can assume the following conclusions:

- As a consequence of high temperatures, places of degradation can be observed on the microscopic images of the used molding sands with the addition of modified starch.
- The addition of modified starch to the green sand causes a two-times-greater electrical conductivity. This is the result of the polar groups present in the modified starch.
- The used green sands without modified starch are characterized by alkaline reactions.
- The detection levels of harmful substances never exceeded the highest permissible concentrations described in the ruling legal regulations.

### Acknowledgements

The work was supported by project AGH no. 11.11.170.318/13.

## References


[1] Grabowska B., Holtzer M., Dańko R., Bilska M.: Masa ze spoiwem akrylowym – ocena pod względem ekologicznym i zdolności do regeneracji. Przegląd Odlewnictwa, 10–11 (2006), 578–583

[2] Izdebska-Szanda I., Żmudzińska M., Faber J., Perszewska K.: Ocena ekologiczna mas formierskich z nowymi spoiwami nieorganicznymi. Archives of Foundry Engineering, 14 (2014), 33–38

[3] Rosik-Dulewska C., Karwaczyńska U., Ciesielczuk T., Głowala K.: Możliwości nieprzemysłowego wykorzystania odpadów z uwzględnieniem zasad obowiązujących w ochronie środowiska. Środkowo-Pomorskie Towarzystwo Naukowe Ochrony Środowiska, (2009), 863–874

[4] Mizerna K., Król A.: Wpływ wybranych czynników na wymywalność metali ciężkich z odpadu hutniczego. Inżynieria Ekologiczna, 43 (2015), 1–6

[5] Grabowska B., Holtzer M., Dańko R., Górny M., Bobrowski A., Olejnik E.: New BioCo binders containing biopolymers for foundry industry. Metalurgija, 52 (2013), 47–50

[6] Holtzer M., Dańko R., Kmita A.: Influence of a Reclaimed Sand Addition to Moulding Sand with Furan Resin on Its Impact on the Environment. Water, Air & Soil Pollution, 227, (2016), article 16

[7] Faber J., Żmudzińska M., Perszewska K.: Oczyszczanie wybranych odpadów odlewniczych metodą biodegradacji (badania wstępne). Prace Instytutu Odlewnictwa, 53 (2013), 27–34

[8] Smolińska B., Król K.: Wymywalność niklu z prób glebowych aglomeracji łódzkiej. Ochrona Środowiska i Zasobów Naturalnych, 49 (2011), 228–239

[9] Holtzer M., Żymankowska-Kumon S., Dańko R., Kmita A.: Elution of Mixed Moulding Sands with the GEOPOL Binder and Core Sands with the Phenolic Resin. Archives of Foundry Engineering, 13 (2013), 53–56

[10] Drożyński D., Kurleto Ż., Kaczmarska K., Grabowska B.: Analysis of selected technological properties of green sands with starch-based additives. Metallurgy and Foundry Engineering, 41 (2015), 65–70

[11] Kaczmarska K., Grabowska B., Drożyński D.: Analysis of selected properties of green sands with modified starch-based additives. Archives od Foundry Engineering, 15 (2015), 127–131

[12] http://xenon.com.pl/pl/polvitex_z.php [12.02.2016]

[13] PN-EN 12457-4:2006 Charakteryzowanie odpadów. Wymywanie. Badanie zgodności w odniesieniu do wymywania ziarnistych materiałów odpadowych i osadów. Część 1: Jednostopniowe badanie porcjowe przy stosunku cieczy do fazy stałej 10 l/kg w przypadku materiałów o wielkości cząstek poniżej 10 mm (bez redukcji lub z redukcją wielkości)

[14] Rozporządzenie Ministra Środowiska z dnia 27 listopada 2002 r. w sprawie wymagań, jakim powinny odpowiadać wody powierzchniowe wykorzystywane do zaopatrzenia ludności w wodę przeznaczoną do spożycia. Dz.U. 2002 nr 204 poz. 1728