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THE ELUTION OF HEAVY METALS (Cd, Cu, Pb AND Zn) FROM USED MOULDING SANDS VS CONDITIONS OF THE ELUTION PROCESS

WYMYWALNOŚĆ METALI CIĘŻKICH (Cd, Cu, Pb I Zn) ZE ZUŻYTYCH MAS FORMIERSKICH W ZALEŻNOŚCI OD WARUNKÓW PROCESU WYMYWANIA

The paper presents the results of studies on the elution process of some selected heavy metals (Cd, Cu, Pb and Zn) from the used moulding sands in respect of the sand type (its composition and chemical reaction) as well as the chemical reaction and duration of the effect of an eluant. The studies were carried out on two different types of the sand, i.e. urea-furfuryl resin sand used for casting of CuZn36AlPb brass and sodium silicate sand used for casting of B555 bronze. Water eluats of these sands were prepared following the specifications valid in this respect in Poland. Additionally, eluats obtained with various times of contact between the sand and eluant (2, 6, 24, 72 and 168 hours) and using eluants characterised by various pH values (distilled water, solutions of pH = 4 and pH = 3) were analysed. The concentrations of the examined metals were determined by the method of potentiometric stripping analysis (PSA). The results of the studies have proved that elution of metals from the used sands depends to a great extent on the acidity of the process environment, i.e. on the chemical reaction proceeding between the sand and eluant. In systems characterised by low pH values (the sand of low basicity and an eluant of acid reaction), the rate of metal elution was much higher and followed by increasing concentration of the eluted metals with prolonged time of contact between the sand and eluant. In the case of sands characterised by a strongly basic reaction, under the examined conditions the effect of time on the volume of the eluted metals was rather insignificant. Irrespective of the conditions under which the process of elution was run, in the group of the metals examined the least resistant to elution has proved to be Zn, the most resistant Cu. In all the produced eluats the concentration of at least one of the examined metals exceeded the admissible value determined by the Polish Standard for water of purity class I. This means that the used moulding sands when disposed to dumping grounds can be a threat to the environment. One fact should be particularly emphasized here, namely that even when the disposed waste materials give water eluats with the content of metals permitted by standards, later this content may increase due to the power of these metals to cumulate in water and soil and contaminate them both.

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W artykule przedstawiono rezultaty badań procesu wymywania wybranych metali ciężkich (Cd, Cu, Pb, Zn) ze zużytych mas formierskich w zależności od rodzaju masy (jej składu i charakteru chemicznego) oraz od charakteru chemicznego i czasu działania cieczy ługującej. Do badań wykorzystano dwie różne masy: masę z żywicą mocznikowo-furfurylową, pochodzącą z produkcji odlewów z mosiądzu CuZn36AlPb oraz masę z sodowym szkłem wodnym z produkcji odlewów z brązu B555. Wyciągi wodne z tych mas przygotowano zgodnie z obowiązującym w Polsce zaleceniem. Dodatkowo analizowano również eluaty otrzymane przy różnych czasach kontaktu masy z czynnikiem wymywającym (2, 6, 24, 72 i 168 godzin) i przy zastosowaniu do wymywania eluentów o różnym pH (woda destylowana, roztwór o pH = 4 i o pH = 3). Stężenia analizowanych metali oznaczano metodą chronopotencjometrii z zatężaniem elektrolitycznym. Wyniki przeprowadzonych badań wskazują, że wymywanie się metali ze zużytych mas w znacznym stopniu zależy od kwasowości środowiska w jakim przebiega proces, czyli od charakteru chemicznego masy i cieczy ługującej. W układzie o małej wartości pH (masa o niskiej zasadowości oraz eluent o charakterze kwasowym) stopnie wymycia metali były znacznie wyższe i występował wyraźny wzrost stężenia wyługowanych metali wraz z wydłużeniem czasu kontaktu masy z eluentem. W przypadku mas o charakterze silnie zasadowym, w badanych warunkach, wpływ czasu na ilość wmywanych metali był niewielki. Niezależnie do warunków prowadzenia procesu ługowania najłatwiej, spośród badanych metali, wymywał się Zn, a najtrudniej Cu. We wszystkich uzyskanych eluatach stężenie co najmniej jednego z analizowanych metali przekraczało dopuszczalną wartość, określoną w polskiej normie dla wód I klasy czystości. Oznacza to, że podczas składowania zużyte masy formierskie mogą stanowić zagrożenie dla środowiska. Należy podkreślić, że nawet przy składowaniu odpadów, których wyciągi wodne spełniają ustalone normy w zakresie zawartości metali, może następować wzbogacanie wód i gleby w te pierwiastki, ze względu na ich zdolność do kumulacji.

1. Introduction

Industrial waste consists of materials characterised by various compositions and properties. Full determination of an effect of the waste on environment is therefore a task very complicated and requires not only a thorough knowledge of the chemical composition of the waste but also and mainly the capability of determining the amount and type of toxic matters which may get liberated from the waste under the conditions of its dumping or industrial application [1—2]. This is also true in the case of the used moulding and core sands, which are foundry waste materials. The used sand often contains toxic matters (among others, phenol, formaldehyde, cyanides and phosphates) originating from binders and hardeners. When the mould is being poured with liquid metal, some of the alloy constituents, heavy metals included, may be transferred from alloy to the sand, and from the used sand they will be next eluted and penetrate into water and soil. So, on one hand, the used moulding sand can be a valuable raw material used by the sectors of industry other than foundry while, on the other, when managed and dumped improperly it may contaminate the environment. Studying the elution process of some toxic compounds from foundary sands (heavy metals included), we can determine the factors which affect the rate and time of the elution process, and which next serve as a basis in determination of the safe conditions of the sand re-use or dumping [3—5].

2. Test materials

Tests were carried out on two types of foundry sands:

- sand designated as M1 based on silica sand with urea-furfuryl resin, used for production of castings in CuZn36AlPb brass. The alloy contained 62.3% Cu, 36.12% Zn, 0.818% Pb, 0.612% Al [6],
- sand designated as M2 with sodium silicate hardened by CO_2, used for production of castings in bronze. The alloy contained 87.07% Cu, 4.78% Pb, 4.76% Sn, 3.03% Zn [7].

The results of an analysis of the content of some selected heavy metals (Cd, Cu, Pb, and Zn) in the examined used sands are given in Table.

TABLE

The content of some selected metals in the used sands M1 and M2

Metal	Sand M1 [mg/kg]	Sand M2 [mg/kg]
Cd	0.57	4.85
Cu	225.66	6.7
Pb	30.32	2.9
Zn	252.10	13.7

3. Methods of investigation

From the used sands eluats were prepared following the specifications valid in this respect in Poland [8]. The obtained eluats were next examined for the presence of some selected heavy metals. To determine a relationship between the rate of metal elution from the used sand and time, the measurements were also made on solutions obtained after various times of contact between the eluant and the sand sample (2, 5, 24, 72, 168 hours). In every case, the dry sand-to-eluant weight ratio was 1 : 10. To determine an effect of the acidity of a medium on the elution process of heavy metals from the waste sands, eluats of the examined sand were prepared with eluants of various pH values. Besides distilled water, eluants of pH = 3 and pH = 4 were used [3]. In all the filtrates obtained, the content of Cd, Cu, Pb and Zn was determined by means of potentiometric stripping analysis [3, 9].

4. Results and their discussion

4.1. Effect of the eluant pH and time on metals concentration in eluats

Metal concentration in eluats of the sand M1 indicates that the amounts of Cd, Cu, Pb and Zn transferred from the examined waste sand depend on the pH value of the eluant and increase very obviously when the pH value decreases (Figs. 1—4).

(Symbol "n" — refers to water extracts prepared in accordance with national standards). The concentration levels of the examined metals in eluats obtained with the use of an eluant of pH = 3 are much higher than those obtained with eluants of higher pH values, and usually exceed many times the admissible limit values established by the Polish Standard for waters of purity class I (Cd — 0.005 mg/dm^3, Cu — 0.05 mg/dm^3, Pb — 0.05 mg/dm^3, Zn — 0.2 mg/dm^3). Specially with longer times of contact between the sand M1 and eluant, the content of metals in filtrates has been high, which clearly indicates a relationship existing between the amount of the eluted impurities and duration of the eluant effect.

The results obtained for the sand M2 do not indicate a pronounced correlation between the amount of metals eluted from the sand and the type of the eluant used. Irrespective of the contact duration between the examined waste sand and eluant and

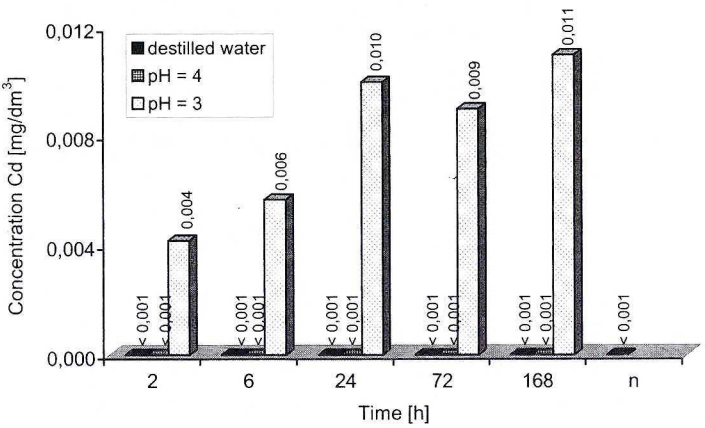

Fig. 1. A relationship between Cd concentration in eluats from the sand M1 and pH value of eluant

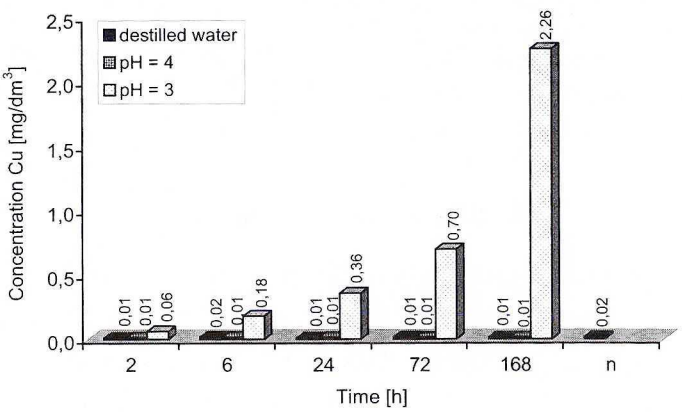

Fig. 2. A relationship between Cu concentration in eluats from the sand M1 and pH value of eluant

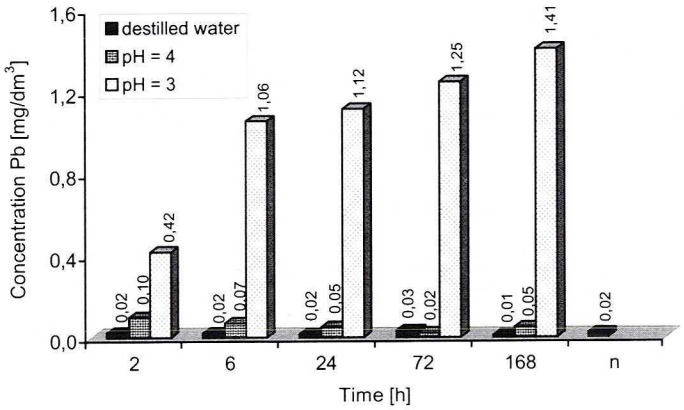

Fig. 3. A relationship between Pd concentration in eluats from the sand M1 and pH value of eluant

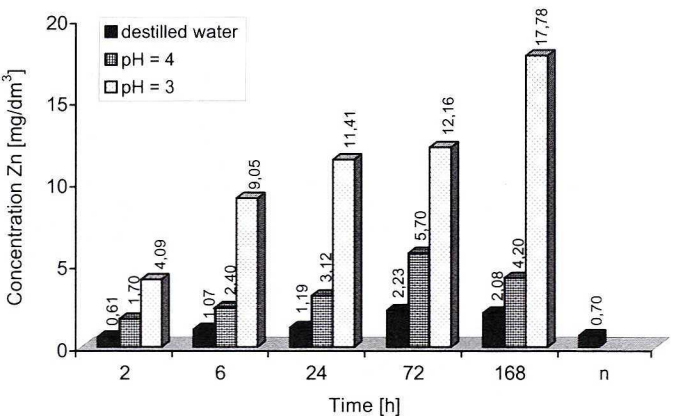

Fig. 4. A relationship between Zn concentration in eluats from the sand M1 and pH value of eluant

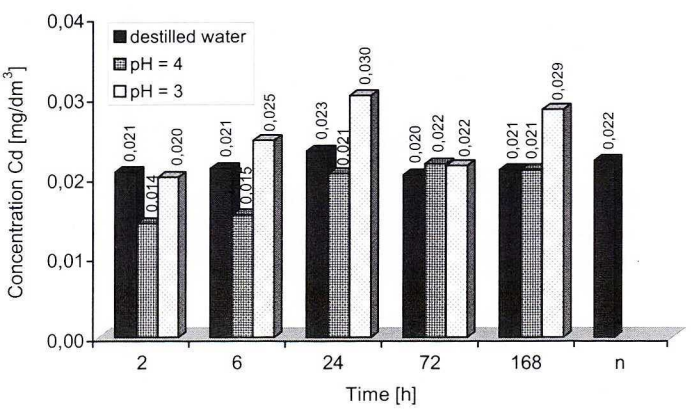

Fig. 5. A relationship between Cd concentration in eluats from the sand M2 and pH value of eluant

the chemical reaction of the eluant, the metal concentration levels determined in filtrates have been similar (Fig. 5). In all eluats obtained from this sand the admissible concentration of Cd was exceeded, the content of other examined metals remained well below the admissible values established by the Polish Standard for waters of purity class I.

4.2. Comparison of the elution rate of individual metals from the examined sands

In all the examined sands and under all the examined conditions, the highest rate of elution among the examined metals proved to have zinc, the lowest — copper (Figs. 6—11) [1]. In eluats from the sand M1, obtained with an eluant in the form of

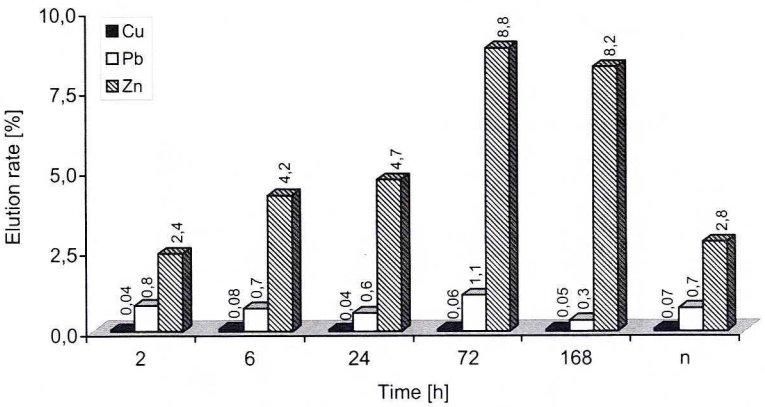

Fig. 6. A comparison of the Cu, Pb and Zn elution rates from sand M1 using distilled water

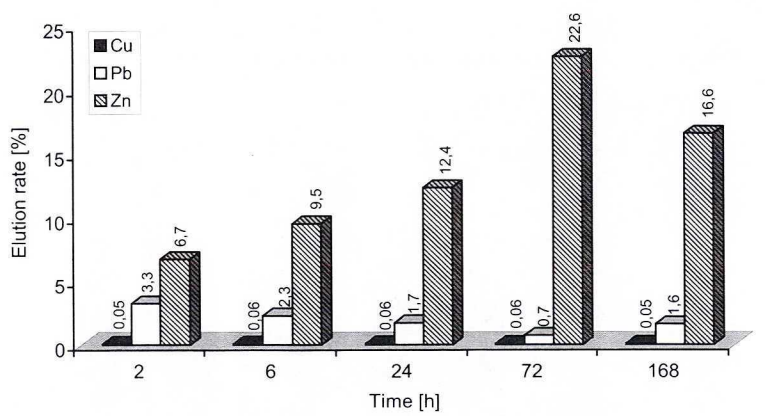

Fig. 7. A comparison of the Cu, Pb and Zn elution rates from sand M1 using eluant of pH = 4

[1] Elution of each metal was estimated on the ground of elution rate $R_{Me} = [c_{Me}/c_{max\,Me}] \cdot 100\%$, where c_{Me} — concentration of metal in eluate, $c_{max\,Me}$ — metal concentration calculated on the base of assumption about complete elution of metal from waste.

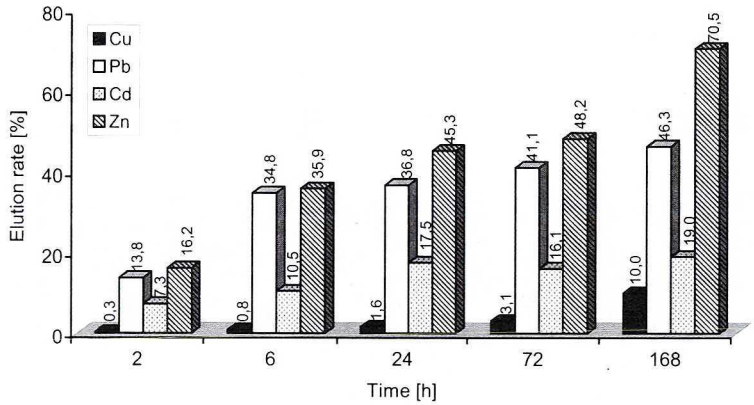

Fig. 8. A comparison of the Cd, Cu, Pb and Zn elution rates from sand M1 using eluant of pH = 3

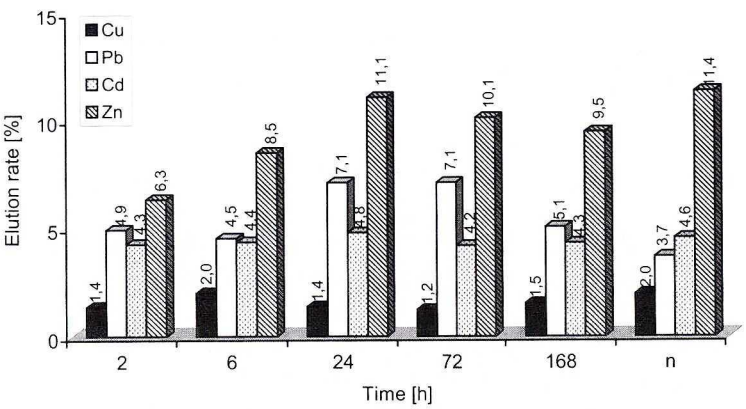

Fig. 9. A comparison of the Cd, Cu, Pb and Zn elution rates from sand M2 distilled water

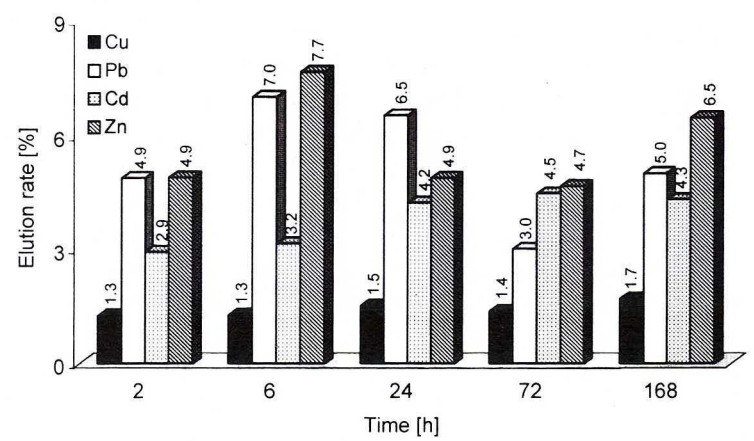

Fig. 10. A comparison of the Cd, Cu, Pb and Zn elution rates from sand M2 using eluant of pH = 4

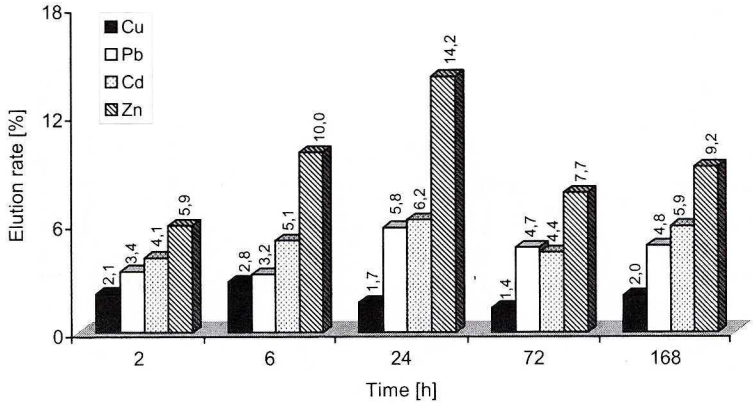

Fig. 11. A comparison of the Cd, Cu, Pb and Zn elution rates from sand M2 using eluant of pH = 3

distilled water or a solution of pH = 4, the concentration levels of cadmium were below the range of determinability.

5. Summary

The studies carried out so far have confirmed that in the used foundry sands various amounts of the heavy metals may occur, depending on the sand origin and type. When eluants are acting on the used moulding sand (on the waste dumping grounds this will be mainly the rainfall water), elution of these metals may take place. The liberation of metals from the sand on dumping grounds may create serious danger to the environment due to contamination of both water and soil.

An analysis of the elution rate of Cd, Cu, Pb and Zn from the waste sand used for casting of brass (sand M1) and bronze (sand M2) indicates that in some eluats from the waste foundry sands the content of these metals may exceed the admissible level of concentration determined by the Polish Standard for water of purity class I. In the case of M1 sand, in all the examined eluats the admissible concentration of Zn, i.e. 0.2 mg/dm^3, has been exceeded (the pH value of the eluant was low); the levels of other examined metals were exceeded as well. In eluats from the sand M2 only cadmium concentration levels were higher than those permitted by the standard, i.e. 0.005 mg/dm^3. Under the examined conditions, the least resistant to elution among the examined metals has proved to be zinc (it had the highest rate of elution in all the eluats obtained from the sand M1 and the sand M2), the most resistant — copper. The rate of metals elution from the sand M1 was changing very sharply along with changes in the conditions of the elution process. Reducing pH of the eluant and prolonging the time of contact between the sand and eluant increased the content of the examined metals in the filtrate obtained. A relationship of this type did not occur in the sand M2, where metal concentration levels were comparable in all filtrates of

this sand, irrespective of the pH values of the eluant used and the duration of its effect on the waste. The reason can be sought in the fact that the sand M2 was of a strongly basic character and even during contact with an eluant of pH = 3, eluats of the pH value = 10 were obtained (eluats made with distilled water and with an eluant of pH = 4 were characterised by similar basicity). The acidity of the filtrates obtained from the sand M1 was changing in the range from 3.1 to 6.7 and depended on the pH of the used eluant.

The obtained results of the analysis have proved that the process of elution of heavy metals from the used sands is very complex in nature. The amount of metals transferred from the sand to the eluat depends on, among others, the content of these metals in the used sand, on the chemical form in which they are present in the sand and on the properties, i.e. the composition and chemical reaction, of the sand and eluant.

It has to be emphasized that when the process of metals transfer from the sand to the eluat is examined, numerous factors have to be taken into consideration.

In the examined system, depending on the physical and chemical factors (pH, type and concentration of all chemical matters present in the examined system), some processes may occur which will affect in a significant way the rate of metals elution and their concentration in eluats. These conditions include, among others, the following parameters:

- reactions between metallic compounds (oxides mainly) and acids (when eluants of low pH are used), in the case of Zn — the element of amphoteric nature — with bases as well,
- the processes of metals sorption on the sand components (depending on numerous factors),
- the possibility of precipitation (in a basic medium) of hardly soluble metallic compounds (mainly hydroxides) and formation of complex compounds.

6. Conclusions

The results of the studies made so far enable drawing of the following conclusions:

1. Due to the effect of liquid cast alloy on foundry sand there is the possibility of transfer of some alloy constituents to the sand, which can make this sand hazardous to the environment.

2. Elution of metals depends to a considerable extent on the acidity of the medium in which the process has been taking place, i.e. on the chemical reaction of the sand and eluant. In the system of a low pH value (the sand characterised by low basicity and an eluant of acid reaction), the observed metal elution rate was much higher and a considerable increase in concentration of the leached metals occured with prolonged time of contact between the sand and eluant. In the case of strongly basic sands, under the examined conditions, an effect of time on the volume of the leached metals was rather insignificant.

3. In the group of the examined metals, the least resistant to elution was Zn, the most resistant Cu, and this was independent of the conditions under which the process of the elution was run.

4. In all the produced eluats the concentration of at least one of the metals examined exceeded the admissible value determined by the Polish Standard for waters of purity class I. This means that the used moulding sands when disposed to dumping grounds can be a threat to the environment. One fact should be particularly emphasized here, namely that even when the disposed waste materials give water eluats with the content of metals permitted by standards, later this content may increase due to the power of these metals to cumulate in water and soil and contaminate them both.

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