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Elution of Mixed Moulding Sands with the GEOPOL Binder and Core Sands with the Phenolic Resin

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Abstract

Out of moulding and core sands used in the foundry industry, sands with organic binders deserve a special attention. These binders are based on synthetic resins, which ensure obtaining the proper technological properties and sound castings, however, they negatively influence the environment. Depending on the kind of the applied resin under an influence of a temperature such compounds as for example BTEX group and polycyclic aromatic hydrocarbons (PAHs) can be formed and released. During storing or economic utilization of used sand is possibility of eluting harmful substances into the environment. Therefore at assessing an influence of the used sand on the environment two above elements should be taken into consideration. Only such investigations provide the complete assessment of the given sand harmfulness.

Keywords: Environment protection, Phenolic resin, Moulding sands, Core sands, BTEX, PAHs

1. Introduction

An assessment of hazards for the natural and work environments caused by moulding sands applied for moulds and cores combines two basic elements:

- emissivity of harmful gases during operations of: preparation of sands, moulding, preparation of cores, moulds pouring with liquid metal, mould cooling and casting knocking out[1];
- possibility of eluting harmful substances from spent moulding sands into the environment e.g. during their storing or economic utilization. Moulding sands with binders, from which none harmful substances are eluted, can be utilized in other domains, which allows to avoid their storage [1, 6-8].

Therefore at assessing an influence of the given sand on the environment the above two elements should be taken into consideration.

Organic harmful substances constitute up to 96 % of all emitted harmful substances from the typical cast iron foundry. Organic compounds are emitted during the preparation process of moulds and cores (preparing moulding sand, core production and storing), when organic binders are applied. However, the largest amount of organic harmful substances is liberated during pouring, cooling and casting knocking out from moulds made of moulding sands with bentonite and additions of lustrous carbon carriers or of moulding sands with organic binders. They can constitute even 90 % of the total emission of dangerous substances in foundry

[1] An assessment of harmfulness of sands in an aspect of emissivity of harmful gases is widely discussed in the monograph: "Assessment of harmfulness of binding materials applied for the new generation of moulding and core sands", M. Holtzer and R. Dańko, Scientific Publishing House AKAPIT, Kraków 2013.

plants, which are using moulding sands with bentonite and lustrous carbon carriers (Fig. 1) [2, 7-10].

Under an influence of a liquid metal high temperature, at unsatisfactory oxygen amounts, the complete decomposition of organic components occurs and numerous new substances are formed. Inorganic dangerous substances are mainly emitted during processes of melting and casting fettling. These are mainly metal oxides.

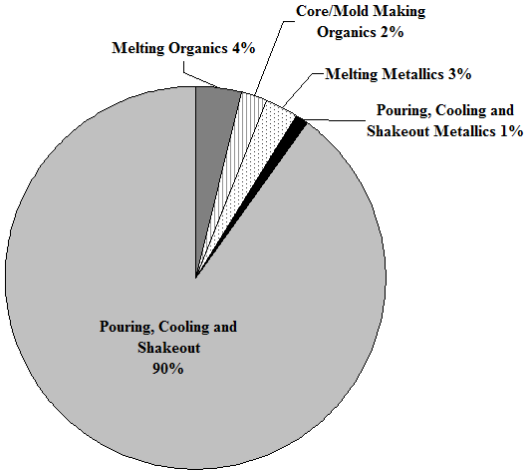

Fig. 1. Participation of individual operations of the process of castings made in moulding sands with bentonite and lustrous carbon carriers - in the emission of contaminations [2]

Among substances generated when high temperatures are influencing binding materials applied in moulding sands, a special group – due to their special harmfulness – constitute polycyclic aromatic hydrocarbons (PAHs) and substances from the BTEX group (benzene, toluene, ethylbenzene, xylene) [3, 11-13].

A lot of these substances - after cooling - condense on sand grains surfaces and together with spent sands are transported outside the foundry plant (e.g. on dumping grounds or as materials used in roads building and in site levelling etc.). Under an influence of atmospheric factors (rain, snow etc.) some of these substances can be washed out into the environment causing its pollution.

An assessment of harmfulness of spent moulding and core sands for the environment during their storing or utilising outside foundry plants - in an aspect of the dangerous substances elusion – is performed on the basis of the elusion test. This test is performed according to the standard: PN-EN 12457-4: 2006. Characterisation of wastes. Elution. Investigation of conformity in relation to eluting granular waste materials and sediments. Part 1: Single-stage batch testing at the liquid to solid ratio 10 l/kg in case of materials of particle dimension below 10 mm (without or with a size reduction).

The obtained test results are compared with the allowance criteria for wastes to be stored on storage yards for the given type of wastes [4] or with values in force for sewages introduced to waters or soils [5].

The above investigations should be performed either by the accredited laboratory or by the laboratory having implemented the quality system or certified qualifications for investigating physical and chemical properties, toxicity and eco-toxicity of substances and preparations.

In the domestic legislation there are three kinds of waste storage yards, differing in their protection degree. Thus, they can accept wastes of different character and different harmfulness for the environment (of course, storage costs are also different). For each of storage yards there are determined allowance criteria, which should be met by deposited wastes. There are the following kinds of storage yards:

- storage yard of dangerous wastes,
- storage yard of neutral wastes,
- storage yard of wastes other than dangerous and neutral.

Criteria deciding on the possibility of storing wastes on the storage yard of the given type of wastes comprise: allowable, limiting elution values and additional parameters.

2. Investigation subject and the applied methodology

Mixtures of spent moulding and core sands applied in Foundry Plant CEMA Myszków constituted the investigation subject. Each of these mixtures contained approximately 30% of the core sand and approximately 70% of the moulding sand (compositions of these mixtures are given in Table 1).

Tests were performed in the accredited laboratory of the Provincial Inspectorate of the Environment Protection in Krakow, according to the binding procedure.

Table 1.
Mixtures of spent sands subjected to elution tests

Moulding sand	Core sand	Symbol
Mixtures od spent sands I		
Binder Geopol + hardener SA 73	Resin Rezolit hardened by Prestal activator	MGR
Mixtures od spent sands II		
Binder Geopol + hardener SA 73	Resin Estrofen hardened by PR 6 activator	MGE
Mixtures od spent sands III		
Binder Geopol + hardener SA 73	Resin Avenol hardened by Katalyzator 7010 activator	MGA

3. The obtained results of elution tests of spent sands mixtures

The obtained results of the elution test of the investigated spent sands mixtures are presented in Table 2. Criteria which must be met by the wastes in the elution test to be allowed to be stored on the storage yard of neutral wastes or wastes other than dangerous and neutral – are also given for comparison. Requirements, which should be met at introducing sewages into waters or soils, are also given. These parameters are given in eluate units mg/dm^3 and dry sand units mg/kg.

Table 2.
Analytical results of eluates originated from a sand elution. Aqueous extract 1:10 [4]

Symbol	MGA	MGE	MGR	P1	R1	R2
		mg/kg dry moulding sand / mg/dm^3		mg/dm^3	*mg/kg dry moulding sand* / mg/dm^3	
pH	10,37	10,36	10,55	6,5 - 9	-	-
cyanides	n.b.	n.b.	n.b.	0,1	-	-
chromium VI	n.b	n.b	n.b	0,1	-	-
orto-phosphates	n.b	n.b	n.b	-	-	-
sulfates	*11,1*/1,11	*18,0*/1,80	*9,6*/0,96	500	*1000*/100	*20000*/2000
TOC	*1120*/112,0	*1253*/125,3	*1486*/148,6	30	*30000*/3000	*5 % dry sand*
nitrates	n.b.	n.b.	n.b.	30	-	-
COD	n.b.	n.b.	n.b.	125	-	-
index phenolic	*0,06*/0,006	*0,11*/0,011	*2,40*/0,240	0,1	*1*/0,1	-
fluorides	*<0,2*/<0,02	*0,6*/0,06	*<0,2*/<0,02	25	*10*/1	*150*/15
chlorides	*39,7*/3,97	*18,9*/1,89	*35,6*/3,56	1000	*800*/80	*15000*/1500
formaldehyde	n.b	n.b.	n.b.	2	-	-
copper	*0,05*/0,005	*0,04*/0,004	*0,03*/0,003	0,5	*20*/2	*50*/5
lead	*0,21*/0,021	*0,05*/0,005	*0,05*/0,005	0,5	*0,5*/0,05	*10*/1
nickel	*<0,05*/<0,005	*<0,05*/<0,005	*<0,05*/<0,005	0,5	*0,4*/0,04	*10*/1
iron	n.b.	n.b.	n.b.	10	-	-
total chromium	*0,012*/0,0012	*0,012*/0,0012	*0,009*/0,0009	0,5	*0,5*/0,05	*10*/1
zinc	*0,016*/0,016	*<0,07*/<0,007	*<0,07*/<0,007	2	*4*/0,4	*50*/5
cadmium	*0,02*/0,002	*<0,001*/<0,0001	*<0,001*/<0,0001	0,4	*0,04*/0,004	*1*/0,1
cobalt	n.b	n.b	n.b	1	-	-
molybdenum	*<0,1*/<0,01	*0,65*/0,065	*0,23*/0,023	1	*0,5*/0,05	*10*/1
antimony	*<0,05*/<0,005	*<0,05*/<0,005	*<0,05*/<0,005	0,3	*0,06*/0,006	*0,7*/0,07
arsenic	*<0,05*/<0,005	*<0,05*/<0,005	*<0,05*/<0,005	0,1	*0,5*/0,05	*2*/0,2
mercury	*0,005*/<0,0005	*0,005*/<0,0005	*0,005*/<0,0005	0,06	*0,01*/0,001	*0,2*/0,02
bar	*0,070*/0,0070	*0,090*/0,0090	*0,030*/0,0030	3	*20*/2	*100*/10
selenium	*<0,1*/<0,01	*<0,1*/<0,01	*<0,1*/<0,01	1	*0,1*/0,01	*0,5*/0,05
BTEX	*<0,06*/<0,006	*<0,06*/<0,006	*<0,06*/<0,006	0,1	*6*/0,6	-
PCB	*<0,00005*/ <0,000005	*<0,00005*/ <0,000005	*<0,00005*/ <0,000005	0	*1*/0,1	-
mineral oil	*<0,5*/<0,05	*<0,5*/<0,05	*<0,5*/<0,05	-	*500*/50	-
PAHs	*<0,0003*/ <0,00003	*<0,0003*/ <0,00003	*<0,00064*/ <0,000064	-	*1*/0,1	-
dissolved organic carbon DOC	*1060*/106	*1190*/119	*1430*/143	-	*500*/50	*800*/80
dissolved solids TDS	*6470*/647	*7470*/747	*8870*/887	-	*4000*/400	*60000*/6000
BOD5	n.b.	n.b	n.b	30	-	-

n.b. – not tested parameter, P1 – The parameters of wastewater discharged into water or soil, R1 – Requirements for waste deposited in a landfill for inert waste, R2 – Requirements for waste deposited in a landfill for non-hazardous and inert

4. Discussion of the obtained elution tests results

Mixture of spent sands: Geopol + SA 73 hardener + Avenol resin hardened by 7010 (MGA) activator

As far as the criteria in force for sewage are concerned, this sand has only a small excess of pH and 3-times excess of the total organic carbon content. In case of storing this spent sand on the storage yard of neutral wastes 2-times exceeding of the dissolved organic carbon parameter and 1.5-times exceeding of the dissolved substances parameter - occurs.

Mixture of spent sands: Geopol + SA 73 hardener + Estrofen resin hardened by PR 6 (MGE) activator

In case of criteria in force for sewages this sand only negligibly exceeds pH value and 4-times exceeds the total organic carbon content. When the criteria of storing this sand on the storage yard for neutral wastes are taken into account, the parameter of dissolved organic carbon is exceeded 2-times and the dissolved substances parameter is also exceeded 2-times. Also a small excess of molybdenum content occurred, which was caused by the fact that castings of cast steel containing this element were produced in these sands (in everyday practice spent

sands from castings of various kinds of cast steel are mixed together and then such situation will not occur).

Mixture of spent sands: Geopol + SA 73 hardener + Rezolit resin hardened by Prestal (MGR) activator

In case of criteria for sewage this sand has only a small excess of pH and 5-times excess of the total organic carbon content. The phenolic index is also exceeded. When criteria of this sand storing on the storage yard for neutral wastes, the dissolved organic carbon parameter is exceeded nearly 3-times and the dissolved substances parameter 2-times. The phenolic index is also exceeded.

5. Summation of elusion tests

All investigated moulding sands (MGE, MGR, MGA) as indicated exceeding the criteria being in force for sewages introduced into waters and soils in the range of the total organic carbon content and had slightly higher than allowable pH values. The sand marked as MGR exceeded in addition the phenolic index.

All tested sands (MGE, MGR, MGA) exceeded several times the total organic carbon parameter, the soluble organic carbon and the soluble substances parameter – in the range of criteria being in force at wastes stored on the neutral wastes storage yard. The MGE sand exceeded a little the Mo content, while the MGR mass exceeded the phenolic index.

6. Conclusions

On the bases on the results of elution tests and the criteria, being in force for sewages introduced into waters and soils as well as for criteria for neutral wastes storage yards it can be stated that:

- All aqueous extracts from spent sands can meet the criteria for sewages introduced into waters and soils as well as the criteria allowing wastes to be stored on the neutral wastes storage yards. However, fractions of core sands prepared with strongly alkaline phenol-formaldehyde resin should be limited in spent moulding sands. This can be obtained by the proper control of the casting process, depending on the cores fraction in the mould.
- The molybdenum content excess found in elution tests was caused by a unitary melt from which the knocked sand was taken. In the real production process sands knocked out from various castings are mixed.
- When analysing the results of elution tests of spent sands mixtures, it should be taken into account that in all investigated mixtures the limiting 30% fraction of spent core sands prepared with the phenol-formaldehyde resin of a very high alkalinity (pH = 12), which introduces organic compounds into the system, was applied. All exceeded criteria were related to the organic compounds presence. The Geopol binder is of inorganic character. In practice the core sand fraction will be much smaller, which will favourably decrease pH reaction and parameters: TOC, SOC and SS. Thus, spent sands should be meeting the criteria concerning their storing on the neutral wastes storage yards as well as the criteria being in force for sewages introduced into waters and soils.

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