

CARBONACEOUS ADDITIVES OF GREEN SAND SYSTEMS

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Abstract:

Use of carbonaceous additives in foundry manufacture is closely connected with moulding mixtures bonded with bentonite. This binding acts well for more than one hundred years. With growing demands to ecology and occupational hygiene the demands to quality of carbonaceous additives that are in a common operation a source of organic pollutants both in working environment and in waste mixtures too are growing. Besides a negative influence on living environment the organic matters affect unfavourably also the human health (carcinogens). This study is aimed at comparing the commonly used and newly developed carbonaceous additives from the point of view of an impact of their use on quality of working environment (BTEX emissions) and surface quality of castings.

1. INTRODUCTION

Moulding mixtures bonded with bentonite are classed with the most extended foundry technologies for the reason of economical and technological simplicity. On a world scale it is about 80 % [1] of casting production, mainly for castings from graphitizing ferrous alloys, lamellar graphite cast iron and spheroidal graphite cast iron.

For the purpose of obtaining the castings of high surface quality the carbonaceous matters are added in bentonite moulding mixtures. That principle is known for more than 100 years. During thermal exposure of the mould the carbonaceous matters (most often sea coal with additives increasing the PC yield) are pyrolyzed with formation of the pyrolysis carbon (PC), semicoke, and gaseous matters.

Solid pyrolysis products – pyrolysis carbon (PC) and semicoke are the cause of the metallophobic behaviour of the mould and they ensure a smooth casting surface. On the other hand the formed gaseous exhalations (HAP – hazardous air pollutant defined in 1990 Clean Air Act Amendment – CAAA) represent a significant danger for living environment and human health. In the group of the HAP matters also so called VOC (volatile organic compounds) ones are classed what is a group of compounds of low molecular weight and high volatility under normal conditions. In addition to it they are a source of increasing the economic costs of depositing the waste moulding mixtures.

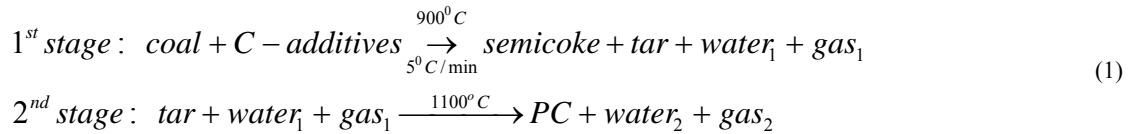
This study is aimed at comparing the traditionally used carbonaceous additives in unit bentonite mixtures with newly developed additives that would replace them in foundry plants.

The decrease of hygienic nuisance (BTEX emissions – benzene-toluene-ethylbenzene and xylenes that form 80 % of HAPs) with keeping the present surface quality of castings has been determined a main criterion.

2. MODEL TWO-STAGE PYROLYSIS

During thermal exposure of a green mould with a casting a whole number of processes run in the mould the most expressive one of which is the formation and movement of the water condensation zone, passivation of the bentonite binder, and pyrolysis of carbonaceous additives.

Based on the [2] the pyrolysis of carbonaceous additives can be divided in two simultaneously running processes. In the mould points where the temperature about 900 °C was achieved the so called first pyrolysis stage is running (equation 1) with formation of semicoke what is a majority part of solid pyrolysis products and a mixture of aromatic and aliphatic hydrocarbons which is designated as gas₁.



Growth of temperature in the mould to about 1100 °C enables the second pyrolysis stage during which pyrolysis carbon (PC) and a mixture of simple hardly decomposable gases designated as gas₂ (CO, CO₂, H₂, CH₄, ...) are formed.

From the point of view of technology, ecology and hygiene the main products of the two-stage pyrolysis of carbonaceous materials can be divided to two groups according to the state as follows:

- a) Solid products:
 - semicoke
 - pyrolysis carbon (PC) – lustrous carbon (LC)
 - amorphous carbon (AC)
- b) Gaseous products

For obtaining a casting of high surface quality the most important is the formation of lustrous carbon that forms a thin film with high adhesion on sand grains (a similarity to a crystal lattice) which prevents the liquid metal penetrating in the mould. Lustrous carbon is formed from volatile hydrocarbons under temperatures above 400 °C in the presence of catalysts (e.g. the acidic surface of quartz sand). Carbon is formed in such a way which with its structure comes near to graphite [3]. Mechanism of lustrous carbon formation corresponds to heterogeneous nucleation.

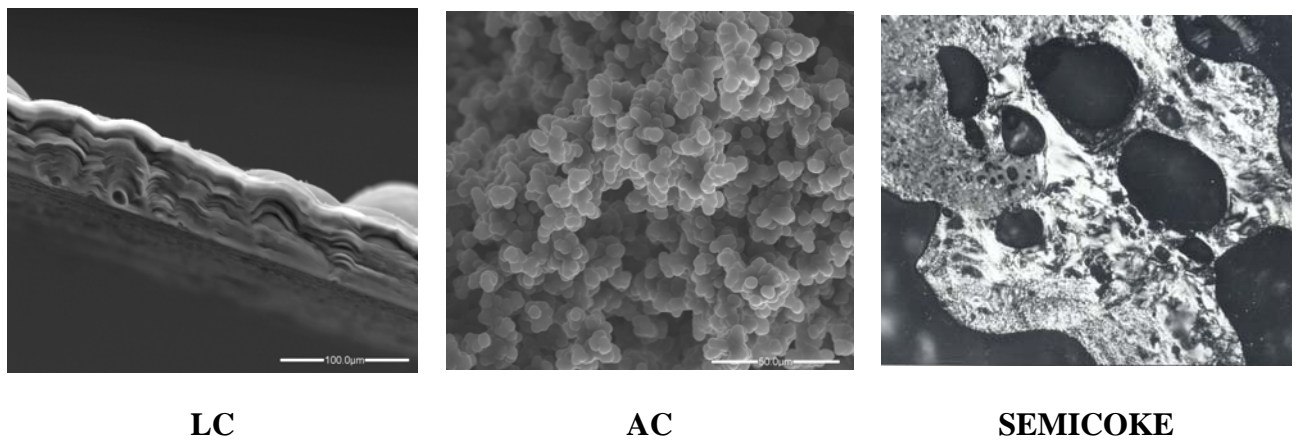


Fig. 1 Solid products of sea coal pyrolysis (LC, AC, semicoke) obtained on a laboratory pyrolysis unit [2]

In the contrary way, i.e. by homogeneous nucleation, the majority part of pyrolysis carbon – amorphous carbon (AC) is formed directly from a gaseous phase. Both forms of PC are morphologically and structurally different (Fig. 1.) and well separable. Besides their structures they also differ with other physical and chemical properties (oxireactivity, density, aromaticity – the C^{at}/H^{at} ratio). Lustrous carbon (LC) thanks to its irreconcilability with metal and high heat resistance (low oxireactivity) plays the main role at the mould/metal interface; amorphous carbon is burnt on the mould face and it forms a part of the oolitic carbon layer of quartz sand (it contributes to the mould metallophobization).

The effect of semicoke which is partially burnt on the mould/metal interface in the same way as amorphous carbon is no less important. The main effect of semicoke in the mould consists in swelling and clogging the intergrain spaces (swelling index) and compensation of thermal stress from microdilatation of sand grains.

Gaseous parts formed during two-stage pyrolysis help to mixture collapsibility. On the other hand as a result of the fact that quantitatively not all gas_1 is consequently pyrolyzed to gas_2 with the formation of simple gases (CO, H₂ etc.) the moulding mixtures produces a certain part of gaseous matters of organic origin. Seal coals, that are complex organic macromolecules, are included among traditional carbonaceous additives in unit bentonite mixtures (UBM). During cracking them the aromatic compounds are liberated in particular that considerably influence both the human health and the neighbouring living environment.

3. CARRIERS OF PYROLYSIS CARBON (PC)

A basic criterion of a suitable PC carrier is ensuring of such amount of solid pyrolysis products (semicoke + PC) that will ensure high surface quality of a final casting. The principle of complex effect of the pyrolysis (PC) or lustrous (LC) carbon carrier is summarized in [4]. The amount of pyrolysis gases or pyrolysis carbon is dependent on a carbonaceous additive type or a degree of its coalification (the C^{at}/H^{at} ratio) [5]. Optimum concentration of pyrolysis carbon liberated in the mixture should range from 0.2 to 0.4 %. Lack of PC in the mixture deteriorates surface quality of castings; on the other hand its excess is a cause of a number of other foundry defects (coldshuts, orange peel etc.) [6].

A conventional carbonaceous additive in bentonite mixtures for castings from graphitizing ferrous alloys is sea coal. Low PC content in coal is solved with the addition of natural (colophony, gilsonite) or synthetic resins. With regard to neighbouring environment the sea coal is a considerable source of emissions of moulding mixtures; in addition to it with the addition of resins the volume of liberated emissions (BTEX) of moulding mixtures is growing too. New materials of organic or inorganic origin are therefore found that would liberate satisfying PC amount with simultaneous decrease of BTEX emissions. Thus such materials can be considered an optimum carbonaceous additive that will liberate an optimum amount of hydrocarbons at the mould/metal interface (the field of high temperatures) needed for the LC formation and in the mould volume distant from the mould/metal interface, i.e. the field of low temperatures, it is subjected to a minimum pyrolysis degree only [7].

3.1 Tested carbonaceous additives

Four carbonaceous additives were chosen for experiments that can be divided in two groups. A carbonaceous additive used in common practice and a newly developed additive which should eventually replace the first one are included in every imaginary group. The reasons for dividing in two groups are different conditions under which the casting experiments run, i.e. taking of pyrolysis gases for the purpose of determining the content of gaseous exhalations in pyrolysis gases. The first group is formed by the Ekosimix (the firm

Šimeček, s. r. o, Czech Republic) and a newly developed mixed carbonaceous carrier of pyrolysis carbon L1 that represents a mixture of Ekosimix, less coalificated coal of different structure, and „process“ carbon. Carboluxon 160 (the firm Hüttenes-Albertus GmbH, Germany) and a newly developed carbonaceous additive Simix 20S were included in the second group. Determination of basic characteristics of carbonaceous materials (volume of liberated PC) was the primary intentions. Further on the influence of chosen pyrolysis carbon carriers on the volume of organic pollutants in gas liberated by the moulding mixture and the impact on surface quality of the final casting were studied.

3.2 Comparison of the PC content

The amount of pyrolysis carbon (PC) liberated by the carbonaceous additive during thermal degradation all the time remains a main criterion of suitability of use the given preparation in bentonite bonded moulding mixtures. The PC amount (Tab. 1) was determined with the aid of a modified retort test (I. Bindernagel, CIATF).

Table 1 Influence of the C – additive kind on the PC content

C – additive	Ekosimix	Carboluxon	Simix 20S	L1
PC content [%]	8 – 10	11.5 – 11.6	15	6.7

With regard to values given in Tab. 1 the optimum carbonaceous additive seems to be the Simix 20S additive which proves the highest content of pyrolysis carbon (PC). But the amount of pyrolysis carbon produced by remaining PC carriers is not negligible either. Palpable difference in PC contents (about 8 %) between Simix 20S and L1 additives is caused by the choice and composition of used carbonaceous materials but in this case it cannot be stated too that the L1 additive doesn't meet the condition for „applicability“ of carbonaceous additives, i.e. the ensuring of sufficient PC amount in moulding mixtures.

3.3 Moulding mixtures emissions

During thermal stress of the mould a number of organic matters (VOCs) are forming that represent a composite mixture of organic compounds with low molecular weight and high volatility.

The main condition of the use of chosen PC carrier is the decrease of absolute amount of BTEX emissions in moulding mixture pyrolysis gas with constant surface quality of the final casting. Concentrations of individual organic pollutants (Fig. 2.) were determined with the aid of a drawing device [8] that was derived on the base of [9 – 11].

The amount of pyrolysis gas liberated by the mould is influenced not only by the carbonaceous additive kind but also by metal casting temperature and the thermal stress of the mould characterized by the mould – metal ratio. For ensuring the reproducibility of experiments the metal casting temperature was constant (1360 ± 5 °C) and similarly the thermal stress for both groups of carbonaceous additives too. Unchanging volume of pyrolysis gas (20 ± 5 l) liberated by the mould was collected for the time of 1 hour on sorption tubes with activated charcoal (Anasorb SKC, 200/400 mg) and further on analyzed on the GC/MS HP 5890 Series II with the MSD 5971 detector.

As the BTEX sum not always represents 100% of emissions in moulding mixture pyrolysis gas the total organic carbon (TOC) was evaluated too that should complete information about impacts of the use of the chosen carbonaceous additive on working environment.

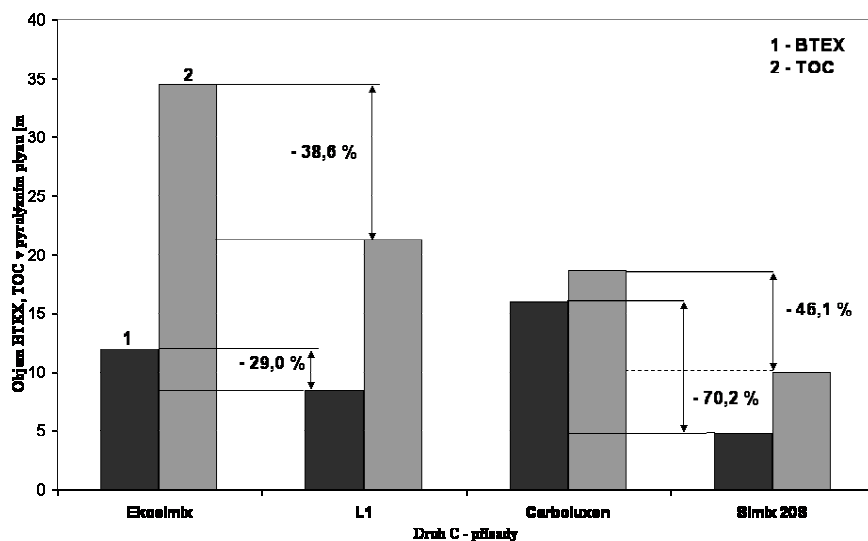


Fig. 2 Influence of the C – additive composition on the BTEX emissions, TOC in pyrolysis gas

Checking of chosen carbonaceous additives in real conditions has brought considerable decrease of organic emissions in pyrolysis gases of newly developed PC carriers. Results of „operating“ experiments have proved presumptions derived on the basis of pyrolyses of pure carbonaceous additives.

The use of L1 mixed carbonaceous additive has brought considerable decrease of BTEX or TOC volume respectively in comparison with Ekosimix commonly used in practice. Explicitly there is a decrease of 29.0 % of BTEX emissions or 38.6 % respectively with determination of total organic carbon TOC. In case of the second group of additives the differences in emission volumes are even more considerable; the decrease by 46.1 % was achieved with determination of total organic carbon (TOC) and in case of BTEX emissions the decrease was even by 70.2 % what considerably influences quality of working environment in foundries.

3.4 Surface quality of castings

The addition of carbonaceous materials in unit bentonite mixtures ensures high surface quality of the final casting. Surface quality of castings is expressed with the aid of mean arithmetic roughness Ra [μm]. For our experiments a model casting [8] of dimensions 150 x 150 x 50 mm was cast from lamellar graphite cast iron EN GLJ-200 and its surface was evaluated on the casting surface from the core that was compacted to a constant compaction degree (to constant volume weight of 1600 – 1610 kg/m^3). Specific area of the casting was fettled with the aid of a steel brush only. Roughness was measured by two ways and namely by a comparative method with the aid of the SVUM standards and with the aid of a digital device Mitutojo Surftest 211 (Japan) on surface trajectories determined in advance.

For depicting the influence of change of the C – material content in the mixture on quality of casting surface the values of PC content in the mixture after casting were determined and compared. For all studied mixtures the PC content value ranged within 0.15 – 0.30 %, which should be ensured a good surface quality.

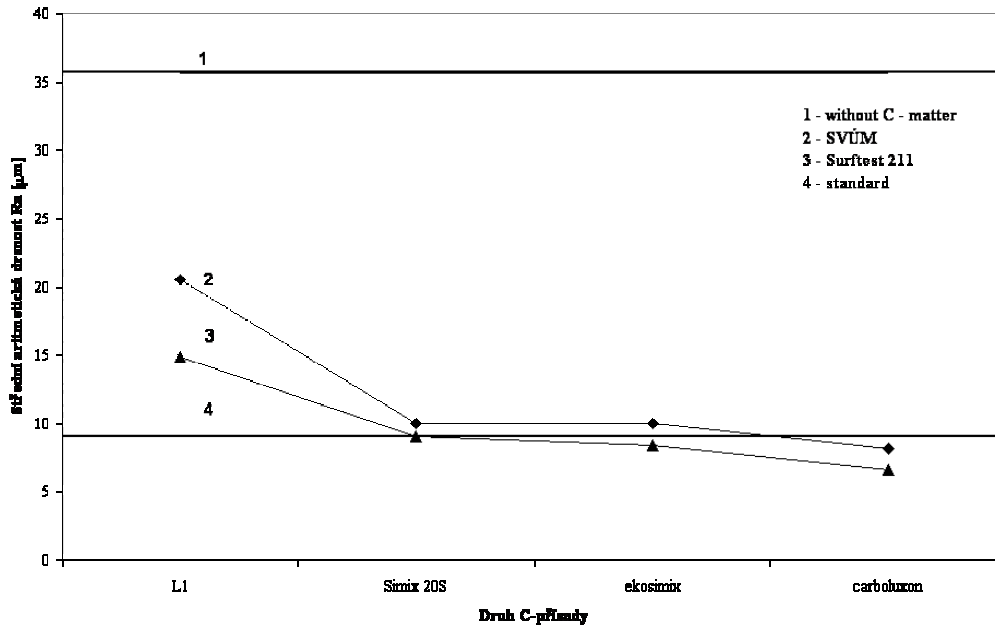


Fig. 3 Surface quality of castings

With regard to determined PC contents of individual additives in pure state it can be expected that all castings will be of high surface quality. Nor the decrease of seal coal by 50 % and its replacing with other carbonaceous materials caused a considerable deterioration of surface quality of castings (Fig. 3.). Achieved values of mean arithmetic roughness Ra are negligible higher (maximum growth by 11.5 μm) in comparison with a standard. Negligible increase of surface roughness is seen with the L1 additive only but in this case too the surface is by about 50 % superior to that one without the use of the PC carrier.

4. CONCLUSION

Carbonaceous additives in bentonite bonded moulding mixtures improve surface quality of castings from grafitizing ferrous alloys. Besides technologically important solid pyrolysis products (LC in particular) the C – additives are a source of organic pollutants.

Comparison experiments were done for the purpose of comparing the carbonaceous additives used in practice and the newly developed ones.

Partial substitution of original carbonaceous additives (sea coal) with other carbonaceous materials or the utilization of process carbon seams to be suitable particularly from the point of view of reducing the ecological and hygienic load of foundry production. The BTEX emission content was decreased with the use of a new C – additive L1 by about 30 % in comparison with commonly used Ekosimix. In case of the second pair of tested additives the decrease of BTEX emissions was even more considerable (about 70 %).

Nor the decrease of original carbonaceous matters content (to 50 %) neither the carbonaceous materials newly used have brought considerable deterioration of surface quality of castings. Achieved values of mean arithmetic roughness Ra of castings are negligibly higher than with a standard carbonaceous additive.

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