

Novel approaches in reducing pouring emissions

J H Helber

IfG - Institute of Foundry Technology,
Dusseldorf, Germany

Abstract

The paper presents a basic understanding of some thermal degradation processes within the mould, i.e. the mechanism of the formation of lustrous carbon was investigated as well as the formation of aromatics. The suppression of those reactions and the state of the art in modelling the gas phase will be addressed respectively the problems which still have to be overcome.

The scope of the presented brand new investigational results is regarded to be fundamental knowledge within the fields of gas defect analysis, emission reduction, and mould material design.

Foreword

The formation of the gas phase in the mould during and after mould filling and its reactions with core gases and hard surfaces are still very much a 'black-box'. The reactions leading to the generation of pouring gas and its constituents are not well understood in detail. Predictions of pouring gas production rates, of gas induced casting defects and, finally, of atmospheric emissions have remained empirically based. These empirical findings ought to be substituted, or at least expanded upon, with reliable knowledge. But to model effects like those mentioned above, it is necessary to possess data that can only be gained via a clear understanding of the thermochemical reactions involved.

It can hardly be expected that these very complex processes will be fully understood anytime soon. However, significant advances may be achieved within the next few years. This presentation is intended to describe a small area of the investigations currently conducted to clarify the physico-chemical processes in the sand mould. A presentation of further experimental results - partly derived from comparative testing of binder and moulding auxiliaries - is to be reserved for another occasion.

Also outlined in this paper are a number of thermal degradation processes taking place within the mould. Besides, the mechanisms underlying the formation of lustrous carbon and aromatics are investigated. The suppression of these reactions and the state of the art in gas phase modelling will likewise be addressed to some extent.

Introduction

The investigations relate to sand moulds with resin-bonded cores and bentonite-bonded moulds for casting iron. The basic thermophysical and thermochemical processes in the gas phase were examined, inter alia, as part of two publicly subsidized projects^(1, 2). The aim was, and still continues to be, the determination of the fundamentals for creating a numeric model whereby the formation of gas as well as the emission of pouring gases could be simulated.

Key questions relate to the in-mould transformation and flow of materials. While the convective gas transport within a sand mould is driven by pressure differences, diffusion processes are based on Braun's molecular movement and gravitation effects. Gas transport is naturally directed from the inside toward the outside, in line with the heat flow (but see notes below). The transformation of materials is driven by the heat flux from the metal into the moulding material.

Since gases and vapours are produced in the mould through the evaporation of water and the thermal decomposition of organic and instable inorganic compounds, transport mechanisms and



Fig. 1. Induction furnace, shown with a gas collecting bag. The bag can be easily replaced with a burette for measurement of gas volumes

chemical processes are directly linked and mutually interdependent. To arrive at a physical description, it is necessary to know the sources and sinks for each material, or in other words, to know which materials will form and disappear where and when. Let us first take a look at the gas phase and the role of gas condensation and adsorption phenomena.

Results

The integral increase in gas volume in the mould which can be observed after the pouring cycle as a result of the casting-to-mould heat transfer is defined by three basic mechanisms, i.e.

1. (Permanent) gas expansion
2. Formation of water vapour
2. Coal decomposition

Given the many influencing factors, this volume increase will vary on a case-by-case basis. On the other hand, components 1 and 2 will become zero once again as soon as a thermal balance with the ambient environment has been achieved (i.e., when room temperature prevails both on the outside and on the inside).

Calculation example:

Composition of the moulding material

Active binder concentrations (binder composition) in the mould:

• Bentonite(B)	8 %
• Water (W)	3 %
• Lustrous carbon former (LCF)	1.7 %
$\Sigma =$	12.7 %

Support medium: Quartz sand	87.3 %
$\Sigma =$	100.0 %

Pouring conditions for modelling calculations:

Pouring temperature 1420 °C
Casting wall thickness 10 mm

Mould characteristics:

Initial mould temperature 20 °C (293 K)
Mould pore volume 35 %
Mould density 1.5 g/cm³.

Simplified physical and chemical effects assumed for the simulation:

Release / decomposition of:

- Water 3.0 % m/m at 100 °C
- Volatiles (FB) from LCF 0.6 % m/m at 400 °C
- Coke (residue) from LCF 1.1 % m/m at 400 °C
- Water from bentonite 0.8 % m/m at 400 °C
- Residue from bentonite (residue) 7.2 % m/m

Total volatiles from LCF and bentonite at 400 °C 1.4 %

It follows from the above that at 400 °C or 673 K, respectively - i.e., during the passage of the (already much diminished) heat front through the moulding material - the surplus gas volumes formed (per 1 ml of moulding material) can be approximately quantified thus:

- 0.45 ml due to thermal expansion of gas in the pore space
- 160 ml due to water vapour
- 29 ml of gases and vapours attributable to coal dust (lustrous carbon former)

This increase in gas volume inside the mould is accompanied by a gas volume increase outside the mould that is commonly known (and can be measured) as pouring gas emissions.

This external expansion results from the different mechanisms mentioned above - but is diminished by condensation, adsorption, and contraction of the gas phase on its way out passing almost cold areas of the mould. So the surface gas release is much smaller than the gas production at the heat front.

Various instruments exist for determining these emissions; the results obtained vary accordingly. For the purposes of this paper, the equipment shown in fig.1 was used.

Below we shall see how these assumptions tally with the experimental findings (fig.2). The diagram shows the measured gas emissions produced by various combinations of moulding material constituents, i.e., pure quartz sand (yellow), moulding sand + bentonite / water (blue), and moulding sand + bentonite / water + lustrous carbon former (red), under identical conditions.

Evidently, there can be no gas release from pre-annealed quartz sand alone. Rather, this volume increase is due to the thermal expansion of the gas (yellow line). The blue line describes the gas expansion plus the permanent gas formation resulting from water (vapour) reactions with the metal, whereas the violet curve additionally plots the emission of gas from the lustrous carbon former and the results of their reactions.

In the trials, about 50 ml of gas was obtained after six minutes of pyrolysis. The calculated gas phase volume is equal to more than four

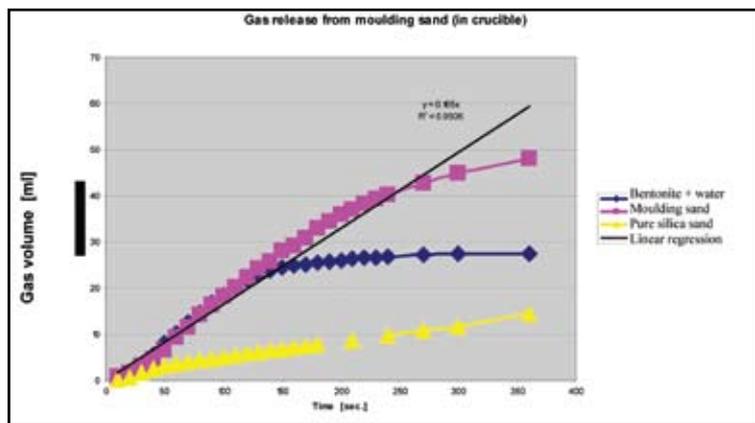


Fig. 2. Comparative study of gas release from moulding sand over 6 min with rapid heating and a temperature gradient in the moulding material (Quartz crucible 14 x 100 mm, 1.4 g Fe surrounded by 6 g moulding sand, sand / bentonite / water and pure quartz sand; induction-heated at full power input; gas volume measured with a water-filled burette)

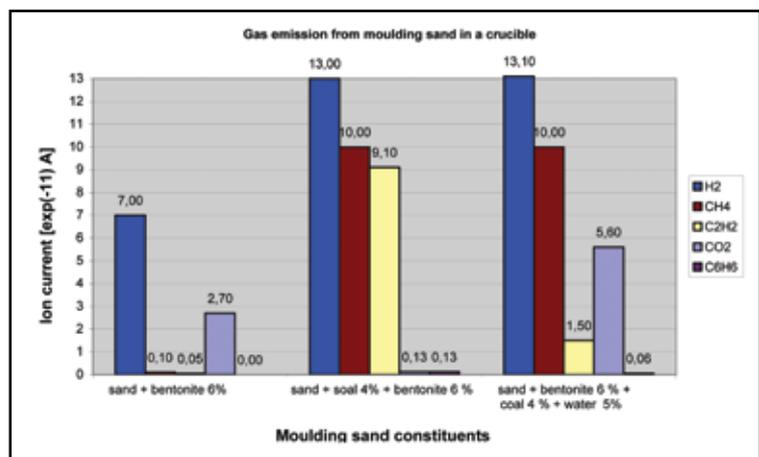


Fig. 3. Coal produces methane, hydrogen, C2 alkanes and aromatics; moist bentonite produces CO₂ and hydrogen (Silica crucible 14 x 100 mm, 1.7-2 g Fe surrounded by 6 g sand with additives, induction-heated)

times the actual measured volume. In the presence of coal, air and (subsequently) water vapour are displaced by the coal pyrolysis gas. As a result, they can no longer react with the metal but only with the remaining gases and with the moulding material. Otherwise the gas volumes measured would have to be much greater since the coal alone cannot be expected, in theory, to produce approx. 20 - 50 ml of gas per gram of coal. However, it is not this effect alone which contributes to the reduced measurements compared with the primary gas formation in the heat zone. Condensation and adsorption effects also function as gas-phase sinks, although the extent to which each of these contributes to the result cannot be determined externally. A clarification of this issue will remain reserved to future studies.

The above raises the question which gases are involved in the formation of gas volumes. The following chart (fig.3) compares the contribution of the individual moulding material constituents to the gas emission. This time, however, the comparison is related not to the total volume but to the composition of the gas phase.

Bentonite in dry sand releases hydrogen and CO₂ by splitting key constituents, i.e., water of crystallisation and (sodium) carbonate. The coal releases further amounts of hydrogen and CO₂ in addition to methane, ethyne, benzene and other aromatics.

Due to the initial uniformity of the gas flow, the concentrations measured simultaneously by mass spectrometry essentially correspond to the amounts of material or gas volumes released at the start of the test.

The addition of water, common in practice, will not change these patterns fundamentally but reduces the levels of unsaturated

Technical Paper

hydrocarbons and CO₂. Thus, moist bentonite as a necessary constituent of green sand results in clearly diminished benzene and ethyne outgassing, whereas the amounts of hydrogen and methane remain unchanged.

At this point let us consider a new generalized gas phase model. Fig.4 gives a graphic explanation of the gas-phase processes we are currently discussing with regard to green sand.

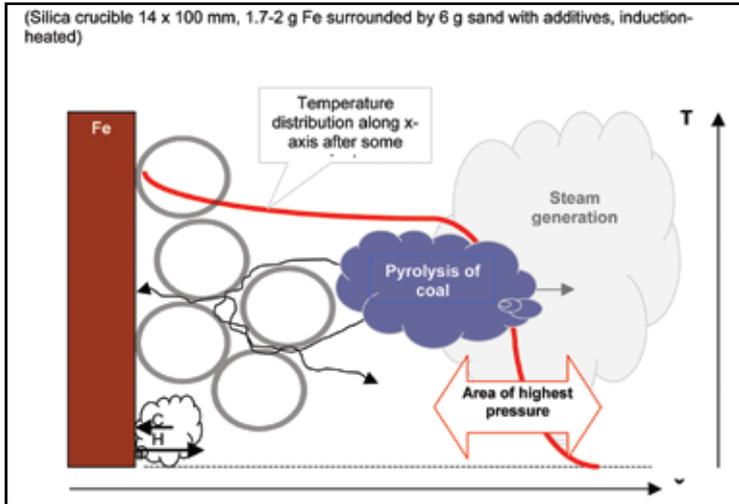


Fig. 4. Simplified heat and gas flow model (x-axis = distance to metal surface)

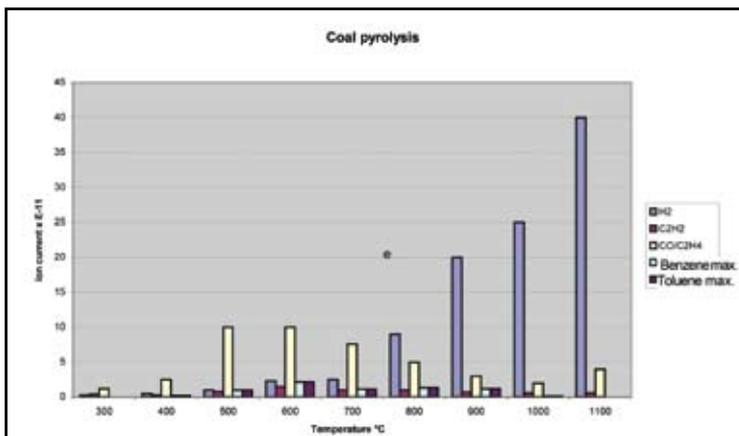


Fig. 5. Coal pyrolysis at different temperatures

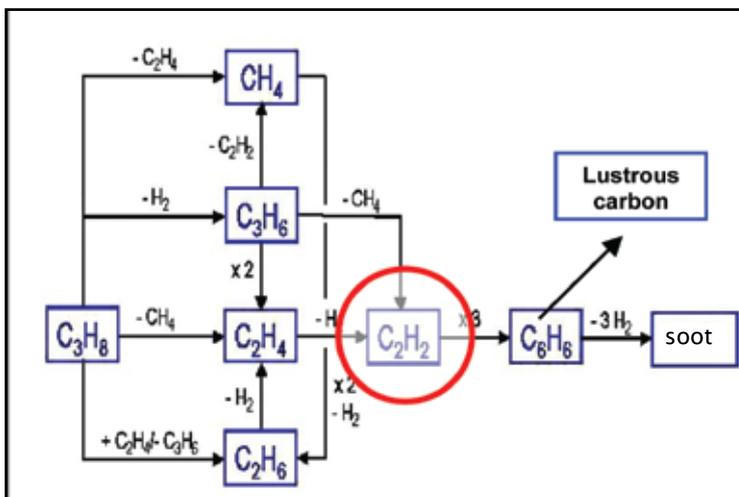


Fig. 6. According to steel carburising trials with propane conducted at EBI Karlsruhe, the carbon deposition process is based on build-up (synthesis) reactions and the formation of benzene⁶⁾

Coal decomposition - lustrous carbon formation

At low temperatures, coal pyrolysis is a very slow process. The composition doesn't become complete until about 1900°C. Depending on the decomposition temperature, different breakdown products are obtained. As the thermal load increases, only the most stable hydrocarbon species 'survive' these harsh conditions (fig.5).

Fig. 6 illustrates a simplified carburising mechanism on a steel surface having a temperature of 900°C. The carburising medium used is propane⁽³⁾. We find that the general reaction mechanism described by other authors in the context of flame investigations, diamond synthesis or case-carburising is fully confirmed with regard to green sand moulds. The synthesis of benzene is only one of several (potential) 'reaction paths' toward the formation of lustrous carbon. Interrupting it would be tantamount to suppressing the formation of lustrous carbon at least partially.

Interruption of formation mechanisms

Generally speaking, the options available for preventing or reducing benzene emissions include the following:

- burn-off or collection of pouring gas outside the mould
- elimination of the use of lustrous carbon formers
- retention of substances in the moulding material by absorption or condensation mechanisms
- destroying substances within the mould before they can be released
- preventing their formation.

The 'Advanced Oxidation' method developed in the U.S, as far as it is understood today, relies on the oxidative degradation of the carbonaceous ingredients of the black water which is re-used for watering the bentonite⁽⁴⁾, and generates porous structures⁽⁵⁾ as well as free surfaces in the inner mould granular structure. Thus it may be regarded a secondary effect.

An interruption of the formation mechanism may be achieved with the aid of carbon dioxide (figs 7a and 7b) as radical scavenger⁽⁶⁾. However, this must be done in such a manner that the deposition of lustrous carbon is not disrupted, i.e. in the central mould section (in the outer mould areas, temperatures are too low for reactions to take place).

The following diagrams illustrate the instant interruption of the benzene formation mechanism upon introduction of CO₂. The formation of benzene resumes as soon as the CO₂ supply is discontinued.

Conclusion

The results aim to provide a differentiated view of the thermally induced processes taking place in green sand after pouring. On the way to establishing a physico-chemical simulation model, some key milestones have been reached:

- The benzene formation process during cooling is now understood in principle. There are different reaction channels at different temperatures T1 < 900 °C; T2 > 900 - 1300 °C.

- Benzene development can be suppressed only gradually.
- Scientific advances have been relied upon to formulate new LCA with reduced benzene emissions.
- The chemical principles can be transferred to polymer binders to some extent.
- A further conclusion has been to interrupt the reaction channels by means of additives.

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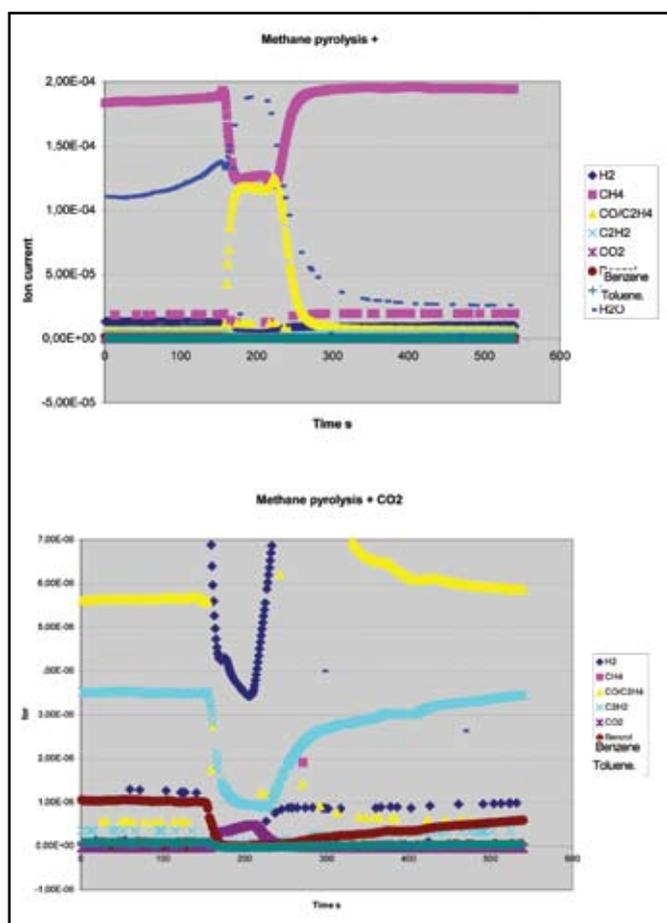


Fig. 7 a/b. Reaction scheme in a laboratory flow reactor system which simulates basic reactions in the mould with respect to benzene suppression

Social dialogue agreement on Respirable Crystalline Silica has both 'carrot' and 'stick' elements

The latest in Health & Safety and Environmental news for the foundry industry from the Cast Metals Federation

Inhalation of Respirable Crystalline Silica (RCS) can result in silicosis. The European Commission now believes there is sufficient information to conclude that the relative risk of lung cancer is increased in persons with silicosis. It is considered therefore that preventing the onset of silicosis will also reduce the risk of cancer.

There are already extensive controls in place to minimise exposure to RCS in foundries and, in the UK, the industry needs to comply with a Workplace Exposure Limit (WEL) of 0.1 mg/m³. However, the European Commission have sought to ensure adequate control across Europe and on 25th October 2006 the European Social Dialogue Agreement on RCS came into force. The Social Dialogue Agreement applies in every member state and is based on a legal document supported by a good practice guide and a series of annexes.

Social Dialogue is a term used to describe the consultation process involving European social partners – representative bodies for employers and employees.

The purpose of the process is to achieve co-operative action by the social partners on the particular issue without resorting to legislation. However, the Social Dialogue is no soft option, as there is both a 'carrot' and a 'stick' involved.

The process does not formally involve the governments of member states but if, despite agreement, the social partners cannot demonstrate compliance, the European Commission may impose a legislative solution and this could well result in a much tighter control level well below the current workplace exposure limit of 0.1 mg/m³.

The agreement applies across a number of industrial sectors, including the foundry industry, where RCS is found in the workplace. It is based on a risk assessment procedure which is intended to identify the potential for an individual to be exposed to RCS in the workplace. The agreement aims to protect the health of employees by minimising exposure to RCS by applying the (appropriate) Good Practices and increasing knowledge about potential health effects of RCS.

The key requirements for companies are to:

- Nominate a responsible person at company (and site) levels
- Organise necessary training
- Identify RCS exposure (risk assessment/dust monitoring/health surveillance)
- Organise reporting

The Cast Metals Federation has already communicated the associated documentation to the UK foundry industry and will be responsible for bi-annual reporting to the European Commission via the CAEF.

It must be emphasised that it is now up to industry across Europe to clearly demonstrate its compliance with the Social Dialogue Agreement. Failure to do so will almost certainly result in tougher legislation.

More information is available from The European Network on Silica (NEPSI) at the website www.nepsi.eu or through the CMF via e-mail to admin@cmfed.co.uk or Tel: +44 (0) 121 601 6392.