The thermal degradation of greensand - preliminary work on a method for measuring the amount of core sand residues

Joss James

Synopsis

The thermal degradation of pure phenolic urethane core sand and mixtures with a laboratory greensand has been analyzed using thermogravimetry and mass spectrometry. A preliminary method for measuring the amount of core sand in greensand has been developed.

Introduction

Greensand moulding remains the most common method of producing iron castings and often it is used in conjunction with cores made from chemically bonded sand. During the recirculation of greensand some of the core sand is inevitably incorporated into the system sand. The core sand will be in various degrees of degradation, having been affected by the heat evolved from the casting. Incorporation of the core sand is likely to affect the properties of the greensand and it is thought that such residues may produce gases which promote the formation of defects in castings.

There is therefore a need for a method for measuring the amount of core sand residues in greensand. The possibility of using thermogravimetry combined with mass spectrometry to measure the amount of core sand residues, is being investigated as part of the BCIRA Collaborative Research Programme on mould-metal reactions. This work is concentrating on a phenolic urethane core sand, because it is arguably the most widely used coremaking process.

Earlier work\(^{(1)}\) has shown that thermogravimetry (TG), a technique that measures the weight of a material during a controlled heating cycle, can provide a detailed analysis of how the various constituents of greensand, including core sand, break down on heating.

Other work\(^{(2)}\) has shown that mass spectrometry (MS) combined with TG can provide a chemical analysis of the gases produced during the thermal breakdown of moulding materials.

In mass spectrometry gaseous compounds are broken down into charged molecular fragments, or ions; it is the amount of these fragments which is measured. Plots of the amount of the fragments against time, or temperature, are known as Evolved Gas Analysis (EGA) curves. It was supposed that if a particular fragment could be identified as being produced by the phenolic urethane core sand, measuring the amount of this fragment would give a method of measuring the amount of core sand present.

The earlier work\(^{(1)}\) showed that phenolic urethane core sand undergoes a distinctive two stage weight loss between 200°C and 400°C. Thus, in this present work, TG-MS analysis has concentrated on this temperature region.

Method

Samples of core sand, a coal dust substitute and mixtures of coesand and greensand were analyzed as follows.

Dried samples of freshly bonded phenolic urethane core sand were analyzed using TG between room temperature and approximately 400°C. The samples were heated in flowing nitrogen at a rate of 20°C per minute. Weight loss (TG) curves were obtained over this temperature range and were differentiated to produce dTG curves which showed the rate of weight loss at any particular temperature. The gases produced were swept directly into a portable mass spectrometer (VG SURVEY) and the gases were analyzed. The experimental arrangement is shown in Fig. 1. In this work the concentrations of molecular fragments with masses in the range 50 to 100 were measured. Mass spectra were obtained over this mass range throughout the degradation period. Evolved gas analysis (EGA) curves, which show how the amount of a particular molecular fragment changes with time, were generated from the mass spectra. The experimental arrangement is shown in Fig. 1.

---

Fig. 1 Schematic of TG-MS equipment.

BCIRA TECHNOLOGY March 1995
Samples of coal dust substitute, a potentially interfering material, were assessed in a similar manner.

After testing the pure materials and selecting a suitable molecular fragment, mixtures of core sand and a virgin laboratory greensand containing the coal dust substitute were analyzed producing TG, dTG and EGA curves for samples containing known proportions of core sand. The amount of the selected fragment was measured from the EGA curves after a time which corresponded to the first stage of weight loss from the core sand. A graph of the amount of the selected fragment against the amount of core sand was prepared.

**Results and discussion**

![Fig. 2 TG and dTG curves for a phenolic urethane core sand.](image)

Fig. 2 shows the weight loss (TG) curve and the rate of weight loss curve (dTG) for a sample of core sand. The distinctive double weight loss in the temperature range 200°C to 400°C can be clearly seen in the dTG curve.

Fig. 3 shows typical mass spectra obtained from the gases evolved in the temperature range of the two stage weight loss, 200°C to 400°C, for samples of phenolic urethane core sand and a coal dust substitute. It can be seen that the core sand generally evolved less gas than the coal dust substitute except for a fragment with mass 60. Hence this fragment was selected as the measure of the amount of core sand present.

The weight loss (TG), rate of weight loss (dTG) and an evolved gas analysis (EGA) curve for the core sand are shown schematically in Fig. 4. The first weight loss can be seen to correspond with the maximum in the EGA curve for mass 60.

![Fig. 3 Mass spectra for core sand and coal dust substitute.](image)

Fig. 5 shows the EGA curves for the core sand and the coal dust substitute. Although the substitute did evolve compounds producing fragments of mass 60 it can be seen that after about 24 minutes the core sand had produced ten times more of these fragments than the substitute. Thus at this particular time the coal dust substitute would not create any serious interference effect. It may be possible to account for any interference by looking at a larger number of peaks.

![Fig. 4 Schematic thermal breakdown of phenolic urethane core sand.](image)

Fig. 6 shows the EGA curves for the mass 60 fragment for the mixtures of core sand and virgin greensand. It can be seen that the amount of mass 60 evolved increased as the proportion of core sand increased.

Each EGA curve shows that the concentration of mass 60 increased with increasing time, and temperature. The maximum concentration is reached after 20 minutes. The samples containing large amounts of greensand show a second peak at about 25 minutes which is thought to be the onset of evolution of mass 60 from the coal dust substitute in the greensand fraction. As a first approximation the concentration of mass 60 at 24 minutes has been taken as the measure of the amount of core sand present.

A graph of the concentration of mass 60 against proportion of core sand is shown in Fig. 7. It can be seen that the concentration of fragment of mass 60 increased as the amount of core sand increased, and this provides the basis for a method of measuring the amount of core sand in greensand. The relationship is approximately logarithmic, the reason for this is not, as yet, understood.
Fig. 5  EGA curves for mixtures containing various proportions of phenolic urethane core sand.

Although the graph in Fig. 7 is reasonably linear it was difficult to obtain consistent measurements for the 100% core sand. However, it is unlikely that a production greensand would contain more than 50% fresh core sand. It should also be noted that the results above were all obtained using fresh core sand in a previously un-degraded state whereas the core sand entering a greensand system would be in various degrees of thermal degradation. Thus measurements obtained using this method would relate to a "fresh core sand equivalent".

It is anticipated that this type of method may be used to measure the amount of residues from other chemical binders. It is also possible that the techniques described above might be used to directly measure the amount of coaldust or coaldust substitutes in a greensand. Such a measurement would be of great benefit to foundrymen replacing the current method for calculating the amount of these materials, which is based on some uncertain assumptions.

The techniques described above have proved in principle that it is possible to determine the amount of phenolic urethane core sand residue in a greensand. The technology is costly and so it seems unlikely that foundries would be able to carry out such analyses individually. However facilities for these measurements could be provided by analytical laboratories.

Fig. 7  Intensity of mass 60 for various levels of phenolic urethane core sand.

Practical implications

1. A method has been devised for determining the amount of phenolic urethane core sand residue in a greensand.
2. Fresh phenolic urethane core sand gives a distinctive, two stage, weight loss during heating.
3. Analysis and quantification of the gases evolved during this weight loss period gives a measure of the amount of core sand present in terms of a "fresh core sand equivalent".
4. The method seems reliable for mixtures containing up to about 50% core sand, the probable maximum for foundry system sands.

References


For a full copy of this report please request Research Report 1886.