



Short communication

Mid-infrared spectroscopic analysis of chemically bound metalcasting sands



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ABSTRACT

Foundries around the world discard millions of tons of sand each year even though they can be beneficially used in manufactured soils and geotechnical applications. Despite their usefulness as an aggregate replacement, some environmental authorities are concerned over potential negative impacts associated with residual organic binders in waste foundry sands (WFSs). In this study, chemically bound molding and core sands were obtained from aluminum, bronze and iron foundries that used alkyd urethane, phenolic urethane, Novolac, and natural organic binders. The aim was to use mid-infrared (MIR) spectrometry to assess binder changes within the sands during the casting process. Bands associated with C–H stretching were detected in most WFSs. Mid-infrared spectra and total carbon data demonstrated that organic binders closest to the molten metal interface and subjected to the highest casting temperatures exhibited the most thermal degradation. Our results also provided preliminary evidence that MIR spectroscopy could potentially be used as a method to quantify residual binder in WFSs.

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1. Introduction

The foundry industry uses silica and other specialty sands (e.g., chromite, olivine, zircon) to create molds and cores for the metalcasting process. Individual sand grains are bound using clays, such as calcium or sodium bentonite, or organic resins. After the hardened castings have been retrieved from the molds, the sands are typically reclaimed and reconditioned to make new molds and cores. To prevent casting defects, a portion of the sand is regularly removed from the metalcasting process and replaced with virgin sands due to abrasion and fracturing of the grains. The waste foundry sands (WFSs) are typically discarded in landfills, but interest in using these sands as aggregate in value-added products (e.g., manufactured soils, hot mix asphalt, concrete, paver stones) is steadily increasing in industrialized countries around the world. In the United States it is estimated that 28% of WFSs are being used annually in geotechnical applications and to produce manufactured soils [1].

Despite the fact that WFSs can be effectively used as aggregate replacement [2,3], regulatory agencies are often hesitant to permit

their beneficial use due to concerns over potential metal and organic contamination in the sands. Research to date, however, has demonstrated that many WFSs are not hazardous, as metal concentrations in leaching extracts were reported to be below regulatory thresholds [4–6]. These results are not surprising since total metal concentrations in waste sands from iron, steel, and aluminum foundries fall within ranges found in native surface soils [7].

Due to the pyrolysis of resins or other carbonaceous sand additives during high casting temperatures, a variety of thermal degradation products are generated [8,9]. While many organics in WFSs are at concentrations near or below detection limits, some compounds are detected at relatively high concentrations [10,11]. In general, naphthalene and phenol are found at the highest concentrations when compared to other U.S. EPA-priority polycyclic aromatic hydrocarbons (PAHs) and phenolics, respectively. Of 43 WFSs analyzed by Dungan [10], the maximum naphthalene concentration was 48 mg kg⁻¹, while the median concentration was 0.73 mg kg⁻¹. Among 17 phenolics analyzed, phenol was found at the highest concentration with a maximum of 186 mg kg⁻¹ (median, 2.3 mg kg⁻¹).

To date, only a few studies have investigated chemical changes within foundry molds and cores using both near- and mid-infrared (MIR) spectrometry [12,13]. It has been proposed that these methods could be used as a qualitative and quantitative measure of

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organic contaminants in WFSs, thus ensuring these materials are acceptable for beneficial use applications. In this study, our objective was to use MIR spectrometry to assess changes within molding and core sands during the casting process, with a specific focus on various organic binder types, proximity from the casting interface, and casting temperature. This information will help improve our understanding of the thermal degradation of resins during the metalcasting process. Insufficient thermal degradation of organic binders could result in WFSs that are potentially unacceptable for beneficial use in various applications, specifically soil-related uses due to high resin levels.

2. Materials and methods

2.1. Waste foundry sands

New and used chemically bonded molding and core sands were obtained from iron, aluminum, and bronze foundries in the province of Buenos Aires, Argentina. The term *new* means that molds and cores were not subjected to the casting process after being regenerated from virgin or reclaimed sands or both. *Used* implies that sands were recovered after casting was completed. Sands analyzed in this study used the following resin systems: alkyd urethane (AU), phenolic urethane (PU) coldbox, Novolac used in the Shell process, and a natural binder (NB) made with soybean oil, corn starch, molasses and sodium bentonite. After collection, the sands were passed through a manual grinder to separate the grains for analysis by MIR spectrometry.

2.2. Mid-infrared spectroscopy

Mid-infrared spectra of the molding and core sands were obtained using a Digilab FTS7000 Fourier transform spectrometer (Agilent Technologies, Inc., Santa Clara, CA) equipped with a DTGS detector, KBr beamsplitter, and a Pike Autodiff autosampler (Pike Technologies, Inc., Madison, WI, USA). Spectra (64 co-added scans) were collected from 4000 to 400 cm^{-1} at 4 cm^{-1} resolution (1868 data points per spectrum) using KBr as the background reference. Spekwin32 (Version 1.71.6.1) was used for spectral visualization and subtraction [14].

2.3. Total carbon analysis

All sands were pulverized in a ball mill for 2 min to reduce the particle size, then a 50-mg sample was analyzed for total carbon in a Flash EA1112 NC Analyzer (CE Elantech, Inc., Lakewood, NJ, USA).

3. Results and discussion

Fig. 1 presents the MIR spectra of virgin silica sand (VSS) and new chemically bonded molding and core sands. Because VSS is used in such large proportion relative to the resin binders (i.e., 97–99%, w/w) its spectrum dominates the spectra of the foundry sands. However, the region between 2800 and 3000 cm^{-1} is free of interference and can be interpreted despite the presence of strong silica bands [15]. The AU and Novolac sands showed very distinct bands at 2851 and 2920 cm^{-1} , while the PU sand showed a band at 2930 cm^{-1} . These bands are characteristic of C–H stretching that is associated with the resins. The NB sand showed a distinct band at 3624 cm^{-1} which can be attributed to the presence of sodium bentonite in the binder [12]. As expected, the VSS had a very low total carbon concentration of 0.241 g kg^{-1} , which was 1–2 orders of magnitude lower than in the new foundry sands with resin binder (Table 1). The Novolac sand had the highest carbon concentration

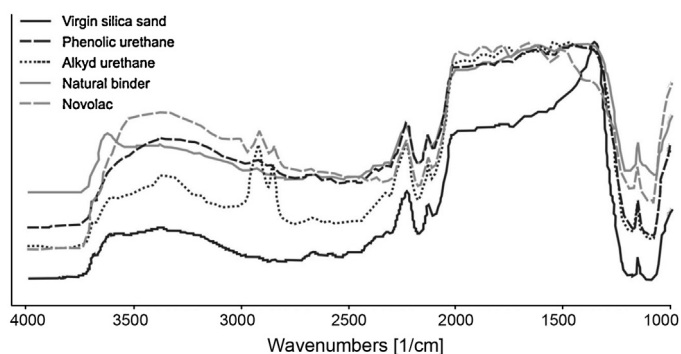


Fig. 1. Mid-infrared spectra of virgin silica sand and organically bound sands prior to casting.

Table 1
Total carbon concentration in the foundry sand samples.

Sand ^a	Total carbon ^b (g kg^{-1})
Virgin silica sand (VSS)	0.24
New phenolic urethane (PU)	6.71
New alkyd urethane (AU)	9.38
New natural binder (NB)	12.5
New Novolac	22.5
New AU	9.38
Used AU iron core	0.93
Used AU bronze core	5.28
Used AU aluminum core	6.78
New NB	12.5
Used NB iron mold–metal interface	5.51
Used NB bronze core	5.01
Used NB aluminum core	10.4
Novolac mold exterior	22.5
Novolac aluminum core	16.8
Novolac iron mold–metal interface	2.79
Used PU mold	6.22
Reclaimed PU mold	3.38
New PU mold	6.71
Used PU mold	6.55
New PU core	9.52
Used PU core	5.57

^a New, casting mold or core; used, casting mold or core; metal interface, molding sand in contact with metal poured.

^b Mean of duplicate samples.

at 22.5 g kg^{-1} , indicating that the sand was prepared with approximately 2% (w/w) resin.

The MIR spectra of new AU sand and used sand poured with different metals, thus being exposed to various casting temperatures, is presented in Fig. 2. Because aluminum, bronze, and iron are poured at about 700, 1000, and 1500 $^{\circ}\text{C}$, respectively, it can be expected that the AU resin will undergo various levels of thermal

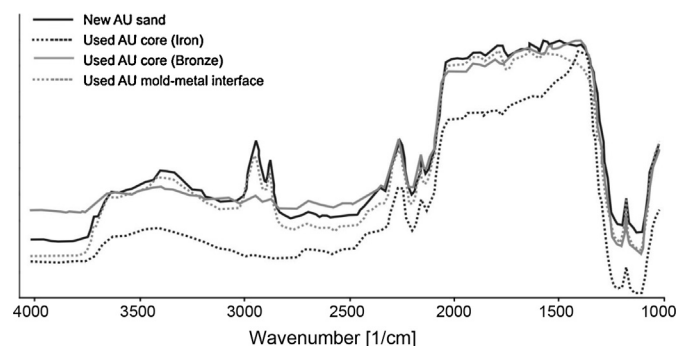


Fig. 2. Mid-infrared spectra of alkyd urethane (AU) sand samples under different thermal conditions.

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