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Short communication

## Mid-infrared spectroscopic analysis of chemically bound metalcasting sands

Roberto E. Miguel<sup>a</sup>, Robert S. Dungan<sup>b,\*</sup>, James B. Reeves III<sup>c</sup><sup>a</sup> Universidad Nacional del Centro de la Provincia de Buenos Aires, Centro de Investigaciones y Estudios Ambientales, Becario CONICET, Pinto 399, Tandil, Bs. As. CP 7000, Argentina<sup>b</sup> USDA-ARS, Northwest Irrigation and Soils Research Laboratory, 3793 North 3600 East, Kimberly, ID 83341, USA<sup>c</sup> USDA-ARS, Environmental Management and Byproduct Utilization Laboratory, 10300 Baltimore Avenue, Beltsville, MD 20705, USA

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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<sup>-1</sup>, while the median concentration was 0.73 mg kg<sup>-1</sup>. Among 17 phenolics analyzed, phenol was found at the highest concentration with a maximum of 186 mg kg<sup>-1</sup> (median, 2.3 mg kg<sup>-1</sup>).

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

\* Corresponding author. Tel.: +1 208 423 6553; fax: +1 208 423 6555.  
E-mail address: [robert.dungan@ars.usda.gov](mailto:robert.dungan@ars.usda.gov) (R.S. Dungan).

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  $\text{cm}^{-1}$  at 4  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$ , while the PU sand showed a band at 2930  $\text{cm}^{-1}$ . These bands are characteristic of C–H stretching that is associated with the resins. The NB sand showed a distinct band at 3624  $\text{cm}^{-1}$  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  $\text{g kg}^{-1}$ , 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

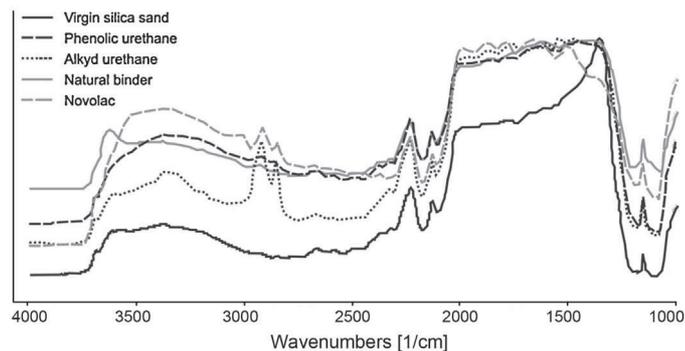


Fig. 1. Mid-infrared spectra of virgin silica sand and organically bound sands prior to casting.

Table 1

Total carbon concentration in the foundry sand samples.

Sand <sup>a</sup>	Total carbon <sup>b</sup> ( $\text{g kg}^{-1}$ )
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

<sup>a</sup> New, casting mold or core; used, casting mold or core; metal interface, molding sand in contact with metal poured.

<sup>b</sup> Mean of duplicate samples.

at 22.5  $\text{g kg}^{-1}$ , 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

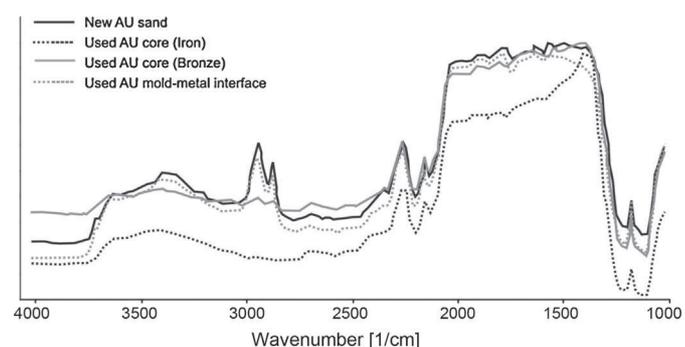


Fig. 2. Mid-infrared spectra of alkyd urethane (AU) sand samples under different thermal conditions.

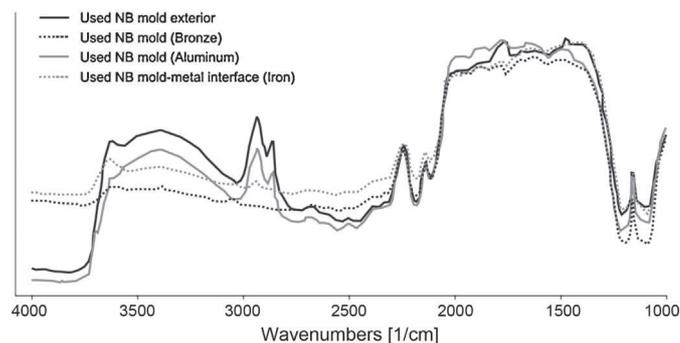


Fig. 3. Mid-infrared spectra of natural binder (NB) sand samples under different thermal conditions.

degradation [16]. The new AU sand and sand from the aluminum mold-metal interface show distinct bands associated with C–H stretching at 2851 and 2920  $\text{cm}^{-1}$ . However, the intensity of these bands decreased in the bronze core sand and were not present in iron core sand, suggesting more degradation of the resin binders occurred. This trend was also supported by the total carbon data, as the respective concentrations in the used AU aluminum, bronze, and iron core sands were 1.4-, 1.8-, and 10.1-fold lower than in the new AU sand (Table 1).

This above mentioned trend also occurred with the NB sand where bands associated with C–H stretching were present in the aluminum core sand, but were not present in the bronze core sand (Fig. 3). The MIR spectrum of NB sand from the mold-metal interface of an iron casting shows small C–H bands, which are likely present because a mold can dissipate heat more quickly than a core which is completely surrounded by molten metal. As a result, incomplete thermal degradation of the NB occurred, but this outcome could vary depending upon the casting and mold size. Similar to the AU results, the total carbon concentrations in the used NB

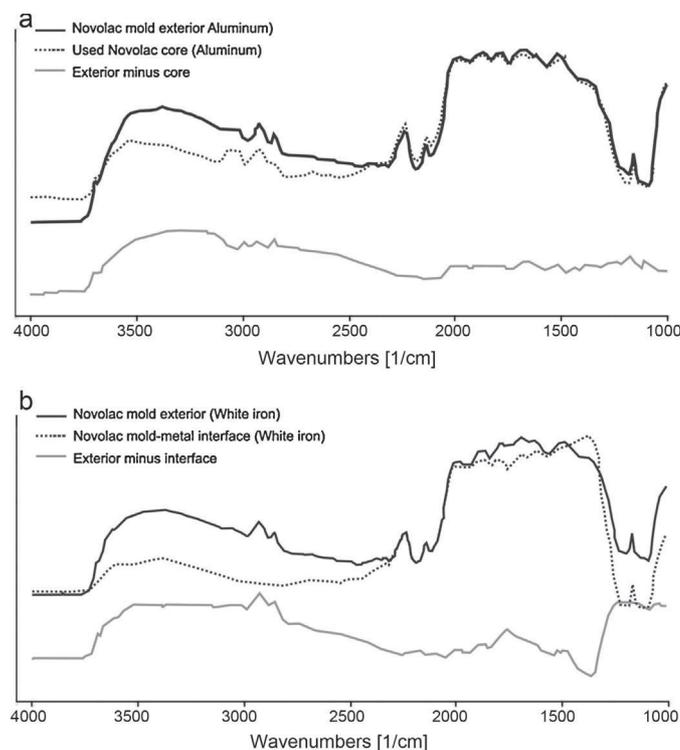


Fig. 4. Mid-infrared spectra of a Novolac molding sand from an (a) aluminum and (b) white iron casting.

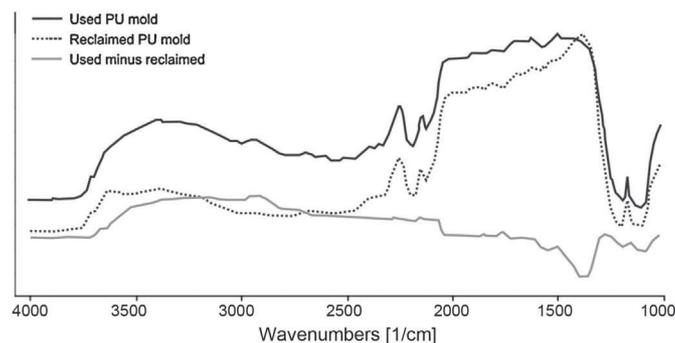


Fig. 5. Mid-infrared spectra of phenolic urethane (PU) molding sand before and after mechanical and thermal recovery.

sands were substantially lower than the new NB sand and lowest in the sand from the bronze and iron castings (Table 1).

Fig. 4a presents the spectra of Novolac sand from the mold exterior (no exposure to molten metal) and a used core from an aluminum casting. The spectra indicate that the used Novolac core sand contains intact resin or associated residuals which are likely present because of the low casting temperature of aluminum. In contrast, Fig. 4b presents the spectra of Novolac sand from a mold exterior and mold-metal interface from a white iron casting, which is poured at more than twice the temperature of aluminum. As a result, binder degradation is more complete as noted by the subtraction spectrum (mold exterior minus used core). This provides evidence that used Novolac sands from iron castings should contain a lower resin content than used sands from aluminum castings. This is supported by the total carbon data, as the respective concentrations in the used Novolac sand from the aluminum and white iron castings were 1.3- and 8.2-fold lower than sand from the mold exterior (Table 1). In addition, the spectrum of sand from the white

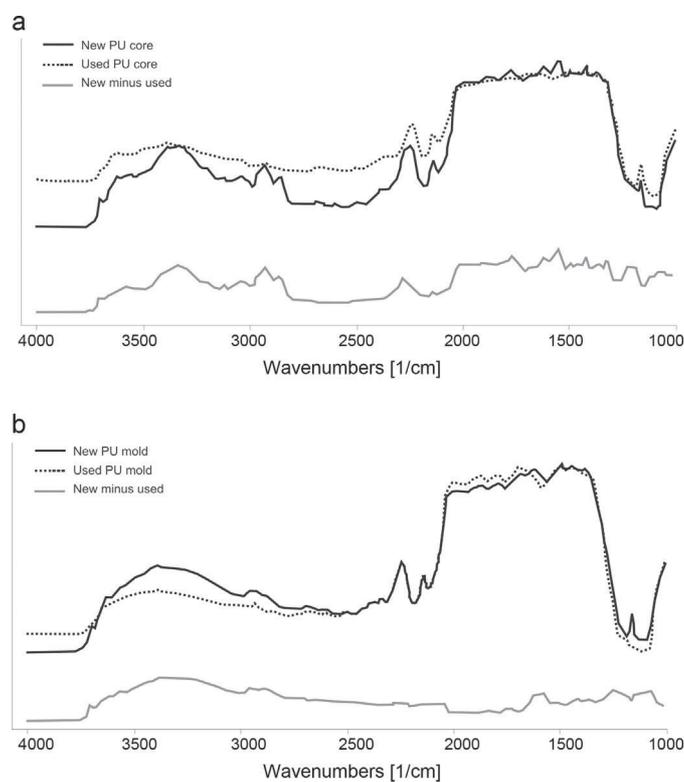


Fig. 6. Mid-infrared spectra of new and used phenolic urethane (PU) (a) molding and (b) core sands from an iron casting.

iron mold–metal interface is similar to Novolac sand that was ashed to remove all organics (data not shown).

As part of the casting processes, used sands are typically reclaimed and reconditioned to make new molds and cores. Fig. 5 presents MIR spectra of PU molding sand before and after recovery by mechanical crushing, thermal treatment (250 °C for approximately 5 min), and removal of silica and binder dust via cyclonic processing. The subtraction spectrum indicates that residual organics were removed during the reclamation process, which was also confirmed by the total carbon data. Reclaimed PU molding sand contained 46% less total carbon than used non-reclaimed molding sand (Table 1).

Fig. 6a and b shows the spectra of the new and used PU molding and core sands from an iron casting, respectively. The spectrum of new PU molding sand contained a small C–H band at 2920 cm<sup>-1</sup> that was slightly reduced in the spectrum from the used molding sand. However, the new PU core sand spectrum contained distinct C–H bands at 2865 and 2930 cm<sup>-1</sup>, which were substantially smaller in the used core sand. This latter result is likely due to greater exposure of the core sands to the molten iron, resulting in increased thermal degradation of the PU binder. Overall, the greatest reductions in total carbon occurred in the core sand.

#### 4. Conclusions

Mid-infrared spectroscopy can be used to show the changes in chemically bound metal casting sands. Virgin silica sand has a significant influence on the spectra of chemically bonded sand because they are largely composed of this material. However, bands associated with C–H stretching in organic binders were detected in most foundry sands. The MIR spectra of the foundry sands showed changes under different metal casting temperatures, which contributed directly to the degradation of the resin binders. While the identity of the thermal degradation byproducts is not known, the determination of total carbon provided additional evidence that changes in the chemical composition of the resin bonded sands occurred during metal casting. The results indicate that molding and core sands from high temperature castings, such as iron, will contain the least amount of residual binder. While speculative, sands with less residual binder should be safer to use in various beneficial use applications from an environmental health standpoint and MIR spectroscopy could potentially be used as a rapid and low cost method to identify those sands.

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