

Pyrolysis of carbonaceous foundry sand additives: Seacoal and gilsonite

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Abstract

Seacoal and gilsonite are used by the foundry industry as carbonaceous additives in green molding sands. In this study, pyrolysis was used to simulate the heating conditions that the carbonaceous additives would experience during metal casting. Gas chromatography–mass spectrometry was used to tentatively identify major organic products generated during their pyrolysis at 500, 750, and 1000 °C. A number of compounds of environmental concern were identified during the pyrolysis of seacoal and gilsonite, including substituted benzenes, phenolics, and polycyclic aromatic hydrocarbons (PAHs). These thermal decomposition products, and especially PAHs, were generated at each pyrolysis temperature in all foundry sands containing seacoal. In gilsonite-amended sand, however, mainly alkanes and alkenes were identified at 500 and 750 °C and PAHs at 1000 °C. Compared to seacoal, the most intense peaks occurred during the pyrolysis of sand containing gilsonite. The greatest loss of pyrolyzable material also occurred during heating of gilsonite-amended sand from ambient temperature to 1000 °C in a thermogravimetric analyzer. The results obtained from this study will be useful to green sand foundries looking to reduce volatile hydrocarbon emissions.

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Keywords: Bituminous coal; Foundry; Gilsonite; Green sand; Phenolics; Polycyclic aromatic hydrocarbons; Pyrolysis; Seacoal

1. Introduction

Green sands are commonly used by the foundry industry to make metalcasting molds and are a mixture of silica sand, bentonite clays, carbonaceous additives, and water [1]. The term green is not related to the color of the sand, but denotes the presence of water in the molding sand prior to the addition of molten metal. Bentonite clay is mulled over the surface of the sand particles, which causes them to adhere to each other when compressed. In addition to clay, carbonaceous materials are added to the molding mixture to produce a reducing atmosphere during the metal casting process and minimize casting defects [2]. One of the most commonly used carbonaceous additives is finely crushed bituminous coal, also referred to as seacoal. Gilsonite, a natural asphaltic material, is another additive used by some foundries.

During the casting process, the molten metal causes thermal decomposition of the carbonaceous additives, which results in the formation of potentially hazardous organics that are emitted to the atmosphere and condense in the molding sand.

To date, many reports have addressed organic emissions from green sand molds [3–7]. In a research foundry operated by the Casting Emission Reduction Program (CERP), it was found that hazardous air pollutant (HAP) emissions were about 13 times higher from molds containing seacoal than those without [8]. Some of the most abundant HAPs identified were benzene, toluene, xylenes, ethylbenzene, and naphthalene, which accounted for roughly 87% of the total mass. Other organics generated during metal casting with green sand molds were phenol, dimethylphenol, trimethylbenzene, propylbenzene, methyl-naphthalene, dimethylnaphthalene, ethyltoluene, and cresol [3,4,8].

Each year the U.S. foundry industry landfills about 10 million tonnes of sand because it is no longer suitable to make metalcasting molds [9]. Alternatively, waste molding sands, such as green sands, can be used as a component in manufactured soils (e.g., topsoil and potting soil) [10,11]. Because there is interest in protecting foundry worker health and using green sands in manufactured soils, concern over potentially harmful thermal decomposition products is warranted. The objectives of this research were (i) to utilize gas chromatography–mass spectrometry (GC–MS) to tentatively identify thermal decomposition products from green sands and silica sand amended with seacoal or gilsonite during pyrolysis at 500, 750, and 1000 °C

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and (ii) assess the loss of pyrolyzable material during gradual heating in a thermogravimetric analyzer. Pyrolysis, when combined with GC–MS, is an effective analytical technique that has been used to investigate thermally produced organic compounds from foundry sand additives and other carbonaceous materials [12–16].

2. Experimental

2.1. Silica sand, carbonaceous additives, and green sands

Silica sand (type F-50), which is specifically graded for use as foundry molding sand, was purchased from U.S. Silica Co. (Ottawa, IL). Seacoal and gilsonite samples were obtained from a foundry. The silica sand was amended with 5% seacoal or gilsonite (w/w), thoroughly homogenized, then crushed to a fine powder with a mortar and pestle before pyrolysis. Fresh green sand was obtained from a major automotive manufacturer and contained 92% silica sand, 4% sodium bentonite, 2% calcium bentonite, and 2% seacoal (w/w, dry wt.). The simulated green sand, which was manufactured in our laboratory to mimic sand used by a Pennsylvania iron foundry, contained 90% silica sand, 7.3% calcium bentonite, 2.5% seacoal, and 0.2% gilsonite (w/w, dry wt.).

2.2. Pyrolysis–gas chromatography–mass spectrometry

Pyrolysis was performed using a Chemical Data Systems Pyroprobe model 2000 (Oxford, PA, USA). Ten mg samples were placed into quartz tubes, which were heated at 500, 750, and 1000 °C for 30 s. The pyrolyzate was swept directly into a GC coupled to an ion trap MS (Finnigan MAT GCQ, San Jose, CA, USA). The GC was equipped with a DB-5ms capillary column (30 m, 0.25 mm × 0.25 μm, J & W Scientific, Folsom, CA, USA). The operating conditions were as follows: carrier gas, helium, 40 cm s⁻¹; splitless injector temperature, 300 °C; pyrolysis–GC interface temperature, 200 °C; GC–MS transfer line temperature, 300 °C; ion trap temperature, 200 °C; column temperature, 50 °C for 10 min, then ramping at 5 °C min⁻¹ to 300 °C. Mass spectra were obtained by electron impact at 70 eV from 40 to 650 *m/z* (1 scan s⁻¹). For tentative peak identification, mass spectra were compared to those in the NIST mass spectral search program (Version 2.0, Chem SW, Fairfield, CA, USA).

2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the sodium bentonite, calcium bentonite, uncoated silica sand, silica sand amended with 5% seacoal or gilsonite, green sand, and simulated green sand was conducted using a TA Q500 analyzer (TA Instruments, New Castle, DE, USA). Dried samples were subjected to a temperature ramping program from room temperature to 1000 °C at a rate of 150 °C min⁻¹. The nitrogen flow rate to the balance and furnace was 40 and 60 mL min⁻¹, respectively.

3. Results and discussion

The pyrolysis of pure silica sand and bentonite clay (both sodium and calcium bentonite) at 500, 750, and 1000 °C resulted in the production of a few low intensity peaks that generally diminished in size with increasing temperature (data not shown). The data suggest that these inorganic molding sand components contain trace quantities of organic material, but this is not the parent material for the large quantity of thermal decomposition products that are generated during metal casting.

Fig. 1a–c shows the gas chromatograms produced during the pyrolysis of seacoal-amend sand at 500, 750, and 1000 °C, respectively. The compounds in the pyrolyzates, which were tentatively identified using MS, can be found in Table 1 along with their respective retention times and molecular weights. At 500 °C the major compounds identified were phenolics, such as methylphenol and dimethylphenol, and various methyl and ethyl substituted naphthalenes. Phenolics and polycyclic aromatic hydrocarbons (PAHs) have been listed as priority pollutants by

Table 1
Tentative GC–MS characterization of products in the pyrolyzates

Peak	RT	Assignment	MW
1	6:10	Ethylbenzene	106
2	12:47	1-Ethyl-2-methylbenzene	118
3	13:07	Phenol	94
4	15:11	1-Propynylbenzene	116
5	16:22	2-Methylphenol	108
6	17:18	1-Ethoxy-4-methylbenzene	136
7	17:20	3- and 4-Methylphenol	108
8	19:53	2,5-Dimethylphenol	122
9	20:47	2,3-Dimethylphenol	122
10	20:51	Naphthalene	128
11	20:55	2-Ethenyl-1,3,5-trimethylbenzene	146
12	21:52	2-Methyl-8-propyldodecane	226
13	23:25	2-Ethyl-4-methylphenol	136
14	24:25	2-Methylnaphthalene	142
15	24:27	(E)-5-Tetradecene	196
16	24:51	1-Methylnaphthalene	142
17	26:42	2,6-Dimethylheptadecane	268
18	26:48	2-Ethenylnaphthalene	154
19	27:13	2-Ethyl-naphthalene	156
20	27:32	1,7-Dimethylnaphthalene	156
21	27:52	1,2-Dimethylnaphthalene	156
22	28:03	1,8-Dimethylnaphthalene	156
23	28:45	Acenaphthylene	152
24	28:52	Tridecanol	200
25	29:01	4-Methyloctadecane	268
26	30:28	Dibenzofuran	168
27	30:37	1,6,7-Trimethylnaphthalene	170
28	31:30	3-Ethyl-1-methylnaphthalene	170
29	31:33	1,4,5-Trimethylnaphthalene	170
30	32:08	Fluorene	166
31	32:09	1,4,6-Trimethylnaphthalene	170
32	32:50	1,2-Dimethyl-4-(phenylmethyl)-benzene	196
33	33:25	1-Methyl-7-(1-methylethyl)-naphthalene	184
34	33:35	2,6,10-Trimethylpentadecane	254
35	34:10	1,6-Dimethyl-4-(1-methylethyl)-naphthalene	198
36	35:25	1-Nonadecane	266
37	36:40	Anthracene	178
38	37:05	2,6,10,14-Tetramethylhexadecane	282
39	38:54	(Z)-9-Octadecenal	266

Table 2
Comparison of the tentative products identified in the pyrolyzates at each of the pyrolysis temperatures

Peak	Assignment	500 °C				750 °C				1000 °C			
		SCL	GIL	FGS	SGS	SCL	GIL	FGS	SGS	SCL	GIL	FGS	SGS
1	Ethylbenzene			+			+					+	
2	1-Ethyl-2-methyl benzene									+			
3	Phenol							+					+
4	1-Propynylbenzene					+				+	+	+	+
5	2-Methylphenol	+			+	+		+	+				
6	1-Ethoxy-4-methylbenzene								+				
7	3- and 4-Methylphenol	+				+		+					
8	2,5-Dimethylphenol	+				+							
9	2,3-Dimethylphenol					+							
10	Naphthalene			+				+	+	+	+	+	+
11	2-Ethenyl-1,3,5-trimethylbenzene				+								
12	2-Methyl-8-propyldodecane		+										
13	2-Ethyl-4-methylphenol					+							
14	2-Methylnaphthalene	+		+		+		+	+	+	+	+	+
15	(E)-5-tetradecene		+				+						
16	1-Methylnaphthalene			+	+			+	+	+	+	+	+
17	2,6-Dimethylheptadecane		+										
18	2-Ethenylnaphthalene									+	+		+
19	2-Ethyl-naphthalene			+									
20	1,7-Dimethylnaphthalene			+				+				+	
21	1,2-Dimethylnaphthalene									+			
22	1,8-Dimethylnaphthalene			+	+	+		+	+			+	+
23	Acenaphthylene									+	+		+
24	Tridecanol							+					
25	4-Methyloctadecane		+										
26	Dibenzofuran									+			
27	1,6,7-Trimethylnaphthalene			+									
28	3-Ethyl-1-methylnaphthalene	+											
29	1,4,5-Trimethylnaphthalene				+	+			+				
30	Fluorene							+		+	+	+	+
31	1,4,6-Trimethylnaphthalene	+			+	+			+				
32	1,2-Dimethyl-4-(phenylmethyl)-benzene			+									
33	1-Methyl-7-(1-methylethyl)-naphthalene					+							
34	2,6,10-Trimethylpentadecane		+					+					
35	1,6-Dimethyl-4-(1-methyl ethyl)-naphthalene	+											
36	1-Nonadecane		+					+					
37	Anthracene									+	+		
38	2,6,10,14-Tetramethylhexadecane		+					+					
39	(Z)-9-octadecenal							+					

SCL, seacoal-amended sand; GIL, gilsonite-amended sand; FGS, fresh green sand; SGS, simulated green sand.

the U.S. Environmental Protection Agency (U.S. EPA). At a retention time >35 min, a series of *n*-alkane and *n*-alkene peaks is easily recognizable in the chromatogram (Fig. 1a). Similar results were obtained by Stankiewicz et al. [17], who found that pyrolyzates from bituminous coal (when pyrolyzed at 610 °C for 20 s) were generally dominated by long-chain alkanes and alkenes, but also contained C₁–C₃ alkyl benzenes, C₀–C₂ alkyl phenols, and C₂ alkyl naphthalene. Organic products generated during the pyrolysis of seacoal at 750 °C, were similar to those at 500 °C (Table 2), except that the peak intensity was considerably higher. The most intense peak was identified as 1,4,6-trimethylnaphthalene (no. 31), followed by 3- and 4-methylphenol (no. 7) and then 1,4,5-trimethylnaphthalene (no. 29). While PAHs containing two condensed rings were identified during pyrolysis of the seacoal at 500 and 750 °C, 3-ring products such as acenaphthylene, fluorene, and anthracene were identified at 1000 °C (Fig. 1c). Dibenzofuran, a heterocyclic

organic compound, which has been detected in emissions during the combustion of coal, diesel fuel, and biomass, was tentatively identified as peak no. 26.

It is well known that the incomplete combustion of coal (as well as other organic materials), results in the formation of PAHs, some of which are human carcinogens [18–20]. Mas-tral et al. [20] found that maximum emission of PAHs during the combustion of a low-rank coal occurred at 750–850 °C. In their study, total PAH emissions were shown to increase about 250 times when the oxygen level was decreased from 20 to 5% during the combustion reaction. During the casting process, the molding sand in close proximity to the metal interface will easily reach temperatures that will cause the pyrolysis of carbonaceous additives, as aluminum is poured at about 750 °C and iron (gray, ductile, and malleable) is poured at 1300–1500 °C. Seacoal and gilsonite are added to the molding sand to produce a reducing atmosphere in the mold, since oxygen

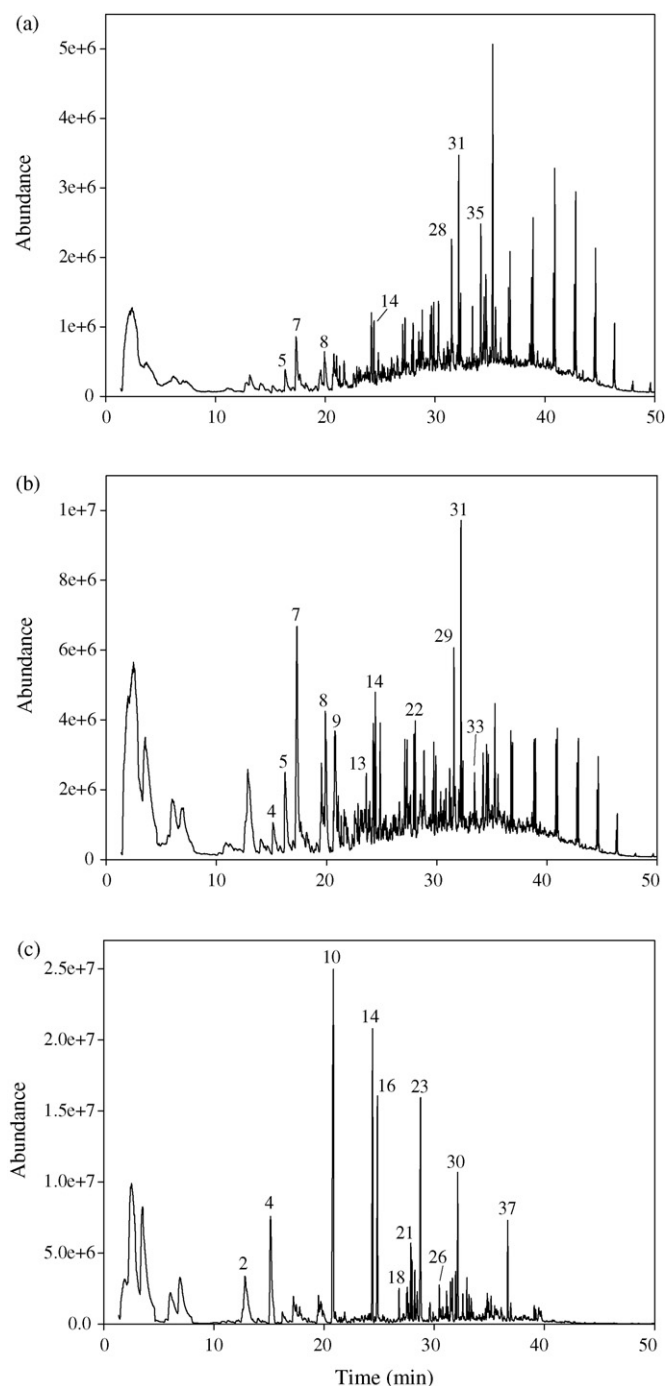


Fig. 1. Gas chromatogram of pyrolysis products from silica sand amended with 5% seacoal (w/w) at (a) 500 °C, (b) 750 °C, and (c) 1000 °C. Assignments of the labeled peaks are shown in Table 1.

causes surface defects on most metals. As oxygen is consumed within the mold during casting, one can expect maximum PAH production to occur. Fabbri and Vassura [15] pyrolyzed bituminous coal at 1000 °C for 60 s; products identified by MS were naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. While we did not identify acenaphthene, phenanthrene, fluoranthene, and pyrene in the pyrolyzates from the seacoal-amended sand at 1000 °C in our study (Table 1),

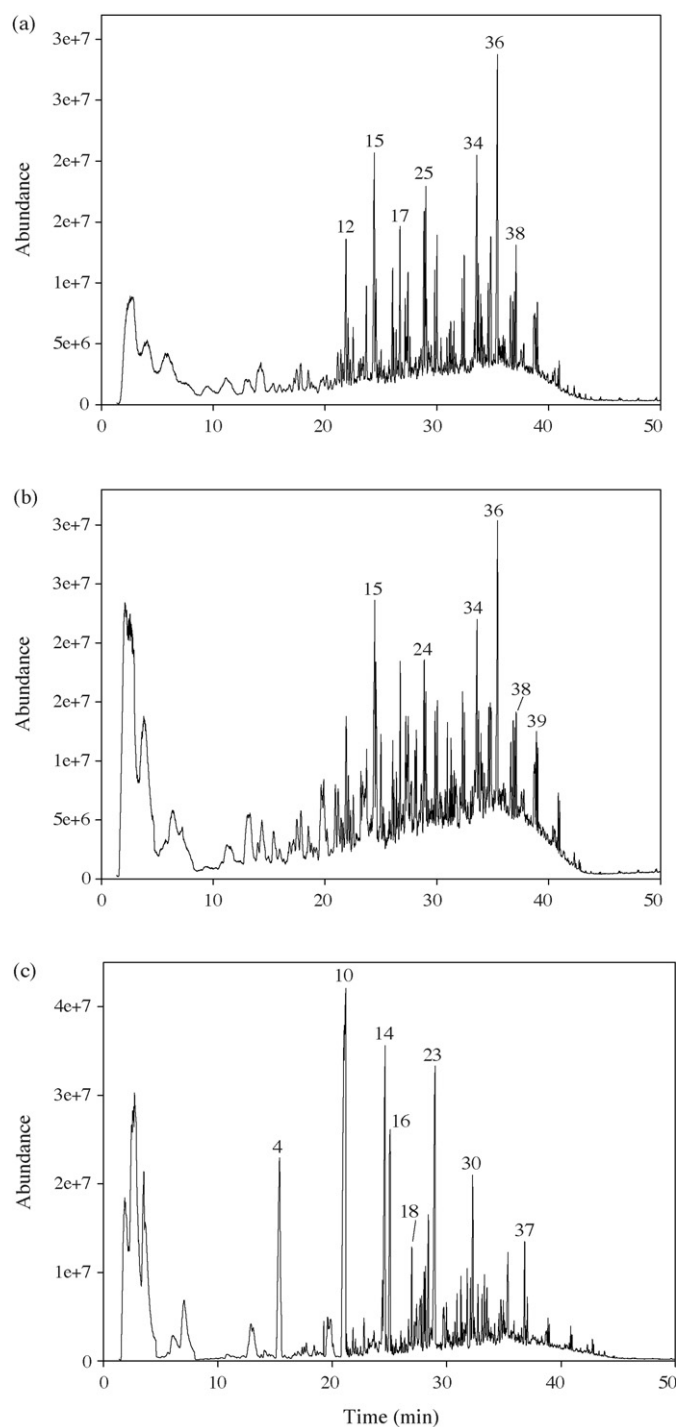


Fig. 2. Gas chromatogram of pyrolysis products from silica sand amend with 5% gilsonite (w/w) at (a) 500 °C, (b) 750 °C, and (c) 1000 °C. Assignments of the labeled peaks are shown in Table 1.

the elution order of the remaining PAHs was the same as obtained by Fabbri and Vassura [15].

The gas chromatograms associated with the pyrolysis of gilsonite-amended sand at 500, 750, and 1000 °C can be found in Fig. 2 (see Table 1 for the tentative peak assignments). Overall, the peak intensity was greater than during the pyrolysis of seacoal-amended sand. Compared to the thermal decomposition products from seacoal-amended sand at 500 and 750 °C, which

were mainly substituted phenolics and naphthalenes, organics in the pyrolyzates from gilsonite-amended sand were mostly identified as alkanes and alkenes. The organic compounds in the pyrolyzate from gilsonite-amended sand at 1000 °C, however, were similar to those from seacoal when pyrolyzed at the same temperature. Compounds identified were 1-propynylbenzene, naphthalene, 2- and 1-methylnaphthalene, 2-ethylnaphthalene,

acenaphthylene, fluorene, and anthracene. The most intense peak was tentatively identified as naphthalene (no. 10), followed by 2-methylnaphthalene (no. 14), acenaphthylene (no. 23), 1-methylnaphthalene (no. 16), and then 1-propynylbenzene (no. 4). Based upon the fact that no major PAH peaks were identified during pyrolysis of gilsonite at 500 and 750 °C, one could speculate that use of gilsonite in green sand molds for aluminum castings (due to the lower casting temperature at around 750 °C) might contribute to fewer PAH emissions when compared to that of seacoal. In contrast, many PAHs were tentatively identified when gilsonite was pyrolyzed at 1000 °C, which is near the casting temperature for iron.

We obtained a fresh green sand sample from a U.S. manufacturer of automotive engine blocks to compare the pyrolysis products to that from the gilsonite- and seacoal-amended sands. The fresh green sand was composed of 92% silica sand, 4% sodium bentonite, 2% calcium bentonite, and 2% seacoal. After pyrolyzing the green sand at 500, 750, and 1000 °C, the organic compounds in the pyrolyzates were tentatively identified. The associated chromatograms are shown in Fig. 3a–c, respectively. At 500 °C, the compounds in the pyrolyzates were mainly identified as methyl and ethyl substituted naphthalenes; the peak with the greatest intensity was identified as 2-methylnaphthalene (i.e., peak no. 14). Similar compounds were obtained at 750 and 1000 °C, except that a 3-ring PAH, fluorene, was also identified at both temperatures. When sand containing only seacoal was pyrolyzed at 750 and 1000 °C, fluorene was also tentatively identified; however, at 1000 °C acenaphthylene and anthracene were identified in addition to fluorene (Fig. 1b and c). In a 1999 CERP study [8], the following PAHs were detected in emissions from a green sand mold (containing about 5% seacoal) for casting with iron: 1- and 2-methylnaphthalene, 1,3-dimethylnaphthalene, naphthalene, and anthracene. The fact that we identified fewer 3-ring PAHs in the pyrolyzates from the green sand at 1000 °C may be related to the lower concentration of seacoal at 2% versus 5% in the silica sand. This is partially supported by the observation that the intensity of the highest peaks (i.e., nos. 10 and 14, naphthalene and 2-methylnaphthalene, respectively) were about

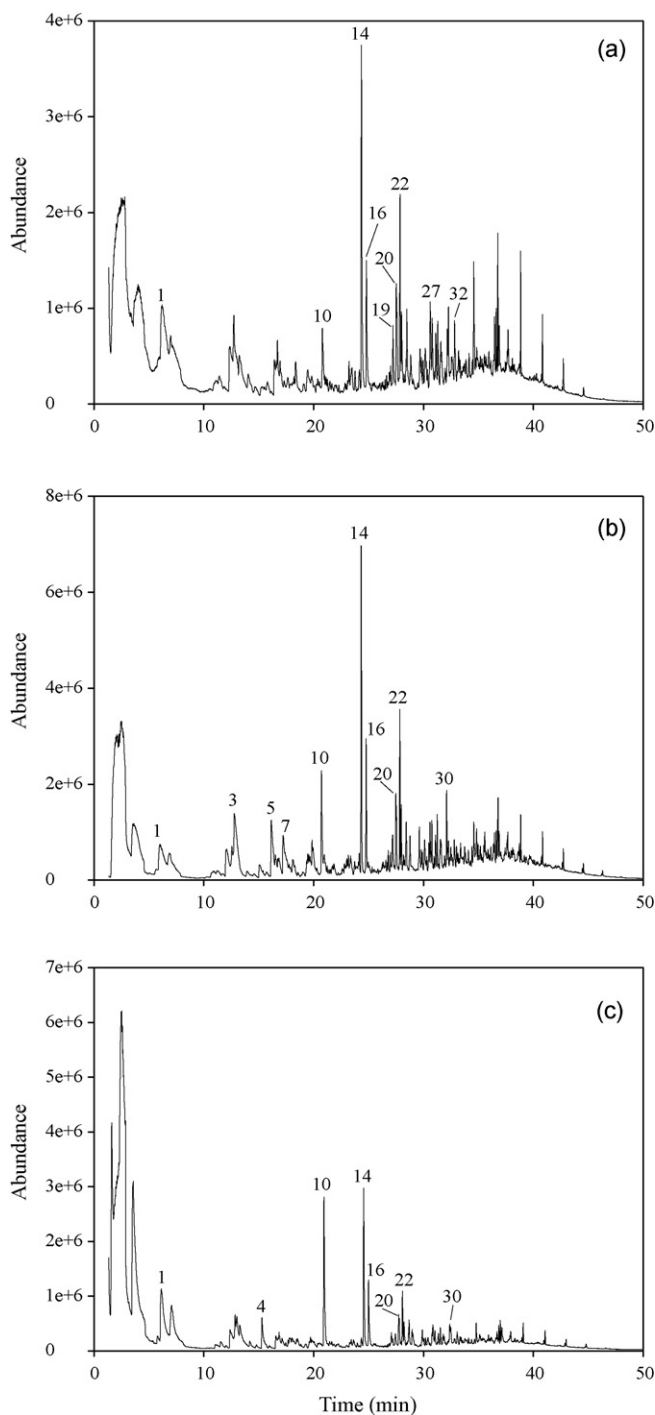


Fig. 3. Gas chromatogram of pyrolysis products from fresh green sand at (a) 500 °C, (b) 750 °C, and (c) 1000 °C. The fresh green sand contained 92% silica sand, 4% sodium bentonite, 2% calcium bentonite, and 2% seacoal (w/w). Assignments of the labeled peaks are shown in Table 1.

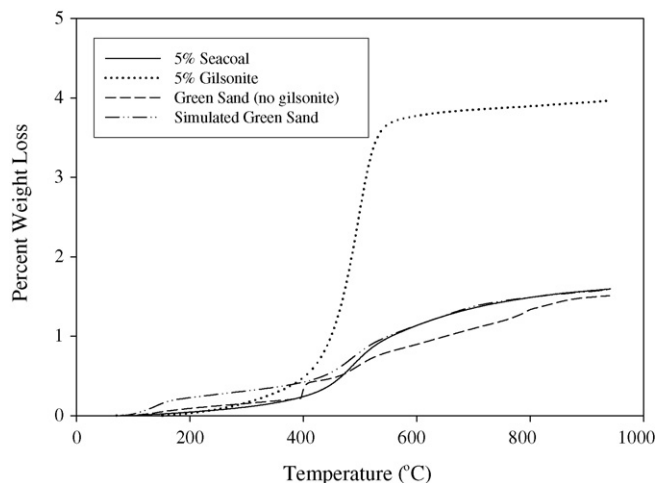


Fig. 4. Thermogravimetric analysis of the seacoal-amended sand, gilsonite-amended sand, fresh green sand, and simulated green sand.

8 times lower in the pyrolyzates from the green sand (Fig. 3c) than from the seacoal-amended sand (Fig. 1c).

The simulated green sand tested in this study contained 0.2% gilsonite along with 2.5% seacoal, 7.3% calcium bentonite and 90% silica sand. When gilsonite is used with seacoal in green sand molds, it is often used at much lower concentrations. Thermogravimetric analysis of the gilsonite-amended silica sand showed that a 4% loss of pyrolyzable material occurred, com-

pared to a 1.6% loss in the seacoal-amended sand (Fig. 4). This means that 80% and 32% of the gilsonite and seacoal in the amended sand were consumed during the TGA, respectively. While material burn off is a beneficial characteristic, the use of too much gilsonite and/or seacoal in a green sand will result in the generation of excess smoke and HAPs within a foundry. Material losses in the green sand and simulated green sand during TGA were similar to the seacoal-amended sand.

The gas chromatograms produced during the pyrolysis of the simulated green sand are shown in Fig. 5. The compounds identified in the pyrolyzates were very similar to those identified in the pyrolyzates from the seacoal-amended sand and fresh green sand sample, which did not contain gilsonite (Table 2). At all three pyrolysis temperatures, the majority of the compounds were tentatively identified as PAHs, especially methyl and ethyl substituted naphthalenes; however, a few of the chromatogram peaks were also identified as phenolics and substituted benzenes. At a retention time >35 min, the characteristic series of peaks associated with long-chain hydrocarbons was present in the 500 and 750 °C chromatograms (Fig. 5a and b, respectively). The peaks with the greatest intensity within these chromatograms (i.e., no. 31) were identified as 1,4,6-trimethylnaphthalene, while at 1000 °C the most intense peak was associated with naphthalene (no. 10). The addition of 0.2% gilsonite to the simulated green sand did not substantially change the composition of the thermal decomposition products, when compared to the fresh green sand without gilsonite. Though the intensity of the peaks in Fig. 5b and c were substantially greater than those in Fig. 3b and c (i.e., pyrolysis temperature of 750 and 1000 °C, respectively).

4. Conclusions

Seacoal and gilsonite are used by the foundry industry as carbonaceous additives in green molding sands, and it appears that these additives will continue to be used well into the foreseeable future. The tentative identification of organics during the pyrolysis of seacoal and gilsonite in foundry sands revealed that a number of compounds of environmental concern were generated, including substituted benzenes and phenolics, and PAHs. Compared to seacoal, gilsonite substantially increased the intensity of the peaks, suggesting that it will cause more volatile hydrocarbon emissions during metal casting. While the pyrolysis technique may not accurately mimic the conditions during metal casting, our results suggest that it is useful to determine the potential of molding sand additives to cause air pollution problems in the foundry environment. To better assess the risks of using molding sands in manufactured soils, efforts are currently underway to quantitatively determine organics in sands from aluminum, iron, and steel foundries [21].

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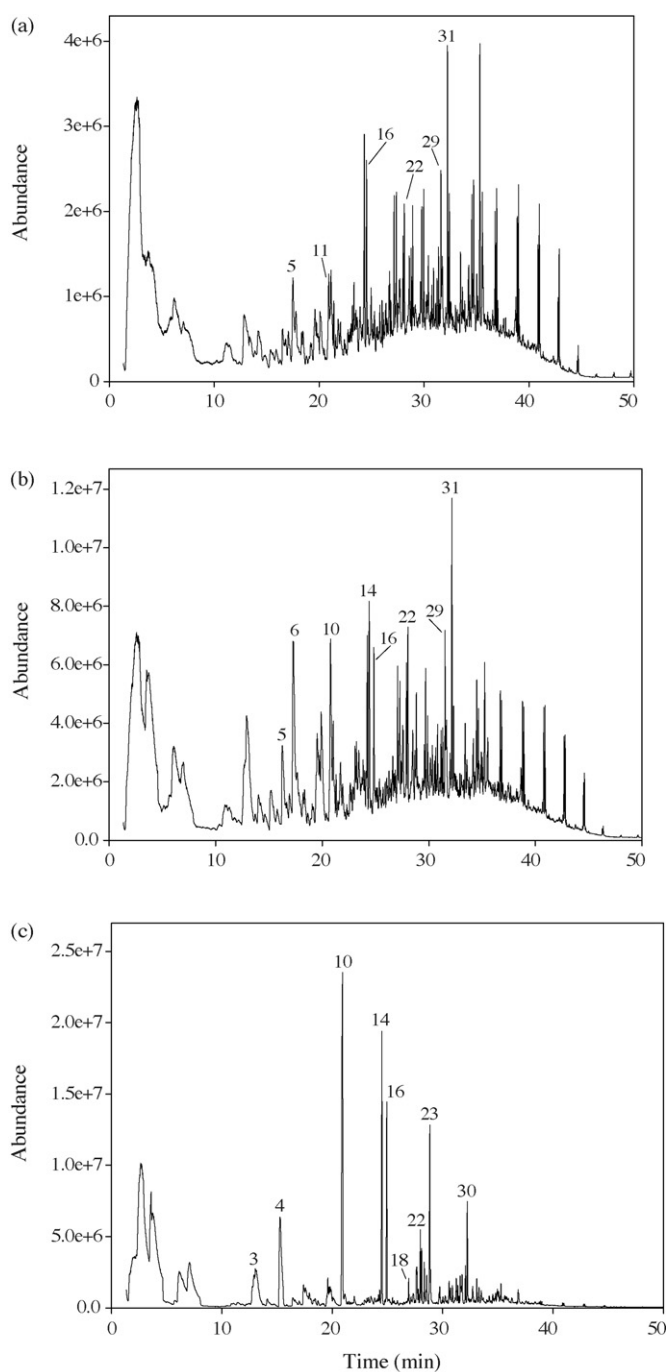


Fig. 5. Gas chromatogram of pyrolysis products from simulated green sand at (a) 500 °C, (b) 750 °C, and (c) 1000 °C. The simulated green sand contained 90% silica sand, 7.3% calcium bentonite, 2.5% seacoal, and 0.2% gilsonite (w/w). Assignments of the labeled peaks are shown in Table 1.

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