Amelioration of Physical Strength in Waste Foundry Green Sands for Reuse as a Soil Amendment

J. P. de Koff* and B. D. Lee Purdue University
R. S. Dungan USDA-ARS

To avoid increasing costs of landfill disposal, it has become increasingly important for U.S. foundries to identify beneficial reuses for the 8 to 12 million tons of waste foundry sand (WFS) generated annually. A major drawback to the reuse of some WFSs as a soil amendment is their high soil strength, under dry conditions, where root growth may be limited. Fifteen WFSs were analyzed for strength to rupture using lab-formed clods, exchangeable cations (Na, Mg, Ca), metal oxide concentration (Fe, Mn, Al, Si), cation exchange capacity (CEC), and % clay. Several WFS samples from gray iron foundries demonstrated high strength to rupture values (> 1.5 MPa), and could potentially restrict root growth in amended soils. The percentage of Na-bentonite exhibited a positive correlation ($R^2 = 0.84$) with strength to rupture values. When WFSs containing more Na-bentonite were saturated with 1 mol L$^{-1}$ Ca ions, strength values decreased by ~70%. Waste foundry sands containing less Na-bentonite were saturated with 1 mol L$^{-1}$ Na ions and exhibited a threefold increase in strength. Additions of gypsum (up to 9.6 g kg$^{-1}$ sand) to high strength waste foundry sands also caused decreases in strength. These results indicate that high strength WFSs have properties similar to hardsetting soils which are caused by high Na$^+$ clay content and can be ameliorated by the addition of Ca$^{2+}$.

Sand is used by the foundry industry to create metalcasting molds. Molten metal at a high temperature is poured into these molds and, once cool, the molds are broken apart to yield the metal casting. The molding sands are often reclaimed and used to make new molds, but eventually the sand particles are no longer useful due to a reduction in grain size. When this occurs, the sands are disposed in private or public landfills around the U.S. at a rate of 8 to 12 million tons per year (Lindsay and Logan, 2005) and at an annual cost of $100 to $250 million (Indiana Cast Metals Association, 2008). The USEPA has deemed 98% of waste foundry sand (WFS) as non-hazardous and believes that other uses can be found for this material outside of landfills (USEPA, 2002).

The majority of foundry sands are made up of uniform, high-quality quartz sand (85–95%) in the fine to medium particle size range. Sea coal (2–10%) is used as an additive to produce a reducing atmosphere and improve the casting finish (Winkler and Bol’shakov, 2000). The main differences in foundry sands lie in how the sands are bonded to each other; either with clay or organic resins. Clay-bonded sands are commonly called ‘green sands’ and contain ben-tonite clay (4–10%) (Winkler and Bol’shakov, 2000). Organic resins are used either to form the entire mold or cores, which create an internal cavity in the metal casting. The core sands are bound together using resins that may contain a variety of organic components, such as phenol, formaldehyde, and furfuryl alcohol (Gardziella et al., 2000). With the high temperatures (750–1000°C) that these cores are exposed to, most of these chemical binders are thermally degraded during casting, especially those closest to the molten metal interface (Dungan and Reeves, 2005, 2006). In foundries using both green sand and cores, the waste stream is generally a homoge-nous mixture of both with lesser quantities of core sand.

One possible use for WFSs is as a component in manufactured soils. A manufactured soil is created through the blending of different mineral and organic components including sand, clay, peat, and compost to create specified properties for a specified purpose (Kool-en and Rossignol, 1998). A manufactured soil containing WFS could then be used in a number of agricultural, suburban, or urban applications (Jing and Barnes, 1993; Lindsay and Logan, 2005). One potential obstacle to this use, however, is that some WFSs may

Abbreviations: CEC, cation exchange capacity; DI, deionized; EM, electron microscope; ESP, exchangeable sodium percentage; WFS, waste foundry sand; XRD, X-ray diffraction.
cause high soil strength. Lindsay et al. (2006) observed some high surface hardness in field plots using WFS for turf growth that was outside the acceptable range for recreational use. High soil strength can lead to adverse effects on turfgrass and crop root growth (Taylor, 1971; Bowen, 1976). Strength values 2.4 MPa can reduce plant emergence (Nabi et al., 2001) while values >2.0 MPa can cause stunted root growth (Lipec and Hakansson, 2000). Impedance to root growth has been linked to decreases in seedling growth rates and productivity (Sallih et al., 1998; Nambiar and Sands, 1992). The strength values for WFSs are currently unknown and may influence the use of these sands as a dominant constituent in a manufactured soil or soil amendment.

Naturally-occurring hardsetting soils exhibit the physical properties outlined above and their associated problems. These soils generally occur in semiarid regions of the world in the E, EB, or BE soil horizons that alternate between seasonally wet and dry conditions (Chartres et al., 1990). A hardsetting soil is typically characterized as having a high strength when dry, with a substantial loss of strength on the addition of water (slaking) (Mullins et al., 1987, 1990). The main contributing factors to this phenomenon are the presence of little or no aggregating agents (i.e., organic matter, iron oxides) (Mullins et al., 1990). Upon drying, the dispersed clay in these soils forms bridges between the sand particles causing high strength (Mullins et al., 1987; Lamotte et al., 1997b). The hardsetting properties are known to cause problems with plant growth due to adverse infiltration, aeration, seedling emergence, root elongation, and waterlogging (Mullins, 1998).

To use WFS in soils for the growth of turfgrass or crops, it is important to determine if WFS has strength properties that can adversely affect plant growth. The composition of WFS is very similar to that of hardsetting soils which makes it likely that WFS will also have similar adverse physical properties as well. For those WFSs that may exhibit high strength properties, the cause should be discovered and ameliorated. This study focused on both of these questions, and examined the chemical and mineralogical properties of WFSs, predominantly from foundries with a mixed green and core sand waste stream. Using hardsetting soils as a possible natural analog, an amelioration procedure was developed to amend the high strength WFSs.

Materials and Methods

The WFSs selected for this study originated from 15 foundries; 5 aluminum foundries and 10 gray iron foundries. The sands were sieved to <2-mm diameter and air dried before use. Particle size was determined by dry sieving the sand fractions after separating them from the silt and clay fractions using Na-hexametaphosphate, (NaPO₃)₆. The silt and clay fractions were determined by pipette (Gee and Bauder, 1986).

For XRD analysis, the clay fraction (<2 µm) was separated by centrifugation and the silt fractions (2–5 µm, 5–20 µm) were separated by sedimentation, following treatment with Na-hypochlorite to remove organic matter (Jackson, unpublished data, 1975). The <2-µm, 2- to 5-µm, and 5- to 20-µm fractions were subjected to several treatments before analysis by XRD. These treatments included K saturation and heating at 25, 350, and 550°C, Mg saturation, and Mg saturation + glycerol solvation. The clay fraction was applied to a glass slide as a paste (Theisen and Harward, 1962) and the silt fractions were applied by pipette as a suspension (Jackson, unpublished data, 1975). Both application procedures were followed by drying. The fine sand fraction was ground and side-packed powder mounted for XRD analysis. Mineralogy of particle size fractions was determined by standard X-ray diffraction (XRD) methods (using Co Kα radiation at 40 keV, 35 mA) using a PANalytical X’Pert Pro MPD diffraction system (PANalytical, Almelo, The Netherlands).

Values for soil strength were determined by testing the strength to rupture for the WFS using an adapted form of the modulus of rupture technique (Cochrane and Aylmore, 1992) used by Franzmeier et al. (1996). Discs for this test were produced by pouring each air-dried, <2 mm WFS, into 12.2-cm diameter holes in a 1-cm thick plastic plate. The samples were moistened with deionized (DI) water by capillarity for ~2 h, then dried in an oven at 40°C for ~48 h. Upon drying, the discs (12 per sample) were cooled in a desiccator for 30 min, removed from the plates, and ruptured using Wagner Force Dial FDK 20 and FDK 40 (Wagner Instruments, Greenwich, CT) force gauges which were able to measure forces between 1.0 and 20.0 kg. This can be converted to a detection range of 0.3 to 6.9 MPa. Those samples (three total) that could not be moistened by capillarity were not analyzed or used in this research.

Iron, manganese, aluminum, and silicon oxide concentrations were determined by citrate–dithionite extractions extracted in triplicate for each sample (Loeppert and Inskeep, 1996). Extracts were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Varian, Inc., Palo Alto, CA) for Fe, Mn, Al, and Si cations. Strength tests (outlined above) were performed on samples after a separate extraction for the removal of free oxides. Extractions were performed on 100-g samples with a citrate–bicarbonate–dithionite solution, washed with DI water, and dried at 30°C for 48 h.

Soluble Ca, Mg, and Na cations were determined by a 1:1 (soil/water, w/w) extraction (Rhoades, 1996). Exchangeable Ca, Mg, and Na cations were determined by a 1 mol L⁻¹ ammonium acetate (pH 7) extraction (Thomas, 1986) and corrected for soluble cations. Cation exchange capacity was determined using a modification of the ammonium acetate (pH 7) method using 1 mol L⁻¹ sodium acetate as the saturating solution and 1 mol L⁻¹ ammonium acetate as the replacing solution. Base cation concentrations were analyzed by ICP-OES (Applied Research Laboratories, Miami, FL).

Three WFSs with strength values ranging from 0.5 to 3.1 MPa were saturated with Ca²⁺, retested for strength, and compared to initial strength test results to identify any changes caused by Ca saturation. This method was used to determine if Na⁺ was causing the high strength properties and if Ca²⁺ could be used to
amend them. Waste foundry sand (~150 g) was added to 200 mL of 1 mol L\(^{-1}\) CaCl\(_2\) in a 250 mL centrifuge bottle, shaken for 10 min., and centrifuged for 10 min. at 1140 \(\times g\). The supernatant was discarded and the Ca saturation was repeated twice. Excess CaCl\(_2\) was removed by shaking the samples with 150 mL DI water for 10 min, centrifugation at 2000 rpm for 10 to 30 min, and discarding the supernatant liquid. This was repeated once more. After the washings, the samples were allowed to air dry, disks were formed, and soil strength was determined.

Three WFSs with strength values <0.3 MPa were saturated with Na\(^+\), retested for strength, and compared to initial stress test results to identify any changes caused by Na saturation. This method was used to determine if exchangeable Na\(^+\) could cause high strength on sands originally having low strength and dominated by exchangeable Ca\(^{2+}\). Waste foundry sand (~150 g) was added to 200 mL of 1 mol L\(^{-1}\) NaCl in a 250 mL centrifuge bottle, shaken for 10 min, and centrifuged for 10 min at 1140 \(\times g\). The supernatant was discarded and Na saturation was repeated twice. Excess NaCl was removed by shaking the samples with 150 mL DI water for 10 min, centrifugation at 2000 rpm for 10 to 30 min, and discarding the supernatant liquid. This was repeated once more. After the washings, the samples were allowed to air dry, disks were formed, and soil strength was determined.

Five WFSs with strength values \(\geq 1.5\) MPa, and similar particle size fractions, were used for amendment with powdered gypsum (CaSO\(_4\) \(\cdot\) 2H\(_2\)O). Based on each individual WFS’s exchangeable sodium percentage (ESP), enough gypsum was added to each WFS to decrease the ESP to 10 and correct for the lack of quantitative replacement and the solubility of gypsum in water as recommended by the U.S. Salinity Laboratory Staff (1954). This resulted in application rates ranging from 6.2 to 9.6 g gypsum per kilogram sand. The gypsum was mixed thoroughly with ~50 g of each WFS in a 100-mL beaker for around 10 min. The same procedure was then conducted for strength tests for each gypsum blend as previously explained above.

Clay dispersivity was calculated using 1:1 (WFS/water) mixtures (in triplicate for each sample) containing 25 g WFS and 25 mL DI water. The mixture was shaken in a 50 mL centrifuge tube for 1 h and centrifuged at 1140 \(\times g\) for 30 to 45 min. The supernatant was collected and flocculated drop-wise with a solution of 2 g L\(^{-1}\) Superfloc N-300 (Cytec Industries, Inc., West Paterson, NJ) polyacrylamide. The number of drops required for flocculation for each sample was recorded. This value was converted to a volume measurement based on the relative number of drops required to make up one mL Superfloc solution.

Images of two of the original clods ruptured by a force gauge were taken using a JEOL JSM-840 electron microscope (EM) (JEOL USA, Peabody, MA) to identify morphological differences between low and high strength sands.

Statistical analyses for error were performed by \(t\) tests performed on sample sizes of 3 (chemical and particle-size analyses) or subsample sizes of 9 to 12 (strength analyses) to give a 95% confidence interval.

Results and Discussion

Particle Size Analysis and X-Ray Diffraction

The greatest proportions of material were found in the fine- (23–69%) and medium- (16–62%) size sand fractions with much lower proportions in the silt- (0–9%) and clay- (1–10%) size fractions (Table 1). The major X-ray diffraction peaks for three aluminum (WFS 1, 2, 3) and three gray iron (WFS 6, 7, 8) WFSs revealed the existence of bentonite with a peak at 14 to 15 Å under Mg-saturation, which collapsed to ~12 Å under K-saturation and expanded to around 18 Å after glycerol solvation in the silt- and clay-size fractions. Quartz (~3.3 Å peak) was observed predominantly in the fine sand- and silt-size fractions (Fig. 1). All spectra were generally the same for each WFS analyzed and no crystalline metal oxides were present that could cause high strength.

The clay content was low among all WFSs and did not correlate with strength values. The EM images, however, showed the binding effect that the clay could have on particles, even at low concentrations (6%) (Fig. 2). The lower strength clod (rupture at <0.3 MPa) had clay flocculated on individual sand particles whereas there was evidence of clay-bridging between sand particles in the higher strength clod (rupture at 3.1 MPa).

Strength

The initial strength values of the measurable WFSs varied between 0.5 and 4.6 MPa (Tables 1 and 2), with higher strength values associated with WFS from gray iron foundries. Strength values increased with oxide removal by dithionite (Table 3). This effect was most likely produced by the Na salts added during the extraction procedure. Though iron, aluminum, manganese, and silicon oxides or hydroxides are known to enhance the strength characteristics of soil particles, the free metal oxides extracted did not correlate with observed strength values (Table 2).

Cation concentrations from soluble and exchangeable base cations and CEC also did not correlate with strength values. There was a correlation \((R^2 = 0.84)\) between the %Na clay (exchangeable Na/CEC \times % clay) in each WFS that was not below detection limits and its respective strength value (Fig. 3). One high strength WFS (#15) was not included in this correlation because it was above the detection limits of the force gauge. Using the upper limit of detection for the force gauge, along with the strength values of the remaining subsamples that were within detection limits, the lowest possible value calculated for WFS #15 would be 6.4 MPa. Based on the trend shown in Fig. 3, this value is higher than that expected for a WFS with an average %Na clay of 2.7%. One possible cause is the presence of colloidal clay which could cause high strength but would be less influenced by the cation present on exchange sites. The dispersivity of WFS #15 required the highest amount of flocculating agent for all replicates of all samples in the study (Table 4). This may indicate that for this particular WFS, smaller colloidal clay particles may have been more prevalent and influential in determining strength than the dominant cation on the exchange sites.

Saturation of lower strength WFS clods with 1 mol L\(^{-1}\) NaCl caused an increase in strength which was most likely due to the
replacement of Ca and Mg on the clays by Na (Fig. 4a). Waste foundry sand #1 was initially below detection limits (<0.3 MPa) and remained that way after Na saturation, which was probably due to its low (1%) clay content (Table 1). Saturation of higher strength WFS clods with 1 mol L\(^{-1}\) CaCl\(_2\) caused a decrease in strength as Ca presumably replaced Na on the clays (Fig. 4b). The high strength caused by Na-bentonite, even at low concentrations (6% clay), has been noted by other researchers (Grim and Güven, 1978; Odom, 1984). The addition of Na salts to Ca-bentonites has been shown to increase strength (Odom, 1984). Alternatively, when Na-bentonites, which are often used in geosynthetic landfill liners, were saturated with Ca, an increase in permeability was observed (Stern and Shackelford, 1998; Dananaj et al., 2005).

Additions of gypsum also decreased strength in the WFSs studied (Table 5), so that all high strength WFSs were below the 1.4 MPa threshold that could potentially stunt root growth. In hardsetting soils, the addition of gypsum has been shown to cause similar effects on strength (Greene et al., 1988). The clays are no longer as dispersive and so are less likely to enter the interstitial spaces between sand grains, forming bridges when dry and redispersing and slaking when wet (Lamotte et al., 1997a,b).

![Fig. 1. Representative X-ray diffraction spectra of one WFS (#6) at <2-μm, 2- to 5-μm, 5- to 20-μm, and 100- to 250-μm fraction. The <2-μm, 2- to 5-μm, and 5- to 20-μm fractions were Mg saturated and the 100- to 250-μm fraction was side-packed as a powder mount. All six WFSs studied (#1,2,3,6,7,8) had similar diffraction results. d-spacing values are listed in Angstroms (Å).](image)

![Fig. 2. Images from electron microscope of ruptured clods containing (a) high strength and (b) low strength sands.](image)
The cause of these observed effects, with respect to strength and exchangeable cation, relate to the chemistries of Na and Ca and their proximity to water and clay (Odum, 1984; Alther, 2004). For Ca\(^{2+}\), during the initial hydration of the cation (called innercrystalline swelling), the interlayer swells to a maximum of 2.0 to 2.3 nm (Weiss, 1989). At this point, the hydration energy is no longer dominant (it has decreased due to decreasing effective charge). Instead, van der Waals forces and the electrostatic attraction between the cation and the negatively charged clay surface (proportional to the square of the cation valency) take over.

For Na\(^{+}\) under innercrystalline swelling, when the spacing reaches ~1.6 nm, the cation moves away from the center of the interlayer toward one of the clay layers where an electrostatic repulsion is created (Weiss, 1989). The electric double layers created on the opposing clay layers overlap and repel one another leading to an increase in water infiltration in the interlayer and the onset of the second swelling phase, called osmotic swelling (Norrish, 1954; Madsen and Müller-Vonmoos, 1989; Weiss, 1989). Under normal innercrystalline swelling, adsorbed water increases to 0.5 g H\(_2\)O g clay\(^{-1}\) and little physical swelling is observed (Mering, 1946). With osmotic swelling in a Na-montmorillonite, this adsorbed water content can increase to 10 g H\(_2\)O g clay\(^{-1}\) (Falcoeur and Mattson, 1933; Norrish, 1954). This explosive expansion is caused by the rapid change in dominating forces from attractive to repulsive, leading to the dispersion of Na-montmorillonite into individual clay platelets (Langmuir, 1938; Verwey and Overbeek, 1948; Weiss, 1989). The dispersivity of the Na-bentonite that coats the surfaces of the WFS allows the clay to bond particles together, similar to that observed in the SEM images (Fig. 2), thereby causing the high strength observed in the Na-bentonite dominated WFSs.
The addition of gypsum to a soil, in this case via a blended gypsum/WFS amendment, should not affect soil properties to a significant degree because the proportion of gypsum present is quite low. These proportions will further decrease as the WFS/gypsum amendment is blended with soil or organic matter. In general, gypsum is beneficial when added to a soil because, in addition to aiding in flocculation, it can also help to reduce aluminum toxicity and exchangeable acidity. Upon dissolution, Ca$^{2+}$ can replace Al$^{3+}$ on exchange sites, forming AlSO$_4$$^{+}$ which is considered nonphytotoxic (Kinraide, 1991). If added to an intensively managed agricultural soil, gypsum will help to replenish sulfate concentrations. It will also reduce the loss of phosphate and ammonium from runoff through the formation of less soluble Ca-P compounds and higher infiltration rates due to flocculation, respectively (Favaretto et al., 2006). In a highly calcareous soil with low phosphate availability, however, the addition of gypsum and formation of Ca-P compounds could bind more phosphate. The use of this amendment may create problems in soils under arid climate regimes. Addition of gypsum to these areas with high salt accumulation, caused by low rainfall and drainage rates, could exacerbate salt toxicity problems. Also, the low moisture content would reduce the dissolution of gypsum and its ability to remediate the WFS.

Conclusions

Of the 15 sands tested, five exhibited high strength characteristics after a wet/dry cycle which could be detrimental to root and plant growth if used as a component in a manufactured soil or as a soil amendment. The presumed cause for the high strength was due to the amount of Na-bentonite found in the WFS rather than the total bentonite present. Higher amounts of Na-bentonite correlated to higher strength values and both were more prominent in WFS from iron foundries. Addition of Ca to the high strength WFS reduced this strength. From our data it is evident that the high strength WFSs are analogous to hardsetting soils in the natural environment with similar physical properties, similar causes for those physical properties, and similar solutions for their remediation.

Most gray iron foundries require the use of Na-bentonites to create strong sand molds that can undergo the high temperatures of the casting process. As there is little possibility of the removal of Na-bentonite from the process, there is great potential to use gypsum or some other calcium-containing waste stream to create a foundry sand soil amendment. From our data, a rate of 9.6 g gypsum per kilogram sand should help amend the WFS from gray iron foundries so that it may be reused. Testing of specific sands would be advised before widespread application. These findings would reduce landfill usage and allow foundries to save money, creating an incentive for foundries to take an active role in the remediation of WFSs.

Table 4. Average volume of Superfloc solution required to cause flocculation. Values in parentheses represent one standard deviation.

<table>
<thead>
<tr>
<th>Foundry</th>
<th>Volume required for flocculation (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.3 (0.6)</td>
</tr>
<tr>
<td>2</td>
<td>0 (0)</td>
</tr>
<tr>
<td>3</td>
<td>0 (0)</td>
</tr>
<tr>
<td>4</td>
<td>0 (0)</td>
</tr>
<tr>
<td>5</td>
<td>0 (0)</td>
</tr>
<tr>
<td>6</td>
<td>5.5 (1.2)</td>
</tr>
<tr>
<td>7</td>
<td>5.5 (1.2)</td>
</tr>
<tr>
<td>8</td>
<td>3.6 (0.8)</td>
</tr>
<tr>
<td>9</td>
<td>7.3 (2.6)</td>
</tr>
<tr>
<td>10</td>
<td>2.9 (0.6)</td>
</tr>
<tr>
<td>11</td>
<td>4.0 (0.9)</td>
</tr>
<tr>
<td>12</td>
<td>0 (0)</td>
</tr>
<tr>
<td>13</td>
<td>3.8 (0.8)</td>
</tr>
<tr>
<td>14</td>
<td>3.9 (0.8)</td>
</tr>
<tr>
<td>15</td>
<td>11.1 (0.9)</td>
</tr>
</tbody>
</table>

Table 5. Average strength for high strength sands (≥1.5 MPa) when gypsum was added to decrease ESP to 10. Values in parentheses represent ± 95% confidence interval.

<table>
<thead>
<tr>
<th>Foundry</th>
<th>Strength (MPa)</th>
<th>Initial</th>
<th>ESP = 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>3.1 (0.3)</td>
<td>&lt; 0.3</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.8 (0.2)</td>
<td>0.5 (0.1)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>4.6 (0.4)</td>
<td>1.2 (0.1)</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1.5 (0.1)</td>
<td>&lt; 0.3</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>ADL</td>
<td>1.1 (0.1)</td>
<td></td>
</tr>
</tbody>
</table>
in reusing their WFXs. This amelioration procedure would also create a value-added product that could be used as an amendment in urban and agricultural applications.

Acknowledgments

This study was funded in part by a USDA-Specific Cooperative Agreement.

References


U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. Agriculture Handbook 60. USDA Print. Office, Washington, DC.

