# Recycling of waste foundry sands by chemical washing method

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Abstract: This study aims to remove the metals (inorganic and heavy metals) in waste foundry sand (WFS) via chemical washing method. Washed waste foundry sand (WWFS) samples were obtained by using triptych washing successively with 5 M HCl, 5 M H $_2$ SO $_4$  and 5M NaOH solutions. Analysis on functional groups, micropores, heavy metals,and inorganic components of WFS and WWFS was carried out by using FT-IR, SEM and XRF. Results show that the concentration values of some inorganic components such as Ca, Fe, Mg, S were decreased, and the maximum removal percentage of these inorganic components are 47%, 19%, 32%, and 8%, respectively. The concentration values for each of the heavy metals of WWFS are below of limit values given in App-3 List of Regulation on General Principles of Waste Management. The removal percentages of Pb, As and Zn elements are 100%, 71%, and 40%, respectively. The findings of this research suggest that WWFS can be used in more applications due to its ability to remove heavy metals and some other inorganic components.

Key words: chemical washing; heavy metal pollutants; waste foundry sand; recycling

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Taste foundry sand (WFS) is produced in large amounts in different parts of the world. Although this type of waste represents a significant problem for the foundry industry, the number of studies addressing its reuse potential is limited. For example, WFS has been investigated as aggregate in terms of asphalt mix, concrete production, adsorbent and agriculture<sup>[1]</sup>. In addition, the applications of waste foundry sand could be seen in areas such as the construction of barrier layers, embankments, flowable fills, roadway construction, agriculture, soil reinforcement/amendments, hot mix asphalt, portland cement manufacturing, mortars, traction materials on snow and ice, vitrification of hazardous materials, smelting, rock wool manufacturing, and fibre glass manufacturing<sup>[2]</sup>. However, as a hazardous by-product of the foundry industry, WFS is often contaminated with potentially toxic elements (PTEs) such as Cu, Pb, Ni and Zn, and is widely re-utilized as a construction material. Therefore, the depollution of WFS has been suggested due to its environmental friendly

reprocessing to avoid potential long-term hazardous impacts<sup>[3]</sup>.

In Turkey, this waste is classified as hazardous waste according to limit values of one or several dangerous chemical elements determined in the App-3 List of Regulation on General Principles of Waste Management. The dangerous chemical elements are As, Cd, Cr(VI), Cu, Hg, Ni, Pb, Sb, Se, Sn, Ti, and Zn [4].

Foundry sand is a by-product of ferrous and nonferrous (e.g., copper, aluminum and brass) metal casting industries, in which sand is used as a molding material<sup>[5]</sup>. Foundries use high-quality specific silica sands in their molding andcasting operations<sup>[6]</sup>. The clay-bonded molding sands, which are also known as green sand, have been predominantly used in foundries and consist of a combination of silica sand (85%-95%), bentonite (4%-10%) and carbonaceous additive (2%-10%). The other category of molding sand is identified as chemically bonded sand, which is produced by mixing 93%–99% silica with 1%–3% chemical binders (e.g., phenolic urethane, epoxy resins, furfuryl alcohol and sodium silicate)[3]. The technique used for the sodium silicate chemical binder is named as CO<sub>2</sub>-sodium silicate method. The principle of the CO<sub>2</sub> process is based on the fact that as CO<sub>2</sub> gas is passed through a sand mixture containing sodium silicate as the binder, immediate hardening of sand takes place as a result of the chemical reaction between sodium silicate and carbon dioxide<sup>[7]</sup>. The method is the

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cheapest among other methods. The molding sand is reused approximately 8 to 10 times in the process depending on the molding utilities and mechanical properties, and the end-of-life molding sand is referred to as WFS <sup>[3]</sup>.

Molten metal preparation process is carried out via mixing together the coke, limestone, puddle iron and scrap iron in a blast furnace. Undesirable metals such as Fe, Si, S, P, Mn, Ca, C, Al, Ti, V, As, Ba, Cl, Cr, Co, Cu, Ni, F, K, Na, Zn are mixed into slag during this process<sup>[8]</sup> and thus they come into the molding sand.

Sawai et al. <sup>[3]</sup> have reported a technique for the removal of PTEs (Pb, Cu, Sn and Zn) from WFS to ensure its environmentally friendly re-utilization. The washing solution used to decontaminate the WFS includes EDTA as the main component, and NaOH and NH<sub>3</sub> were added to adjust the solution pH and enhance the removal efficiency (%RE). The optimum washing performance was achieved using the following extractant composition: EDTA, 50 mol·L<sup>-1</sup>; NaOH, 0.2 mol·L<sup>-1</sup>; and NH<sub>3</sub>, 0.3 mol·L<sup>-1</sup>. The overall %RE values of the PTEs were as follows: Cu, 98; Pb, 81; Sn, 83; and Zn, 50 <sup>[3]</sup>.

Balbay and Acikgoz<sup>[9]</sup> have studied the removal of metallic contaminant and other pollutants from WFS. In their study, a 1 g sample was washed 3, 8 and 16 hours for each of 5 M HCl, 5 M H<sub>2</sub>SO<sub>4</sub> and 5M NaOH solutions at 25 °C. The washing times for HCl, H<sub>2</sub>SO<sub>4</sub> and NaOH solutions were determined at 8 h, 16 h and 8 h, respectively. After that, two-stage washing (successively washing with two different chemicals) and triptych washing (successively washing with three different chemicals) were applied to WFS. The experimental studies concluded the reduction of metallic contaminant and other pollutants were much better in case of triptych washing with H<sub>2</sub>SO<sub>4</sub>-NaOH-HCl solutions and the maximum reduction of metallic contaminant and other pollutants was 40% <sup>[9]</sup>.

The objective of this research is to investigate the removal of undesirable metals (pollutant) from WFS by using a chemical washing process. These metals were determined by X-ray Fluorescence technique, FT-IR spectrophotometer and SEM analysis. WWFS was compared with the raw silica sand (RSS), which has a wide range of applications, in order to instruct new studies.

# 1 Experimental

Waste foundry sand (WFS) used for the experiment was taken from a ferrous foundry located in Turkey. The WFS is grayish in color with irregular shape and the particle size distribution of WFS was determined to be  $D_{\rm p}{<}1.18$  mm. First of all, the WFS was washed with distilled water and then dried overnight. Determination of ash, moisture, and volatile matter of WFS was performed according to ASTM D3174-12, D3173, D3175-11 Standards, respectively. The triptych washing (successively washing with three different chemicals) was applied to WFS. The 1, 5, 10 and 20 g of WFS samples were extracted with 100 mL of 5 M HCl, 5 M H<sub>2</sub>SO<sub>4</sub> and 5 M NaOH washing solutions for 8 h, 16 h and 8 h consecutively to remove the metallic contaminant and other pollutants. Chemical washing of WFS

was performed at 25 °C.

Each sample was well mixed by mechanical stirrer at a speed of 300 rpm. At the end of the extraction process, WFS samples were washed with distilled water until they reached neutral pH and filtered through over  $0.45~\mu m$  membrane filters. Afterward, samples were dried in an oven at  $105~^{\circ}\text{C}$  for 2 h.

The removal percentage of contaminants was calculated by using the following formula:

Removal (%) = 
$$\frac{(A_i - A_f)}{A_i} \times 100$$

where  $A_{\rm i}$  and  $A_{\rm f}$  are the initial and final sample amounts, respectively. The pH was measured using a pH meter (Hanna HI 991001). WFS has low absorption capacity and is non-plastic<sup>[10]</sup>. The functional group compositional analysis of WFS samples before and after washing was carried out using FT-IR spectrophotometry (Perkin Elmer, model spectrum 100). The pore structure of WFS samples was determined by SEM scanning electron microscopy (SEM-ZEISS Supra 40VP).

The compositional analysis of the raw silica sand (RSS), molding sand before casting (MSBC), WFS, and washed WFS samples was investigated by using XRF (Wavelength Dispersive X-ray Fluorescence; PANalytical, Axios max minerals model).

## 2 Results and discussion

Table 1 shows the result of proximate analysis of WFS sample.

The removal percentages of pollutants from various amounts of WFS washed using the triptych washing method (successively washing with 5 M HCl, 5 M  $\rm H_2SO_4$  and 5 M NaOH solutions at 25 °C) are given in Fig. 1.

Table 1: Proximate analysis results of WFS

Fixed carbon Volatile matte (wt.%) (wt.%)		Ash (wt.%)	Moisture (wt.%)
56.88	6.64	30.55	5.93

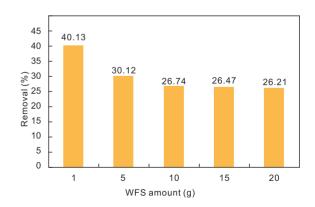


Fig. 1: Effect of WFS amount on pollutant removal (Solution concentration: 5 M, temperature: 25 °C)

The highest removal percentage of pollutant (40%) was obtained for 1 g WFS amount in  $H_2SO_4$ -NaOH-HCl sequence of triptych washing. Anyway, the removal percentage of pollutants from the amount of 10, 15, 20 g WFS was also as high as ~26%.

Chemical reactions involved in the washing process by using

three different solutions 5 M HCl, 5 M H<sub>2</sub>SO<sub>4</sub> and 5M NaOH are grouped according to the following:

(i) Reaction of sodium silicate with hydrochloric acid solution

$$SiO_3^{2-} + 2 HCl \rightarrow SiO_2 + 2Cl^{-} + H_2O$$
 (1)

 $n[Si_7O_{18}H_4Na_4] + 4nHCl \rightarrow n[Si_7O_{18}H_4] + 4nNaCl + nH_2O$  (2) Sodium silicate reacts with HCl through polycondensation actions and leads to a silica gel by releasing water and NaCl<sup>[10-11]</sup>.

(ii) Reaction of sodium silicate with sodium hydroxide solution

$$Na_{0.38} SiO_{2.19} + 1.62NaOH \rightarrow 2Na_2^+ + H_2SiO_4^{2-}$$
 (3)

Sodium silicate reacts with NaOH through polycondensation reactions and thus causes break of the siloxane bridges and disintegration of the silica<sup>[11-12]</sup>.

(iii) Reaction of sodium silicate with sulphuric acid solution

$$n[\text{Na}_2\text{SiO}_3 + (1-x)\text{H}_2\text{O} + \text{H}_2\text{SO}_4] \rightarrow n\text{Na}_2\text{SO}_4 + [\text{SiO}_x(\text{OH})_{4-2x}]_n$$
 (4)

The formation process of a semi-solid network silicate gel (pH 10) consists of the acidification of the diluted sodium silicate solution via  $\rm H_2SO_4$  as shown in Eq. (4)  $^{[13]}$ .

Sodium silicate is alkaline in nature having a pH of  $\sim 12^{[13]}$ . Sodium silicate solution, under acidic conditions is polymerized to silica and acts as an inorganic binder <sup>[14]</sup>. According to the

reaction of sodium silicate with sulphuric acid solution, the silicate gel consists of a network of polymerized Si-O-Si-OH group that traps water via solvation and hydrogen bonding forces [Eq. (4)]. The structure of sodium silicate consists of silicate tetrahedral along with sodium that is not bonded into the structure and therefore can be washed out of the formed silicate gel [13].

Silica is known to be more soluble in a basic medium. A chemical reaction between the silica surface and the hydroxyl groups present in the basic solution could be considered by breaking the Si-O-Si leading to the formation of Si-OH and Si-O groups [Eq. (3)] [10].

Chemical composition of the waste foundry sand depends on the type of cast metal at the foundry, type of binder and combustible materials used. The chemical composition of the foundry sand may influence its performance <sup>[15]</sup>.

The effects of washing technique on chemical bonding in the WFS were studied using FT-IR spectroscopy. FT-IR spectra of the WFS and WWFS are shown in Fig. 2 and Table 2. The Si-O-Si and -OH ligand metal complex was not found from 1400 to 1450 cm<sup>-1</sup> in WWFS (H<sub>2</sub>SO<sub>4</sub>-NaOH-HCl of triptych washing, Table 2). This result shows that undesirable metals in WFS are removed from WWFS.

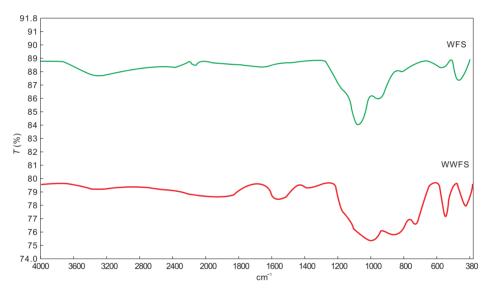


Fig. 2: FT-IR spectrum of WFS and WWFS

The limit concentration values for each of the heavy metals that have a feature ecotoxic coded H14 were given as 0.25 % in the App-3 List of Regulation on General Principles of Waste Management <sup>[4]</sup>. The value of As in WFS is higher than the recommended limit value in WFS. Values of heavy metals in WWFS are below the limit value (Table 3).

Removal percentages of heavy metal in the waste foundry sands are given in Fig. 3. It can be seen that the removal percentages of Pb, As and Zn elements are 100%, 71%, 40%, respectively.

The inorganic metal concentrations in the raw silica sand, molding sand before casting, WFS, and WWFS are shown in Table 4. Maximum removal percentages of some inorganic components such as Ca, Fe, Mg, S are 47%, 19%, 32%, 8%, respectively.

Figure 4 shows the SEM microstructure of the WWFS and WFS samples of 20 g. The SEM images were obtained from the surfaces of the specimens and magnified 30000 times. In the interior structure of the WWFS, the crystalline structure was observed to be denser.

## 3 Conclusions

In this study, the concentrations of heavy and inorganic metals of washed waste foundry sand (WWFS) by chemical washing method were investigated. Functional groups, micropores of

Table 2: Attribution of FT-IR absorption for WFS and WWFS

WFS (cm <sup>-1</sup> )	WWFS (cm <sup>-1</sup> )	Assignment	
3376.86	-	O-H stretching vibration of molecular water in the sample <sup>[16]</sup>	
-	3232.75	Si-O-H bands <sup>[17]</sup>	
2921.11	-	C-H stretching vibrations <sup>[17]</sup>	
2844.82	-	C-H stretching vibrations <sup>[17]</sup>	
1619.82	-	C-O bands <sup>[18]</sup>	
-	1555.18	C = C bands <sup>[19]</sup>	
1441.82	-	Si-O-Si and - OH ligand metal complex <sup>[20]</sup>	
1162.01	1146.23	Si-O-Si unti-asymmetric stretching of bridging oxygen atom within tetrahedral <sup>[21-22]</sup>	
1023.36	995.05	within tetrahedral <sup>[21-22]</sup>	
913.78	-	Si-OH bands <sup>[17-23]</sup>	
-	839.16	Si-O-Si symmetric stretch of bridging oxygen atoms between tetrahedral [24]	
797.88	-	Si-C stretching vibration <sup>[19]</sup>	
-	721.5	Si-O-Si symmetric stretch of bridging oxygen atoms between tetrahedral <sup>[24]</sup>	
-	542.8		
512.07	-	the rocking motion of Si-O-Si bridging oxygen which connects the various Qn species of silicates <sup>[18]</sup>	
464	-		
420.77	419.22		

Table 3: Comparison of heavy metal concentrations (%) in raw silica sand (RSS), molding sand before casting (MSBC), WFS and WWFS

Metals	RSS	MSBC	WFS	wwfs
Cr	0.486	0.121	0.17	0.204
Ni	0.032	0.033	0.16	0.142
Cu	-	0.027	0.114	0.085
Zn	-	0.05	0.11	0.066
As	-	-	0.527	0.154
Pb	-	-	0.151	0

WFS and WWFS were studied by using FT-IR and SEM. The Si-O-Si and -OH ligand metal complex was not observed in WWFS during FT-IR analysis. Due to the breakage of Si bonds in WWFS, it was observed that WWFS was transformed into a porous structure in SEM analysis. The total metal concentration in WFS was determined by using XRF. The concentration values of some inorganic components such as Ca, Fe, Mg, S were decreased, and the maximum removal percentages

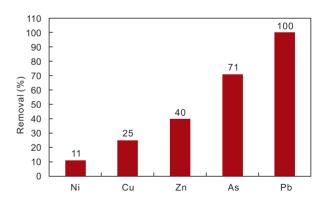


Fig. 3: Removal percentages of heavy metal in waste foundry sands

of these inorganic components are 47%, 19%, 32%, 8%, respectively. The concentration values for each of the heavy metals of WWFS are below of limit values given in the App-3 List of Regulation on General Principles of Waste Management. The removal percentages of Pb, As and Zn elements are 100%, 71%, 40%, respectively.

The findings of this research suggest that WWFS can be used in more applications due to its ability to remove heavy metals and some other inorganic components. For example, WWFS can be used to blend in various ratios in different areas where raw silica sand is used, such as foundry moulding sand,

Table 4: Inorganic metal concentrations (%) in the raw silica sand (RSS), molding sand before casting (MSBC), WFS, and washed WFS

Metals	RSS	MSBC	WFS	wwFS
0	12.633	14.661	10.596	13.658
Na	0.107	3.863	0.103	0.173
Mg	0.156	0.272	0.895	0.606
Al	1.816	1.527	7.693	9.392
Si	71.336	64.804	7.75	11.631
Р	4.312	5.287	1.832	2.354
S	0.042	0.159	5.257	4.824
CI	0.135	0.336	0.153	12.61
К	0.544	0.79	2.037	3.14
Ca	2.125	4.752	39.64	21.013
Ti	4.838	1.332	6.067	5.611
Mn	0.031	0.054	0.073	0.071
Fe	1.077	1.709	15.331	12.381
Sr	-	-	0.552	0.187
Zr	0.329	0.224	0.409	0.136
Ва	-	-	0.377	0

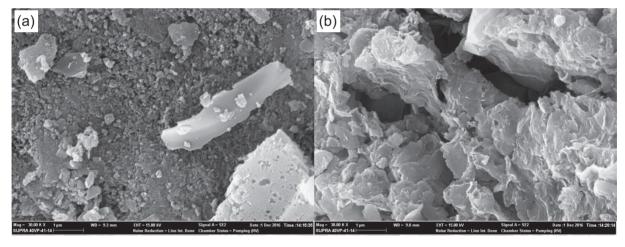


Fig. 4: SEM images of WFS samples before (a) and after (b) washing

agriculture, portland cement manufacturing and fiberglass manufacturing.

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