Spain 02/2019 to 04/2020

Inorganic binder system to minimize emissions, improve indoor air quality, purify and reuse of contaminated foundry sand

LIFE17 ENV/FI/173 “Green Foundry LIFE”

Action B4.3 Cleaning by washing method

Deliverable DeB4.3 Washing test results of sand samples in Spain

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Content

1. Introduction

Due to the unexpected closure of Ecofond shortly after the kick-off of the Green Foundry project, Tecnalia, originally subcontracted to investigate the composting method in the Green Foundry project, took over also their role in waste sand washing tests.

With this 4000 tons volume of washed green sand supplied by Ecofond, Tecnalia carried out composting tests (Deliverable DeB4.1B). And more than 100 kilos was kept back for analysis purposes and washing tests.

In addition to have data from Ecofond's washed green sand , in order to have also results of the contaminated green sand prior to and after washing tests, Tecnalia sourced comparable green sand from three Spanish foundries (DeB4.3).

In this document we analyze and report:

- Washing tests following Tecnalia´s cleaning method prior to and after washing (laboratory process, sourced from three Spanish foundries). Tests with green sand and inorganic silicate sand types.
- Green sand washed from Ecofond (industrial process, from Spanish foundries), and analysed by Tecnalia.

- Unwashed sand from green foundries, which means foundries using green sand moulding process (due to lack of data on Ecofond's sand prior to washing). Analysed and washed by Tecnalia.

In order to obtain results relevant for different types of foundries, we used both organic binder system, green sand and inorganic binder system, silicate sand.

2. Tecnalia sand washing method

The principle behind our method was that by using basic chemical products (***5M hydrochloric acid and distilled water***), the contaminated moulding sand could be washed cost-effectively and made reusable back in foundry processes.

The quantities of unwashed sand started at 30 grams, and as the experiments progressed, the scale was up to 450 grams. In total, approx. 100 kilos of unwashed sand was used.

Equipment and materials

In the washing test experiments following equipment and devices were used: the Mufla furnace, pH equipment, and regular lab items such as beakers, flasks and filters etc. Process materials were 5M hydrochloric acid and distilled water.

Method

Step one was to wash the sand with distilled water. This was then analyzed for pH and rewashed using fresh water until the level obtained by washing in water stabilized, i.e. no further reduction. Once pH did not anymore change, step two was to add the damp sand to an Erlenmeyer flask containing HCl (hydrochloric acid). This was then mixed with a magnetic agitator for eight hours. The solution was filtered to separate the sand from the acid, and the pH level of the sand was monitored. The sand was returned to an Erlenmeyer flask containing fresh HCl to repeat the washing, agitation and analyzing process until the desired pH range was obtained twice, i.e. no further change occurred.

The final stage was to dry the sand by using a Mufla furnace. Chemical analyses were carried out of the washed and dried sand.

The method explained in detail below shows the experiment conducted with a 450 gram sample of contaminated sand.

Equipment and materials:

- 5M HCl*
- Distilled water
- Mufla furnace Tª max 230ºC
- pH equipment
- Filter paper of 0.45 µm
- Precipitate glass of 2 litres
- Magnetic mixer (300rpm)
- Büchner funnels of 2 litres
- Erlenmeyer flasks of 2 litres
- Vacuum filtren system

*Data: Molecular mass=36.46 g/mol and mass density 1.18g/ml→ 633.19 ml HCl

Process for 450 gram sand (chemical quantities can be scaled up proportionately)

1. Wash the sand with distilled water in a ratio of one-part sand to two parts water
2. Check pH and repeat washing until ≤ 9.35 pH is achieved
3. Filter the sand from the water and allow to air-dry
4. Mix the air-dried sand with HCl 5M** for 8 hours using a magnetic agitator at 300rpm
   ** (7.5 mol → 276.45 (37%)→ 747.16 grams HCl)
5. The sand is further washed with the same ratio of distilled water to sand until the pH becomes neutral (≥7)
6. The sand is filtered using filter paper of 0.45 µm
7. Dry the sand in a mufla furnace at 105ºC for a further 3 hours
8. Grind the wash sand and analyze it

The following figures show the different equipment used for washing sand.

Figure 1: Washing sand with distilled water

Figure 2: pH test during first washing

Figure 3: Büchner funnels equipment

Figure 4: Filtering the sand

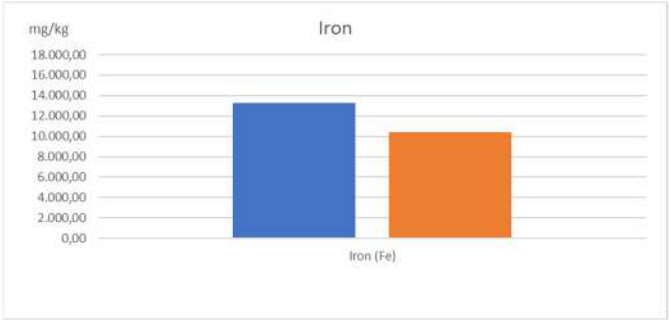
Figure 5: Sand after filtering

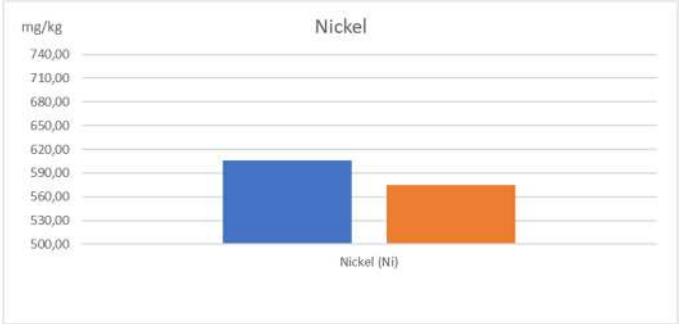
Figure 6: Sands after washing

3. Results of inorganic binder system silicate sand washing tests

The following table shows the results of analyzing of 30 gram of silicate waste sand before and after being washed by the Tecnalia process against the limit value for their use as fertilizer class C.

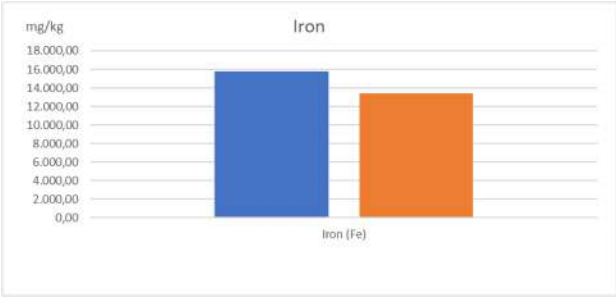
Total metal (mg/kg)	Silicate sand before washing by Tecnalia process	Silicate sand after washing by Tecnalia
Aluminum (Al)	288.00	314.00
Antimony (Sb)	<1.00	<2.00
Arsenic (As)	<1.00	<2.00
Barium (Ba)	2.87	<2.00
Cadmium (Cd)	<1.00	<2.00
Chromium (Cr)	16.80	<2.00
Copper (Cu)	1.48	<2.00
Iron (Fe)	13,300.00	10,400.00
Lead (Pb)	1.48	<2.00
Mercury (Hg)	<0.10	<0.50
Molybdenum (Mo)	<1.00	<2.00
Nickel (Ni)	606.00	575.00
Selenium (Se)	<1.00	<2.00
Zinc (Zn)	8.50	6.81
pH (u. pH)	10.40	7.05

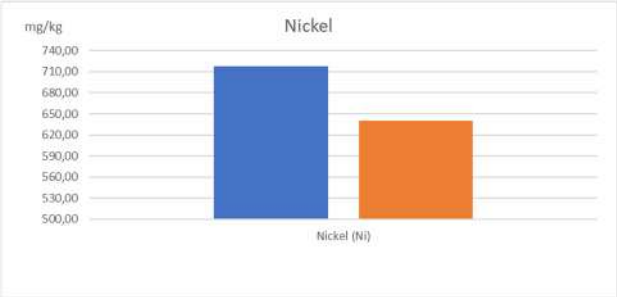




The following table shows the results of scaling up to 450 gram sand before and after being washed by the Tecnalia method against limit value for their use as fertilizer class C.
*Silicate sand means waste sand from silicate moulding process (inorganic binder system)

Total metal (mg/kg)	Silicate sand before washing by Tecnalia process	Silicate sand after washing by Tecnalia process
Aluminum (Al)	850.00	352.00
Antimony (Sb)	<2.00	<2.00
Arsenic (As)	<2.00	<2.00
Barium (Ba)	7.85	4.55
Cadmium (Cd)	<2.00	<2.00
Chromium (Cr)	15,800.00	163.00
Copper (Cu)	2.45	<2.00
Iron (Fe)	15,800.00	13,400.00
Lead (Pb)	718.00	<2.00
Mercury (Hg)	-	<0.50
Molybdenum (Mo)	3.24	<2.00
Nickel (Ni)	718.00	640.00
Selenium (Se)	<2.00	<2.00
Zinc (Zn)	13.20	10.50
pH (u. pH)	10.47	7.56





4. Results of Ecofond washed green sand and Tecnalia washed green sand

The table below shows the analysis results of both washed sand one waste green sand (from Ecofond, from foundries with green sand moulding process) and the other waste silicate sand (from foundry that use silicate moulding process)

Total metal (mg/kg)	Sand washed by Ecofond	Sand washed by Tecnalia
Aluminum (Al)	3,480.00	352.00
Antimony (Sb)	<1.00	<2.00
Arsenic (As)	<1.00	<2.00
Barium (Ba)	24.70	4.55
Cadmium (Cd)	<1.00	<2.00
Chromium (Cr)	14.70	163.00
Copper (Cu)	18.30	<2.00
Iron (Fe)	5,750.00	13,400.00
Lead (Pb)	4.40	<2.00
Mercury (Hg)	<0.1	<0.50
Molybdenum (Mo)	1.01	<2.00
Nickel (Ni)	51.30	640.00
Selenium (Se)	<1.00	<2.00
Zinc (Zn)	56.00	10.50
pH (u. pH)	7.50	7.56

5. Comparative results unwashed and washed green sand

The washed sand was supplied by Ecofond sourced from foundries with green moulding sand process

The following table shows the comparative results of unwashed green sand and washed green sand.

Sand types	Unwashed green sand	Washed green sand (Ecofond)
Fe_2O_3	1.10	1.40
Al_2O_3	3.40	2.70
MnO	<0.05	<0.05
MgO	0.56	1.40
Cr_2O_3	0.28	0.87
TiO_2	0.12	0.12
NiO	-	<0.05
CaO	0.55	<0.05
Na_2O	0.30	0-28
K_2O	0.76	0.53
P_2O_5	-	<0.05
C	3.00	0.62
S	0.04	0.02
N	-	0.03

The following table shows soluble metals in both unwashed and washed green sand from the same source compared to limit values for classification as inert waste.

Leached metal (mg/kg)	Unwashed contaminated green sand	Washed contaminated green sand (Ecofond)	Limit value for inert waste
Antimony (Sb)	-	<0.01	0.06
Arsenic (As)	-	<0.01	0.50
Barium (Ba)	-	<0.20	20.00
Cadmium (Cd)	<0.01	<0.01	0.04
Chromium (Cr)	0.20	<0.20	0.50
Copper (Cu)	<0.20	<0.20	2.00
Iron (Fe)	2.30	<0.20	-
Lead (Pb)	<0.20	<0.20	0.50
Mercury (Hg)	<0.01	<0.01	0.01
Molybdenum (Mo)	-	<0.20	0.50

Nickel (Ni)	<0.20	<0.20	0.40
Selenium (Se)	-	<0.05	0.10
Zinc (Zn)	<0.20	<0.20	4.00

Results

- washing reduces metal content to be further below limit values

The following table shows hazardous parameters in unwashed and washed green sand compared to limit values for classification as inert waste.

Other hazardous parameters (mg/kg)	Unwashed green sand	Washed green sand (Ecofond)	Limit value for inert waste
Chlorides	-	<50.00	800.00
Fluorides	7.80	<5.00	10.00
Sulphates	-	<50.00	1,000.00
Phenol	0.80	<0.50	1.00
DOC	480.00	169.00	500.00
TOC	8,900.00	<1,000.00	30,000.00
BTEX	0.22	<0.04	6.00
PCB	-	<0.10	1.00
Mineral oil	-	<20.00	500.00
PAH	0.21	<0.160	55.00
pH (U. pH)	8.60	7.50	>6.00
Conductivity (µS/cm)	254.00	<45.00	-

Results

- In the Ecofond washed sand DOC and TOC values were lower than in unwashed sand
- Ph values were found to be similar (depending on binder type and the alloy being cast)

The following table shows the values for Total Heavy Metals in unwashed and washed green sand from Ecofond.

Total metal (mg/kg)	Unwashed green sand	Washed green sand (Ecofond)
Aluminium (Al)	15,580.00	3,480.00
Antimony (Sb)	2.88	<1
Arsenic (As)	3.50	<1
Barium (Ba)	70.60	24.70
Cadmium (Cd)	<1.00	<1.00
Chromium (Cr)	31.20	14.70
Copper (Cu)	22.10	18.30
Iron (Fe)	11,500.20	5,750.00

Lead (Pb)	4.40	4.40
Mercury (Hg)	<0.10	<0.10
Molybdenum (Mo)	1.11	1.01
Nickel (Ni)	22.60	51.30
Selenium (Se)	1.53	<1.00
Zinc (Zn)	106.00	55.90

Results

- The washing process reduced total metal values for Al, Fe, Ba, Cu, Cr. Nickel increased (reason unknown at this stage)

Conclusions

In contaminated foundry sands (green sand washed by Ecofond and silicate sand washed by Tecnalia, the process was found to reduce metal content in most metal compouds. In sand washed by Ecofond, other hazardous parameters, notably DOC, TOC and BTEX, were reduced, between 15-25%.

The chemical washing of contaminated sand reduces its toxicity and could be a viable option for the foundry industry in terms of environmental sustainability and the circular economy. Washing the foundry waste sands could extend its useful life and the washed sand could be reused in foundry processes and reduce the need of virgin sand.