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Characterisation of South African Waste Foundry Moulding Sand: Metallic Contaminents

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Abstract -Waste foundry sands are invariably contaminated to some extent during the manufacturing of cast alloys. As such the sand is regarded as a hazardous material that requires exceptional precautions for its disposal. Therefore, the study is initiated to identify, quantify and to classify metallic contaminants present in these sands. To achieve these objectives in conjunction with the South African Waste Management Act which plays as the guide line for industrial waste disposal, samples were collected from various South African foundries. In the present study, ten waste sand samples were characterised using XRF, XRD, SEM-EDS and Sulphur analyser. It was found after comparison with a virgin sand used as control or reference sand, that the cast alloy and the moulding additives are the main pollutants present in the waste foundry sand. The additional sulphur and acid potential characterisation, showed that the waste foundry sand has a low potential for sulphuric acid and acid sulphate soil formation when submerged in aquatic medium. The leaching behaviour and the total metallic concentration of the waste was similar to the virgin soil thus their similar classification in the same waste class category.

Keywords**:** Foundry Waste; sand; Characterisation; Pollutants; Toxicity Leach Procedure

1. Introduction

The SA foundry industry is facing a problem with waste management, especially concerning the waste foundry sand, which has been classified as hazardous waste material for landfill under the South Africa Environmental waste Management Regulation Act rather than inert waste as is the case in other country such as Germany and United Kingdom. The classification regarding the SA waste foundry has an economic impact on foundries: over prize for waste disposal, when comparing to other countries: U$34 in SA while U$ 4.3 in the United Kingdom (Mohamadi A. E., 2011) The annual waste foundry sand generated by foundry has been estimated to 350,000 tons of Silica sand and 25,000 tons of Chromite sand. The utilization of waste material and by-products has become an attractive alternative to disposal therefore understanding chemical characteristics of spent foundry sands and their environmental impacts before a beneficial utilization of the waste can serve as weighbridge control information.

So far, some studies were conducted in the same direction and they was demenonstrated that waste foundry sands contain regulated pollutants which are in general metals and in most of the cases they are part of the sand matrix and not only brought up by the metal casting processes (B. S. Q Alves et al, 2014). Futhermore, ferrous foundry waste togheter with alluminun are low in metallic contaminants (Deng, 2004) while casting of brass and bronze reported a significant metalic concentration in terms of Cd, Pb, Cu, Ni and Zn as mentioned by Craig H Benson and S. Bradshaw.

Accordinng to the brazilian standard norms, waste sand has proven to be inert and are classified as non hazardous (J. M. Pablos and E. P. Sichieri, 2010). The statement was in strong agreement with the classification conducted by Zhang et al, (2014) when comparing the pollution magnitude in the waste sand against the chinise regulation standard. Portugese and European legislation, also classifies the waste sand as inert and non-hazardous material as reported by F. castro and T. Teixeira, (2014). Futhermore, under the Argentina regulation, to the exception of modified resin, notably alkyd urethane which contaminates the sand with high Pb concentration, the majority of waste sand is classified as inert material (Roberto E. Miguel, et al 2013). The existing SA repot, classifies the waste sand has hazardous since its metallic concentration was found exceeding the class of general or inert waste.

To provide experimental data addition, to existing South African waste foundry sand classification report, the objective of this study is to identify, quantify and classify the waste sand in terms of heavy and hazardous metallic content from ferrous and non-ferrous casting. The waste sands were subjected to the Toxicity Characteristic Leaching Procedure (TCLP), with the obtained results compared against the South African National Enviromental Management Regulation (Act 59 of 2008). The primary issue faced by foundries is the classification of their waste streams thereof, the selected protocol, TCLP (Method 1311) has been used in several research work for better waste classification, management and their beneficial reuse (Siddique et al,2010).

2. Materials and Characterisation

2. 1. Material

A total of 20 samples were collected from 10 different local foundries around Johannesburg. There were composed of 10 waste sands (after the casting process) and their corresponding virgin sands. The collected sand varies in terms of the cast alloy, this included ferrous and non-ferrous.

2. 2. Method

2. 2. 1. Physicochemical Properties

Field sampling and laboratory sample homogeneiazation, were conducted according to the prescribed procedure as published by the science and Ecosystem Support Division (Simmons, 2014), aproximately 0.2kg of each sand was used as the final sample and were dried for 2 hours at 105^0 C.

The chemical composition of the sand samples was analyzed using a Rigaku, ZSX Primus II X-ray Fluorescence (XRF) spectrometer. Phase identification of the chemical composition of the sand samples were obtained by comparing the diffraction signature of the sample with a database of X-ray Diffraction (XRD) mineral patterns. XRD patterns were recorded on a Rigaku Ultima IV X-ray diffractometer equipped with a graphite-monochromated Cu Kα radiation source (40 kV, 30 mA). A diffractogram was collected in the 2θ range between 3^o and 90^o with a step size of 0.01^o, and a scan speed of 1^o/min. The XRD analysis was conducted to detect the mineralogical and the crystal structure of the different phases. The XRD pattern was processed using JCPDS card numbers. Sample preparation for XRD analysis entailed the following steps: sample was milled to less than 212 microns, pelletized using the an hydraulic press and then subjected to chemical analysis under X-ray analysis while for the XRD the sample was only flattened in the sample cup after milling. The microstructure and the chemical analysis of the sand sample was analyzed using a scanning electron microscope (SEM) model TESCAN equipped with Oxford instrument X-Max (EDS). The sand morphological analysis together with the energy dispersed spectrum (SEM-EDS) was obtain after the as received sand were carbon coated before being subjected to the analysis. A thin section of the sand sample was prepared along with crushed samples of the rock; the samples were then mounted on a stud and carbon coated and irradiated with a beam of electrons at 20 kV. Secondary electron (SE) and backscattered electron (BSE) micrographs were used for optimum imaging of samples.

2. 2. 2. TCLP, Sulfur Content, and the pH,

Secondly, the sand samples were subjected to the TCLP test method in order to assess eventual amount of heavy metal associated with the polluted sand under Atomic Absorption Flame Spectrometer (AAFS)**.** Furthermore, one virgin sand was used and the obtained results were used as control result. Lastly, the waste molding sand sulfur content was determined after weighing 50 grams of each sand and analyzed at 1150 ^{0}C under the U-Therm Sulphur Analyzer YX-DL equipment.

The pH was recorded after starring 5 grams of waste sand in 96.5 ml of distilled water while the hazardous specified metallic content was evaluated after the waste sands had been subjected to the TCLP protocol method as publish by the USEPA. The procedure, TCLP involves rotary agitation of 5 % solid to liquid ratio for 18 hours and it intends to dissolve hazardous regulated metallic traces in the leachates. 100 grams of each sands was leached and their metallic quantification was processed under Atomic Absorption Flame Spectrometry after the leachate were collected by filtering through filter paper.

3. Results and Discussion

Table-1- summarizes the chemical composition of the waste sand samples in comparison to its virgin sand. As expected and reported, the chemical composition of waste foundry sand consist primarily of silica and varies in nature depending on the cast alloy modeled at the foundry site as it has been investigated by Siddque (R. Siddique et al, 2010). Analysis revealed a metallic contamination of the sand from the main ingredient of the cast alloy. The waste sands exhibit high metallic content when compared to its corresponding raw sand in terms of the following metals Al, Cu, Cr, Fe, Mn, Ni and Zn. The existence of the metals within the sand matrix were brought in by the casting process. The presence of the main cast alloy ingredient observed under XRF was in good agreement with the mineralogical analysis by XRD and the additional under SEM-EDS.

Table. 1. Waste foundry sand elemental chemical composition

Foundry	1		2		3		4		5	
Cast Aloy	Aluminum		High Chrome		Brass		Cast Iron		High Chrome	
	Shell		Greesand		Urethane		Greesand		Greensand	
Analysis	Waste	Raw	Spent	Raw	Spent	Raw	Spent	Raw	Spent	Raw
Al	**3.93**	0.09	2.36	0.28	0.55	0.61	8.15	0.59	1.65	0.59
Cr	0.00	0.00	**0.96**	0.01	0.14	0.01	0.00	0.00	**2.72**	0.00
Fe	0.83	0.47	**1.43**	0.24	0.42	0.51	**5.25**	0.53	**1.66**	0.53
Ni	0.02	0.00	0.00	0.00	0.04	0.04	0.00	0.00	0.02	0.00
Zn	0.02	0.00	0.00	0.00	**0.07**	0.00	0.09	0.00	0.02	0.00
Cu	0.00	0.00	0.00	0.00	**0.33**	0.00	0.00	0.00	0.00	0.00
Mn	0.02	0.00	0.02	0.00	0.01	0.01	0.06	0.01	0.00	0.01

Table. 1. Continues

Foundry	6		7		8		9		10	
Cast Aloy	Steel		Cast Iron		Steel		Cast Iron		Cast Iron	
	Alcaline		Pepset		Phenolic		Greensand		Furan	
Analysis	Spent	Raw	Spent	Raw	Spent	Raw	Spent	Raw	Spent	Raw
Al	2.45	2.09	3.78	2.09	1.97	0.61	3.26	0.59	0.63	0.59
Cr	**4.52**	1.02	0.91	0.01	**3.38**	0.52	**0.49**	0.04	**0.52**	0.04
Fe	**5.50**	1.09	**7.54**	1.09	**2.15**	0.61	**2.19**	0.53	2.34	0.53
Ni	0.03	0.03	0.02	0.03	0.02	0.00	0.00	0.00	0.00	0.00
Zn	0.03	0.18	0.00	0.18	0.00	0.00	0.01	0.00	0.03	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.03	0.01	0.14	0.01	0.04	0.01	0.24	0.01	0.27	0.01

Table. 2. RXD Mineral Phase Quantification

X-Ray Diffraction Quantitative Analysis Results (RIR)										
Sand	**Main Cast Alloy** in %			**Mineral Phases** in %						
	Al	(Y/α) Fe	Cu/Zn	Anorthite	Albite	Microline	Preiclase	Magnesioferrite	Magnesiochromite	Wustite
1	2.99	***	***	6.13	***	***	***	***	***	***
2	3.51	0.01	***	0.04	***	***	2.87	***	***	0.79
3	***	***	0.27	***	***	***	***	***	***	0.01
4	***	3.18	***	***	0.59	1.05	***	***	***	***
5	***	1.43	***	1.94	1.61	***	***	***	***	***
6	***	5.08	***	1.09	***	***	***	***	***	1.22
7	***	2.56	***	***	0.52	***	***	***	***	1.09
8	***	1.19	***	***	5.26	***	3.11	3.89	***	0.28
9	***	1.52	***	0.56	***	***	4.30	***	***	0.11
10	***	1.10	***	0.37	***	***	***	**	***	0.08

3. 1. Waste Moulding Sand Morphological Analysis

The first set of pictures summarizes the morphology of raw (virgin) while the second set represent the waste moulding sand. The morphological analysis revealed the surfaces of the raw sand are much cleaner and smooth when compared to their corresponding waste grains. The latter possess coating of residual binder as expected and as reported by J.C. Dainezi de Oliveira and A. A. Bernadez Pecora, (2005). The waste grains also exhibits incrustation of bright coulors as depicted in the second set of pictures, suggecting that the observed incustation derived from the main cast alloy ingrient as reported by G. Penkaitis and J. S. Barbujiani, (2012). It was in strong agreement with the XRF, XRD and EDS since the analysed were alluminum, chromium, copper and lastly zin and were the cast alloy produce in the foundry from where the sand was collected.

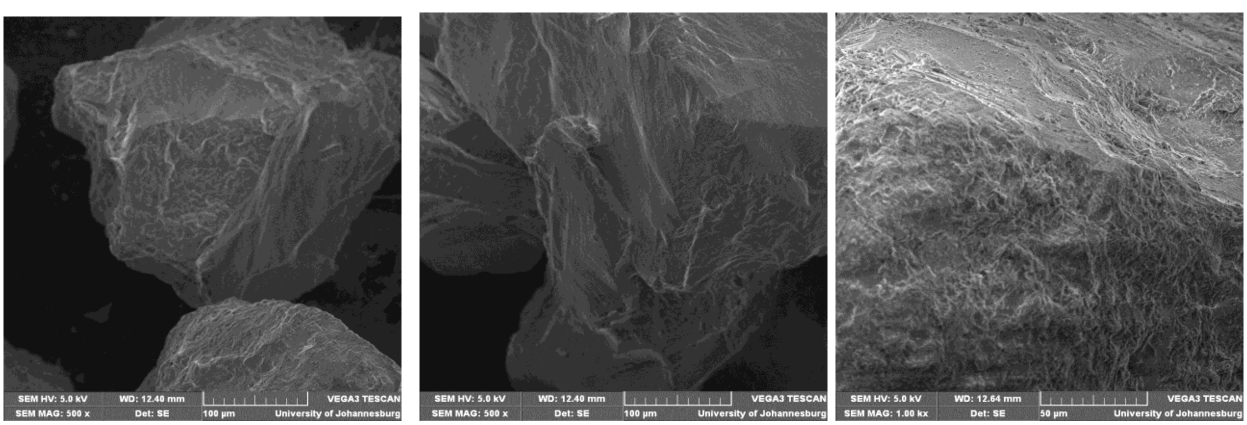

Fig. 1. Moulding virgin sand surface morphology

3. 2. Sulfur and Acid Potential Determination

The waste sand elemental sulfur had an average content of 0.101%, with greensand having the highest content due to the coal dust addition, the latter brings froth sulfur as its impurity. The maximum potential acidity as a function of the obtained Sulfur %, assuming that all the Sulphur react as pyrite to the completion revealed that waste sand had an average maximum acidity is 3.1 kg/t according to the reaction:

$$FeS_2 + \tfrac{15}{4} O_2 + \tfrac{7}{2} H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \tag{1}$$

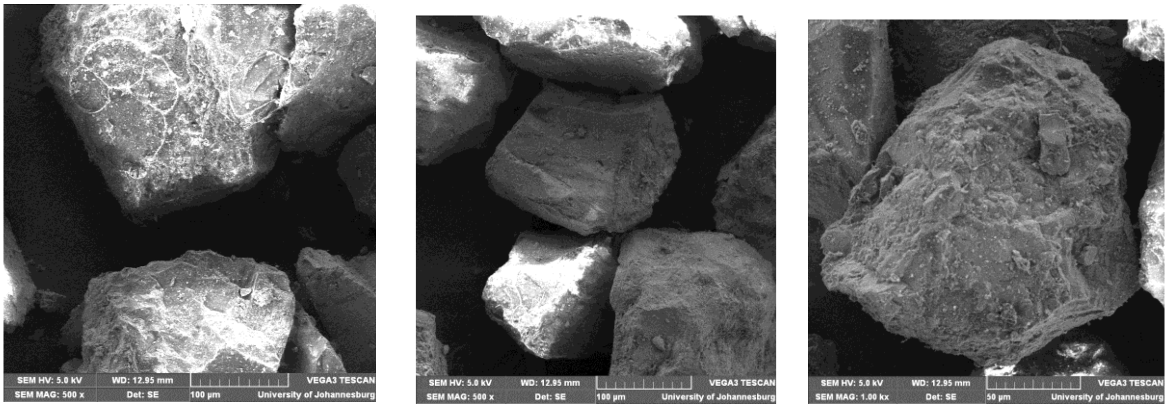

Fig. 2. Waste Moulding Sand surface Morphology

Table. 3. Waste Moulding Sand Sulfur content, pH and acid potential determination

Samples	% Sulphur Waste	% Sulphur Raw	Waste Sand pH As Received	Waste Sand pH After HCl	Acid Potential $CaCO_3$/ 1000 (WFS)	Waste Molding Sand System
1	0.09	< 0.01	6.02	< 5	-2.81	Shell
2	0.18	< 0.01	7.89	< 5	-5.62	Greesand
3	0.05	< 0.01	6.32	< 5	-1.56	Phenolic Urethane
4	0.01	< 0.01	7.03	< 5	-0.31	Greesand
5	0.22	< 0.01	9.01	< 5	-6.87	Greesand
6	0.15	< 0.01	10.1	< 5	-4.68	Alcaline Phenolic
7	0.04	< 0.01	7.02	< 5	-1.25	Pepset
8	0.06	< 0.01	6.91	< 5	-1.87	Alcaline Phenolic
9	0.15	< 0.01	10.1	< 5	-4.68	Greesand
10	0.06	< 0.01	6.03	< 5	-1.87	Furan

However, even though the waste sand contains elemental sulfur, able to promote sulfuric acid formation when exposed to rain and other marshy or swampy terrain (in-situ environment), foundry waste sand do not exhibits corrosivity characteristics.

Foundry Waste Moulding Sands Effluents Characters

Since all waste sand pH values were within the stipulated range when recorded during the appropriate leaching media choice for the TCLP (table-3). The regulation had rate precipitation to occur at high pH value than 12 while corrosive waste able to form acid poses a pH less than 6. Waste sand pH was within the stipulated regulatory range being 6-12 as summarized in table-3.

Out of the sixteen regulated metals, six were found present in the waste sand, these metals included Cu, Cr, Mn, Ni, Pb, and Zn. From the observation relating to the waste sand leachate composition, the results revealed that the waste foundry sand does not meet any toxic characters for the rest of the regulated metals which are: As, B, Ba, Cd, Co, Hg, Mo, Sb, Se and V.

Table. 4. Summarizes the metallic trace concentration

AAS Elemental Analysis	Waste Sand					Virgin Sand	SA Act (Limit Concentration)			
	S_1	S_2	S_3	S_4	S_5		LCT 0	LCT 1	LCT 3	LCT 4
Mn	0.00	0.85	0.52	0.00	0.00	0.89	0.5	25	50	200
Cr	0.07	0.04	0.05	0.00	0.07	0.04	0.05	2.5	5	20
Fe	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
cu	0.00	0.13	0.09	2.57	0.00	0.00	2	100	200	800
Ni	0.00	0.46	0.39	0.00	0.01	0.98	0.07	3.5	7	28
Mg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Pb	0.00	0.00	0.09	0.71	0.00	0.00	0.01	0.5	1	4
Zn	0.00	0.00	0.00	7.62	0.00	0.05	5	250	500	2000
Co	0.00	0.00	0.00	0.00	0.00	0.79	0.5	25	50	200

Table. 4. Continues

AAS Elemental Analysis	Waste Sand					Virgin Sand	SA Act (Limit Concentration)			
	S_6	S_7	S_8	S_9	S_{10}		LCT 0	LCT 1	LCT 3	LCT 4
Mn	0.00	0.49	2.55	0.14	1.94	0.89	0.5	25	50	200
Cr	0.10	0.05	0.06	0.01	0.06	0.04	0.05	2.5	5	20
Fe	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
cu	0.00	0.00	0.00	0.09	0.16	0.00	2	100	200	800
Ni	0.00	0.03	0.51	0.42	0.23	0.98	0.07	3.5	7	28
Mg	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.5	1	4
Zn	0.00	0.01	0.00	0.00	0.00	0.05	5	250	500	2000
Co	0.00	0.00	0.00	0.01	0.00	0.79	0.5	25	50	200

Table-4- summarizes the metallic traces concentration magnitude irrespective of the used binder, against a control virgin sand leachate and lastly, the South African regulation. The control sand was obtain by mixing all collected virgin sand and was used as standard sample while the comparison with the regulatory, intended the classification of the waste foundry sand.

Apart from Cu and Zn, the waste sand leachate had similar composition with the control sand in terms of polluting metallic elements, as previously mentioned by H. Merve Basar and A. Nuran Deveci, (2012) that the waste foundry sand, exhibits similar chemical characters as regular sand. The large majority of analysed leachates did measured high manganese and nickel concentration suggesting that, these elements are contained in the sand matrix or bentonite clay and increase in their magnitude within the waste foundry sand during the metal casting process (Barbara S.Q. Alves et al, 2014), their highest proportion was observed in greensand (bentonite clay bonded sand). Chrome was present in all waste sand samples and can also be related to the sand grain matrix as observed during chemical analysis table 1.

3. 3. Metallic Traces Quantification and Sand Classification

Both sands waste and control had at least one metallic trace above the limits concentration thresholds zero (LCT0) and well below limits concentration thresholds one (LCT1). This suggests that the sands slightly exceed the class of inert waste and fall within the class of low hazardous risk waste. As reported by Mariana L. Marchioni et al, (2012) that waste foundry sand is classified as not inert waste. Contrary to the conducted waste classifications, the present study support the existing waste sand classification and under the local regulation, the foundry sand is hazardous from its origin well before the casting process is conducted.

4. Conclusion

Regardless of the fact that metallic content was found relatively high in the waste sand than in the control sand, and they both sand (waste and virgin control) fall in the same class. The experimental dataset provide additional evidence that very low metallic contamination takes place during the casting process and can therefore be reused in other application since it possess a very low hazardous characters.

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