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RESEARCH ARTICLE

Characterization of landfilled stainless steel slags in view of metal recovery

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Abstract The slag samples taken from landfill, which originated from different metallurgical processes, have been characterized in this study. The slags were categorized as electric arc furnace (EAF) slag, argon oxygen decarburization/metal refining process slag and vacuum oxygen decarburization slag based on chromium content and basicity. EAF slags have higher potential in metal recovery than the other two slags due to its higher iron and chromium contents. The size of the iron-chromium-nickel alloy particles varies from a few µm up to several cm. The recoveries of large metal particles and metal-spinel aggregates have potential to make the metal recovery from landfilled slags economically viable.

Keywords landfilled stainless steel slag, metal recovery, characterization

1 Introduction

Since the beginning of the new millennium, due to environmental and economical incentives, research devoted to recycling of metallurgical slags has increased dramatically [1]. Slags are no longer considered as end-wastes, but actually as secondary resource materials, which have been applied in various areas [2]. An excellent example for slag valorisation is the complete recycle of blast furnace slag as gravel for road construction or raw material in cement production [3]. In contrast, the application of stainless steel slags is rather limited [2,3]. One of the major reasons hindering the valorisation of stainless steel slags is their heavy metal content, such as chromium, which is restricted in many applications [3–6]. Although in some cases [7–9], the results of environmental leaching tests on stainless steel slags with various origins are below the values of hazardous material, the potential release on the long term of the heavy metals is still a concern [9]. In the case of chromium, despite it is mainly sealed in stable spinel phases and at non-hazardous trivalent state, it can still be gradually oxidised to highly soluble and carcinogenic hexavalent state in atmospheric environment [7,10,11]. Hence, it is preferable to remove chromium, or at least reduce its content to rather low level, before applying stainless steel slags to landfill. Besides the reduction of potential risk to the environment, the effective recovery of metals from slags also has economical importance due to the constantly rising demand of chromium in metallurgy [3,12]. The importance of metal recovery plants is rising with the increasing size of the slag dumps worldwide. Metal recovery from slags has been in vogue since mid-1990s. In some cases, the smelter can even shut down a furnace during times of poor metal price and still keep up capacity through metal recovery from slags at a reduced operation cost [13].

The REMO landfill site in Houthalen-Helchteren is owned by Group Machiels and stores 16 million tons of waste materials, among which about 1 million tons are stainless steel slags generated from metal production plant of Aperam (a stainless steel maker in Belgium) during 1990s and early 2000s. The slags originated from various metallurgical processes, including electric arc furnace (EAF), argon oxygen decarburization (AOD)/metal refining process (MRP) and vacuum oxygen decarburization (VOD). The aim of this project is to recover valuable metals, including iron, chromium, nickel and other alloying metals from the landfilled stainless steel slags. A

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lot of research has been carried out in metal recovery from metallurgical wastes, through physical processes [13,15,16], pyrometallurgical processes [17–19] and hybrid processes of both techniques [20]. Promising results have been reported and economical benefits have been claimed. However, prior to study the feasibility of various processes in metal recovery from slags, it is necessary to understand the properties of the material. Therefore, this study has been conducted to study the characteristics of the landfilled stainless steel slags, supporting the design of subsequent metal recovery flowsheet.

2 Sampling and characterisation methodology

The slags were stored in the landfill and covered with a layer of 1-meter-thick soil and vegetation. There are no clear records of the details of operations at that time, such as from which process the slag was produced or where it was stored. To acquire more knowledge about the slags, a 1-meter-deep pit (Fig. 1 (a)) was excavated on the top of the slag heap to obtain samples for further characterization. The slags stored in the heap exhibited heterogeneous colours and appearances (Fig. 1 (b)), indicating their various origins and properties.

Two buckets of slag samples obtained from the excavated slag pit, indicated “ALZ” and “STAAL2” respectively, were received. Slags from these two buckets were then crushed, from pieces with size between 5 and 15 cm, into different size ranges. During crushing, the slags were categorized into seven categories based on their respective colours and morphologies. Characterization of these slags is the first step towards metal recovery and utilization. Chemical composition, microstructure and mineralogy of the stainless steel slags were determined through different techniques. Besides the slag pit, samples were also taken from four other locations on the landfill to compare their differences in chemical composition.

The received slags were crushed using a hammer (down to < 3 cm) and ground with a jaw crusher (down to < 1 cm). Large metal pieces were picked out by hand for the ease of the subsequent material handling steps. The samples were then prepared through fine grinding with roll mill (with roll gap of 500 μm) and subsequent sieving. When passing through the roll mill, instead of being ground, the metal particles (> 500 μm) were only deformed into flake shape with enlarged surface. The metal flakes were then separated through sieving and not included in this study. Metal particles below 500 μm could pass through the roll mill together with slag material. This mixture of small metal particles and slag material was then ground in centrifugal mill (down to < 100 μm) for chemical composition analysis. The overall chemical composition of the slag was determined with X-Ray fluorescence (XRF, Philips PW 2400) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 720 ES). Metal particles larger than 500 μm were excluded from the chemical composition of the slags by grinding and sieving. The microstructure of the slag was characterized with scanning electron microscopy (SEM, Philips XL30 FEG) equipped with energy-dispersive X-ray spectroscopy (EDX). The mineralogical composition of the slag was characterized with X-Ray Diffraction (XRD, Seifert 3003 TT). The quantification of minerals was carried out through Rietveld refinement with the help of TOPAS Software (Bruker).

(a) (b)

Fig. 1 (a) Sampling operation on slag heap; (b) cross section of slag heap

3 Characterisation results—On-site sampled slags

3.1 General description

The slags from the two received buckets were categorized into seven categories based on their respective colours and morphologies, which can be the first indications of their respective composition and origin. The categories and concise descriptions are listed in Table 1. It is extremely difficult to estimate the mass fraction for each category, because the slags were randomly mixed.

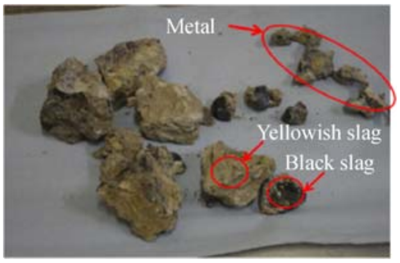
3.2 Chemical and mineralogical composition

Slag samples (5 kg per spot) from various locations on the landfill were collected and the respective overall chemical compositions were measured. To obtain the chemical composition representing the whole slag body, the samples were crushed and ground from a bulk sample into powder below 100 μm without selective sieving or separation. However, the large metal particles (> 500 μm) were picked out, due to difficulties caused by them during grinding. The results are listed in Table 2. Except sample from location 2, the other samples have similar CaO and SiO_2 compositions and basicities. However, the contents of other oxide components vary from each other to a great extent. This indicates the complexity of the slag types in the landfill.

Close studies were performed on the seven slag samples from the excavated slag pit. The overall chemical compositions of these samples are listed in Table 3.

Slags from different stainless steel making processes, such as EAF, AOD, MRP and VOD have similar slag systems. CaO, SiO_2, Al_2O_3 and MgO are the major slag components in stainless steel slags. Depending on the processing parameters, feeding materials and production period, the composition of slag from a certain process can

Table 1 Categories and concise descriptions of slags

Slag	Description
"ALZ" bucket	
A aggregate	 "A aggregate" is composed of a yellowish slag and a black slag. Large pieces (up to several cm) of metal can be observed.
A black	 "A black" is a dense hard solid slag. White dots can be observed in the black slag matrix. Small pores can be found in the slag, but not in vast amounts.
"STAAL2" bucket	
S aggregate	 "S aggregate" appears to be a yellowish porous solid material with loose bonding structure.

(*Continued*)

Slag	Description
S black	 "S black" is a porous black solid slag. Small metal particles can be observed visually on the surface when it was crushed.
Green	 "Green" is a dense hard slag, which gives a greenish color.
Yellow	 Slag "Yellow" is a solid that contains large pores. The surface of the slag is in a yellowish color.
Hybrid	 Slag "Hybrid" is an aggregate of two types of slags, which appear in black and yellow respectively.

Table 2 Overall chemical composition of slag samples from different locations (wt-%)

Location	CaO	SiO_2	MgO	Al_2O_3	Cr_2O_3	Fe_2O_3	MnO	Basicity
1	48.3	29.4	5.5	5.3	6.5	1.7	1.9	1.6
2	37.8	41.1	4.5	4.9	5.8	2.6	1.6	0.9
3	47.2	30.9	5.5	6.9	4.4	1.9	1.2	1.5
4	47.7	31.2	7.2	6.9	3.3	0.7	1.7	1.5
5	46.7	32.9	6.7	3.6	6.4	1.0	1.6	1.5

vary over a wide range and even overlap with the composition of slag generated from other processes. The phases exist in slags depends on the cooling process. Different cooling process can generate different phases or phase ratio in the same slag. Hence, the mineralogy of a certain slag is not necessarily according to its original process. The determination of the process from which the slag is produced, is therefore difficult but can be inferred based on two factors: basicity of the slag and Cr_2O_3 content. In general, AOD slag contains more CaO but less SiO_2 than EAF slag [14]. Hence, AOD slag has relative high basicity (around 2). The MRP process is similar to AOD process and the slag composition is close to that of AOD. The basicity of EAF slag can be up to 2 and sometimes it can even overlap with that of AOD/MRP. For example, for sample "Green", the basicity was 1.9. In that case, the content of Cr_2O_3 is used as the second criteria. In EAF slags, the content of Cr_2O_3 is relatively high because there is no reduction step to recover oxidised Cr in the EAF process as it is applied in AOD/MRP and VOD processes [14]. At the same time, the content of Cr_2O_3 is more than twice of that of AOD/MRP. Hence, the slag "Green" can still be assumed to be EAF slag. VOD slag normally has very low basicity (close to 1) and low Cr_2O_3 content [14]. Based on these criteria, the origin processes of the slags were inferred and listed in Table 3.

Table 4 lists the major phases in various slag samples. Dicalcium silicate (C_2S) is the matrix mineral for most of the slags applied in stainless steel production. Among the samples categorized as EAF slag, a relatively large amount of magnesiochromite can be detected. The slags "Hybrid" and "A black" lack Cr containing phases due to their low overall Cr content (Table 2). All the slags have relatively low gamma C_2S and quartz (silica) content, because they were selected large bulk materials with integrated shape. The slags in the landfill are mixture of materials from fines to large bulk materials. As shown in the following characterizations of the physically separated samples represented the general slag composition in the landfill, quartz content increases with decreasing of size of ground

Table 3 Overall chemical composition of slag samples (wt-%)

Slag	CaO	SiO_2	MgO	Al_2O_3	Cr_2O_3	Fe_2O_3	MnO	Basicity	Presumed slag type
A aggregate	46.5	28.0	7.4	4.3	8.0	2.7	1.7	1.7	EAF
S aggregate	44.8	30.1	5.7	6.1	7.5	2.6	1.7	1.5	EAF
S black	35.1	21.0	4.5	3.9	19.4	8.9	2.5	1.7	EAF
Green	48.8	26.2	9.1	6.9	5.8	0.7	1.1	1.9	EAF
Yellow	44.5	29.0	5.9	7.1	6.8	2.1	1.7	1.5	EAF
Hybrid	51.3	26.7	8.2	9.1	2.3	0.6	0.5	1.9	AOD/MRP
A black	40.6	37.3	7.9	6.8	2.3	0.3	3.2	1.1	VOD

Table 4 Mineralogical composition of various slag samples (wt-%)

Mineral	Chemical formula	A aggregate	S aggregate	S black	Green	Yellow	Hybrid	A black
C_2S beta	Ca_2SiO_4	21.6	23.2	44.5	65.5	43.7	43.2	< 1.0
C_2S gamma	Ca_2SiO_4	9.6	3.8	5.0	3.9	8.3	< 1.0	< 1.0
Magnesiochromite	$MgCr_2O_4$	12.7	7.2	16.9	4.9	6.7	1.6	1.6
Quartz	SiO_2	1.3	1.4	1.2	< 1.0	5.1	< 1.0	1.5
Gehlenite	$Ca_2Al_2SiO_7$	6.2	20.7	2.0	< 1.0	1.6	1.4	48.9
Bredigite	$Ca_7MgSi_4O_{16}$	8.6	4.8	3.9	5.7	4.4	27.7	< 1.0
Magnesite	$MgCO_3$	3.7	2.5	2.9	< 1.0	2.5	5.0	< 1.0
Merwinite	$Ca_3MgSi_2O_8$	10.3	3.7	2.7	< 1.0	4.4	2.1	< 1.0
Calcite	$CaCO_3$	1.3	5.1	1.5	2.3	3.3	< 1.0	< 1.0
Cuspidine	$Ca_4F_2Si_2O_7$	12.5	8.8	4.4	3.4	4.5	6.1	19.2
Akermanite	$Ca_2MgSi_2O_7$	3.2	3.7	< 1.0	2.0	< 1.0	< 1.0	15.3
Iron carbide	Fe_5C_2	2.1	2.9	3.4	4.2	4.2	2.0	4.3
Magnetite	Fe_3O_4	< 1.0	< 1.0	2.0	1.7	1.5	2.1	1.7
Calcium chromate	$CaCr_2O_4$	< 1.0	2.8	2.1	< 1.0	2.9	1.7	4.2
Wollastonite	$CaSiO_3$	4.2	7.7	4.8	1.9	3.7	3.4	< 1.0

*Values < 1.0 are considered as inaccurate due to the limitation of the QXRD method.

materials, whereas gamma C_2S content does not show significant changes. Hence, the conclusion can be drawn that the sand and gravels mixed in the slag deposit would end up in the fines after physical separations.

3.3 Microstructure

The microstructure of the slag samples from the excavated pit was characterized with SEM. The composition of specific phases was studied with EDX. The images for each individual sample are listed and discussed below. The identification of various phases was carried out based on EDX data and overall mineralogical composition was obtained through XRD. Although magnesiochromite ($MgCr_2O_4$) was the major chromium containing phase observed during XRD analysis, calcium chromate ($CaCr_2O_4$) was also detected during EDX characterizations, which is in line with XRD analysis (Table 4). Hence, the label "Cr spinel" is selected to indicate the group of spinel phases.

3.3.1 A aggregate

"A aggregate" is composed of two kinds of slags. One is lean in metal alloy particles and Cr spinel (Fig. 2(b)). The matrix of this slag is composed of merwinite, gehlenite and dicalcium silicate. This slag has low basicity and Cr content (Table 3). The other slag in this sample is rich in metal particles and well developed Cr spinel grains (Fig. 2(c)). The matrix of this slag is bredigite. It can be observed that metal droplets are normally associated with Cr spinel particles. Hence, there is a potential for them to be recovered together.

3.3.2 S aggregate

Figure 3 shows the complex microstructure of sample "S aggregate". The matrix of the slag is dicalcium silicate and bredigite. Needle shape calcium chromite and cubic shape periclase grains can be observed throughout the slag.

3.3.3 S black

As indicated in Fig. 4, dicalcium silicate, Cr spinel and bredigite are the major phases of slag "S black", which is in line with the analysis delivered by XRD (Table 4). This type of slag is rich in metal value, which reveals its high Cr and Fe content (XRF results). Large Cr spinel grains (grain size up to 200 μm, Fig. 4 (a)) can be observed throughout the slag body.

3.3.4 Green

The matrix of slag "Green" is dicalcium silicate. The magnesium content of this slag sample is relatively high due to the large amount of periclase existing in the slag (Fig. 5). The other phases existing in this slag are bredigite, Cr spinel and Fe-Cr-Mn alloy.

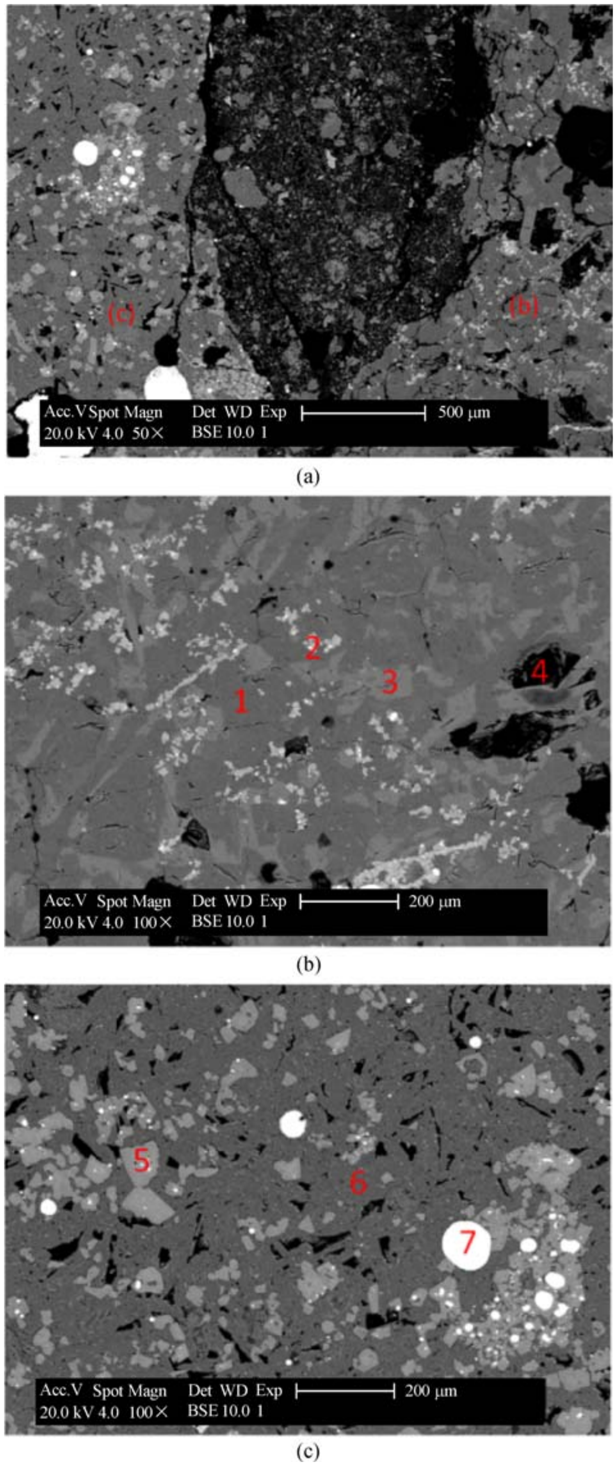


Fig. 2 Slag "A aggregate": (a) overall microstructure; (b) detailed microstructure of metal lean part; (c) detailed microstructure of metal rich part. 1: merwinite; 2&5: Cr spinel; 3: C_2S; 4: pores; 6: bredigite; 7: Fe-Cr-Ni alloy

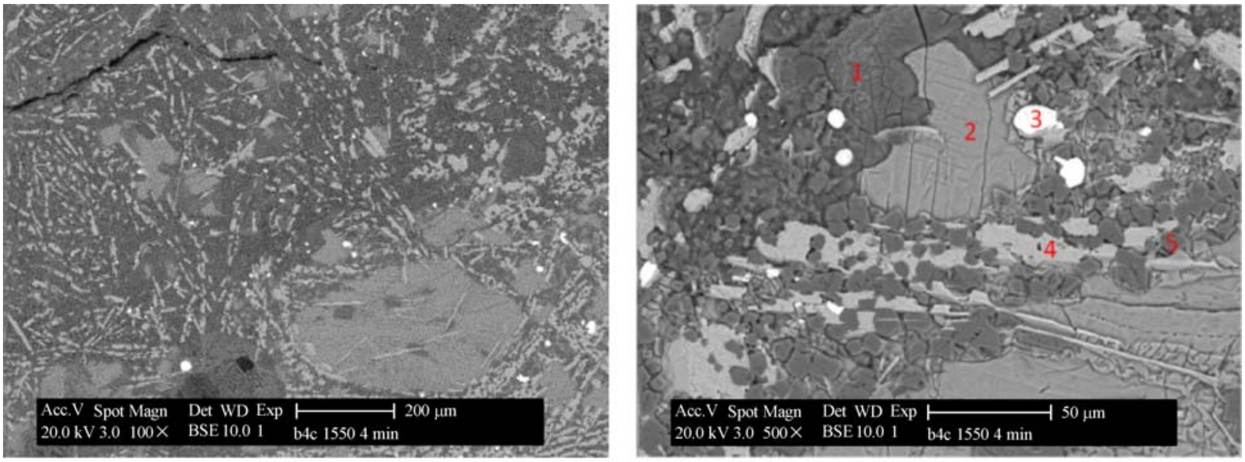


Fig. 3 Slag “S aggregate”: (a) overall microstructure; (b) detailed microstructure. 1: bredigite; 2: C_2S; 3: Fe-Cr-Ni alloy; 4: Cr spinel; 5: periclase

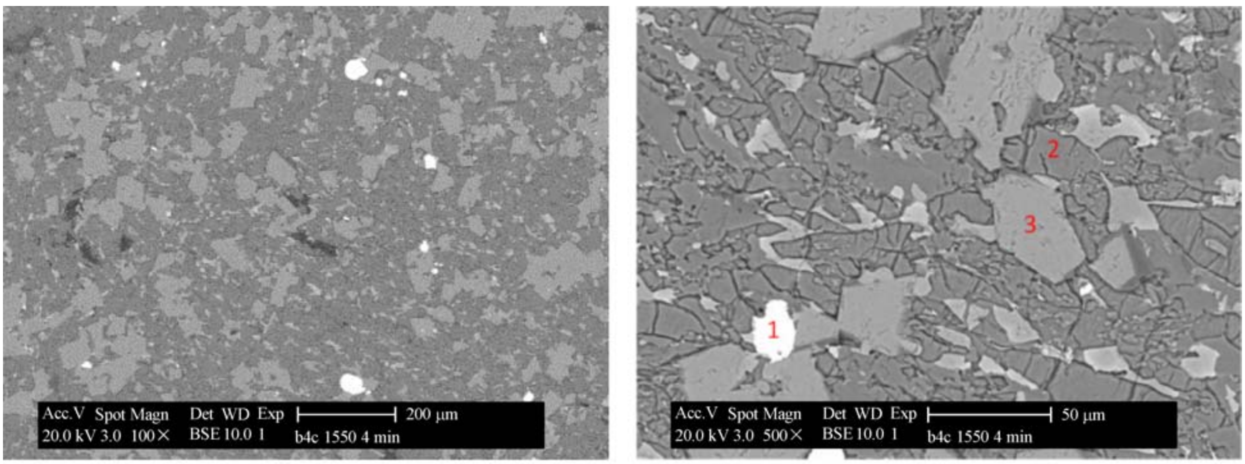


Fig. 4 Slag “S black”: (a) overall microstructure; (b) detailed microstructure. 1: Fe-Cr-Ni alloy; 2: C_2S; 3: Cr spinel

3.3.5 Yellow

The sample was very lean in metal phase. The matrix minerals of this sample are dicalcium silicate and merwinite. Relatively large Cr spinel grains (up to 200 µm) can be observed (Fig. 6 (a)). Metals are in the form of fine droplets. Magnesium aluminate can be observed as single crystal or accumulated with merwinite and magnesiochromite. This phase was not indicated in the XRD results.

3.3.6 Hybrid

Slag “Hybrid” is composed of two slags. One has black colour (named H-black) and the other has yellowish colour (named H-yellow). These two slags were contained in the same slag bulk and cannot be separated mechanically. Both of them lack metal droplets (Figs. 7(a) and (c)), which is also revealed by their low iron content (Table 3). The major phases in H-black slag are dicalcium silicate, periclase, bredigite and Cr spinel. The chromium spinel grains are relatively fine (10−50 µm) and associated with other phases in skeleton shape. Cuspidine can be observed in H-yellow slag, whereas chromium spinel is absent. Low chromium and iron content and fine grain size of slag “Hybrid” indicate its low potential in metal recovery.

3.3.7 A black

Gehlenite, cuspidine and akermanite are the major phases in slag “A black”. Fine Cr spinel grains (<50 µm) and metal droplets (<20 µm) can be observed (Figs. 8(a) and (b)), but in limited amount. This indicates the low potential of this slag in metal recovery.

As can be concluded from the discussions, the slags with different characteristics have been randomly mixed and landfilled. The average chromium and iron contents are

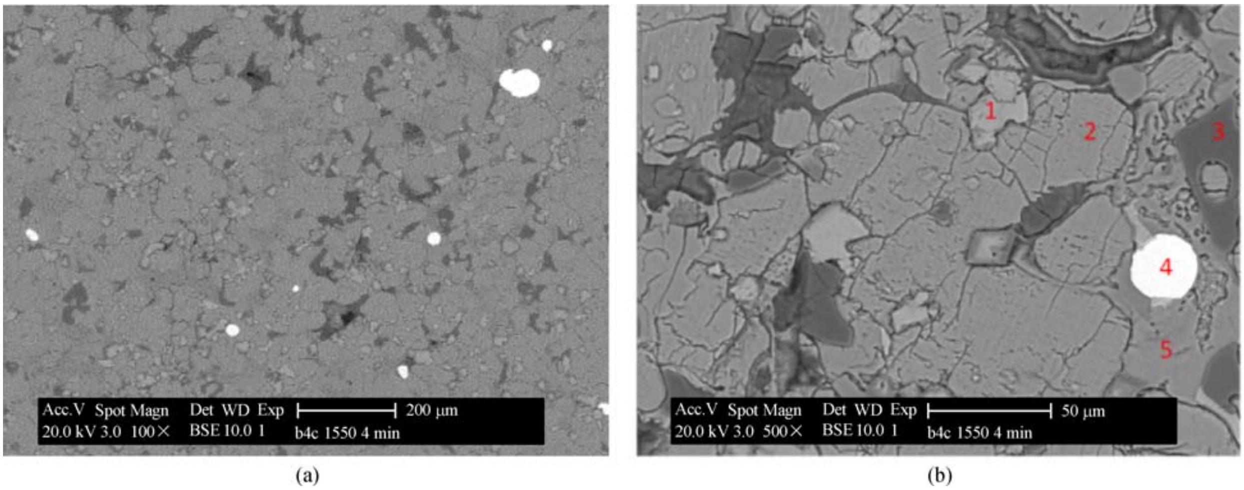


Fig. 5 Slag “Green”: (a) overall microstructure; (b) detailed microstructure. 1: Cr spinel; 2: C2S; 3: periclase; 4: Fe-Cr-Ni alloy; 5: bredigite

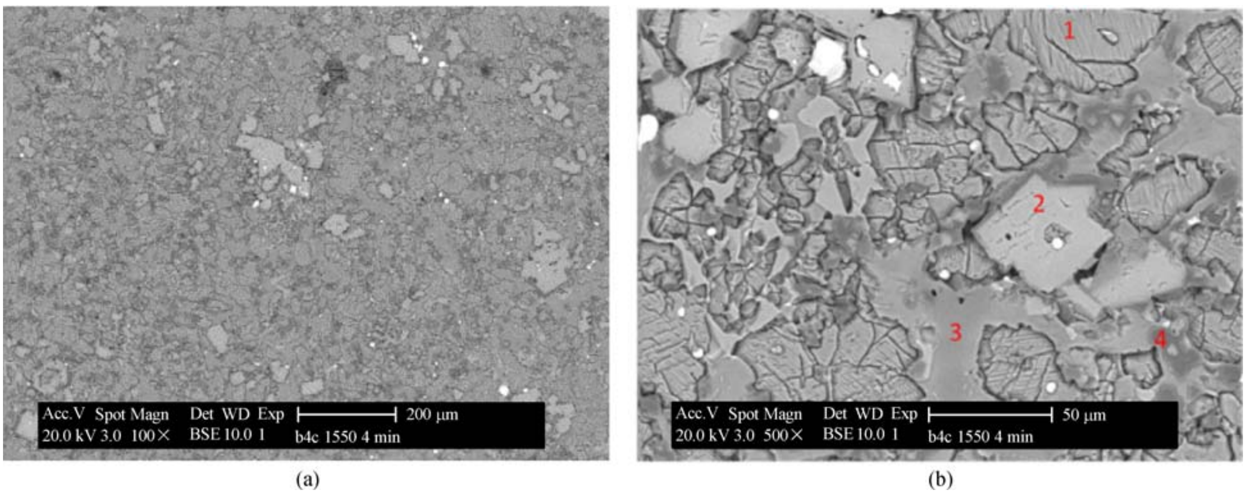


Fig. 6 Slag “Yellow”: (a) overall microstructure; (b) detailed microstructure. 1: C_2S; 2: Cr spinel; 3: merwinite; 4: magnesium aluminate ($MgAl_2O_4$)

relatively low in various slag streams (as shown in Table 1). However, these are the values obtained after removing the large (>500 µm) metal alloy particles. These particles contain large amount of iron, chromium and nickel. They can be easily recovered through conventional physical separation processes and generate economical benefits for the landfill owner. Due to the limited size of this study, where only kilos of materials were studied, the mass fraction of the large metal alloy particles could not be accurately quantified. On the other hand, based on the SEM images, it can be observed that metal alloy particles mostly coexist with chromium spinel grains. These metal-spinel aggregates can potentially be separated from the slag matrix through physical separation, based on their differences from other minerals in terms of density and hardness. The obtained chromium-iron rich fractions can be fed back to the metallurgical processes as a concentrate. Therefore, a pilot scale campaign on the metal recovery from these landfilled slags is proposed to study the feasibility and economical value of separating large metal particles and metal-spinel aggregates from landfilled slags.

4 Conclusions

The slag samples taken from landfill site originate from different metallurgical processes. Their chemical compositions and microstructures were studied. The slags were categorized as EAF slag, AOD/MRP slag and VOD slag based on chromium content and basicity (the weight ratio of CaO/SiO_2). Generally, EAF slags have high chromium and iron contents and low basicity. AOD/VOD slags have low chromium content but high basicity. VOD slag has both low chromium content and low basicity. The size of the iron-chromium-nickel alloy particles varies from a few

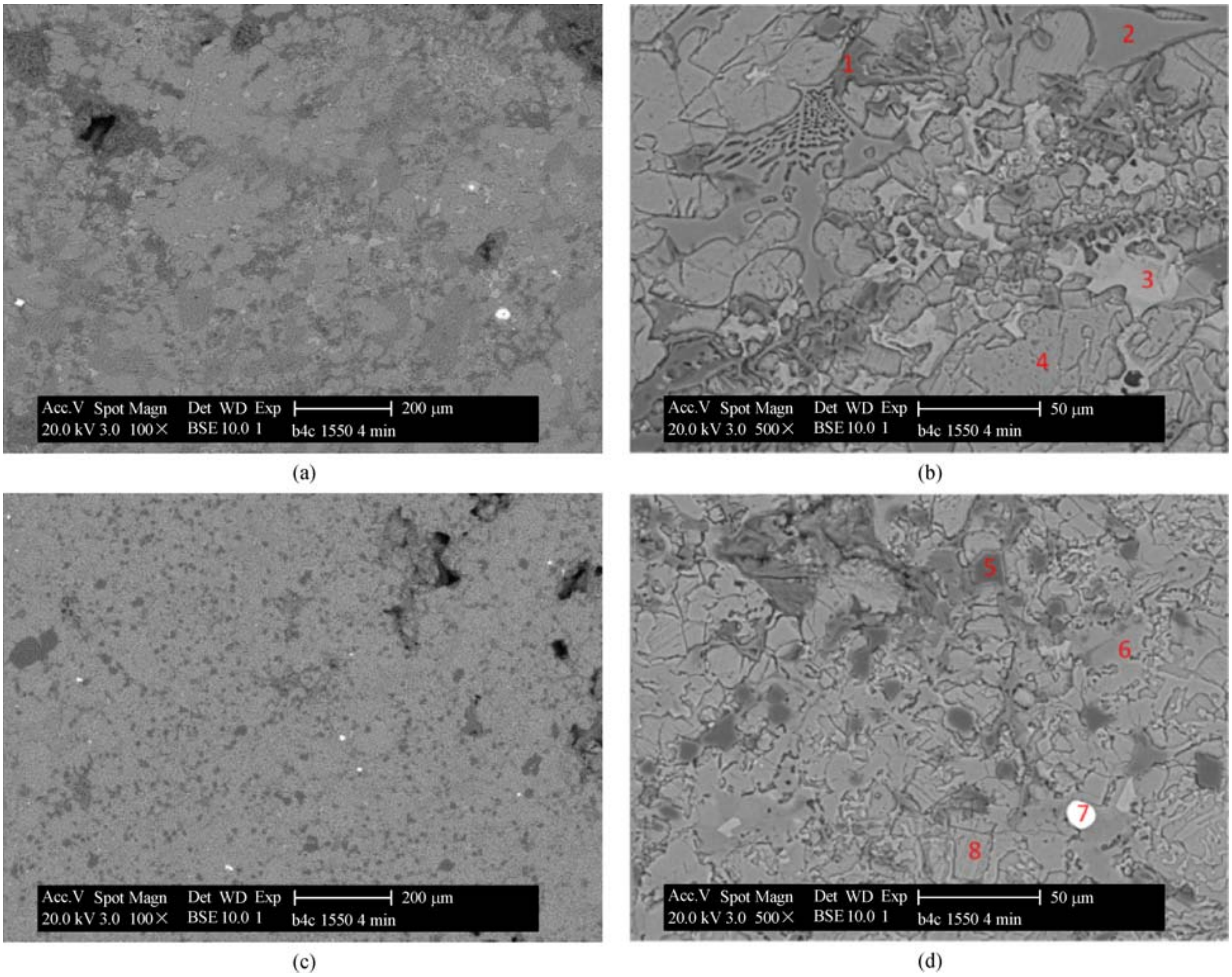


Fig. 7 Slag "Hybrid": (a) overall microstructure of H-black slag; (b) detailed microstructure of H-black slag; (c) overall microstructure of H-yellow slag; (d) detailed microstructure of H-yellow slag. 1&5: periclase; 2: bredigite; 3: Cr spinel; 4&8: C_2S; 6: cuspidine; 7: Fe-Cr-Ni alloy

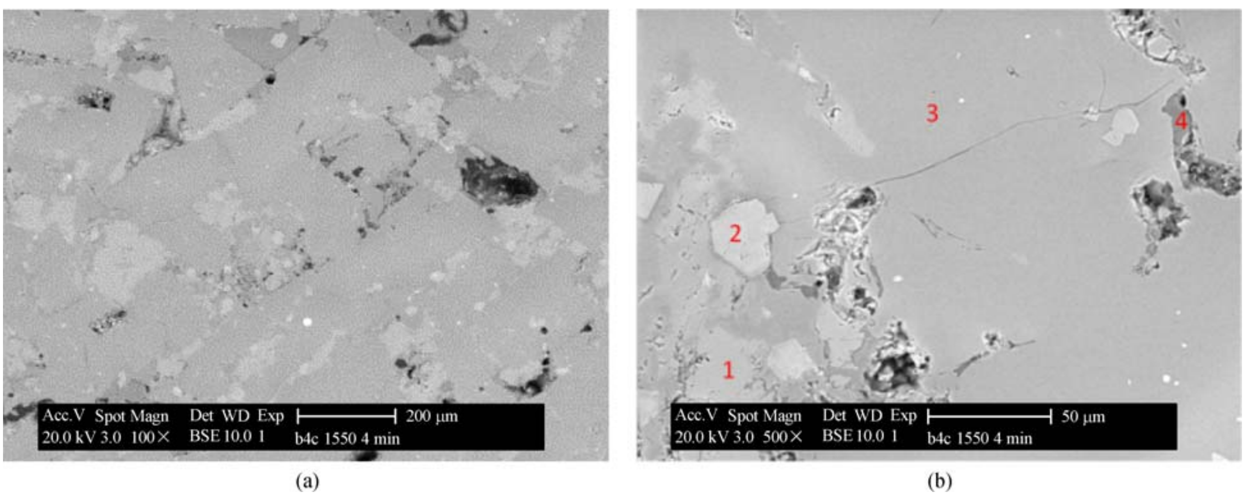


Fig. 8 Slag "A black": (a) overall microstructure; (b) detailed microstructure. 1: cuspidine; 2: Cr spinel; 3: akermanite; 4: gehlenite

μm up to several cm. EAF slags have higher potential in metal recovery than the other two slags due to its high iron and chromium contents. The recoveries of large metal particles and metal-spinel aggregates have potential to make metal recovery from landfilled slags economically viable. A larger scale campaign on the metal recovery from these landfilled slags is suggested to be carried out.

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