

## EVALUATION OF LADLE SLAG AS A POTENTIAL MATERIAL FOR BUILDING AND CIVIL ENGINEERING

### OCENA POTENCIALA PONOVCNE ŽLINDRE KOT SUROVINE ZA UPORABO V GRADBENIŠTVU

Vesna Zalar Serjun<sup>1</sup>, Breda Mirtič<sup>1</sup>, Ana Mladenovič<sup>2</sup>

<sup>1</sup>University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Geology, Aškerčeva c. 12, 1000 Ljubljana, Slovenia

<sup>2</sup>Slovenian National Building and Civil Engineering Institute, Dimičeva 12, 1000 Ljubljana, Slovenia  
vesna.zalar@geo.ntf.uni-lj.si

*Prejem rokopisa – received: 2013-02-22; sprejem za objavo – accepted for publication: 2013-03-20*

An important step in secondary metallurgy of stainless steel is ladle metallurgy. Ladle slag is a by-product of ladle refining, typically specific for each steelmaking plant. Industrial secondary materials can be used for different applications, including construction and civil engineering. The use of industrial by-products requires the knowledge of the characteristics of the materials. Using metallurgical by-products that fulfil the relevant requirements can save natural resources, as well as helping to avoid impairment of the landscape through their excavation and, thus, minimizing the adverse landfilling of such materials. This paper provides an overview of possible uses of ladle slag (the slag from a ladle furnace and vacuum-oxygen-decarburization processes). As a preliminary research, ladle slag has been investigated using SEM/EDS. The commonly known hydraulic minerals, such as tricalcium aluminate, mayenite, tricalcium silicate and dicalcium silicate, were detected in this analysis. Since a large proportion of the mineral phases of ladle slag exhibit hydraulic properties, ladle slag could also have a potential use in the bonded composites in construction.

Keywords: ladle (ladle furnace, vacuum oxygen decarburization) slag, reuse, recycling, building sector, civil engineering

Ponovna tehnologija je pomemben proces sekundarne metalurgije pri produkciji nerjavnih jekel. Stranski produkt rafinacije jekla v ponovci je ponovčna žindra, ki je bolj ali manj specifična za posamezno jeklarno. Industrijski stranski produkti se lahko uporabijo v različnih panogah, vključno z gradbenim sektorjem. Ključni pogoj za uporabo tehnoloških odpadkov je poznanje njihovih lastnosti. Ponovna uporaba stranskih produktov iz proizvodnje jekla z ustreznimi lastnostmi je pomemben element zmanjševanja obremenjenosti okolja, saj se s tem ohranjajo neobnovljivi naravni mineralni viri, ki se pridobivajo iz naravnih kopov ter hkrati razbremenjujejo deponije. V članku je podan pregled mogoče uporabe ponovčne žindre (žindre iz ponovčne peči in žindre iz procesa vakuumskega razogljčenja (VOD)). Preliminarna raziskava ponovčne žindre je bila izvedena s SEM/EDS. Določene so bile mineralne faze, ki izkazujejo hidravličnost, kot so trikalcijev aluminat, mayenit, trikalcijev silikat ter dikalcijev silikat. Ker ima velik del mineralnih faz v preiskovani ponovčni žindri hidravlične lastnosti, je žindra zato dodatno potencialno zanimiva za vezne kompozite v gradbeništvu.

Ključne besede: ponovčna (ponovčna peč, proces vakuumskega razogljčenja) žindra, ponovna uporaba, recikliranje, gradbeni sektor, nizke gradnje

## 1 INTRODUCTION

In 2010, the EU steelmaking industries generated about 21.8 million tonnes of different types of slag.<sup>1</sup> About 13 % of this amount was generated as secondary metallurgical slag<sup>1</sup>, arising from various secondary-metallurgy processes. One of the secondary processes in the production of high-alloyed steel is known as ladle refining or ladle metallurgy. Ladle refining consists, generally, of a ladle furnace (LF) and vacuum oxygen decarburization (VOD).<sup>2</sup> The slag resulting from this process is called ladle slag (LS) and is also known as basic, refining, reducing, or falling slag, and also as white slag.<sup>1,3-9</sup>

Land disposal restrictions are becoming increasingly stringent (due to the environmental harm, the use of valuable landfill space, resources and costs). The current EU policy encourages and promotes the reuse and recycling of waste. The EU Waste Framework Directive (2008/98/ES)<sup>10</sup> earmarks land disposal as the least acceptable alternative. Implementation of this concept

means that a material originating as waste can either be characterized as waste, or declared as a by-product.

In many EU states slag has already been declared as a by-product, a non-waste material, or a product.<sup>1,11</sup> Different types of slag have different capabilities for recycling and reuse; ladle slag has the lowest such capability.<sup>6</sup> Due to its fine grain size and adverse properties with regard to leaching (the presence of harmful elements such as Cr), ladle slag has a low potential for recycling.<sup>12-15</sup> For this reason about 80 % of it is currently landfilled, taking into account the whole of the EU.<sup>11</sup>

The recycling of industrial by-products has two important goals: a reduction in the amount of waste material and the minimization of the exploitation of natural resources. In order to minimize consumption in a production process, it is necessary for every country to exploit, to the maximum, every available industrial by-product.<sup>16,17</sup> In the case of the concrete industry, an industrial by-product of fine gradation can be used as a filler or as a fine aggregate. Of course, there is a higher benefit, when it can be used as a binding agent, replacing

a percentage of the cement.<sup>17</sup> Following this concept, an extensive research is in progress in order to create new opportunities for the reuse of LS.

Environmental challenges have become a key issue for the steelmaking industry, too. In recent years, methods for the recycling of slags have been improved, as the recycling approach is not only an opportunity but also a necessity for the survival of steel production,<sup>7,18</sup> since, among other factors, it is not possible to return slag, or at least not all of it, into the primary steelmaking process. The ideal sector for the consumption of the excess slag is the building industry. In the construction sector two synergetic effects are achievable: large amounts of material can be consumed and, at the same time, in the case of bonded composites (e.g., concrete) the harmful elements such as Cr can be permanently immobilized through the solidification/stabilization (S/S) technology.<sup>14,15</sup> An additional benefit lies in the fact that LS has (latent) hydraulic components and may be considered as a cementitious material. This attribute can be positive in the binder mixtures used in bonded composites.<sup>3,5,19–25</sup> Steelmaking slags could be either low-cost materials in the applications where low demands are expected, or products with a high-added value that could improve the properties of the final products.<sup>17</sup> At present, LS is still an innovative option, being less extensively used in the building sector than the other steelmaking slags.<sup>6</sup> The applications of LS are diverse and can be extended to any realm where their use is allowed, advised or even recommended by imagination, common sense and/or good practice.<sup>8</sup>

Each type of steel slag has its own characteristics. Not all steel heats are similar, nor do all steel manufacturers share the same working practices, giving rise to variations in the composition of LS at different steel works, and even at the same works, due to different heats.<sup>8</sup> Furthermore, local conditions, batch syntheses and scrap-metal variations also affect the composition of the produced slag.<sup>17,21,22</sup> The exposure of slag stockpiles to the atmosphere must also be taken into account.<sup>8</sup> Another aspect is the physical or practical procedure of dealing with the logistics of slag. Slags from different processes are sometimes mixed together in the liquid phase before being transported to the slag yard. Last but not least is the question of the handling of the slag at the slag yard. Water is often used to lower the temperature of the slag and/or to avoid the formation of dust.<sup>2,23</sup> This means that every different LS must be considered as a case study.

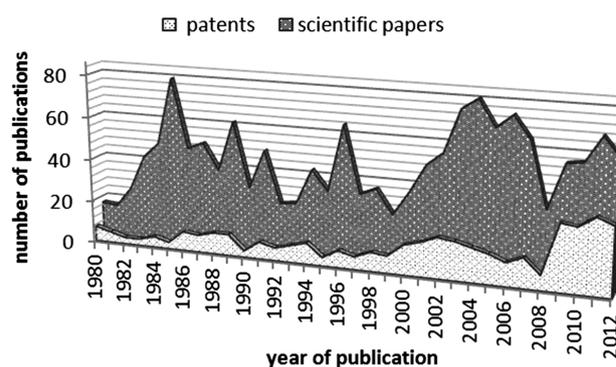
Accurate knowledge about the chemical, mineralogical and morphological properties of steel slags is essential because their cementitious and mechanical characteristics, which play a key role in their possible reuse, are closely linked to these properties.<sup>19,20</sup>

This paper provides a literature review of possible fields of application, as well as reviewing the chemical and mineralogical composition of ladle slag (LF and

VOD slag). The most common mineral composition of the LS studied by means of SEM/EDS is presented. The purpose of this work is to explore the potential (latent) hydraulic properties of LS.

## 2 FIELDS OF APPLICATION

The number of publications per year on the topic of ladle slag (**Figure 1**) indicates that LS has been intensely studied in recent years, from the point of view of both fundamental and applied research.



**Figure 1:** The number of publications per year and the publishing trend regarding the dynamics of the development in the field of ladle slag is presented using a value-added processing method. The relationship between the number of published articles and the number of patents indicates the proportion of fundamental and applied research. The data were collected from the databases: Engineering Village (Compendex) and Espacenet, for the period of 1980–2012.

**Slika 1:** Za sledenje usmeritev raziskav, tako temeljnih kot aplikativnih, ter za spremljanje dinamike razvoja s področja ponovne žindre, smo uporabili metodo procesiranja z dodano vrednostjo. Razmerje med članki in patenti nakazuje delež temeljnih in aplikativnih raziskav. Podatki so bili zbrani iz podatkovne baze Engineering Village ter Espacenet za obdobje 1980–2012.

According to Manso et al.<sup>26</sup> two main groups can be identified among the possibilities for the reuse of LS: those involving its industrial transformation with a significant economic cost (mainly recycling in the electric-arc furnace), and those aimed at finding an inexpensive use of LS as a construction material.

### 2.1 Reuse of LS

The steel-making industry can recycle LS by using it as a flux in the steel production instead of lime.<sup>27–30</sup> This kind of reuse of LS is performed by injecting it into EAF, representing the so-called "hot recycling" of LS.<sup>7,29</sup> Such recycling of LS can sometimes achieve interesting and advantageous results: besides decreasing the amount of dumped material and the cost of fluxes (by about 35 %), it can improve the foaminess of the EAF slag, and also increase electricity-consumption efficiency. Additionally, there is no more need for lime or this need is reduced to at least 70 %.<sup>16,18,29</sup> The LS recycling using the BOF process and a LD-converter has also been shown to be a viable procedure.<sup>30</sup>

## 2.2 Recycling of LS

In the second group, research has been performed into the use of LS in cement and the concrete industry, as well as in the slag-soil mixes in civil engineering.

2.2.1 Bricks, granulated slag: Some researchers have investigated the technology for recycling different steelmaking wastes including LS, by mixing them in furnaces to produce bricks.<sup>31</sup> The manufacturing technology of granulated slag particles was introduced by Kojimori et al.<sup>32</sup>

2.2.2 Cement: LS can be used as a raw material for the production of Portland cement (PC).<sup>3,8,26</sup> LS has also been assessed as a raw material for the production of sulphoaluminate belite cement.<sup>33</sup>

2.2.3 Mortar, concrete: There has also been research into the use of LS in other sectors of the construction industry, e.g., in the manufacturing of mortars with lime<sup>17</sup>, the application of LS as a screed material in internal premises, where there is a need for a quick repair of floors or walls<sup>23</sup>, and for other similar products that can facilitate masonry work.<sup>3,26</sup> LS could also be used, in the case of manufacturing hydraulic concrete without additives, for individual precast urban elements that have no load-bearing capacity, e.g., barriers, bannisters and curbs for pedestrianized areas<sup>6</sup>, and for developing concrete blocks that are used in aquiculture.<sup>34</sup> Studies on the hydraulic concrete matrixes made using LS, other residual materials and PC have also been performed.<sup>5</sup> Shi and Hu<sup>9</sup> investigated the hydraulic reactivity of LS fines in combination with siliceous materials (silica flour, FA, PC and hydrated lime). LS can also be used as a filler in the self-compacting concrete exposed to elevated temperatures.<sup>35</sup> The behaviour

of masonry mortars containing LS in aggressive environments was evaluated by Manso et al.<sup>4</sup> A study of the physical, mechanical and durability properties of the concrete made of a combination of EAFS and LS without chemical activators against the external agents has been carried out by Polanco et al.<sup>6</sup> LS can also be used as a supplementary cementing material in briquettes, containing iron and steelmaking residues<sup>33</sup>, and as an alternative binder for low-strength applications.<sup>3,21,26</sup> In order to increase the final strength of the cement composites containing LS, researchers have suggested several ways of processing LS such as re-melting<sup>21</sup>, the use of activators<sup>17,36</sup> and screening or grinding.<sup>21,36</sup>

2.2.4 Civil engineering: Surveys have proposed alternative uses of LS in landfill applications<sup>21</sup>, as a landfill covering structure<sup>24,37,38</sup>, as filtering beds<sup>26</sup> and in other civil-engineering works, e.g., for the stabilization of soft clayey soils<sup>39</sup> in the construction of embankments.<sup>40</sup> Studies of the paving mixes for rural roads with low levels of traffic<sup>26</sup> have also been performed. Branca et al.<sup>41</sup> investigated an addition of glazing powder to LS for the potential use of slag in the road construction. A survey performed by Bignozzi et al.<sup>42</sup> revealed that LS is also suitable for geopolymerization.

2.2.5 Environmental engineering: There is also a further line of study, which proposes the use of LS in environmental engineering, for the fixation of ions in water depuration<sup>3,8</sup>, as a neutralizing agent in bioleaching with the aim of replacing commercial-grade slaked lime in agriculture<sup>43</sup> and for acidity corrections of soil.<sup>3,6,8</sup> A study published by Sun et al.<sup>44</sup> indicated a possibility of using LS as an industrial waste material for treating another kind of industrial waste in order to produce a high-value-added product.

**Table 1:** Chemical compositions of ladle slags according to the literature in mass fractions, w/%

**Tabela 1:** Kemijska sestava ponovčne žlindre iz literature v masnih deležih, w/%

CONSTITUENTS			w/%			REFERENCE		
A	B	C	A	B	C	A	B	C
CaO	CaO <sub>free</sub>	CaO <sub>total</sub>	26–66	max 20	max 51	3, 4, 6, 8, 9, 17, 20–23, 25, 26, 33, 35, 36, 40, 42, 45–52	4, 6, 8, 25, 45, 49, 52	26, 41
SiO <sub>2</sub>	Si <sub>reactive</sub>	Al <sub>2</sub> O <sub>3</sub>	2–50	max 20.4	1–37	3, 4, 6, 8, 9, 17, 20, 23, 25, 26, 33, 35, 36, 40–42, 45–52	25	3, 4, 6, 8, 9, 17, 20–23, 25, 26, 33, 35, 36, 40–42, 45–52
MgO	MgO <sub>free</sub>	MgO <sub>total</sub>	1–13.2	max 10	max 11	3, 4, 6, 8, 9, 17, 20–23, 25, 26, 33, 35, 36, 40, 41, 42, 45–52	4, 6, 8, 45	26
Fe <sub>2</sub> O <sub>3</sub>	FeO	Fe <sub>total</sub>	max 4	max 15	max 4	4, 8, 9, 21, 22, 36, 41, 42, 47, 52	17, 20, 25, 33, 35, 46, 47, 50–52	23, 49, 52
Mn <sub>2</sub> O <sub>3</sub>	MnO	TiO <sub>2</sub>	max 8.1	max 10	max 2.5	33	8, 9, 20, 22, 23, 36, 42, 46, 47, 50–52	8, 9, 20, 22, 23, 33, 36, 41, 42, 50
Cr <sub>2</sub> O <sub>3</sub>	Cr	F	max 8.1	max 0.27	max 4.4	8, 19, 35, 49, 50	46, 47	9, 36, 48
SO <sub>3</sub>	S	Na <sub>2</sub> O	max 2.4	max 1.5	max 0.9	6, 9, 20, 22, 25, 26, 41, 42, 45	8, 36, 40, 46, 51, 52	8, 17, 20–22, 25, 33, 35, 41
P <sub>2</sub> O <sub>5</sub>	P	K <sub>2</sub> O	max 0.87	max 0.4	max 0.42	8, 20, 35, 42, 52	46	8, 17, 20–22, 33, 35, 40–42

Works concerning LS that characterize the product as a material, have also been published.<sup>5</sup>

### 3 CHEMICAL COMPOSITION

The chemical compositions of ladle slags (ladle-furnace slag (LFS) and vacuum-oxygen-decarburization slag (VOD)) from various studies<sup>3,4,6,8,9,17,20,21-23,25,26,33,35,36,40-42,45-52</sup> are presented in **Table 1**. The contents of the major oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and MgO) point to a diverse composition of LS.

Typically, LS is mostly constituted of calcium oxides, as well as silica, aluminium and magnesium oxides. Beside the major components, minor amounts of Fe, Ti, Mn, Cr and S oxides, as well as P, Na and K oxides can be present in LS.

Some other elements, such as Mo, Zn, Ni, Cu, P<sub>2</sub>O<sub>5</sub>,<sup>46,47</sup> soluble salts (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>)<sup>17,21,42</sup>, CO<sub>2</sub>,<sup>22</sup> C<sup>8,40</sup>, ZrO<sub>2</sub>,<sup>9,36</sup> and V<sub>2</sub>O<sub>3</sub>,<sup>42</sup> have also been detected, all in the quantities of less than 2 %.

The bulk chemical composition for the oxide chemical analysis was, in most cases, determined with X-ray fluorescence (XRF).<sup>8,20,22,40,42,47</sup> Chemical composition was also determined by means of the inductively coupled plasma-atomic emission spectroscopy (ICP-AES).<sup>47,50</sup> Papayianni and Anastasiou<sup>17</sup> presented the chemical composition of the acid-soluble phases. Tossavainen et al.<sup>47</sup> used titration for an analysis of Fe and FeO and infrared adsorption spectroscopy (IR) for carbon and sulphur. Carbon and sulphur contents were also determined with a combustion analysis.<sup>25,33,40</sup> Hot ethylene glycol titration for determining CaO was performed by Monkman et al.<sup>22</sup> Manso et al.<sup>26</sup> performed specific determinations of free lime on LS according to the ASTM C 114 standard. For a quantification of the CO<sub>2</sub> content, an automated carbon analyzer with an induction furnace and an infrared detector has been used.<sup>22</sup> Papayianni and Anastasiou<sup>21</sup> determined the reactive silica according to the European standard EN 197-1: 2000. Chloride and sulfate contents and loss on ignition (LOI) were determined following the specific procedures for the cement chemical analysis reported in the EU standard EN 196-2 by Bigozzi et al.<sup>42</sup> Böhmer et al.<sup>49</sup> noted the Czech standard CSN 72 2041-1.

### 3.1 Basicity

Chemical composition is one of the important parameters determining the hydraulic properties of slags. It is generally agreed that the reactivity and the cementitious properties of steel slag increase with its basicity/alkalinity.<sup>46,53</sup> Different authors have defined basicity in slightly different ways. According to Shi<sup>46</sup> the mass concentration  $V = w(\text{CaO})/w(\text{SiO}_2)$  is often used to characterize basicity. Posch et al.<sup>54</sup>, Setien et al.<sup>8</sup> and Manso et al.<sup>5</sup>, however, interpret basicity as  $B = w(\text{CaO})/w(\text{Al}_2\text{O}_3 + \text{SiO}_2)$ , whereas Wang et al.<sup>55</sup> and Xu and Li<sup>56</sup> have stated that the commonly used parameter for evaluating the activity of steel slag is alkalinity:  $M = w(\text{CaO})/[w(\text{SiO}_2) + w(\text{P}_2\text{O}_5)]$ . Yet another way of defining basicity is  $M_b = w(\text{CaO} + \text{MgO})/w(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ .<sup>47, 57</sup>

The mineralogical composition of steel slag changes with its chemical composition. The relationship between basicity, the main mineral phases and the reactivity of steel slag are summarized in **Table 2**.<sup>46,55,58,59</sup>

Basicity, defined as  $B$ , also defines the main mineral phases in each basicity range ( $B < 0.8$  spinels;  $B > 0.8$  periclase, (Mg, Fe)-wüstite;  $0.6 < B < 2.1$ : C<sub>3</sub>A, C<sub>12</sub>A<sub>7</sub>, C<sub>2</sub>S, C<sub>3</sub>S;  $B > 2.1$  CaO<sub>free</sub> occurs).<sup>54</sup> If the  $M$  alkalinity of the slag is higher than 1.8, it should be considered as a cementitious material.<sup>59,60</sup> If  $M_b$  exceeds the value of 1, the slag is basic, which, according to Tossavainen et al.<sup>47</sup>, results in a mainly crystalline slag. The value of  $M_b$  for LS is 1.5.<sup>47</sup> LS has the  $V$  basicity of around 2<sup>36</sup>, the  $B$  basicity in the range of 1.6–2.4 according to Setien et al.<sup>8</sup>, and in the range of 0.45–2.1 according to Posch et al.<sup>51</sup>

### 4 MINERAL COMPOSITION

As the chemical composition of LS is variable, the mineral composition of LS also varies. LS is most frequently characterised by high calcium and alumina contents, which suggests a likely formation of calcium aluminates as the main phases, along with dicalcium silicate and some other phases.<sup>23,33</sup>

According to the available literature reviews of the mineral compositions of ladle slags<sup>5,6,8,20-23,26,33,36,38,40,42,47,51</sup>, the most common minerals are C<sub>2</sub>S ( $\beta$  and  $\gamma$ ), maye-

**Table 2:** Relationship between basicity, the main mineral phases and the reactivity of steel slag

**Tabela 2:** Razmerje med bazičnostjo, glavnimi mineralnimi fazami in reaktivnostjo jeklarske žlindre

Reactivity	Types of steel slag	Basicity [Reference]			Main mineral phases
		$V = w(\text{CaO})/w(\text{SiO}_2)$ 46, 58, 59	$M = w(\text{CaO})/w(\text{SiO}_2 + \text{P}_2\text{O}_5)$ 46, 58, 59	$M_b = w(\text{CaO} + \text{MgO})/w(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ 55	
LOW	olivine	0.9–1.5	0.9–1.4	< 1.8	olivine, RO phase, merwinite
	merwinite	1.5–2.7	1.4–1.6		RO phase, merwinite, C <sub>2</sub> S
MEDIUM	dicalcium silicate		1.6–2.4	1.8–2.5	C <sub>2</sub> S, RO phase
HIGH	tricalcium silicate	>2.7	>2.4	> 2.5	C <sub>3</sub> S, C <sub>2</sub> S, C <sub>4</sub> AF, C <sub>2</sub> F, RO phase

\*The following abbreviated formulae are used in the text: C= CaO; A= Al<sub>2</sub>O<sub>3</sub>; S= SiO<sub>2</sub>; F= Fe<sub>2</sub>O<sub>3</sub>; M= MgO; H= H<sub>2</sub>O

**Table 3:** Mineral compositions of ladle slags according to the literature**Tabela 3:** Mineralna sestava ponovne žindre

	PHASE		METHOD	REFERENCE
BEFORE WEATHERING	most common	calcium silicates (C <sub>2</sub> S, CS, C <sub>3</sub> S), calcium aluminates (C <sub>12</sub> A <sub>7</sub> , C <sub>3</sub> A, CA), periclase, portlandite	XRD, DTA/TGA, FTIR, SEM/EDS	5, 6, 8, 20- 23, 26, 33, 36, 38, 40, 42, 47, 51
	common	calcium magnesium silicates (C <sub>3</sub> MS <sub>2</sub> , CMS <sub>2</sub> , C <sub>2</sub> MS <sub>2</sub> ), RO and R <sub>3</sub> O <sub>4</sub> phase, fluorite, calcite, jasmundite, spinel		5, 6, 8, 20-23, 26, 33, 36, 38, 40, 51
	minor	C <sub>2</sub> AS, dolomite, C <sub>20</sub> A <sub>13</sub> MS <sub>3</sub> , brucite, CaO, C <sub>2</sub> F, amorphous phase, C <sub>3</sub> AH <sub>6</sub> , garnet, anhydrite, uvarovite, oldhamite, quartz, iron magnesium (calcium) silicate, calcium fluoroaluminate, iron, Al metallic, C <sub>54</sub> MAS <sub>16</sub>		5, 8, 20-23, 26,33, 36, 38, 40, 42, 47, 51
AFTER WEATHERING	primary	calcium silicates (C <sub>2</sub> S), calcium magnesium silicates, calcium aluminates (C <sub>12</sub> A <sub>7</sub> , C <sub>3</sub> A), spinel, jasmundite, fluorite, iron oxides, portlandite, periclase	XRD, DTA/TGA, FTIR, ISOTHERMAL CALORIMETRY	6, 8
	secondary	CAH phases (CAH <sub>10</sub> , C <sub>2</sub> AH <sub>7.5</sub> , C <sub>2</sub> AH <sub>8</sub> , C <sub>4</sub> AH <sub>19</sub> , C <sub>3</sub> AH <sub>6</sub> , C <sub>4</sub> AH <sub>13</sub> ), AH <sub>3</sub> , C <sub>2</sub> ASH <sub>8</sub> , amakinite, portlandite, periclase, vaterite, calcite, spurrite		6, 8, 22, 23, 33

nite, tricalcium aluminate, portlandite and periclase (Table 3).

In order to investigate the self-cementing capacity of LFS, a slag paste was produced by mixing water with LFS, and the compressive strength of the hardened paste was measured. The SEM/EDX, DTA/TG analyses and X-ray diffraction analysis were used to determine the latent hydraulic character of LS.<sup>21</sup> The results showed the presence of ettringite and the C-S-H compounds in small amounts and a decrease in the content of portlandite.<sup>21</sup>

A quantification of the LS mineral compounds was calculated directly from the chemical-composition data and X-ray diffraction data<sup>8,26</sup>, and also determined by means of the semi-quantitative SEM-EDS analyses<sup>50</sup> and the Rietveld analysis.<sup>33</sup> The amorphous-phase content was determined separately, using pure quartz as an internal standard.<sup>33</sup> Free lime was determined by deducting the amount of Ca(OH)<sub>2</sub> determined with the DTA-TG analysis from the amount of CaO<sub>f</sub> determined by using the relevant European standard EN 451-1.<sup>21</sup> DTA-TG was also applied for the quantifications of CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, MgO and Mg (OH)<sub>2</sub>.<sup>22,23,41</sup> Monkman et al.<sup>22</sup> applied a TGA analysis for the quantifications both before and after the accelerated carbonation.

## 5 VOLUME STABILITY

The presence of C<sub>2</sub>S as a mineral phase in the slag microstructure drives the disintegration of slag into a very fine powder.<sup>61</sup> Free C<sub>2</sub>S can be present in LS in different phases, such as  $\alpha$ ,  $\alpha'$ ,  $\alpha'$ ,  $\beta$  and  $\gamma$ . C<sub>2</sub>S undergoes several polymorphic transformations up until the cooling process. During the cooling down of slag,  $\alpha$ -C<sub>2</sub>S undergoes a polymorphic solid-phase transition to  $\beta$  type larnite, at a temperature of about 630 °C. At the temperatures within the range of 450–500 °C larnite is partially or fully converted into the low-temperature stable form of  $\gamma$  C<sub>2</sub>S.<sup>8,12,31,41,61</sup> The high internal stress of LS, caused

by the conversion of the  $\beta$  into the  $\gamma$  polymorph, arising from a different crystal structure and density, results in the shattering of the matrix, accompanied by a 10–12 % volume increase. This phenomenon is responsible for the initial cracking of the LS monolithic mass and the following disintegration/self-pulverising process during the further cooling. This is the reason why LSs are also known by the name of "self-dusting" or "falling" slags.<sup>8,20,46,57,61</sup>

It should be emphasized that this disintegration occurs during the cooling, making it clearly distinct from the swelling of the slag after the cooling due to lime and/or periclase, which is further discussed below.

The hydration and carbonization reactions of lime and periclase, present in LS, are, in fact, also liable to expansion. The oxides can cause long-term volume instability of the slag. Free lime, or periclase, present in the slag microstructure after the cooling, tends to react with water and CO<sub>2</sub> in a humid environment. The volume of the hydrates and carbonates is almost double the volume of the oxides, so that a 100 % increase in the volume can occur. Both of these ageing reactions cause a volume expansion or 'swelling', which can lead to severe valorisation issues for the reuse of this slag.<sup>8,31,61</sup> The fact that lime hydrates quickly suggests that the majority of the free lime in LS will hydrate within a few days if it has access to water. The residual free lime and/or free periclase can be embedded in small pockets or inside the pits in the slag particles. Delayed volume instability (weeks to months) will occur if hydration takes place. In comparison with lime, periclase hydrates at a much slower rate.<sup>4,5</sup> The spontaneous hydration of periclase requires several years.<sup>5</sup> However, the vast majority of the slags generated in modern steelmaking plants have a low periclase content. If the fluxing agent used is dolomite, the periclase content in the slag increases, so that a long-term volumetric expansion is possible.<sup>20,46,61</sup> Potential spontaneous changes at a later stage, such as the

hydration of calcium aluminates, do not, however, produce any further changes in the morphology (grain size) of LFS.<sup>8</sup>

The potential treatments of the slags containing lime and/or periclase and  $C_2S$  can be divided into two main groups: firstly, a group where the aim is to prevent the expansive transformation of the mineral, and secondly, a group where there is an outright avoidance of the presence of the mineral in the first place.

The usual way to ensure the long-term volume stability of slag particles is weathering in outdoor conditions for an extended period of time (over 6 months).<sup>61</sup> Tossavainen et al.<sup>47</sup> confirmed that LS can become stable after a performance of rapid cooling, due to the formation of glass. The use of LS in ternary systems with siliceous materials and cement, as well as mixing LS with an inert material, is one of the proposed methods of avoiding the expansion phenomena.<sup>9,21</sup> The carbonation treatment reduces the amounts of portlandite and extractable CaO in slag in an energy-efficient manner.<sup>22</sup> However, action can also be taken to actually prevent the presence of lime/periclase in slag.<sup>61</sup>

Inhibiting the  $\beta$ - to  $\gamma$ -polymorph transformation of  $C_2S$  is an option that stabilizes the high-temperature  $C_2S$  polymorphs at an ambient temperature. This is carried out by depressing the required migrations of the  $Ca^{2+}$  ions and the rotations of  $SiO_4^{4-}$  tetrahedrons, using either physical or chemical methods. Physical stabilization methods for free  $C_2S$  particles include limiting the grain size, rapid cooling and constraining the particles in a matrix.<sup>12,23,47,62</sup> Chemical-stabilization techniques are based on an incorporation of doping elements in the

crystal structure.<sup>12,62</sup> Alternatively, slag disintegration can be averted by an outright avoidance of the presence of  $C_2S$  by modifying the slag composition.<sup>63</sup>

## 6 PRELIMINARY/CASE STUDY

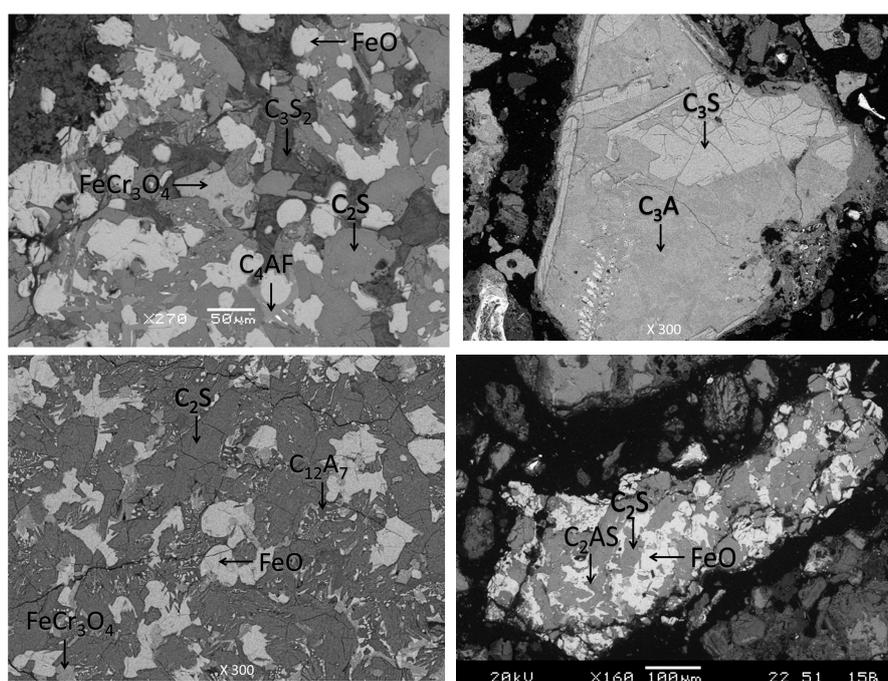
### 6.1 Material and methods

The analysis carried out in this study was preliminary and was based on the samples of slowly cooled (air atmosphere), wetted and aged LS. The investigated ladle slag consisted of a mixture of slags from two different ladle refining operations; the majority of the slag was the ladle-furnace slag, whereas a smaller part was the slag from the vacuum-oxygen-decarburization process. The LS used in this work was supplied by an Italian steel manufacturer, ABS.

The identification and characterization of the mineral phases and the microstructure of the samples were conducted by means of a scanning electron microscope using back-scattering electrons. The JEOL 5600 LV microscope model of was used, with a spectrometer for the chemical composition using energy dispersive spectroscopy (EDS). The excitation voltage was 20 kV and the pressure was between 10 Pa and 20 Pa.

### 6.2 Results and discussion

The most common mineral phases observed in the investigated LS (**Figure 2**) were  $C_3A$ ,  $C_2S$ ,  $C_3S$ , the melilite group (gehlenite ( $C_2AS$ )-åkermanite ( $C_2MS_2$ )), FeO (wüstite),  $C_4AF$  (brownmillerite),  $C_{12}A_7$  (mayenite)



**Figure 2:** SEM/EDS analysis of the investigated LS  
**Slika 2:** SEM/EDS analiza preiskovane ponovčne žindre

and  $C_3S_2$  (rankinite). Calcite, periclase and chromium spinel ( $FeCr_3O_4$ ) were also observed.

Solid solutions of gehlenite and åkermanite are considered to be weakly hydraulic.<sup>23</sup> The presence of  $C_3S$ ,  $C_2S$  and  $C_4AF$  endorses the cementitious properties of the steelmaking slags.<sup>59</sup> The presence of  $C_3A$ ,  $C_{12}A_7$ ,  $C_2S$  and  $C_3S$  implies that LS may serve as a binder supplement, or at least make a contribution to a short-term strength development. The fact that calcium aluminates react instantaneously with water implies that it is important to reconsider the method of slag handling, especially in terms of avoiding any exposure to weathering.<sup>33</sup> The spinel phase and iron oxide 2+, wüstite, do not exhibit hydraulic properties.<sup>8</sup> As regards periclase, hydration and carbonation processes are expected in the presence of air moisture. The expansive hydration reaction from lime to calcite is obviously completed.

## 7 CONCLUDING REMARKS

According to the descriptions given in the literature, LS can develop cementitious hydraulic properties, so that it could have several benefits for the construction and civil-engineering applications.

A detailed analysis of LS from its ABS properties in terms of chemical, mineralogical and physical characterization should be performed to define its (latent) hydraulic properties. From the results of the performed SEM/EDS analysis it can be concluded that the investigated LS has a potential as a supplementary cementing material, but consideration should also be given to the quantity of the hydraulic mineral phases, as well as to the potential hydration and carbonation reactions of the expansive components.

## 8 REFERENCES

- <sup>1</sup> The European slag association: Position Paper on the Status of Ferrous Slag complying with the Waste Framework Directive (Articles 5/6) and the REACH Regulation [online]. 2012, [cited 2012-11-27]. Available at: <http://goo.gl/3XEnB>
- <sup>2</sup> R. Remus, M. A. Aguado-Monsonet, S. Roudier, L. Delgado Sancho, Best Available Techniques (BAT) Reference Document for Iron and Steel Production [online]. 2013, [cited 2013-01-16]. Available at: <http://goo.gl/EVZon>
- <sup>3</sup> Á. Rodríguez, J. M. Manso, Á. Aragón, J. J. González, Resources, conservation and recycling, 53 (2009), 645–651
- <sup>4</sup> J. M. Manso, Á. Rodríguez, Á. Aragón, J. J. González, Construction and Building Materials, (2011), 3508–3519
- <sup>5</sup> J. M. Manso, D. Hernández, M. M. Losáñez, J. J. González, ACI Materials Journal, 108 (2011), 673–681
- <sup>6</sup> J. A. Polanco, J. M. Manso, J. Setién, J. J. González, ACI Materials Journal, 108 (2011), 196–203
- <sup>7</sup> O. Bonetti, C. Mapelli, M. Guzzon, Recycling of ladle slag in the EAF: improvement of the foaming behaviour and increase of the environmental impact [online]. [cited 2012-11-16]. Available at: <http://goo.gl/SRdgZ>
- <sup>8</sup> J. Setién, D. Hernández, J. J. González, Construction and Building Materials, 23 (2009), 1788–1794
- <sup>9</sup> C. Shi, S. Hu, Cement and Concrete Research, 33 (2003), 1851–1856
- <sup>10</sup> EU Waste Framework Directive (2008/98/ES) [online]. 2008, [cited 2013-02-14]. Available at: <http://goo.gl/YYSYSi>
- <sup>11</sup> Technical University of Crete: PREWARC- Strategic Plan for the Prevention of Regional Water Resources contamination from Mining and Metallurgical Industries in Western Balkan Countries [online]. 2008, [cited 2012-09-18]. Available at: <http://goo.gl/tm8vq>
- <sup>12</sup> D. Durinck, P. T. Jones, B. Blanpain, P. Wollants, Journal of American ceramic society, 91 (2008), 3342–3348
- <sup>13</sup> S. Fiore, M. C. Zanetti, B. Ruffino, American journal of applied sciences, 1 (2008), 512–518
- <sup>14</sup> B. Batchelor, Waste Management, 26 (2006), 689–698
- <sup>15</sup> Q. Y. Chen, M. Tyrer, C. D. Hills, X. M. Yang, P. Carey, Waste management, 29 (2009), 390–403
- <sup>16</sup> M. Guzzon, C. Mapelli, V. Sahajwalla, N. Saha-Chaudhury, F. Memoli, M. Pustorino, The behaviour of the secondary metallurgy slag into the EAF. How to create a good foamy slag with the appropriate basicity using a mix of lime and recycled ladle slag as EAF slag former [online]. 2011, [cited 2012-11-14]. Available at: <http://goo.gl/SurH5>
- <sup>17</sup> I. Papayianni, E. Anastasiou, Optimization of ladle furnace slag for use as a supplementary cementing material, In Measuring, Monitoring and Modeling Concrete Properties, Edited by M. S. Konstadoutos, Springer, Netherlands 2006, 411–417
- <sup>18</sup> P. L. Cavallotti, C. Mapelli, F. Memoli, M. Pustorino, La metallurgia Italiana, 99 (2007), 41–48
- <sup>19</sup> M. P. Luxán, R. Sotolongo, F. Dorrego, E. Herrero, Cement and concrete research, 30 (2000), 517–519
- <sup>20</sup> I. Z. Yildirim, M. Prezzi, Chemical, Mineralogical, and Morphological Properties of Steel Slag. Advances in Civil Engineering [online]. 2011, 10pp [cited 2012-11-14]. Available at: <http://goo.gl/43LUQ>
- <sup>21</sup> I. Papayianni, E. Anastasiou, Cement and concrete composites, 34 (2012), 400–407
- <sup>22</sup> S. Monkman, Y. Shao, C. Shi, Journal of materials in civil engineering, 21 (2009), 657–665
- <sup>23</sup> D. Adolfsson, E. Engström, R. Robinson, B. Björkman, Steel research international, 82 (2011), 398–403
- <sup>24</sup> I. Herrmann, L. Andreas, S. Diener, L. Lind, Waste and management research, 28 (2010), 1114–1121
- <sup>25</sup> I. Papayianni, E. Anastasiou, Construction and building materials, 24 (2010), 1412–1417
- <sup>26</sup> J. M. Manso, M. Losáñez, J. A. Polanco, J. J. González, Journal of materials in civil engineering, 17 (2005), 513–518
- <sup>27</sup> R. Dippenaar, Industrial uses of slag—The use and re-use of iron and steelmaking slags, VII International Conference on Molten Slags Fluxes and Salts [online]. 2004, 57–70 [cited 2012-08-26]. Available at: <http://goo.gl/1vsyg>
- <sup>28</sup> T. S. Lee, I. S. Choi, W. Y. Song, Stahl und Eisen, 123 (2003), 113–117
- <sup>29</sup> F. Memoli, M. Guzzon, Metallurgical plant and technology international, 3 (2006), 42–49
- <sup>30</sup> A. Dahlin, Influence of Ladle-slag Additions on BOF-Process Parameters, Licentiate Thesis, Stockholm, 2011, 40
- <sup>31</sup> M. Shinkai, M. Tsuno, N. Ogawa, Denki Seiko (Electric Furnace Steel), 68 (1997), 295–299
- <sup>32</sup> M. Kojimori, K. Nemoto, T. Fukuokaya, S. Uchida, H. Matumoto, T. Mori, Denki Seiko (Electric Furnace Steel), 74 (2003), 55–59
- <sup>33</sup> D. Adolfsson, R. Robinson, E. Engström, B. Björkman, Cement and concrete research, 41 (2011), 865–871
- <sup>34</sup> H. Sasamoto, A. Tsubone, Y. Kamiya, K. Sano, Tetsu to Hagane, 89 (2003), 416–465
- <sup>35</sup> N. Anagnostopoulos, K. K. Sideris, A. Georgiadis, Materials and structures, 42 (2009), 1393–1405
- <sup>36</sup> C. Shi, Cement and concrete research, 32 (2002), 459–462
- <sup>37</sup> S. Diener, L. Andreas, I. Herrmann, H. Ecke, A. Lagerkvist, Waste management, 30 (2010), 132–139

- <sup>38</sup> S. Diener, L. Andreas, I. Herrmann, A. Lagerkvist, Mineral transformations in steel slag used as landfill cover liner material, Proc. of the Eleventh International Waste Management and Landfill Symposium, Sardinia, 2007, 9
- <sup>39</sup> A. Kanagawa, T. Kuwayama, Denki Seiko (Electric Furnace Steel), 68 (1997), 261–267
- <sup>40</sup> J. M. Montenegro, M. Celemín-Matachana, J. Cañizal, J. Setién-Marquín, Journal of Materials in Civil Engineering, 25 (2013) 8, 972–979
- <sup>41</sup> T. A. Branca, V. Colla, R. Valentini, Ironmaking and Steelmaking, 36 (2009), 597–602
- <sup>42</sup> M. C. Bignozzi, L. Barbieri, I. Lancelotti, Advances in Science and Technology, 69 (2010), 11–122
- <sup>43</sup> S. C. Gahan, M. L. Cunha, A. Sandström, Hydrometallurgy, 95 (2009), 190–197
- <sup>44</sup> D. D. Sun, J. H. Tay, H. K. Cheong, D. L. Leung, G. Quian, Journal of hazardous materials, 87 (2001), 213–23
- <sup>45</sup> J. M. Manso, D. Hernández, J. M. Losáñez, J. A. González, ACI materials journal, 108 (2011), 673–681
- <sup>46</sup> C. Shi, Journal of Materials in Civil Engineering, 16 (2004), 230–236
- <sup>47</sup> M. Tossavainen, F. Engström, Q. Yang, N. Menad, M. Lidstrom, M. Larsson, B. Bjorkman, Waste Management, 27 (2007), 1335–1344
- <sup>48</sup> Y. Yu, N. Wang, China's Refractories, 15 (2006), 25–28
- <sup>49</sup> S. Böhmer, M. Gertraud, N. Christian, P. Milla, S. Elisabeth, T. Maria, W. Birgit, W. Brigitte, Aggregates case study, final report [online]. 2008, 282 pp [cited 2012-5-11]. Available at: <http://goo.gl/EwGPq>
- <sup>50</sup> M. Guo, S. Parada, P. T. Jones, E. Boydens, J. Van Dyck, B. Blanpain, P. Wollants, Journal of the European ceramic society, 29 (2009), 1053–1060
- <sup>51</sup> W. Posch, H. Presslinger, H. Hiebler, Ironmaking & steelmaking, 29 (2002), 308–315
- <sup>52</sup> Ľ. Mihok, P. Demeter, D. Baricová, K. Seilerová, Metalurgija, 45 (2006), 163–168
- <sup>53</sup> I. A. Altun, I. Yilmaz, Cement and concrete research, 32 (2002), 1247–1249
- <sup>54</sup> W. Posch, H. Preblinger, M. Mayr, K. Klepp, H. Hiebler, Sulphur bonding in solidified ladle slags, Proc. of the VII International Conference on Molten Slags Fluxes and Salts, The South African Institute of Mining and Metallurgy, 2004, 249–254
- <sup>55</sup> Q. Wang, P. Y. Yan, S. Han, Science China Technological Sciences, 54 (2011), 388–394
- <sup>56</sup> D. Xu, H. Li, Journal of Wuhan University of Technology-Materials Science Edition, 24 (2009), 411–417
- <sup>57</sup> F. Engström, D. Adolfsson, Q. Yang, C. Samuelsson, B. Björkman, Steel Research International, 81 (2010), 362–371
- <sup>58</sup> C. Shi, J. Quian, Resources, Conservation and Recycling, 29 (2000), 195–207
- <sup>59</sup> H. Alanyali, M. Çöl, M. Yilmaz, S. Kargöz, International journal of applied ceramics technology, 6 (2009), 736–748
- <sup>60</sup> W. Xuequan, Z. Hong, H. Xinkai, L. Husen, Cement and Concrete Research, 29 (1999), 1103–1106
- <sup>61</sup> D. Durinck, P. T. Jones, S. Arnout, B. Blanpain, Stainless steel slag valorisation: on volume stability and disintegration, Proc. of the first international slag valorisation symposium, Leuven, 2009, 81–92
- <sup>62</sup> Y. Pontikes, L. Kriskova, X. Wang, D. Geysen, S. Arnout, E. Nagels, Ö. Cizer, T. Van Gerven, J. Elsen, M. Guo, P. T. Jones, B. Blanpain, Additions of industrial residues for hot stage engineering of stainless steel slags, Proc. of the second international slag valorisation symposium, Leuven, 2011, 313–326
- <sup>63</sup> D. Durinck, S. Arnout, G. Mertens, E. Boydens, P. T. Jones, J. Elsen, B. Blanpain, P. Wollants, Journal of the American ceramic society, 91 (2008), 548–554