VALORISATION OF STAINLESS STEEL SLAGS AS A HYDRAULIC BINDER

Lubica Kriskova[1),2)*], *Yiannis Pontikes*[1),2)], *Fei Zhang*[1)], *Özlem Cizer*[1),2)], *Peter Tom Jones*[1)], *Koen van Balen*[3)], *Bart Blanpain*[1)]
[1)] KU Leuven, Department of Metallurgy and Materials Engineering, Belgium
[2)] KU Leuven, Secondary Resources for Building Materials, Consortium in Sustainable Inorganic Materials Management, SIM2, Belgium
[3)] KU Leuven, Building Materials and Building Technology Division, Department of Civil Engineering, Belgium

Received: 29.03.2013
Accepted: 20.05.2013

[*]Corresponding author: e-mail: lubica.kahalova@mtm.kuleuven.be, Tel.: +32 16 32 12 18, Department of Metallurgy and Materials Engineering, Kasteelpark Arenberg 44 bus 2450, 3001 Heverlee, Belgium

Abstract

This work is focused on exploring various cold and hot stage treatment paths of stainless steel slag as a tool to improve its hydraulic properties. At a cold stage, mechanical and chemical activation was applied on industrial stainless steel slag; and it was found that both activation methods effectively improve the reactivity of the studied slag. In addition, the detailed investigation of hydration on two major phases, γ – C_2S and merwinite, revealed that their hydration resulted in the formation of C – S – H gel, typically formed during the hydration of OPC. Regarding the hot stage treatment, the combination of the chemistry modification with the addition of fly ash at 30 wt. % and fast cooling by means of water quenching resulted in a complete amorphisation of the material. Ultimately, the produced material possessing similar properties to granulated blast furnace slag could be used as a latent hydraulic material in blended cements.

Keywords: stainless steel slag, γ – dicalcium silicate, merwinite, hydration, SEM

1 Introduction

Stainless steel production consists of the following three steps: melting of stainless steel scrap in an electric arc furnace (EAF), carbon removal via argon oxygen decarburization (AOD) or vacuum oxygen decarburization (VOD) process and final steel treatment and alloying in a ladle, called ladle metallurgy (LM) [1]. A relatively large amount of slag is generated in each of these steps resulting in an annual worldwide stainless steel slag production of more than 10 Mt [2].

EAF slag is typically valorized as aggregate for road constructions, while slags from secondary refining processes (AOD, LM) are more problematic to be valorized because of their powdery nature, free CaO and MgO content and a potential leaching of heavy metals. A promising higher value applications such as their use as a hydraulic binder, have been proposed for these slags [3]. Secondary stainless steel slags mainly consist of γ – dicalcium silicate (γ – C_2S) and merwinite (C_3MS_2), while both these phases are considered to be non – hydraulic or only mildly hydraulic [4, 5]. Thus, the reactivity of these phases needs to be improved in order to valorise them as a binder.

DOI 10.12776/ams.v19i3.159

p-ISSN 1335-1532
e-ISSN 1338-1156

Both mechanical and chemical activation have been proposed by several authors [6 – 9] to be effective ways to increase the hydraulic reactivity of various materials. The principle of mechanical activation lies in increasing the reactive surface area as well as in introducing structural disorder into the material. In this way, the material is shifted into a metastable state resulting in its higher reactivity. An enhanced reactivity of various materials such as fly ash [7] or blast furnace slag [6] after the mechanical activation have been observed before. Chemical activation improves the reactivity through altering the pH of the solution, where the hydration reaction should occur. Typically, various alkalis are used to increase the pH of the solution and thus enhancing the Si – O and Ca – O bonds breakage in the material [8]. Alkalis, however, show "selectivity" towards materials, meaning the same activator may have different effects on various materials [10]. It has been reported elsewhere in [11] that Na_2CO_3 should be especially suitable for C_2MS rich slags, whereas NaOH should be better for slags rich in C_2AS. However, a general rule to select the most suitable activator does not exist yet.

The aim of this work is to explore possible routes to increase the hydraulic properties of a stainless steel slag by means of detail analysis of the hydration of pure minerals composing this slag. In addition, a possible route to improve the hydraulic properties of the slag via hot stage treatment is also discussed.

2 Experimental materials and methods

2.1 Materials

The chemical composition of the industrial as – received LM slag, used for mechanical and chemical activation, is listed in **Table 1**. The as – received slag was sieved and only the fraction below 125 μm was used. Pure minerals (γ – C_2S and merwinite) were prepared using the laboratory grade oxides and carbonates, which were wet mixed in corresponding stoichiometric proportions (**Table 1**). Mixtures were fired for 20 h at 1450 °C and 1500 °C for γ – C_2S and merwinite, respectively; and cooled to the room temperature at 1 °C/min.

Material used for hot stage experiment was prepared by mixing a synthetic slag mixture with 30 wt. % of fly ash (**Table 1**). This mixing proportion was chosen to fit in the typical compositional range of granulated blast furnace slag. Mixed materials were heated up to 1550 °C, homogenized for 1.5 h and water quenched.

Table 1 Chemical composition of studied materials, in wt. %

	CaO	SiO_2	MgO	Al_2O_3	Cr_2O_3	Fe_2O_3	others
LM slag	51.5	28.3	11.3	1.2	3.9	–	3.8
γ – C_2S	65.1	34.9	–	–	–	–	–
Merwinite	51.2	36.6	12.2	–	–	–	–
slag + 30 wt.% FA	43.3	32.7	6.2	7.8	–	2.0	8.0

2.2 Experimental Methods

Mechanical activation was performed by extensive milling in a bead mill (Dispermat SL-12-C1, VMA). Approximately 100 g of material was milled in 500 ml of ethanol for 6 h at 5000 rpm using 1 mm ZrO_2 milling balls. Chemical activation was performed by means of NaOH, Na_2CO_3 and $Na_2O.3.4(SiO_2)$ solution, keeping the Na_2O to binder ratio equivalent to 8 wt. %.

The surface area was determined by the nitrogen sorption method BET (Micromeritics TriStar 3000 V6.04 A) after drying at 150 °C for 12 h. X – ray diffraction analyses was performed (Philips, PW 1830) using CuK_α radiation of 45 kV and 30 mA. The X – ray patterns were collected with a step size of 0.02 ° and step time of 2 s. To determine the amorphous fraction of the materials, 10 wt. % ZnO was interground with the sample as an internal standard.

Hydraulic properties were studied using isothermal calorimetry (TAM Air device, TA Instruments) on pastes prepared with binder to liquid (b/l) ratio of 1. To study the hydration at later stages, paste samples were kept in plastic containers for the designated time period and then dried at 0.035 mbar for 2.5 h using a vacuum – freeze dryer (Alpha 1 – 2 LD, Martin Christ). Thermogravimetric analysis (TGA) was performed on samples using simultaneous TGA/DSC (STA 409 PC Luxx®, Netzsch). The samples were heated at 10 °C/min in a continuous N_2 flow up to 1000 °C. Microstructural investigations were carried out on bulk samples employing a scanning electron microscope (SEM, XL30, Philips). The specimens were prepared by drying for at least 2 days at 40 °C in air. Fourier transform infrared spectroscopy (FTIR) was used to study the hydration products.

3 Results and discussion

3.1 Mechanical and chemical activation

Both mechanical and chemical activation of LM slag resulted in enhanced hydraulic properties, as it can be seen from **Fig. 1**. In case of the mechanically activated sample, the released heat was higher compared to the heat released when the sample was activated chemically. Heat release that occurs during hydration reactions is partially connected to the surface area of the studied powders. The surface area of the mechanically activated sample was 10 times higher than the original sample. This explains the higher heat release of this sample compared to the chemically activated one. In addition, it has been reported [8] that alkali activated cements have a lower heat release rate compared to OPC, which may also be the case here.

Similar behaviour was also observed on the pure $\gamma - C_2S$ sample, where the heat release of the mechanically activated sample was three times higher than the one of the alkali activated sample (using NaOH). In case of pure merwinite, the heat release was slightly higher for the alkali activated sample (using NaOH) than for the mechanically activated sample.

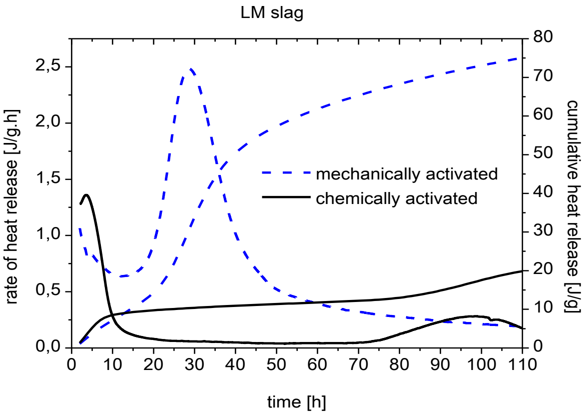

Fig. 1 Heat release of the mechanically and the chemically activated LM slag

X – ray Diffraction (XRD) analyses showed that the content of crystalline phases originally present in the LM slag decreased, and the content of amorphous increased with the hydration time. In addition, new phases, CaOH and MgOH, were formed in the mechanically activated sample, **Table 2**. Regarding the chemically activated sample (using Na_2CO_3), the XRD analysis revealed the formation of other crystalline phases, such as gaylussite ($Na_2Ca(CO_3)_2.5H_2O$), eitelite ($Na_2Mg(CO_3)_2$), $CaCO_3$ and $MgCO_3$, **Table 3**. It can be seen, that no carbonated phases were detected in hydrated mechanically activated samples, while the carbonation in the hydrated chemically activated sample was quite substantial. This observation is consistent with previously published findings on alkali activated cements, where it was reported that the carbonation of alkali activated slag cements is more pronounced when compared to the Portland cements [8, 12, 13]. This phenomenon can be simply explained with the fact that high alkalinity facilitates the capture and the hydration of the carbon dioxide from the atmosphere into the pore solution where the carbonate ions are released and readily react with the calcium ions to form calcite.

Table 2 The mineralogical composition of the LM slag after mechanical activation and after mechanical activation and hydration (D = days), in wt. %

	mechanically activated	**hydrated 3D**	**hydrated 7D**	**hydrated 28D**
γ – C_2S	24	17	16	13
β – C_2S	4	< 1	< 1	–
Merwinite	5	4	3	3
Bredigite	6	4	4	2
Periclase	12	6	4	1
Cuspidine	12	8	9	7
Portlandite	< 1	1	1	2
Brucite	–	1	2	3
others/amorphous	29	51	53	64

Table 3 The mineralogical composition of the as – received LM slag and during hydration after chemical activation (D = days), in wt. %

	as – received	**hydrated 3D**	**hydrated 7D**	**hydrated 28D**
γ – C_2S	36	25	16	9
β – C_2S	< 1	3	1	< 1
Merwinite	7	5	2	2
Fluorite	2	1	< 1	< 1
Cuspidine	10	9	6	5
Magnesiochromite	3	4	< 1	< 1
Periclase	16	11	3	< 1
Wollastonite	2	1	1	< 1
Bredigite	7	5	3	3
Magnesite	–	3	3	3
Calcite	–	3	7	8
Eitelite	–	5	4	3
Gaylussite	–	9	8	8
others/amorphous	17	25	40	53

The increase in the fraction of the amorphous phase could indicate the formation of C – S – H gel, a hydration product typically formed during the hydration of OPC [14]. TGA analyses supported the theory of C – S – H gel formation by revealing an increasing weight loss in the C

– S – H gel decomposition region (50 – 450 °C [15]). However, the complexity of the LM slag mineralogy did not allow us to clearly identify the origin of this newly formed amorphous phase. Nevertheless, it has been mentioned elsewhere [16, 17] that γ – C_2S may hydrate and indeed forms the C – S – H gel. The presence of C – S – H in the hydrated γ – C_2S was also observed by FTIR during our investigation of pure mineral phase, **Fig. 2 a**).

Limited studies performed on merwinite hydration indicated, that under hydrothermal conditions this mineral phase hydrates to form a calico – chondrodite ($Ca_5(SiO_4)_2(OH,F)_2$) and other crystalline C – S – H phases [18]. In our study, mechanically and chemically activated (with NaOH) merwinite hydrated at ambient temperature and detailed analyses of hydrated materials were performed. Similarly to LM slag, in the case of pure merwinite hydration, the XRD analysis revealed that the amount of amorphous phase increased over time. In addition, a clear peak at about 815 cm^{-1}, assigned to Si – O vibration in the C – S – H phase [19, 20], was identified in the FTIR, **Fig. 2 b**).

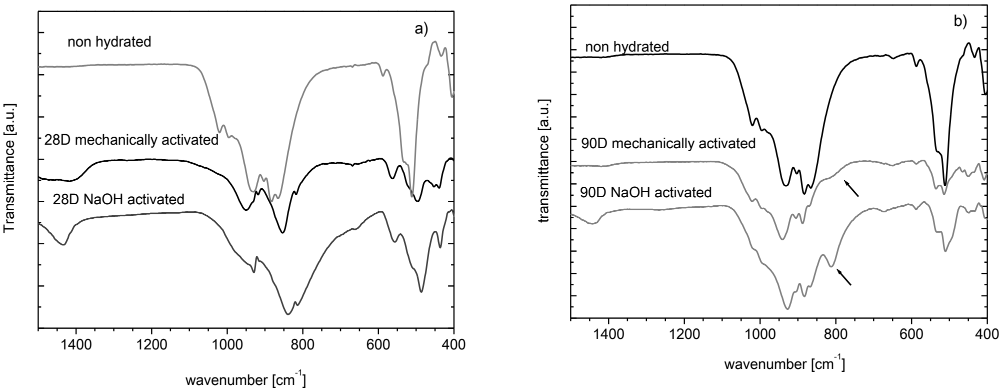

Fig. 2 FTIR patterns of non – hydrated and activated hydrated pure phases a) γ – C_2S; b) merwinite

Since it has been shown that two main phases of LM slag hydrate to form C – S – H gel, it can thus be concluded that the C – S – H gel was also formed during the hydration of both mechanically and chemically activated LM slag.

Supporting the above findings regarding the C – S – H gel formation, the typical fibrillar structure of the gel was also observed in hydrated LM slag in SE micrographs, **Fig. 3**. As the hydration progressed, a reticular network was formed and the densification of the gel structure was observed.

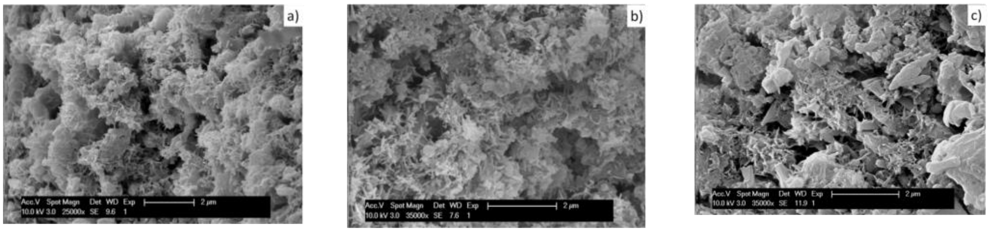

Fig. 3 SE micrographs of mechanically activated LM slag after a) 3D; b) 7D and c) 28D of hydration

3.2 Hot stage treatment

If the increased hydraulic reactivity of the stainless steel slag resulting from the mechanical and/or chemical activation is not sufficient, modification of the stainless steel slag chemistry is another option to improve its hydraulic activity. Water quenched slag prepared from a synthetic slag mixture and 30 wt. % fly ash (FA) shows a glassy, dark brownish appearance. XRD analyses revealed that the material to be completely amorphous, similarly to granulated blast furnace slag which has typically more than 90 wt. %. of glassy phase [8]. Calorimetry measurements revealed that the quenched material possessed latent hydraulic properties, as only minimum heat was produced, when mixed with water only. Three various activators, NaOH, Na_2CO_3 and sodium silicate ($Na_2O.3.4(SiO_2)$) were used to activate the hydration reaction, **Fig. 4**. All three activators could effectively activate the hydraulic properties of the FA + slag mixture as it was demonstrated by exothermic peaks. When the NaOH activator was used, the exothermic peak occurred only two hours after mixing. In addition, the largest heat was generated when NaOH activator was used, thus it has been concluded, that this was the most suitable activator for this material.

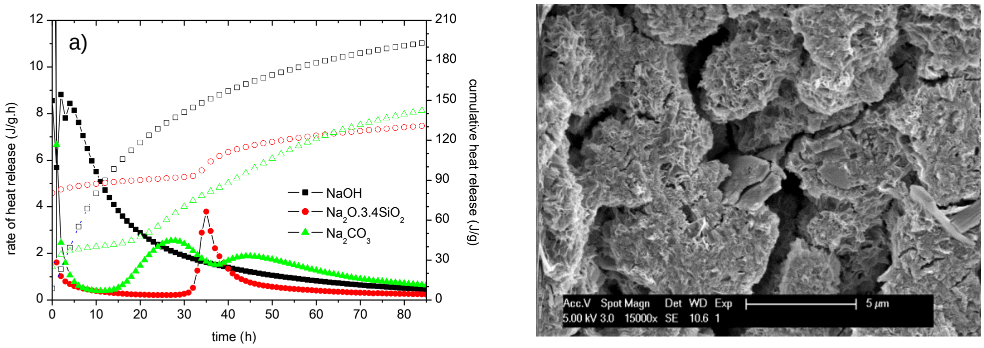

Fig. 4 a) Heat release of the quenched FA and synthetic slag mixture activated with NaOH, Na2CO3 and Na2O.3.4SiO2; b) SE micrograph of NaOH activated hydrated FA + slag mixture after 3D of hydration.

SE micrograph, Fig. 4b), shows the structure of the hydrated material after 3 days of hydration. It can be seen that the gel structure is very dense although some cracks, most probably resulting from too high molarity of the used solution, were present in the structure. Based on the above findings, it can be concluded, that the newly produced material shows high hydraulic activity once it is properly activated. In addition, similar properties compared to granulated blast furnace slag (described in more detail in [21]) indicate, that this material can be used as a hydraulic binder in similar applications as a granulated blast furnace slag.

4 Conclusions

Both mechanical and chemical activation resulted in an enhancement of the hydraulic properties of an industrial stainless steel slag. During the hydration, the amount of originally present crystalline phases decreased and the amount of amorphous phase increased. Dedicated analyses performed on the pure mineral phases provided evidence on that both main phases ($\gamma - C_2S$ and merwinite) hydrated to form C – S – H gel, thus this hydrated phase was most probably also formed during the hydration of the activated LM slag.

Adaptation of the slag chemistry by FA addition at hot stage and subsequent water quenching of FA + slag mixture resulted in the formation of completely amorphous material possessing latent hydraulic properties, similar to that of the granulated blast furnace slag.

References

[1] T. A. Engh, C. J. Simensen, O. Wijk: *Principles of metal refining*, Oxford University press, 1992
[2] [online], Available at <http://www.worldstainless.org/Statistics/Crude/>
[3] L. Kriskova et al.: Cement and Concrete Research, Vol. 42, 2012, No. 6, p. 778-788
[4] S. N. Ghosh, P. B. Rao, A. K. Paul, K. Raina: Journal of Materials Science, Vol. 14, 1979, No. p. 1554-1566
[5] Q. Wang, P. Yan, J. Feng: Journal of Hazardous Materials, Vol. 186, 2011, No. 2-3, p. 1070-1075
[6] S. Kumar et al.: Cement and Concrete Composites, Vol. 30, 2008, No. 8, p. 679-685
[7] N. Bouzoubaâ, M. H. Zhang, A. Bilodeau, V. M. Malhotra: Cement and Concrete Research, Vol. 27, 1997, No. 12, p. 1861-1874
[8] C. Shi, P. K. Krivenko, D. Roy: *Alkali – Activated Cements and Concretes*, Taylor & Francis, NY, USA, 2006
[9] S. Kumar, A. Bandopadhyay, T. C. Alex, R. Kumar: Ceramics International, Vol. 32, 2006, No. 5, p. 555-560
[10] C. Shi, R. L. Day: Cement and Concrete Research, Vol. 25, 1995, No. 6, p. 1333-1346
[11] C. Shi: Cement and Concrete Research, Vol. 26, 1996, No. 12, p. 1789-1799
[12] S. A. Bernal, et al.: Cement and Concrete Research, Vol. 42, 2012, No. 10, p. 1317-1326
[13] F. Puertas, M. Palacios, T. Vázquez: Journal of Materials Science, Vol. 41, 2006, No. 10, p. 3071-3082
[14] Lea's Chemistry of Cement and Concrete, 1998
[15] M. Castellote, C. Alonso, C. Andrade, X. Turrillas, J. Campo: Cement and Concrete Research, Vol. 34, 2004, No. 9, p. 1633-1644
[16] H. F. W. Taylor: *Cement Chemistry*, Academic press, London, UK, Vol. 1990.
[17] J. Bensted: Cement and Concrete Research, Vol. 8, 1978, No. 1, p. 73-76
[18] G. Qian, A. Li, G. Xu, H. Li: Cement and Concrete Research, Vol. 27, 1997, No. 12, p. 1791-1797
[19] I. García Lodeiro, A. Fernández – Jimenez, A. Palomo, D. E. Macphee: Cement and Concrete Research, Vol. 40, 2010, No. 1, p. 27-32
[20] I. García Lodeiro, D. E. Macphee, A. Palomo, A. Fernández – Jiménez: Cement and Concrete Research, Vol. 39, 2009, No. 3, p. 147-153
[21] Y. Pontikes, L. Kriskova, Ö. Cizer, P. T. Jones, B. Blanpain: Advances in Cement Research, Vol. 25, 2013, No. 1, p. 21-31

Acknowledgements

Authors are grateful for the financial support from the IWT O&O project 090594. Y. Pontikes is thankful to the FWO for a post – doctoral fellowship.