

EAF STEEL SLAG AS SUPPLEMENTARY CEMENTING MATERIAL

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Abstract

Large scale recycling of steel slag as a cementitious additive to cement mortar and/or concrete was investigated in this paper. As the material component of steel slag is highly variable, this EAF slag is gathered from plant site of Dong Tien steelmaker in Ba Ria-Vung Tau province. Chemical compositions of slag consist almost the high content of free CaO, MgO and iron, Fe_xO_y . Lower content of cementitious mineral C3S, C2S endorses relative low hydraulic reactivity in comparing with Portland cement. After grinding slag to particle size $<90\mu\text{m}$ (Blaine $3400\text{ cm}^2/\text{g}$), blended cement–steel slag with 10 to 40% by mass of slag were formulated. Both steel slag-cement Portland and steel slag-granulated blast furnace slag (GBFS)-cement Portland system were introduced to analyze early age and later age property of mortar sample. Preliminary results of resistance remark appropriate formulation of 20% of slag. By adding 20% GBFS in such product, practical application could be considered due to the typical enhancement of durability property of cement mortar in severe condition (sulfate, chlorhydric acid). Others, by considering an approach of slag treatment to improve hydraulic reactivity as the GBFS materials model present. The mineralogical composition and some cementitious properties of obtained product would be discussed for a perspective of new clinker steel slag.

Keywords: Accelerated corrosion environment, GBFS, SCM, Slag clinkerization, Steel slag

Introduction

Steel slag is a by-product from the processing of iron (pig iron and/or steel-scrap) to steel in conversion furnace. By removing impurities such as Al, Si, P... during this process, steel products show higher resistance as we need. The amount of slag released is around 15% of the final steel product [1]. In Vietnam, an estimation of 1-1.5 million tons of steel slag is discharged each year [2]. This solid waste occupies large area of land and leads to serious environmental impact due to high content of heavy metal. Thus, to recycle steelmaking slag is truly necessary in the both context of economic demand and environment issue. For large scale recycling, steel slag could be used as filler of cement or also as aggregates for asphalt concrete [1,3]. Steel slag aggregates improve their intrinsic properties (e.g., mechanical properties and durability) due to hardening process. In many case, practical application of slag did not take full advantage of their attributes from viewpoint of material science.

Adopting a model of granulated blast furnace slag (GBFS), we could directly incorporate in Portland cement (OPC). According to ASTM, slag cement type IP is characterized as low heat, slow strength developing. They favor high resistance in long term to aggressive environment. Rapid cooling condition (jet of cold air or water) of molten stream of slag at $1400\text{-}1600^\circ\text{C}$ will prevent the crystallization of the slag and simultaneously cause vitreous phase. The specific granulation process of blast furnace essentially settles the hydraulic character of the glassy slag [4]. High quality steel slag in

term of hydraulic reactivity could be ground with OPC clinker. To improve slag characteristic, we introduce on the other hand the stage of clinkerization of mixture and others appropriate components. The heating condition of oxy-acetylene welding torch was used directly on mixing material. The resulted liquid slag was subjected to rapid quench cooling in water and/or also natural cooling in air. Ground clinker products were then analyzed by XRD, SEM, and FTIR to observe the mineralogical composition. We compared slag clinker with OPC in term of composition, setting time, compressive strengths at 3 and 7 days. Based on the result, the methodology that serves a purpose of steel slag recycling in construction materials will be discussed in the last paragraph.

Cementitious Properties of EAF Steel Slag

Bulk slag after cooling phase in air was reduced to gravel size in hammer. This semi-product was continued storing outside and jetting water for volumetric stability. In almost case, steel slag is considered as poor crystallize including abundant phase of amorphous [5]. On figure 1-right, XRD analysis of slag sample Dong Tien (DT) reveal a complex structure with many overlapping peaks. These peaks reflect the crystalline phases present in steel slag or from feed steel scrap (EAF converter), for example SiO_2 , FeO and Fe_2O_3 . Since EAF slag DT has high iron oxide content, solid solution of FeO , typically one of the main mineral phases.

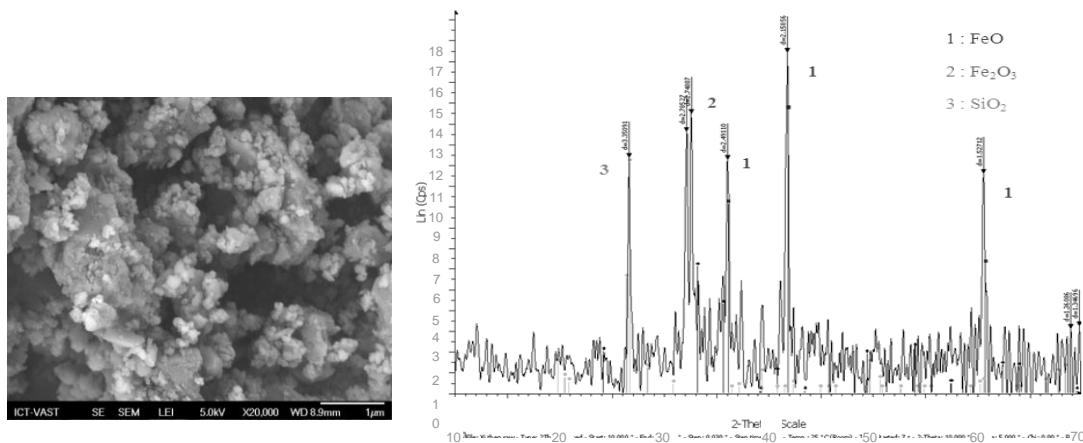
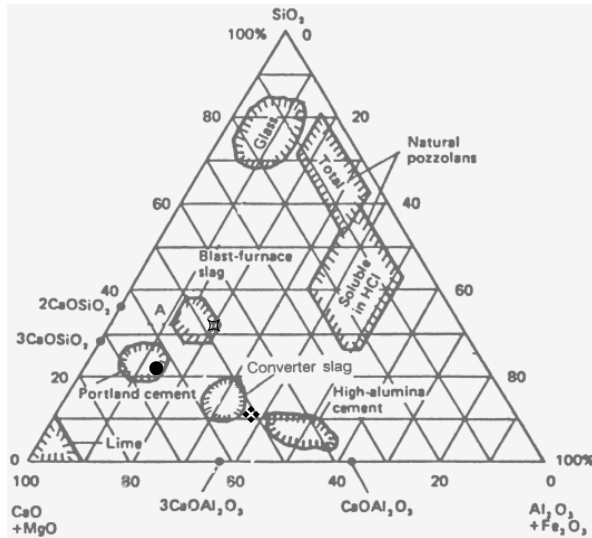


Figure 1. SEM photo of ground steel slag powder (left) and XRD spectrum of slag DT, CuKα (right)

The chemical composition of EAF slag DT is showed on the table (Figure 2-right). Typically, the Fe_xO_y , CaO , SiO_2 , Al_2O_3 , and MgO contents are major; respectively 27.34%, 35.98%, 14.85%, 6.58% and 5.19% by mass. Others minor components include other oxidized impurity such as MnO , SO_2 . As indicated, CaO could be found in both crystallized phase C-S and also free lime [5,6]. Free lime converts normally to $\text{Ca}(\text{OH})_2$ that induces major dimensional instability of slag gravel. The chemical composition is introduced on the common ternary $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ (reference [7])



Sample	Slag DT (◆)	GBFS (♠)	OPC (●)
CaO	35.98	39.50	64.80
SiO ₂	14.85	35.40	20.99
Al ₂ O ₃	6.58	15.50	4.90
Fe ₂ O ₃ / /FeO	12.09 /15.25	1.30	3.58
MgO	5.19	3.60	2.12
Others	10.06	4.70	3.61

Figure 2. Chemical composition of steel slag DT (◆), GBFS (♠) and OPC (●) on the common ternary diagram of CaO-Al₂O₃-SiO₂

Approximately, the positions of steel slag DT (◆), GBFS (♠) were evaluated in compared with reference cementitious properties of OPC (●) on Figure 3. Steel slag DT stayed quite far from the reference OPC that could be explained by higher content of iron oxide in steel slag sample. Otherwise, SiO₂+CaO oxide content in GBFS and OPC are quite similar. They are in general compatible for producing a blended cement slag type.

Before serving as a supplementary cementing material (SCM), resistance index of slag DT must be superior to acceptable value 75% as requirement of TCVN 6882:2001. Compressive strength of two samples series at 7 days are respectively 30.1MPa (reference) and 28.5MPa (replacing 10% OPC cement by steel slag DT). The index of 94.5% (>75%) was calculated from fraction of two resistance values. Furthermore, according to TCVN 3735-1982 pozzolanic reactivity of slag DT was measured by the reaction of silica with hydrate lime. Result of 71.82mg CaO/1g slag deduces moderate reactivity of SCM steel slag. Filling effect of fine particle of steel slag might also improve mechanical resistance of blended cement [8,9].

Materials and Experimental Method

Schema of Experimental Study

Figure 4 shows the whole experimental study of slag recycling process. Steel slag after passing the common stage of material processing could follow two steps of recycling. The first one consists of formulating a system of blended cement OPC-steel slag and/or GBFS. The purpose of second one was to determine the influence of composition, heating condition and cooling rate on the microstructure and mineralogy of clinkerized slag. The final objective of this experimental work is a practical clinkerization process of melted steel slag from EAF converter.

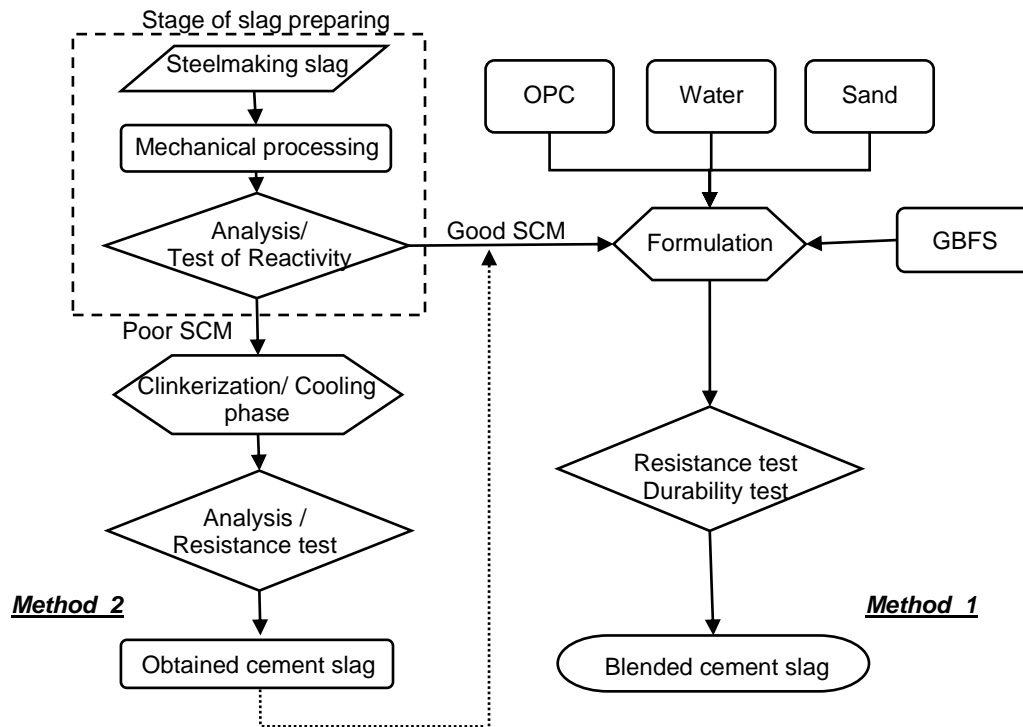


Figure 3. Experimental study of steel slag recycling with simultaneously two approaches

Materials for Producing Blended Cement Slag

Steel slag DT was used in the formulation stage after passing 90 μ m sieve. According to aforementioned analysis, it is classified as moderate in the range of reactive SCM.

OPC and GBFS in this study were supplied by Ha Tien 1 cement company (Vincem). They were ready used in-situ to produce blended cement OPC-GBFS respecting the requirement of TCVN 4315:2006. Materials composition is mentioned on the table (figure 2) by adopting method of XRF analysis. The standard ready-mix sand is used in the stage of mortar sampling with respect to TCVN 6227:1996; module size of granulometry is 2.9 in average. Fresh water is also used in the mixture according to the requirement of TCVN 4506-1987. Prismatic samples (40x40x160mm) were produced for specific test at early and later age of hardening period. Table 2 lists mixing composition of steel slag, OPC and GBFS in different samples series.

Table 1. Formulation Table of Slag Cement Mortar Samples for Test at Early and Later Age

Sample Series	% Slag DT	% GBFS	% OPC	Water /Solid	Sand /Solid	Curing Condition
S0	0		100	0.4	3	Normal + corrosion
S10	10		90	0.4	3	Normal
S20	20		80	0.4	3	Normal + corrosion
S30	30		70	0.4	3	Normal
S40	40		60	0.4	3	Normal + corrosion
S20+G20	20	20	60	0.4	3	Normal + corrosion
G40		40	60	0.4	3	Normal + corrosion

It is noted that hardened mortars was cured in both normal condition and accelerated corrosion, respectively for resistance test and durability test.

Materials for Clinkerizing Steel Slag

Raw materials needed for slag clinkerization process compose of steel slag DT, limestone and aluminum hydroxide. Limestone is extracted from Thanh Luong mine in Binh Phuoc province. After crushing and grinding step, material went through XRF analysis for chemical composition (XRF-SPECTRO XEPOS). In this preliminary study, an industrial product of aluminum hydroxide was used to provide Al_2O_3 component. Chemical composition of this hydroxide is also obtained by XRF analysis.

Table 2. Chemical Composition and Raw-Mix Design

	% by Mass of Oxide					% by Mass in mix design
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	
Limestone	91.24	1.97	-	-	3.77	26.63
Aluminum hydroxide	-	-	63.03	-	0.23	10.52
Steel slag DT	35.98	14.85	6.58	12.09	5.19	62.85

We noted that our objective of slag clinkerization is to improve cementitious reactivity as the reference of Portland cement. Raw-mix design was calculated by using theoretical Portland cement's composition [4, 7]. Thus, the expected slag clinker powder would be able to blend directly in OPC due to their conformity of mineralogy composition.

Results of Mixed Cement-Slag

SCM slag blends into Portland cement at different rate of replacement could modify radically the physio-mechanical behavior of cement mortar.

At Early Age (Fresh Cement Mortar)

Water serves for hydration reaction and to maintain workability of mortar sampling. Water demand of cement mortar decreases by varying replacement rate of steel slag in the range 10-40%. Blending 40% of steel slag, result of water reducing is highest around 9.8%. In contrast, there is no difference in result of water reducing of G40 and OPC samples. It seems that steel slag is truly low reactive in compared with GBFS and OPC.

Setting-time of cement mortars was measured with Vicat needle apparatus according to TCVN 3735-82/ASTM C618-92 standard. Relating to steel slag sample (S0 → S40), larger content of slag retarded the setting-time of cement paste (Figure 4-a). Relating to GBFS sample (SG20, G40), initial and final setting time also increased but still moderate in comparison with those of steel slag sample.

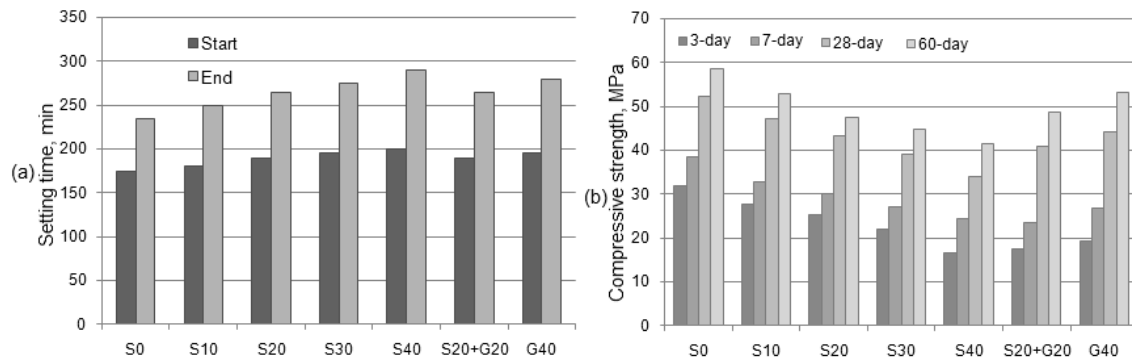


Figure 4. (a) Setting time period of cement paste and (b) compressive strength at 3, 7, 28, 60 days of curing time (prism 40x40x160mm)

At Later Age (Hardened Cement Mortar)

Figure 4-b shows normal strength developing of control sample S0 (prism 40x40x160mm). All others blended cement slag sample also show good behavior of mechanical resistance at later age, especially 28 and 60 days of curing time. Considering that there is a small gap between 3-day strength of G40 and S40 but 60-day strength of G40 is very high by comparing with S40 sample (40% steel slag). Others sample S10, S20, S30, S40 show clear evolution of later strength. S20 sample (20% steel slag) appears good formulation for blended cement slag, especially in the present of GBFS 20% (S20+G20). Relating to hydrated product in the cement matrix, both steel slag and GBFS behave differently with hydraulic Portland cement. Steel slag which is moderate in reaction with mixing water, still existing consequently in the hardened product. After 28 days, a typical microstructure of cement matrix combines most hydrated product of C-S-H and others particle filler of steel slag [10]. In the presence of GBFS, more C-S-H product would be formed by incorporating with the main hydrated product C-H of steel slag [11].

Furthermore, chemical ageing experiments were introduced to evaluate the relative durability of blended cement mortars. Three kind of accelerated corrosion environment Na_2SO_4 5%, MgSO_4 5%, HCl 0.5M have been prepared for test according to ASTM C1012. The solutions were regularly agitated and their pHs were controlled to maintain the desired value during 60 days of test. There exists net degradation of all mortar samples when exposed to corrosive solution. Longer time immersion in curing bath, higher deterioration rate is. In fact, Figure 5 reveals a slight difference (around $\pm 5\%$) of compressive strength of cement slag curing in corrosion environment by comparing with control sample S0. It is possible that new reaction product with sulfate ion (SO_4^{2-}) contribute to their higher strength of cement slag [12]. However, compressive strength of cement mortars decreases sharply in permanent contact with chlorhydric acid. The result is logic due to both the acid-base reaction with releasing portlandite and iron oxide leaching in acid solution [13]. Longer curing time in acid environment resulted lower compressive strength. There are no similar consequence in case of G40 sample (40% GBFS). The last one behaves well and develops strength in curing condition. Typically, using both iron and steel slag in S20+G20 sample improves durability property of cement mortar in the accelerated corrosion environment.

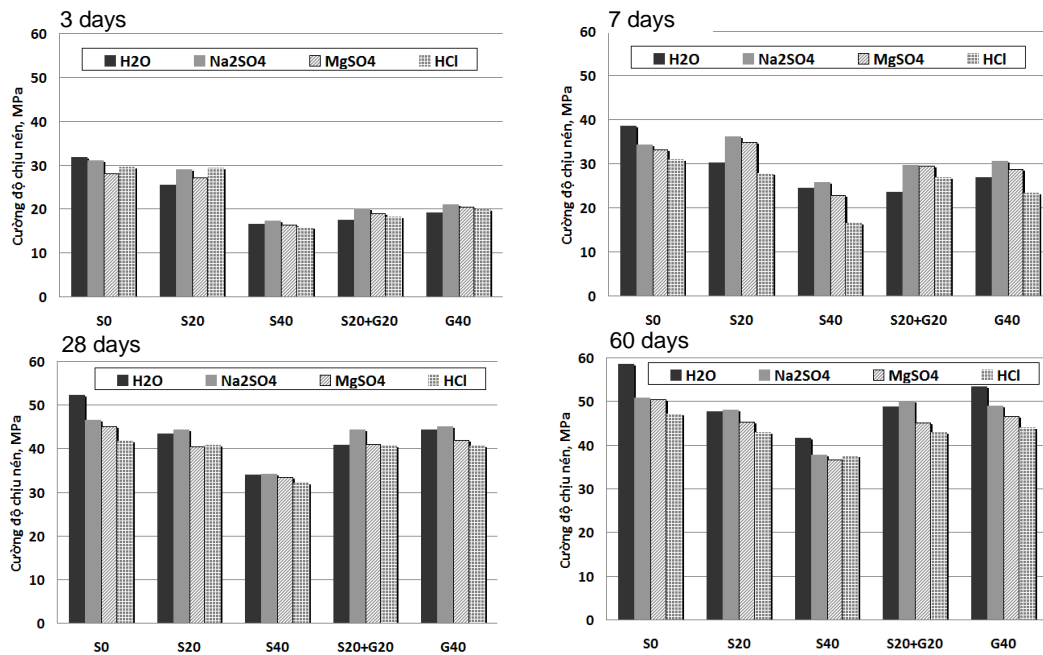


Figure 5. Compressive strength of mortar samples (prism 40x40x160mm) curing in water and others accelerated corrosion environment Na₂SO₄ 5%, MgSO₄ 5% and HCl 0.5M at 3-7-28-60 days

Results of Slag Cement

Clinkerization and Cooling Phase of Slag Cement

As mentioned, the iron slag GBFS played a model role in steel slag processing. GBFS material is generated from blast furnace technology causing its natural reactivity. Improving hydraulic reactivity of steel slag was objective of clinkerization step. For this purpose, mineralogical composition of new product need contain high amount of silicate calcium phase C₃S, C₂S. Free lime and magnesia would be fixed mainly in these crystallized products in solidified slag. Rapid cooling rate in the generating method was realized with cold water jetting/emerging. The existing of glassy phases deduced from cooling phase favored to grinding process of new clinker steel slag.

Mineralogical and Chemical Composition

On the figure 6-a, XRD analysis of slag cement shows a majors peaks of iron oxide. Except that, there was a glassy phase of amorphous base of spectrum. Others trace of C₃S at $2\theta = 32.0889; 33.8095; 29.06220$, C₂S at $2\theta = 32.2912; 41.1858; 35.1952$ and CA at $2\theta = 23.459; 47.231; 32.015$ were also recognized on the spectrum. These existing hydraulic minerals could contribute to hardening reaction of slag cement type [4].

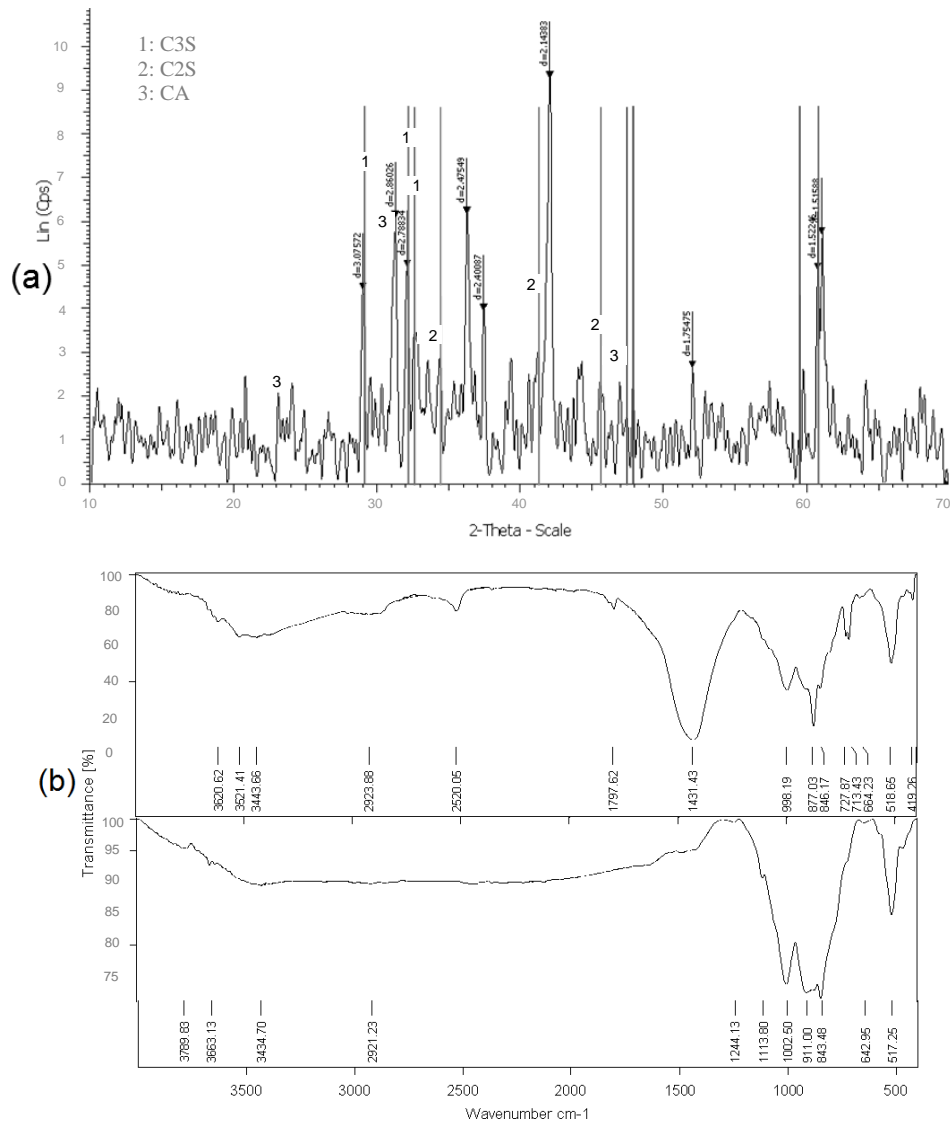


Figure 6. Spectrum of (a) XRD analysis, $\text{CuK}\alpha$ and (b) from up to bottom IR spectrum of raw materials mixture - new clinker steel slag

By comparing IR spectrum of raw materials and obtained clinker product (Figure 6-b), the effect of different parameters (raw-mix composition, sintering temperature, cooling phase) in slag clinkerizing would be analyzed. In the range of $500\text{-}1000\text{cm}^{-1}$, there exist some Si-O bond at 1247.04 ; 1114.55 ; 997.89 ; 434.45 ; Al-O bond at 844.29 ; Si-O-Si bond at 614.04 and Al-O, Si-O, Fe-O bonds at 518.8 . Considering the result of XRD analysis, they could stay in crystalline products of C-S. Typically, C2S phase still existing in both raw material of steel slag and new product. Higher temperature condition permits to improve sintering degree in general [4].

Setting-time, W/C and Compressive Strength

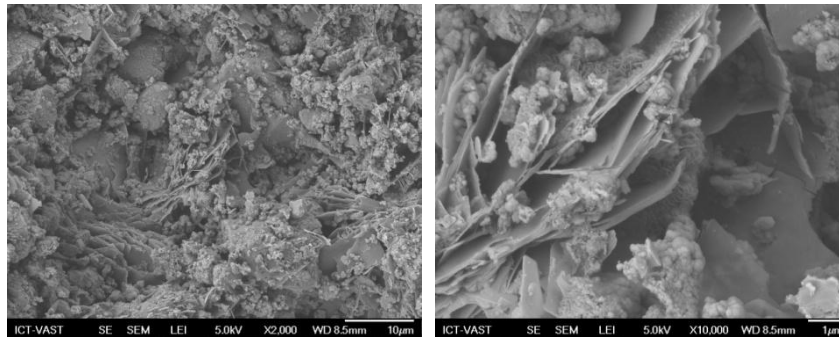


Figure 7. SEM photo(x2000 and x10,000) of hydrated product at 3 days

Slag cement was characterized according to specific requirement of TCVN 2682-1999. Water to cement ratio was estimated at 0.25. Initial and final setting time of cement paste were respectively 5 and 9 minutes. It seems very quick hardening cement in compared with OPC mortar sample. The results of compressive strength at 3 and 7 days are respectively 0.95MPa and 1.31MPa. These values are small and far from the requirement of TCVN standard of cement materials. At least, cement paste sample showed hardening period after 3 days of curing time but the intensity of hydrated product still low in term of both quality and quantity after clinkerization process. Others C-H plates were generated in the SEM photo of cement matrix (Figure 7).

Conclusions

Thanks to the existing silicate calcium C₂S, steel slag DT in this study shows moderate reactivity considering both resistance index and pozzolanic reaction. Well-selected fine slag gravel could be ground with cement OPC after storage time for dimensional stability. In term of mechanical resistance, blended cement including 20% steel slag attain 80% of compressive strength of control sample OPC. Hydrated product in cement matrix is abundant; moderate steel slag content was distributed between crystalline phases. At later age, it was noted that a remarkable degradation of microstructure of cement paste directly contact with accelerated corrosion environment. Using a mixture of steel slag and GBFS ameliorated durability properties in sulfate environment. Moreover, In comparison with the anti-corrosive character of GBFS cement (40% GBFS), blended slag cement behaves worse in HCl 0.5M due to leaching iron oxide in acid. Mixture 20% steel slag and 20% GBFS could be an appropriate candidate for producing anti-corrosive cement.

By adopting clinkerization prototype of GBFS, obtained results of materials analysis presented trace of C-S mineral as in material model GBFS and OPC. Raw-mix composition, sintering temperature and the following cooling phase in cold water bath could influence on hydraulic reactivity. Results of XRD analysis and IR analysis of in clinkerized slag product offered in depth discussion about the existing of reactive C₂S and C₃S component. Others characteristic properties did not conform to the requirement of normal cement Portland but it could be served as rapid setting cement type. Further study on heating and/or cooling condition will be needed for the purpose of producing new steel slag cement.

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