

Study on cementitious properties of steel slag

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Abstract: The converter steel slag chemical and mineral components in China's main steel plants have been analysed in the present paper. The electronic microscope, energy spectrum analysis, X-ray diffraction analysis confirmed the main mineral compositions in the converter slag. Converter slag of different components were grounded to obtain a powder with specific surface area over 400m²/kg, making them to take place some part of the cement in the concrete as the admixture and carry out the standard tests. The results indicate that the converter slag can be used as cementitious materials for construction. Furthermore, physical mechanic and durability tests on the concrete that certain amount of cement be substituted by converter steel slag powder from different steel plants are carried out, the results show that the concrete with partial substitution of steel slag powder has the advantages of higher later period strength, better frost resistance, good wear resistance and lower hydration heat, etc.

This study can be used as the technical basis for "Steel Slag Powder Used For Cement And Concrete", "Steel Slag Portland Cement", "Low Heat Portland Steel Slag Cement", "Steel Slag Road Cement" in China, as well as a driving force to the works of steel slag utilization with high-value addition, circular economy, energy conservation and discharge reduction in the iron and steel industry.

Keywords: Steel slag, cementitious property, admixture

1. Introduction

As byproduct of steel manufactory industry, steel slag is discharged 0.12-0.13 t/t•steel of steel produced. China's steel slag output in 2011 was 90.42 million tons, of which the utilization ratio was about 25%. Resource recovery has become an important issue of steel manufactory industries.

Since 1971, Scientists and engineers of Central Research Institute of Building and Construction have carried out continual researches on the relationship between steel slag components and its cementitious property, and also techniques for its process and utilization. Series of products of 'steel slag Portland cement' and technique for 'steel slag powder used for cement and concrete' have been developed and applied in construction engineering.

Ministry of Industry and Information Technology of the People's Republic of China published '12th Five-Year Plan for major industrial solid waste comprehensive utilization', in which the utilization ratio of slag should reach 75%, technique and complete equipment of steam pyrolysis and self-slaking technology of steel slag and producing steel slag powder, ground iron and steel slag(GISS) should be strongly promoted. The key projects involve construction of steel slag treatment and comprehensive utilization and producing GISS.

National Development and Reform Commission published 'Guidance on 12th Five-Year Plan for resource comprehensive utilization' and 'Implementation plans for major industrial solid waste comprehensive utilization', in which the iron and steel slag used for cement, concrete, construction and road regarded as the main application, the primary mission is to develop steam pyrolysis and self-slaking technology of steel slag and increase the recovery rate of metal, promote and construct ten demonstration projects on the technique of producing steel slag powder, GISS used for cement and concrete.

In order to achieve the goal, it is significant to undertake the research on cementitious property of steel slag.

2. Steel slag chemical composition

During steel manufacture process, main raw materials (liquid iron and scrap steel), auxiliary raw materials (lime, ore, dolomite and fluorspar) and ferroalloys melt into two incompatible parts under high temperature. Meanwhile, phosphonium, sulfur, carbon and harmful gases and some impurities of molten iron are removed to meet the standard requirements of different types of steel. Impurity, which is called steel slag indeed, composing various minerals, separates from steel due to the difference from densities.

Main chemical composition of steel slag is CaO, SiO₂, Al₂O₃, FeO, Fe₂O₃, MgO, MnO, P₂O₅ and f-CaO. Some kind of steel slag may contain a small amount of TiO₂, V₂O₅, etc.

Chemical compositions of converter steel slag are listed in Table 1.

Table 1 Chemical Compositions of Converter Steel Slag of Some Steel Plants in China(wt%)

	SHOU STEEL	BEN STEEL	TANG STEEL	TAI STEEL	MA STEEL	AN STEEL	NANJING STEEL	SHAO STEEL
SiO ₂	14.86	15.99	15.38	14.22	11.48	15.43	17.19	18.38
Fe ₂ O ₃	10.37	12.29	12.73	8.79	6.47	10.71	7.43	7.46
Al ₂ O ₃	3.88	3	2.54	2.86	2.1	2.44	1.48	3.04
CaO	44	40.5	40.3	47.8	41.29	39.29	40.14	40.77
MgO	10.04	9.22	9.05	9.29	7.26	11.04	8.79	3.14
FeO	12.3	7.34	14.06	13.29	15.83	16.48	16.94	15.49
MnO	1.11	1.34	1.88	1.06	1.79	1.27	1.99	5.38
P ₂ O ₅	1.31	0.56	1.1	0.56	1.06	0.74	1.51	1.27
f-CaO	1.8	2.8	1.84	1.57	12.77	2.02	4.31	8.57
Alkalinity	2.72	2.45	2.45	3.13	3.29	2.43	2.15	2.07

Remark: Alkalinity = CaO/(SiO₂+P₂O₅)

Because of the short converter process of smelting and slag tapping, steel slag was put into slag ladle together without distinguishing early or later periods of slag, and then, transported to processing production line.

From Table 1, (1) Steel slag chemical compositions from different plants were different, and alkalinities were among 2.07-3.29; (2) Major contents were CaO and SiO₂, Fe was found in the forms of FeO and Fe₂O₃; (3) P₂O₅ existed in slag. At first, P₂O₅ reacted with CaO and SiO₂ forming 7CaO·P₂O₅·2SiO₂, which adsorbed a lot of CaO. As a result, generation of 3CaO·SiO₂(C₃S) was slowed. Further more, P₂O₅ might lead to decomposition of C₃S, which reduced activity of steel slag; (4) Activity of steel slag could be derived roughly by its composition. Generally, steel slag with high alkalinity had high activity (see Table 2).

Table 2 Relationship Between Alkalinity and Activity

Alkalinity	Principal Minerals	Strength of Cement Mortar /Mpa	
		R7	R28
1.80	C ₂ MS ₂ 、C ₂ S、RO	15.1	36.8
2.75	C ₃ S、C ₂ S、RO、C ₂ F	17.8	55.0
3.6	C ₃ S、C ₂ S、RO、C ₂ F	32.9	56.4

Remarks: a. Alkalinity = CaO/(SiO₂+P₂O₅)

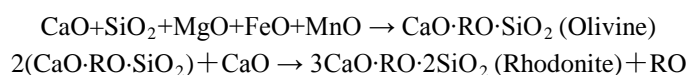
b. Mortar — 35% steel slag powder, 40% blast furnace slag, 20% Portland cement clinker, 5% gypsum

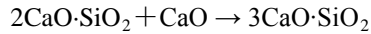
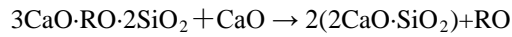
c. Specific surface area of steel slag – 420m²/kg

3. Steel slag mineral constituents

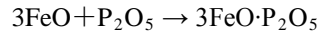
3.1 Mineral forming process

During the early stage of smelting, part of liquid iron is oxidized into FeO or Fe₂O₃ and silicon in liquid iron and burden are oxidized into SiO₂ and then the main constituents of steel slag are SiO₂, CaO and FeO+Fe₂O₃. As lime added, alkalinity rises and reactions go as follows.





Where: RO -- oxide of (Mg^{2+} , Fe^{2+} , Mn^{2+} , etc) continuous solid solution



When the temperature T is lower than 1470 °C, $3\text{CaO}\cdot\text{SiO}_2$ and $\text{CaO}\cdot\text{SiO}_2$ react to generate kinds of solid solution like $7\text{CaO}\cdot\text{P}_2\text{O}_5\cdot 2\text{SiO}_2(\text{C}_7\text{PS}_2)$, etc.

Activity of steel slag is related to its chemical compositions, especially the content of active minerals (C_3S , C_2S and C_2F).

Part of FeO exists in RO-phase and fayalite ($\text{CaO}\cdot\text{FeO}\cdot\text{SiO}_2$) which has no activity. But $2\text{CaO}\cdot\text{Fe}_2\text{O}_3$, which generates from Fe_2O_3 and CaO, is active mineral.

Main minerals of steel slag were confirmed by the means of electron microscopic analysis, X-ray energy spectrum analysis, X-ray diffraction analysis and ore phase analysis, and then steel slag cementitious property could be assessed.

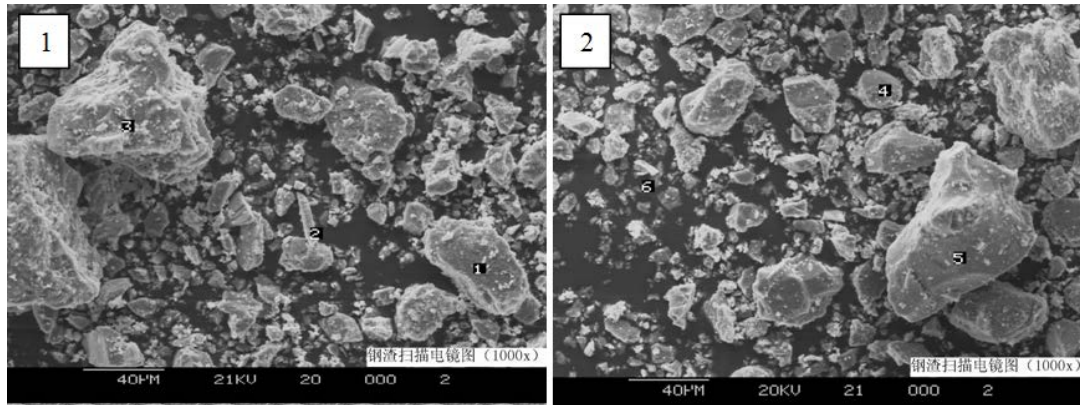
3.2 Main mineral components

Main mineral components in steel slag are tricalcium silicate (C_3S), dicalcium silicate (C_2S), RO-phase, rhodonite (C_3RS_2), olivine (CRS), dicalcium ferrite (C_2F), calcium ferrite (CF), free CaO (f-CaO) and free MgO (f-MgO). Some of steel slag may also have melilite (C_2AS), spinel, etc.

3.3 Mineral feature analysis

3.3.1 Electron microscope analysis

The result of analysis on SEM photos of converter steel slag (see Fig. 1-5) is presented in Table 3.



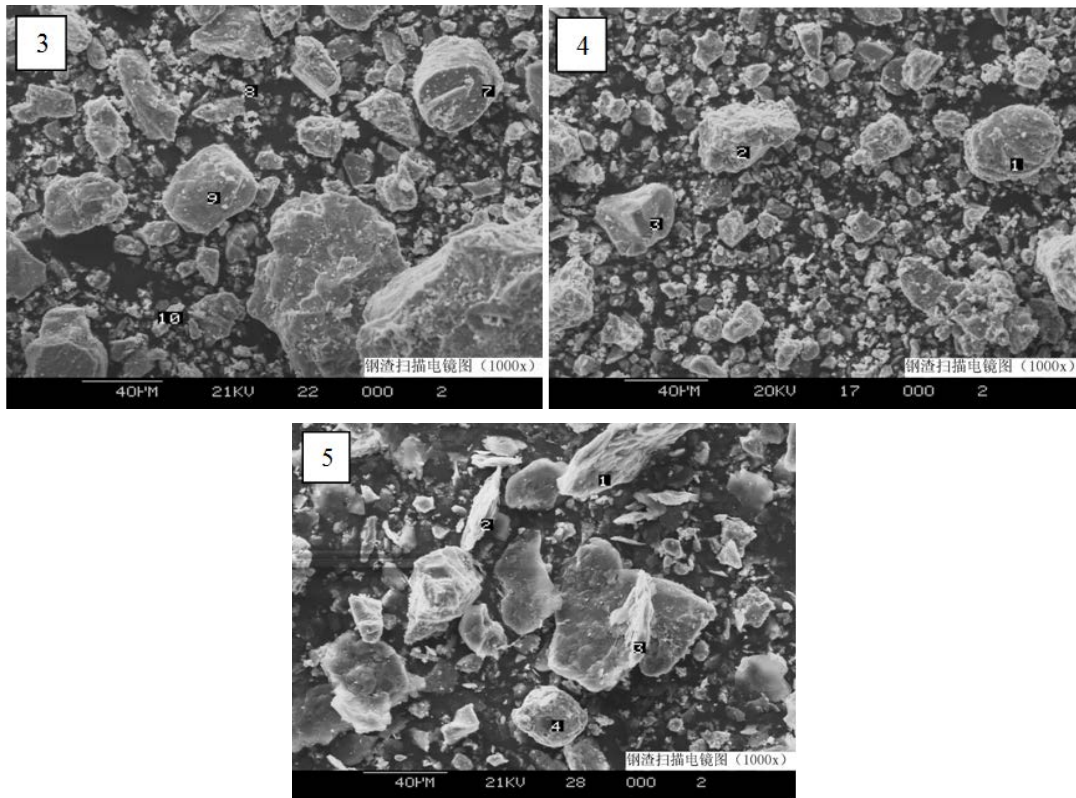


Fig. 1-5 Scanning Electron Microscope photos of converter steel slag (1000×)

Table 3 Mineral analysis of SEM photos

Figure Number	Ore-phase Number	Mineral Analysis
1	1#	massive - fayalite(CFS) probably
	2#	elongated - CFS-MgO solid solution
	3#	Irregular - CFS and C ₂ S
2	4#	rounded, granular - RO-phase and f-CaO
	5#	massive - f-CaO and RO-phase
3	7#	columnar - RO-phase
	8#	short columnar - C ₂ S and RO-phase
	9#	square - C ₃ S
4	10#	columnar - C ₃ S
	1#	rounded, granular - C ₂ S
	2#	massive - C ₂ F
5	3#	short columnar - CFS
	1#	massive - rhodonite(C ₃ MS ₂) and ferrosipinel(FeO·Al ₂ O ₃)
	2#	massive - rhodonite(C ₃ MS ₂) and ferrosipinel(FeO·Al ₂ O ₃)
	3#	fusiform - rhodonite(C ₃ MS ₂)
	4#	rounded - metallic Fe

3.3.2 X-ray energy spectrum analysis

Mineral phases are confirmed by energy spectrum analysis in Table 4.

Table 4 X-ray energy spectrum analysis

Figure number	Phase number	Energy spectrum analysis (%)
1	1#	Ca 64.814, Si 15.021, Mg 11.943, Fe 7.223
	2#	Mg 39.829, Fe 25.085, Ca 24.413, Si 3.820
	3#	Ca 64.176, Si 21.354, Fe 7.437, Mg 5.804

2	4#	Mg 43.701, Fe39.286, CaO 7.945, Mn 6.576, Si 1.402
	5#	Ca 86.378, Mg 6.543, Fe 4.890, Mn 1.707
	6#	Ca 52.712, Al 20.946, Fe 16.486, Si 5.381
3	7#	Fe 53.653, Mg 35.722, Ca 6.353, Mn 2.763, Si 1.370
	8#	Ca 87.230, Si 3.028, Fe 6.244, Mn3.267
	9#	Ca80.281, Si 16.710
	10#	Fe 15.489, Ca 60.385, Si 16.931, Mg 2.349, Mn 0.918
4	1#	Ca 61.636, Si 25.620, Fe 8.440, Al 2.466, Mn 1.843
	2#	Ca 53.868, Fe 45.337
	3#	Ca 49.318, Fe 27.953, Si 11.211, Mn 7.777, Al 2.256
5	1#	Ca 24.727, Fe 22.103, Si 19.009, Mg 9.938, Al 8.565
	2#	Si 28.279, Mg 19.659, Ca 16.077, Fe 10.600, Al 10.041
	3#	CaO 51.827, Si 20.378, Fe 11.099, Al 5.810, Mg 4.259
	4#	Fe 97.032

3.3.3 X-ray diffraction analysis

Analyses of X-ray diffraction patterns (see Fig.6, 7) are summarized in Table 5, 6 separately.

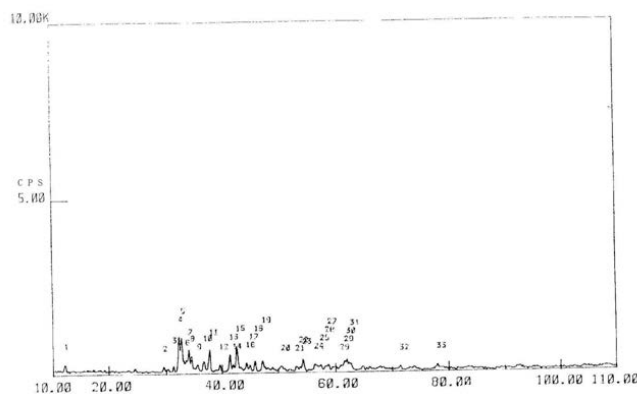


Fig. 6 X-ray Diffraction Patterns on Converter Steel Slag

Table 5 D-value of X-ray Diffraction Patterns on Converter Steel Slag

No.	d	Mineral	No.	d	Mineral
2	3.0135	C ₂ S	2	3.0135☆	C ₃ S
18	1.9746		3	2.8554	
24	1.6284		4	2.7643	
28	1.5195		11	2.3768☆	
7	2.6256	f-CaO	28	1.5195	MgO
20	2.4403		29	1.5034	
21	1.7209		31	1.4797	
3	2.8554	CFS	15	2.1177	C ₂ F
6	2.6635		10	2.4403	
20	1.8024		30	1.4956	
25	1.6020		17	2.1167	
11	2.3768	RO-phase	22	1.9302	C ₂ F
14	2.1475		31	1.4797	
29	1.5034				

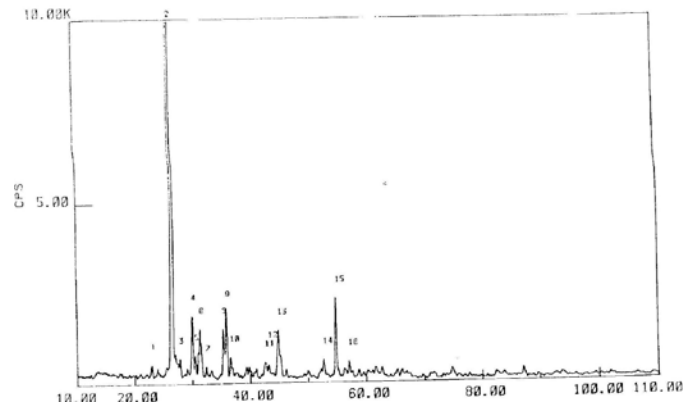


Fig. 7 X-ray Diffraction Patterns of Steel Slag

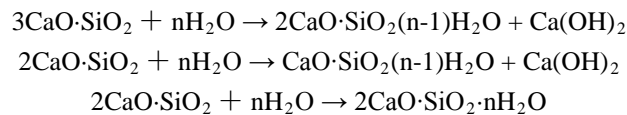
Table 6 D-value of X-ray diffraction Diffraction Patterns of Steel Slag

No.	D	Mineral
3	3.31863	3CaO·MgO·2SiO ₂
7	2.7577	
16	1.6112	
6	2.8413	FeO·Al ₂ O ₃
10	2.4493	
15	1.6715	

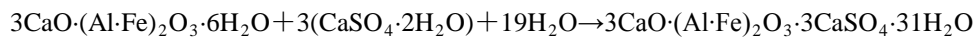
From the results above, it can be confirmed that main mineral components in steel slag were C₃S, C₂S, C₂F, CFS, RO-phase (solid solution of Mg²⁺, Fe²⁺ and Mn²⁺), f-CaO, f-MgO, C₃MS₂ and FeO·Al₂O₃.

4. Steel slag cementitious property and hydration process

Steel slag comprises cementitious minerals as C₃S and C₂S, which take up more than 50%, and also 3CaO·(Al·Fe)₂O₃, so it can be used to produce steel slag powder for cement and concrete. Hydration process proceeds as follows.



In the case of gypsum presenting,



By means of X-ray diffraction, the steel slag powder paste was tested (see Table 7).

Table 7 D-value and Diffraction of X-ray Diffraction of Steel Slag Powder Paste

Experimental data		Foreign reference data	
d/n	I/I ₀	d/n	I/I ₀
9.1905	8	9.3000	weak
—	—	7.2300	weak
5.3917	7	5.6600	medium
—	—	5.2000	weak
4.5109	2	4.6800	weak
—	—	4.2600	much weak
3.8045	8	3.9200	medium
3.0057	10	3.0300	medium
2.7590	8	2.8100	medium
2.6547	5	—	—

Experimental data		Foreign reference data	
2.5473	7	2.5700	medium
2.1785	7	2.2260	medium
2.1263	5	2.1550	weak
1.9170	4	1.9670	much weak
1.8187	3	1.8500	weak
1.6640	1	1.6730	weak

After grinding and separating the liquid, the sample of specific gravity 2.0-3.2 was picked out for X-ray diffraction (see Table 8).

Table 8 D-value and Diffraction of XRD of Steel Slag Powder Paste After Hydration

D/n	4.2737	3.3708	3.0488	2.8735	1.9170	1.8102	1.7161
I/I ₀	7	2	10	3	5	4	4

To sum up, CSH(B) was generated after steel slag powder hydration.

4.1 Mechanism of steel slag powder used as admixture of cement and concrete

As known, hydration process and hydration products of steel slag powder are similar to Portland cement. But the formation temperature of steel slag is 200-300 °C higher than that of cement, which leads to C₂S and C₃S with larger and more compact crystals and lower hydration speed. Chinese scientists put forward the name 'overburnt Portland cement clinker' for steel slag in the paper on Cement Materials International Conference in Belgium, 1983.

After grinding, median diameter of steel slag powder reached 14.16μm, of which 76.42% was less than 30μm (see Fig. 8). Grinding process, mechanical activation indeed, not only made particles even smaller, but also caused changes of crystal structure and characterization of particle surfaces. Specific area became larger, as energy came from grinding transfers into internal and surface energy of new particles, which led to changes of bond energy of crystal. As a result, rapid decrease of lattice energy generated lattice defect, dislocation and recrystal. Then structure of amorphous state was formed on the surface.

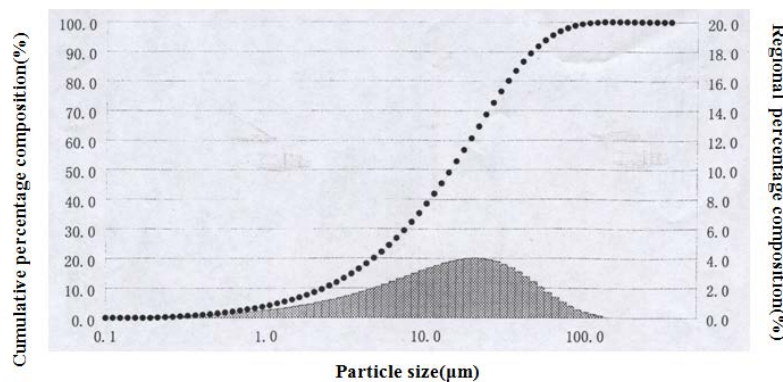


Fig.8 Distribution of grain size of converter steel slag powder (400m²/kg)

Lattice structure changes are mainly presented as reduced size, increased strain and structural deformation of lattice, which respectively lead to the increased contact area of mineral and water, enhanced interactions between mineral and water and reduced number of bonding among minerals, which makes it easier that hydrone enters and hydration accelerates.

Different chemical compositions of steel slag have different structural changes during grinding process, which is relevant to lattice stability. For example, granulated blast furnace slag and steel slag of the same fineness have a big difference in activity.

4.2 Relationship between alkalinity and activity of steel slag

Experiments were conducted on the relationship between alkalinity and activity of steel slag (see Table 9).

Table 9 Relationship between alkalinity and activity of steel slag

No.	Alkalinity	Compressive strength MPa		Activity index (%)	
		7d	28d	7d	28d
1	Comparison sample of cement	34.6	53.8	100	100
2	2.68	22.1	45.6	64	85
3	2.02	21.8	39.4	63	73
4	1.69	21.4	37.9	62	70

Remarks: a. Alkalinity = $\text{CaO}/(\text{SiO}_2+\text{P}_2\text{O}_5)$

b. Specific surface area of steel slag: $400\text{m}^2/\text{kg}$

c. Cement strength grade: 42.5 Portland cement

d. Test sample: 70% cement and 30% steel slag powder in mass ratio

As alkalinity of steel slag reduced, samples compressive strength dropped accordingly.

4.3 Relationship between alkalinity of steel slag and activity of GISS

Experiments were conducted on the relationship between alkalinity of steel slag and activity of GISS (see Table 10).

Table 10 Relationship between alkalinity of steel slag and activity of GISS

No.	Alkalinity of steel slag	Compressive strength MPa		Activity index (%)	
		7d	28d	7d	28d
1	Comparison sample of cement	34.6	53.8	100	100
2	GGBFs	26.3	52.3	76	97
3	2.68	25.95	51.2	75	95
4	2.02	23.1	48.3	67	90
5	1.69	21.7	45.7	63	85

Remarks: a. Alkalinity = $\text{CaO}/(\text{SiO}_2+\text{P}_2\text{O}_5)$

b. Specific surface area of GISS: $420\text{m}^2/\text{kg}$

c. Test sample: 70% cement and 30% GISS in mass ratio

d. GISS: 70% GGBFs and 30% steel slag powder in mass ratio

Therefore, it can be seen that the activity index of GISS can be improved with alkalinity of steel slag increasing. When alkalinity of steel slag was 2.68, the activity index of GISS reached Grade S95 according to the requirements in 'Ground granulated blast furnace slag powder used in cement and concrete' GB/T 18046-2008 in China. When alkalinity of steel slag was under 2.02, the activity index of GISS could reach Grade S75 in the standard above.

4.4 Relationship between content of steel slag powder and concrete compressive strength

Experiments were conducted on the relationship between content of steel slag powder and concrete compressive strength (see Table 11).

Table 11 Relationship between content of steel slag powder and concrete compressive strength

No.		1	2	3	4
Amount of materials for concrete (kg/m^3)	cement	480	384	360	336
	steel slag powder	0	96	120	144
	water	144	144	144	144
	sand	764	764	764	764
	stone	1012	1012	1012	1012
Content of steel slag powder (%)		0	20	25	30

Water reducing agent JG-2 (%)		1.2	1.2	1.2	1.2
water to binder ratio		0.3	0.3	0.3	0.3
Sand ratio (%)		43	43	43	43
Slump (cm)		0	0.5	0.5	1
Compressive strength (MPa)	7d	65.4	62.7	61.3	60.2
	28d	71.4	75.1	72.6	68.8

When steel slag powder took place of 20%-50% cement, the concrete compressive strength of 7d was lower, but that of 28d was enhanced. 20% of the cement was replaced by steel slag powder in producing concrete, which could reach C70, higher than that produced by pure cement. Similarly, when the percentage came to 25% and 30%, concrete reached C60.

5. GISS – the best admixture for concrete

5.1 Effect of GISS as admixture on concrete compressive strength

Relationship between GISS and concrete compressive strength are concluded in Table 12.

Table 12 Relationship between content of GISS and concrete compressive strength

No.		1	2	3	4
Amount of materials for concrete (kg/m ³)	cement	480	384	360	336
	GISS	0	96	120	144
	water	144	144	144	144
	sand	764	764	764	764
	stone	1012	1012	1012	1012
Content of GISS (%)		1.2	1.2	1.2	1.2
Water reducing agent JG-2 (%)		0	20	25	30
Water to binder ratio		0.3	0.3	0.3	0.3
Sand ratio (%)		43	43	43	43
Slump (cm)		0	1	1.5	1.5
Compressive strength (MPa)	7d	65.4	70.6	69.8	66.4
	28d	71.4	82.3	81.5	78.6

Remarks: GISS - 70% GGBFs and 30% steel slag powder in mass ratio

When GISS took place of 20%, 25%, 30% cement to make up concrete, compressive strength of 7d and 28d were both enhanced, which reached C70 a grade higher than that made of pure cement. Compared with steel slag powder admixture, concrete of GISS admixture showed higher compressive strength under the same conditions. Moreover, concrete made up by GISS presented increased slumps.

Concrete compressive strength in the hardened state mainly depended on the strength of aggregate, hardened cement paste and interface bond between aggregate and cement paste. If only the impact of GISS was considered, strength of hardened cement paste depended on the situation of particles accumulation and bond. As a reason of increased strength of concrete, GISS of 400m²/kg acted as filling materials, by which porosity of concrete decreased and strength increased.

Besides, fine particles of GISS had a quick and deep hydration, which was also important for strength increasing. When amount of replaced cement was large, concrete showed a lower strength, as the result of the lower strength of GISS hydration products. Concrete of GISS admixture showed higher compressive strength than that of steel slag powder admixture, because glassy network structure of GGBFs was solid, which made it easier to hydrate when steel slag powder presented to form a higher alkalinity.

C₃S and C₂S within steel slag generated much Calcium silicate hydrate(CSH) gel and Tobormorlit during hydration process, which had expansive action to some degree. Therefore, the paste was more compact, and the strength was enhanced.

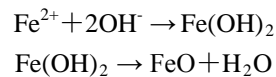
5.2 Durability of GISS as admixture in concrete

Concrete not only demands enough strength, but also requires good durability. Durability is a primary factor in guaranteeing construction safety.

Cementitious property of GGBFs comes from its glassy structure. By the action of $\text{Ca}(\text{OH})_2$, hydration product comprises CSH(B), hydrogarnet ($\text{C}_3\text{AS}_{1.2}\text{H}_{3.6}$) and C_2SH_2 .

Carbonization of CSH(B) is fast and then strength reduces more than 30%. The reason is that CSH decomposes to fine calcite and amorphous silica gel. According to ore phase analysis, lattice size of calcite was much larger than that of CSH(B). Carbonization process took place by Ca^{2+} and CO_3^{2-} within liquid phase among the interspaces of sample. Calcite came out through crystallization and precipitation from liquid phase. Solubility of CSH(B) was stronger than that of other CSH.

Steel bar corrosion in concrete is a kind of electrochemical corrosion. Steel bar always has impurity and surface defect, which result in inhomogeneity of electrochemistry. Much tiny primary cells are formed because of the difference of electric potential between steel and impurity. Generally, impurity has higher electric potential acting as negative pole of the primary cells. Potential difference is considered as electromotive force. Electric current and corrosion will appear when there are water and oxygen around.



Solubility of FeO is so small that this kind of sparingly soluble substance accumulates on the surface of steel bar forming a film to prevent the reaction, which is usually called passive film. For that reason, steel bar will not get rusty.

Low alkalinity of concrete liquid phase can cause damage of passive film of steel bar surface. Generally, passive film will not be broken when pH is above 12.2.

According to the tests, when 40% cement was replaced by GGBFs to produce concrete, the alkalinity of concrete liquid phase reduced from 12.2 to 10.6. But during hydration C_2S and C_3S composed in steel slag powder released $\text{Ca}(\text{OH})_2$, which maintained the alkalinity. Besides, hydration product of steel slag powder was Tobermorit ($\text{C}_5\text{S}_6\text{H}_5$), which was slower than CSH(B) during carbonization and improved strength more than 50% after carbonization.

Content of steel slag powder and GGBFs in GISS seriously impacted the amount of CaO in the mixture and then influenced pH value (see Fig. 9). pH was 10.75 when content of CaO was 29.5, and pH reached 12.5 when there was 40.5% CaO. Meanwhile, influence of f-CaO was also found in tests (see Fig. 10). In a certain range, along with the increase of f-CaO content, pH increased correspondingly.

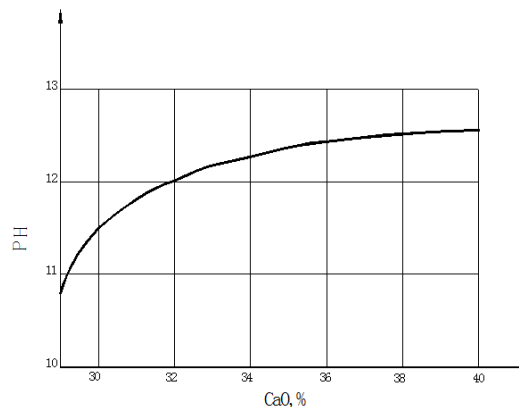


Fig.9 The relationship between content of CaO in steel slag powder and pH

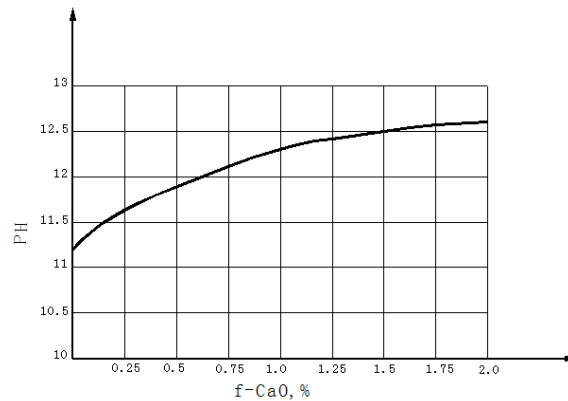


Fig.10 The relationship between content of f-CaO in steel slag powder and pH

6. Conclusions

(1) As byproduct of steel manufacture industry, steel slag is a valuable resource which is called 'overburnt Portland cement clinker'. Formation temperature of steel slag is 1650 °C, which is high. Therefore, C_2S and C_3S in steel slag comprise large and compact crystals, and also hydrate slowly.

(2) Contents of C_2S and C_3S in steel slag act as an important factor that influences activity of steel slag powder. The more their contents are, the higher activity is.

(3) Activity of steel slag powder rises with increase of its alkalinity ' $CaO/(SiO_2+P_2O_5)$ '.

(4) Steel slag has a hydration process similar to cement. Strength comes from hardening of CSH.

(5) Concrete produced by steel slag powder as admixture can obtain an increased strength.

(6) GISS is the best admixture for concrete which avoids low alkalinity and poor durability caused by GGBFs as the only admixture.

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