Utilization of converter steel slag by remelting and reducing treatment

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Abstract. In China, as by-products of iron and steel industry, the utilization rate of steel slag is still relatively low and its open-air stacking occupies a lot of land, where there is a quite different situation of blast furnace slag as supplementary cementitious material in concrete. Considerable amount of metallic iron and iron oxide are lost within slag. In addition, undesirable volume change occurs when slag used as admixture in construction due to high free-CaO content, limiting its application in cement and concrete industry. In this study, remelting and reducing treatment was conducted to recycle iron and modify the chemical composition of the residue. Results showed that iron oxide could be reduced to iron and adjusting materials were found to promote reduction of iron oxide and stability of slag and separation of iron and slag.

1. Introduction

Since 2000, crude steel production has kept increasing throughout the world. Especially after 2013, China's crude steel output has taken up half of the global production, yielding considerable amounts of byproducts as blast furnace slag, converter steel slag, etc. Utilization of these byproducts has attracted researchers' attention all over the world. Concrete would improve particle size distribution and pore structure by adding mineral materials, leading to a good performance in liquidity, resistance to chloride ion permeability [1-3], etc.

Converter steel slag has certain cementitious activity due to the components of C_3S ($3CaO{\cdot}SiO_2$), C_2S ($2CaO{\cdot}SiO_2$), *etc*. But different from the cement clinker, the temperature of its formation is about 1650℃. Minerals crystallize performs more complete and compact, leading to its slow hydration. What's more, undesirable volume change occurs when slag used as admixture in construction due to high f-CaO (free-CaO) content, limiting its application in cement and concrete industry [4-6].

Durability is an essential factor of concrete structures life and safety [7]. Corrosion of reinforcement that is usually caused by carbonation or chloride is considered as the direct reason of concrete durability failing.

2. Materials and Methods

2.1. Raw materials

Converter steel slag (SS) used in the experiment was sampled from a large iron and steel corporation in Hebei province, China. Chemical composition show in Table 1, metallic iron was 10.81% of original slag. Slag were ground for experiments by a ball mill to the specific surface area of 400 ± 5 m^2/kg, when density of steel slag was 3350 kg/m^3. As seen from **Fig. 1**, Fe_xO_y mainly exists in Ca-Fe phase. Peaks of C_2S, C_3S and f-CaO were outstanding in the pattern. Coke was used as the reducing agent (**Table 2**).

Table 1. Main Chemical composition of slag (%)

Sample	CaO	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	P_2O_5	MnO	f-CaO
Steel slag	38.83	12.14	2.14	8.97	14.32	11.22	2.45	1.48	8.46

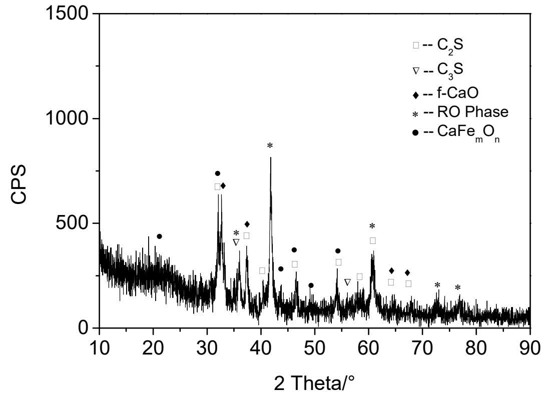

Figure 1. XRD pattern of converter steel slag.

Table 2. Analysis of coke (%).

Index	Air dried base	Dry base	Dry ash-free base
Water component	0.20	/	/
Ash component	15.89	15.92	/
Volatile component	0.94	0.94	1.12
Fixed carbon	82.97	83.14	98.88

2.2. Experimental apparatus

According to theory of metallurgical thermodynamics, iron oxide in molten slag can be reduced priorly. Researches on factors of amount of reducing agent and adjusting materials were carried out. Remelting and reducing process were conducted in melting furnace of DC graphite electrode. As strong alkaline substances, CaO/SiO_2 value reached 3.20. Thus, SiO_2 was added in remelting process as the adjusting materials.

Slag samples were ground to diameter smaller than 10mm.Then chemical and XRD analysis were undertaken according to Chinese standard YB/T 4188-2009, YB/T 140-2009 and GB/T 1346-2001.

3. Results and Discussion

3.1. Reduction of iron oxides

During remelting, metallic iron of steel slag settled down to bottom of the reactor. Iron oxides could be reduced to iron and separate from slag. Metallization rate and metal recovery rate could reach 87.01% and 96.12% when only coke was used (**Fig. 2**). From the change of curve, 2% coke was enough to reduce the slag to an adequate level of metallization and recovery. In consideration of system loss, 5% coke was regarded as the reducing agent quantity standard in the following experiments.

As for adjusting materials added in **Fig. 3**, SiO_2 was found to promote reduction and separation of iron and slag. When the amount of SiO_2 was 10%, metal recovery rate came to a head of 96.45% and metallization rate came to a head of 87.30%. Recovery of iron of steel slag was proved practicable. But when amount of SiO_2 reached 20%, both of the two indexes tend to worsen due to the dilution effect.

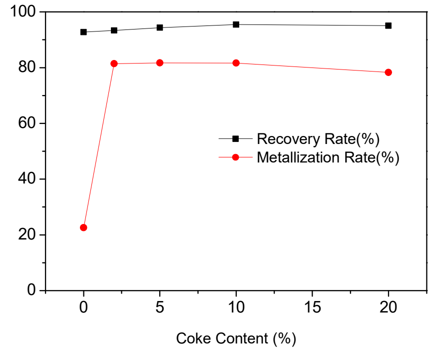

Figure 2. Reduction of iron dioxides by coke.

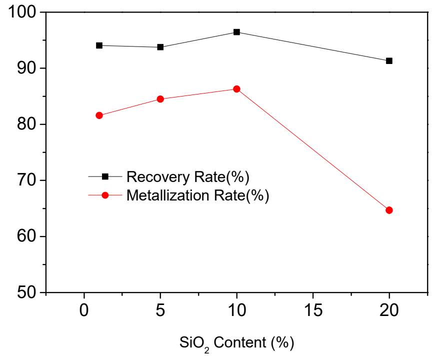

Figure 3. Reduction of iron dioxides with SiO_2 adjusting materials.

3.2. *Chemical and mineral analysis*

Chemical analysis of recycled iron of original and 10% SiO_2 samples was concluded in **Table 3**. Fe and Si drops as C, Mn, P and S increases, which indicates the reaction of reduction by carbon. From the chemical composition of slag (as seen in **Table 4**), CaO/SiO_2 ratio decreases with the increasing proportion of SiO_2 admixture. Obviously, f-CaO reduces to lower than 1% when 10% SiO_2 added.

Table 3. Chemical analysis of recycled iron (%).

Sample	Fe	C	Si	Mn	P	S
Original	95.96	1.25	0.43	0.49	0.15	0.0190
10% SiO_2	94.92	2.53	$<$0.10	0.14	1.54	0.1500

Table 4. Chemical composition of treated slag (%).

Sample	CaO	SiO_2	Al_2O_3	MgO	FeO	Fe_2O_3	f-CaO
1% SiO_2	61.01	16.27	2.73	4.49	3.19	0.39	13.48
5% SiO_2	56.76	18.77	3.52	6.42	2.20	0.91	4.35
10% SiO_2	52.23	29.00	2.51	7.16	1.17	0.20	0.87
20% SiO_2	38.40	31.84	2.35	9.95	4.15	0.43	0.73

From **Fig. 4**, it is found that as the proportion of SiO_2 increases, C_3S decreased but C_2S increased, which suggested a possibility of conversion of C_3S to C_2S. The patterns also supports the results come from the chemical analysis.

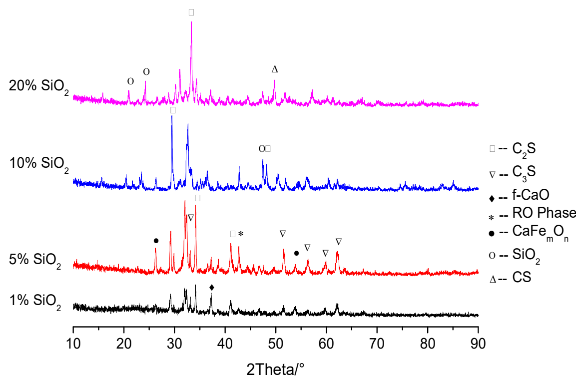

Figure 4. XRD patterns of treated slags.

3.3. *Stability tests*

In the tests of stability (**Table 5**), sample of 5% SiO_2 reached highest amount of slag up to standard. Volume change was only 3.00 mm when the amount of tested sample reached 80%, which sustained that stability of steel slag could be improved during the iron recovery process. Taken together, the best result was the sample with adjusting material of 10% SiO_2, melting time of 30 min, coke of 5%, correspondingly metallization rate was 87.30%, metal recovery rate was 96.45%.

Table 5. Results of stability tests.

Sample	Volume stability	
	Maximum content（%）	Expansion amount（mm）
Original Slag	40	3.00
1% SiO_2	30	×
5% SiO_2	80	3.00
10% SiO_2	80	1.00
20% SiO_2	80	1.00

4. Conclusions

As inevitable byproducts of iron and steel industry, metallurgical slag needs to be utilized as reasonable resource through technical means in order to avoid dumping, occupation of land and environmental pollution. Iron oxides in steel slag could be recycled by reduction method and metallic iron could settle down to bottom of the reactor. Metal recovery and metallization rate could reach 96.45% and 87.30% respectively. Moreover, the treated slag could obtain a good stability which enhances the safety in utilization. Besides, if the energy of molten slag could be used effectively, process cost would take a further reduction.

References

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