Utilization of converter steel slag by remelting and reducing treatment

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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 C₃S (3CaO·SiO₂), C₂S (2CaO·SiO₂), etc. But different from the cement clinker, the temperature of its formation is about 1650 °C. 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 m²/kg, when density of steel slag was 3350 kg/m³. As seen from Fig. 1, Fe₅O₇ mainly exists in Ca-Fe phase. Peaks of C₃S, C₄S 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  | SiO₂ | Al₂O₃ | Fe₂O₃ | FeO  | MgO  | P₂O₅ | MnO  | f-CaO |
|--------------|------|------|-------|-------|------|------|------|------|-------|
| Steel slag   | 38.83| 12.14| 2.14  | 8.97  | 14.32| 11.22| 2.45 | 1.48 | 8.46  |

![XRD pattern of converter steel slag.](image)

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/SiO₂ value reached 3.20. Thus, SiO₂ 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, SiO₂ was found to promote reduction and separation of iron and slag. When the amount of SiO₂ 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 SiO₂ reached 20%, both of the two indexes tend to worsen due to the dilution effect.
3.2. Chemical and mineral analysis

Chemical analysis of recycled iron of original and 10% SiO₂ 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/SiO₂ ratio decreases with the increasing proportion of SiO₂ admixture. Obviously, f-CaO reduces to lower than 1% when 10% SiO₂ added.

| Sample     | Fe   | C     | Si   | Mn   | P    | S     |
|------------|------|-------|------|------|------|-------|
| Original   | 95.96| 1.25  | 0.43 | 0.49 | 0.15 | 0.0190|
| 10% SiO₂   | 94.92| 2.53  | <0.10| 0.14 | 1.54 | 0.1500|

| Sample     | CaO  | SiO₂ | Al₂O₃| MgO  | FeO  | Fe₂O₃| f-CaO |
|------------|------|------|------|------|------|------|-------|
| 1% SiO₂    | 61.01| 16.27| 2.73 | 4.49 | 3.19 | 0.39 | 13.48 |
| 5% SiO₂    | 56.76| 18.77| 3.52 | 6.42 | 2.20 | 0.91 | 4.35  |
| 10% SiO₂   | 52.23| 29.00| 2.51 | 7.16 | 1.17 | 0.20 | 0.87  |
| 20% SiO₂   | 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 SiO₂ increases, C₃S decreased but C₂S increased, which suggested a possibility of conversion of C₃S to C₂S. The patterns also supports the results come from the chemical analysis.

| Sample     | 2Theta/° |
|------------|----------|
| 1% SiO₂    | 10       |
| 5% SiO₂    | 15       |
| 10% SiO₂   | 20       |
| 20% SiO₂   | 25       |

Figure 2. Reduction of iron dioxides by coke.

Figure 3. Reduction of iron dioxides with SiO₂ adjusting materials.

Figure 4. XRD patterns of treated slags.
3.3. Stability tests

In the tests of stability (Table 5), sample of 5% SiO₂ 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% SiO₂, melting time of 30 min, coke of 5%, correspondingly metallization rate was 87.30%, metal recovery rate was 96.45%.

| Sample       | Maximum content (%) | Expansion amount (mm) |
|--------------|---------------------|-----------------------|
| Original Slag| 40                  | 3.00                  |
| 1% SiO₂      | 30                  | ×                     |
| 5% SiO₂      | 80                  | 3.00                  |
| 10% SiO₂     | 80                  | 1.00                  |
| 20% SiO₂     | 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.

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