Reactivity of Carbon Reductants for Smelting Applications

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Carbon reductants are used in the carbothermic reduction of quartz to produce metallurgical grade silicon. A primary factor for determining the silica reduction process efficiency is the reactivity of the carbon reductants. A thermogravimetric analysis test was developed to determine the relative reactivity of various kinds of reductants and minimize the need for full scale furnace evaluations.

Introduction

Carbon reductants, consisting mainly of coal, petroleum coke, and wood chips, are used in the carbothermic reduction of quartz to produce metallurgical grade silicon. A primary factor for determining the silica reduction process efficiency is the reactivity of the carbon reductants. A test was developed to determine the relative reactivity of various kinds of reductants and minimize the need for full scale furnace evaluations.

Process Reactions

The reductants and quartz are combined in an electric arc furnace to produce silicon metal by the overall reaction:

$$SiO_2 + 2C = Si + 2CO \qquad (1)$$

Carbon reductants do not react directly with quartz as indicated in equation (1), but react with gaseous SiO to form an intermediate, SiC, which reacts with SiO_2 and/or SiO to produce silicon metal.

The true test of a reductant's reactivity would be it's reaction with SiO:

$$SiO_{(g)} + 2C_{(s)} = SiC_{(s)} + CO_{(g)} \qquad (2)$$

Producing SiO gas to react with the carbon reductant requires high temperature and elaborate apparatus.[1,2] A carbon dioxide reactivity test could be performed at much lower temperatures easily, and is expected to allow the prediction of SiO reactivity. Development of this CO_2 test was undertaken.

Theoretical Discussions

Reaction Descriptions

The carbon/carbon dioxide reaction examined in this test was a heterogeneous reaction[3] of the type:

$$\text{solid} + \text{gas} \rightarrow \text{gas}. \qquad (3)$$

The surface or intrinsic reaction was of the most interest. The pore diffusion effect on the reaction had to be minimized to allow determination of the intrinsic reactivity of the reductant. The rate of coal oxidation had been found to increase with an increase in surface area for large particles (>1mm), the rate became proportional to the sample weight for particle sizes <0.1mm.[4]

Upon reaction of CO_2 with a carbon sample of the particle size greater than 1.0 mm, the oxidation of carbon on the surface and within the particle increases its pore volume and surface area thus resulting in a relatively constant reaction rate. When gaseous SiO reacts with carbon, a solid reaction product of silicon carbide is formed which covers the reductant particle. The reaction rate will slow as it becomes dependent on the diffusion of the gases through the product layers. These reaction mechanisms produce different ranking of reduction materials with the exception of extremely reactive reductants which react equally well with either gas.[6] In order to equalize these effects due to oversized particles, the reductant particle size used in the test was the size fraction of 200 x 325 M (0.07 - .04mm).

It was hoped that CO_2 and SiO reactivities would correlate better throughout the entire range of reductant reactivity by improving sample preparation and test procedures.

Reactivity Calculations

Modifications of an experimental procedure and equation developed by Mannesmann Demag Hüttentechnik to determine the reactivity of carbon reductants in silicon smelting[7] lead to the present reactivity test. Reactivity (K_R) was calculated as:

$$K_R = \ln \frac{C_A}{C_E} \qquad (4)$$

C_A = Fixed carbon=Reductant-volatiles-ash.

C_E = Fixed carbon-Carbon which reacted with carbon dioxide.

Experimental Results

Three experimental configurations were used in determining the best procedure for testing reductants.

Two configurations, a vertical fluid bed reactor and a horizontal fixed bed reactor, consisted of vessels which contained the reductant samples. The vessel was placed in a furnace and heated sequentially with nitrogen, carbon dioxide, and finally air to determine volatile content, reactive carbon, and ash. Weighings took place between every change of gas to determine weight loss during every cycle.

The vertical fluid bed reactor was a faster test which gave inconsistent results. Problems with material loss and small reactivity ranges lead to the use of the horizontal reactor.

The horizontal fixed bed reactor was a slower test but highly repeatable. No major problems were encountered with this test, but only two tests per day could be completed.

Thermogravimetric analysis (TGA), the third configuration used to predict reactivity, was based on instantaneous weight loss versus time information during each cycle. TGA used a CO_2 reaction temperature of 1070°C for petroleum cokes as in the horizontal reactor. Since TGA indicated when the sample had completed its reaction in the CO_2 cycle, time, t, could then be introduced as another variable in the reactivity calculation. The original K_R equation was multiplied by 60/t to incorporate this variable in the determination. The Demag test required 60 minutes in the CO_2 cycle, but if 60 minutes were not needed for complete reaction the equation could now be adjusted to the actual time required.

The different gas cycles operated at 950°C except for the CO_2 cycle with petroleum coke reductants in the horizontal fixed bed and TGA configurations. Initial reactivity results found petroleum cokes to be the least reactive carbon reductants, by an order of magnitude, as compared to coals and charcoal. Because of the low reactivity and the very compressed range between different sources of petroleum coke, a higher temperature of 1070°C was used to determine their reactivity.

Comparison to Smelting Performance

The low amount of petroleum coke added to the smelter does not make its reactivity a significant factor. All petroleum cokes performed equally well in production except for one which performed below normal in the smelter and in the reactivity test.

Only two coals have been both tested and used in the smelter. There was no direct comparison of the two in the production smelter, but direct comparisons of the coals were made on a pilot scale smelter and the coals performed just as predicted by the reactivity test results.

Conclusion

Thermogravimetric analysis is the preferred test for determining reactivity.

TGA gives information on CO_2 reaction rate versus time during the test which is not known with the other test configuations. This information is used to further define reductant reactivity.

The reactivity test should not be considered a pass/fail test, but it will help identify the risks of running a reductant in a plant trial.

References

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