

The interaction of silicon monoxide gas with carbonaceous reducing agents

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SYNOPSIS

The rate of reaction between different carbonaceous reducing agents and silicon monoxide gas was studied by the use of a technique developed in Norway by Tuset and Raaness. Argon carrier gas was used to pass a known fixed concentration of silicon monoxide gas through an 11 cm³ sample of precalcined reducing agent at 1650°C. Silicon monoxide gas was generated by the heating of a mixture of silica and silicon carbide, and the progress of the reaction was followed by monitoring the carbon monoxide in the off-gas with an infrared spectrometer.

The reactivity of silicon monoxide gas towards a number of carbonaceous reducing agents (charcoal, Iscor coke, Lurgi char, and petroleum coke) was shown to be similar to results obtained with the carbon dioxide reactivity test. The silicon monoxide reactivity test was able to indicate the extent to which fines were generated when the reducing agent was converted to silicon carbide. Of the reducing agents studied, Lurgi char appeared to be the most suitable for the production of ferrosilicon because it has a high reactivity towards silicon monoxide gas and high strength when converted to silicon carbide.

So that industry could be given some indication of the suitability of certain reducing agents for the production of ferrosilicon and silicon metal, a reactivity scale similar to that of Tuset and Raaness was constructed that compares the volume of silicon monoxide gas required by a reducing agent to reach a carbon monoxide content of 10 per cent in the off-gas during the conversion of the reducing agent to silicon carbide. This scale assists in the selection of those reducing agents that require less silicon monoxide gas for conversion to silicon carbide, and that give savings in material and power costs because less silicon monoxide gas need be generated in the furnace.

SAMEVATTING

Die reaksietempo tussen verskillende koolstofreduseermiddels en silikonmonoksiedgas is bestudeer met gebruik van 'n tegniek wat Tuset en Raaness in Noorweë ontwikkel het. Argondragas is gebruik om 'n bekende vaste konsentrasie silikonmonoksiedgas by 1650°C deur 'n monster van 11 cm³ van 'n vooraf gekalsineerde reduseermiddel te stuur. Silikonmonoksiedgas is ontwikkel deur 'n mengsel van silika en silikonkarbid te verhit en die vordering van die reaksie is gevolg deur die koolstofmonoksied in die losgas met 'n infrarooi spektrometer te monitor.

Daar is getoon dat die reaktiwiteit van silikonmonoksiedgas teenoor 'n aantal koolstofreduseermiddels (houtskool, Yskor-kooks, Lurgi-sintel en petroleumkooks) ooreenstem met die resultate wat met die koolstofdiksiedreaktiwiteitstoets verkry is. Die silikonmonoksiedreaktiwiteitstoets kon ook aandui in watter mate fynstof afgegee is by die omsetting van die reduseermiddel in silikonmonoksied. Van die reduseermiddels wat bestudeer is, is Lurgi-sintel blykbaar die geskikste vir die produksie van ferrosilikon vanweë sy hoë reaktiwiteit teenoor silikonmonoksiedgas en sy hoë sterkte by die omsetting daarvan in silikonkarbid.

Ten einde die bedryf 'n aanduiding te gee van die geskiktheid van sekere reduseermiddels vir die produksie van ferrosilikon en silikonmetaal is daar 'n reaktiwiteitskaal soortgelyk aan dié van Tuset en Raaness opgestel wat die volume silikonmonoksiedgas wat 'n reduseermiddel nodig het om 'n koolstofmonoksiedinhoud van 10 persent in die losgas tydens die omsetting van die reduseermiddel in silikonkarbid te bereik, vergelyk. Hierdie skaal help met die keuse van reduseermiddels wat minder silikonmonoksiedgas vir die omsetting in silikonkarbid nodig het en so tot 'n besparing van materiaal en kragkoste lei omdat daar minder silikonmonoksiedgas in die oond ontwikkel hoef te word.

Introduction

Silicon metal and various grades of ferrosilicon are usually produced in submerged-arc furnaces by the reduction of high-purity quartz with a suitable carbonaceous reducing agent. The selection and preparation of suitable raw materials, and operational problems in the production of silicon and its alloys with iron, are discussed elsewhere^{1, 2}.

The main aim of the investigation reported here was to develop a suitable test that would provide a scale of the reactivity towards silicon monoxide of the carbonaceous reducing agents that are being used, or could be used, by South African producers of silicon metal and ferrosilicon. The development of such a scale of reactivity should help in the selection of the most suitable reducing agents to minimize the loss of silicon, in the form of silicon monoxide gas, from the furnace. These silicon losses may be as high as 20 per cent of the mass of silicon charged to the furnace. It was also hoped that this investigation would eventually provide more information on the influence of the reaction between silicon monoxide and

carbon on the overall reactions in the furnace.

Paull^{2, 3} has given a detailed description of the thermodynamics and phase equilibria in the Si-O-C system, and of the reactions in ferrosilicon and silicon submerged-arc furnaces, together with a discussion of the role of silicon monoxide.

Limitations of Conventional Reactivity Tests

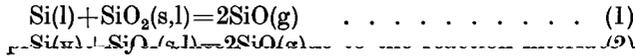
The conventional method for the determination of the reactivity of carbonaceous reducing agents involves the measurement of the rate at which the reducing agent burns to form gaseous products under standard conditions in a stream of oxidizing gas such as carbon dioxide, air, or steam⁴. In such tests, the reducing agent is burnt with the active surface of the reducing agent remaining open. Particles (ash oxides) are extracted, and the pore structure of the reducing agent remains accessible to the oxidizing gases^{5, 6}.

The results from conventional tests for the determination of reactivity are applied mainly to the selection of reducing agents for blast-furnace operation and for other carbon-metal oxide reactions in which the metal oxide is reduced by carbon monoxide. The carbon dioxide produced from this reduction step reacts with the carbon

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to regenerate carbon monoxide⁷, and hence the reactivity of the reducing agent towards carbon dioxide is important.

The sequence of reactions for the reduction of metallic oxides with carbon contrasts with the sequence of reactions in the production of silicon and its alloys. In the production of silicon, silica (quartz) is not reduced by carbon monoxide. However, silica is gasified by a series of reactions to the lower oxide form silicon monoxide:



Therefore, when the performance of reducing agents for the production of silicon and its alloys is assessed, it would be more relevant to the process if the classification of these reducing agents were based on their reactivity towards silicon monoxide gas.

Thermogravimetric^{8, 9} and gas-analysis⁶ techniques can be used in studies of the reaction of silicon monoxide gas with carbonaceous reducing agents. In the thermogravimetric technique, the mass of the carbonaceous reducing agent is monitored continuously while silicon monoxide gas passes over the briquetted reducing agent. The gas-analysis technique involves the continuous determination of the content of carbon monoxide in the gas leaving a reaction chamber in which silicon monoxide gas has passed through a packed bed containing a known volume of reducing agent.

This type of study provides a direct comparison between the performance of different reducing agents when they are reacted with silicon monoxide gas, the classification technique reported by Tuset and Raaness⁶ being based on the quantity of silicon

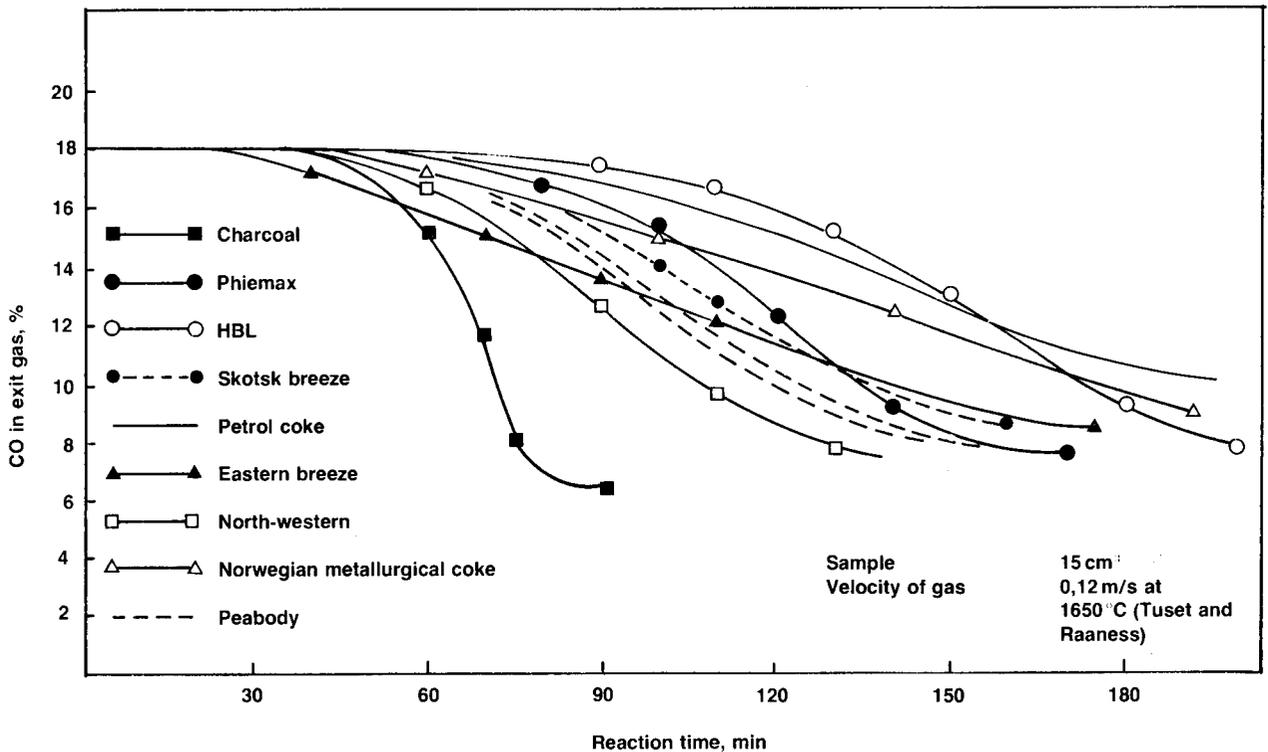


Fig. 1—Concentration of carbon monoxide in effluent gas versus time for some selected types of reduction materials

monoxide gas that passes unreacted through a bed of reducing agent before the carbon monoxide in the product gas has fallen to 10 per cent. Hence, this test compares the efficiency of each reducing agent in limiting the escape of silicon monoxide gas from the furnace.

The initial stages of this test do not distinguish between the different reducing agents. The carbon is readily accessible at the surface of the reducing agent, and the reaction between silicon monoxide gas and carbon at temperatures above 1600°C is thought to be extremely rapid⁶. Each reducing agent reacts with silicon monoxide gas to produce the equilibrium partial pressure of carbon monoxide.

When the free surface of the reducing agent is covered by a layer of silicon carbide, the reaction rate is reduced considerably and each reducing agent reacts to form silicon carbide at a different rate during this stage. This difference in the rate of reaction between silicon monoxide gas and carbon is then used to differentiate between the capacity of various reducing agents to react with silicon monoxide gas near the final stages of conversion of the reducing agent to silicon carbide.

The variation in the content of carbon monoxide in the exit gas with time shows the rate and manner in which the conversion of the carbonaceous reducing agent to silicon carbide proceeds up to 100 per cent conversion. It can be seen from the typical graph shown in Fig. 1 that the reducing agents react with silicon monoxide gas in the early stages to produce an equilibrium carbon monoxide content of 18 per cent at a total pressure of 1 atm. The carbon monoxide content decreases from the equilibrium value after approximately 40 minutes. This decrease in the content of carbon monoxide coincides with the formation of a

layer of silicon carbide round each particle in the bed of reducing agent. There is a considerable difference between the rates of reaction to 100 per cent conversion to silicon carbide after the initial period has ended. For example, charcoal has reacted fully to silicon carbide after 90 minutes, whereas the content of carbon monoxide in the effluent gas from a packed bed of petroleum coke has reached 11 per cent after 170 minutes.

The results shown in Fig. 1 were used by Tuset and Raaness⁶ to develop the reactivity scale shown in Fig. 2, which is based on the quantity of silicon monoxide gas that passes unreacted through a bed of reducing agent before the proportion of carbon monoxide in the exit gas drops to 10 per cent. This scale describes the individual efficiencies of reducing agents in limiting the escape of silicon monoxide gas from the furnace.

The most effective method for the selection of reducing agents for the production of silicon and silicon-rich alloys is a test that determines the rate of reaction of that reducing agent with silicon monoxide gas. The gas-analysis technique has the most advantages, which include larger sample and particle sizes, as well as the provision of an estimate of the efficiency of the reducing agent in reducing the loss of silicon monoxide gas from a furnace.

Experimental Method

Considerable effort was devoted to the development of an experimental technique similar to that of Tuset and Raaness⁶, and in particular to the development of the reactor. Details of the techniques used in the attainment of the temperatures in the region of 1650°C, problems with thermocouples and refractories, and the development of the reactor are given by Paull².

The reactor used for the reactivity tests was placed inside a Degussa vacuum graphite resistance furnace as shown in Fig. 3. The reactor housing was a graphite cylinder with two removable ends screwed to each end of the cylinder. The internal surfaces of the graphite reactor were lined with alumina components to protect the graphite housing from attack by silicon monoxide gas. The exit tube for the off-gas at the top of the reactor was graphite lined with alumina. A detailed diagram of the reactor is shown in Fig. 4. A Pt-6%Rh/Pt-30%Rh thermocouple housed in a recrystallized-alumina sheath was fitted through the inlet tube of the generation chamber, the tip of the thermocouple being located in the middle of this chamber.

The silicon monoxide gas and carbon monoxide were generated from pellets containing 2 moles of silica and 1.05 moles of silicon carbide. The charges of silicon carbide and silica to the generation chamber, and of the reducing agent to the reaction chamber, were first weighed and placed in their respective chambers. The reactor was then assembled and located within the heating element of the Degussa furnace.

The furnace and the reactor were sealed and evacuated, and were then back-filled three times with spectrographic argon. The furnace was heated to 1550°C over approximately 1½ hours, with the pressure buildup being released through the off-take tube from the reactor. The

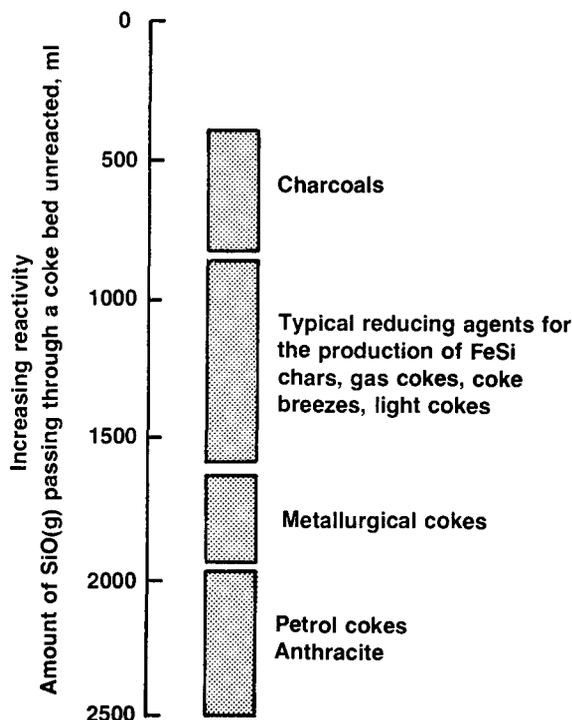


Fig. 2—The silicon monoxide reactivity scale based on the curves given in Fig. 1 (after Tuset and Raaness⁶)

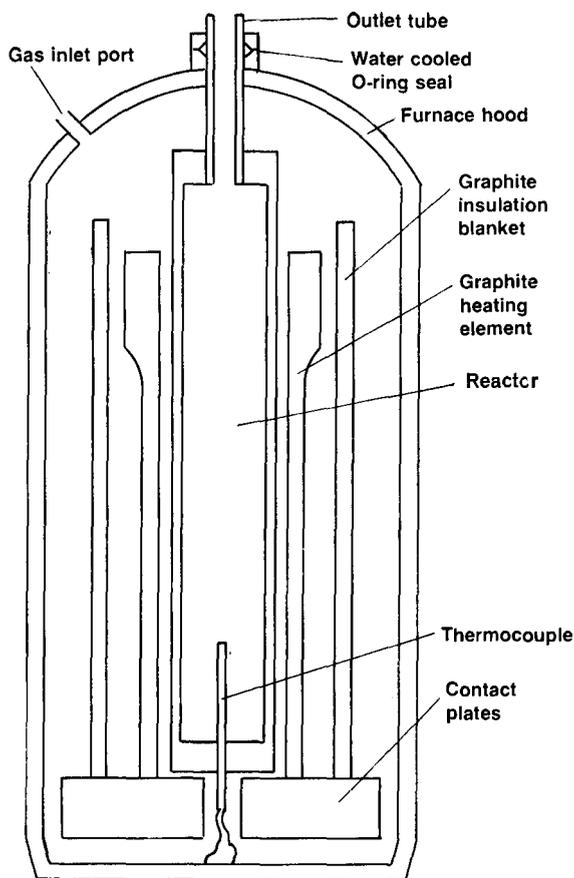


Fig. 3—The location of the reactor inside the Degussa furnace

furnace temperature was kept constant at 1550°C for 45 minutes to ensure the reduction of ash oxides of the reducing agent. A low, controlled flow of pure argon was passed through the reactor during this period. The temperature was then raised to 1650°C and the argon flowrate was adjusted to 23,7 l/h, which corresponds to a linear velocity of 0,12 m/s through the packed bed of reducing agent.

The gas leaving the reactor was filtered and continuously analysed for carbon monoxide by a Wilks infrared spectrometer. When the carbon monoxide in the off-gas fell below 10 per cent, the flow of argon was stopped and the furnace was cooled before the reactor was dismantled and the constituents of the generation and reducing-agent chambers were weighed.

Results and Discussion

Reactivity tests were carried out on 11 cm³ samples of four reducing agents: charcoal, petroleum coke, Iscor coke, and Lurgi char with particle sizes from 3,36 to 4,76 mm. The Lurgi char was produced at AECI Ltd by a low-temperature carbonization process, and the Iscor coke was undersized metallurgical coke from the South African Iron & Steel Industrial Corporation Ltd. These two reducing agents were obtained from Palmiet Chrome Corporation (Pty) Ltd, and a detailed description of their properties is given elsewhere¹⁰. The reducing agents were selected so that the extremes of the rates of reaction would fall between various forms of carbon and

silicon monoxide gas. Charcoal was chosen as the most reactive, Iscor coke and petroleum coke as the least reactive, and Lurgi char as having intermediate reactivity towards silicon monoxide gas.

Table I gives the proximate analyses of the reducing agents, and Table II shows the reactivities of these reducing agents towards carbon dioxide.

Details of the reactivity tests with silicon monoxide gas are given in Table III, and Fig. 5 shows the variation with time in the carbon monoxide content of the exit gas for these tests. The marked fluctuations in the plots of carbon monoxide content in the off-gas versus time in Fig. 5, particularly at the beginning of each test, were

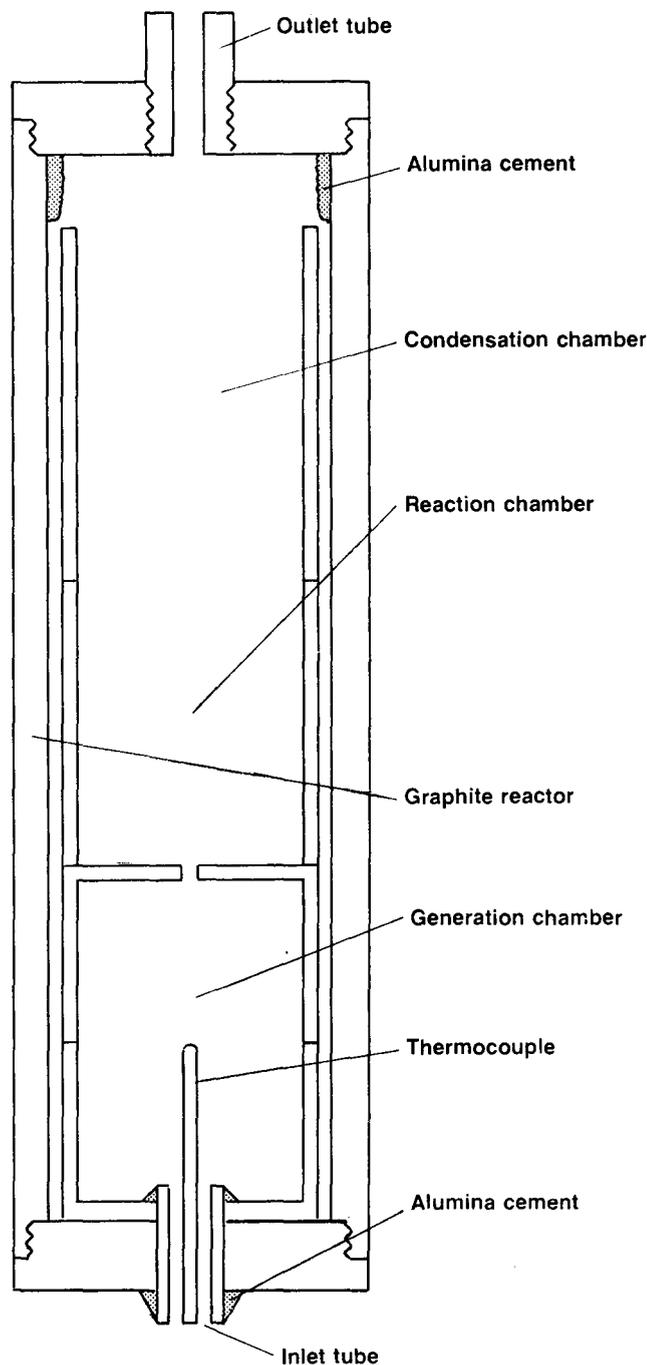


Fig. 4—Details of the reactor used in the reactivity tests

TABLE I
PROXIMATE ANALYSES OF REDUCING AGENTS

Type	Proximate analysis, %			
	Moisture	Ash	Volatiles	Fixed carbon
Charcoal*	8,62	1,36	21,08	68,94
Petroleum coke*	2,46	0,43	10,16	86,95
Iscor coke†	0,60	17,00	0,90	81,50
Lurgi char†	4,10	23,40	7,00	65,50

*Analysis conducted by the National Institute for Metallurgy, Randburg.

†Analysis conducted by the Fuel Research Institute, Pretoria.

TABLE II
REACTIVITIES* OF REDUCING AGENTS TOWARDS CARBON DIOXIDE

	Reactivity constant, k_m ($\text{cm}^3/\text{g} \cdot \text{s}$)		
	Reaction time of 15 min	Reaction time of 30 min	Reaction time of 60 min
Charcoal	13,46	15,34	17,76
Petroleum coke	0,58	0,35	0,32
Iscor coke	0,18	0,19	0,19
Lurgi char	2,98	2,39	1,84

*Tests conducted by the Fuel Research Institute, Pretoria.

caused by difficulty in the control and maintenance of constant temperature during the tests. This difficulty arose because there was no temperature controller on the Degussa furnace, and manual compensation² had to be used in an attempt to maintain the temperature at 1650°C. Since the partial pressure of silicon monoxide is very sensitive to temperature^{2, 3} in the region around 1650°C, temperature control is very important.

The differences between the initial tests and the

additional tests performed on charcoal and Iscor coke as a check on the reproducibility of the test are thought to be a result of the temperature fluctuations during the test. These fluctuations as shown in the curves of Fig. 5 made the construction of a reactivity scale similar to that of Tuset and Raaness⁶ very difficult. However, a reactivity scale has been proposed that will permit the comparison of reducing agents. This scale is based on the volume of silicon monoxide gas that has to be generated before the level of carbon monoxide in the off-gas has fallen to 10 per cent. Table III gives the results for these calculations, and the proposed scale is shown in Fig. 6. This form of reactivity scale does not indicate the expected losses of silicon monoxide gas for reactions with different reducing agents at a constant degree of conversion to silicon carbide, but it does give the volume of silicon monoxide gas required to produce an off-gas containing 10 per cent carbon monoxide for a sample size of 11 cm^3 .

This proposed scale of reactivity has a correlation with the reactivity scale of Tuset and Raaness⁶ between the reactivities of the reducing agents towards silicon monoxide gas. Both scales indicate that the most reactive reducing agent towards silicon monoxide gas is charcoal, followed by char (Lurgi char), metallurgical coke (Iscor coke), and petroleum coke. A similar order exists for the reactivity of the reducing agents towards carbon dioxide as shown in Table II, with the exception of Iscor coke.

Tuset and Raaness⁶ found that, at the extremities of either of the reactivity scales, the reactivities of the reducing agents towards either silicon monoxide gas or carbon dioxide are similar. However, they found discrepancies between the results given by the tests of reactivity towards silicon monoxide gas and carbon dioxide for the reducing agents of medium reactivity, which constitute the bulk of the reducing agents used in the production of ferrosilicon.

One important feature of the reactivity test for silicon monoxide gas is that it reveals any abnormal behaviour of the reducing agent during the conversion to silicon carbide.

TABLE III
REACTIVITY OF SILICON MONOXIDE GAS TOWARDS SOUTH AFRICAN CARBONACEOUS REDUCING AGENTS

Run no.	Reducing agent	Consumption of generation mix g	Duration of test min	Mass charged g	Mass after test g	Percentage of material less than 3,36 mm after test %	Volume of SiO (g) generated for a 10% CO level in off-gas ml
50	Charcoal	6,36	55	2,54	2,85	55,40	1842
51	Iscor coke	6,95	65	6,21	6,76	5,02	2510
52	Petroleum coke	7,36	70	5,73	6,30	29,20	2867
54	Iscor coke	7,90	80	6,20	6,97	4,30	2900
55	Charcoal	5,87	50	2,50	2,83	57,7	1971
56	Lurgi char	6,54	55	7,29	6,38	12,5	2893
57	Iscor coke	7,10	65	6,22	6,89	7,75	2565

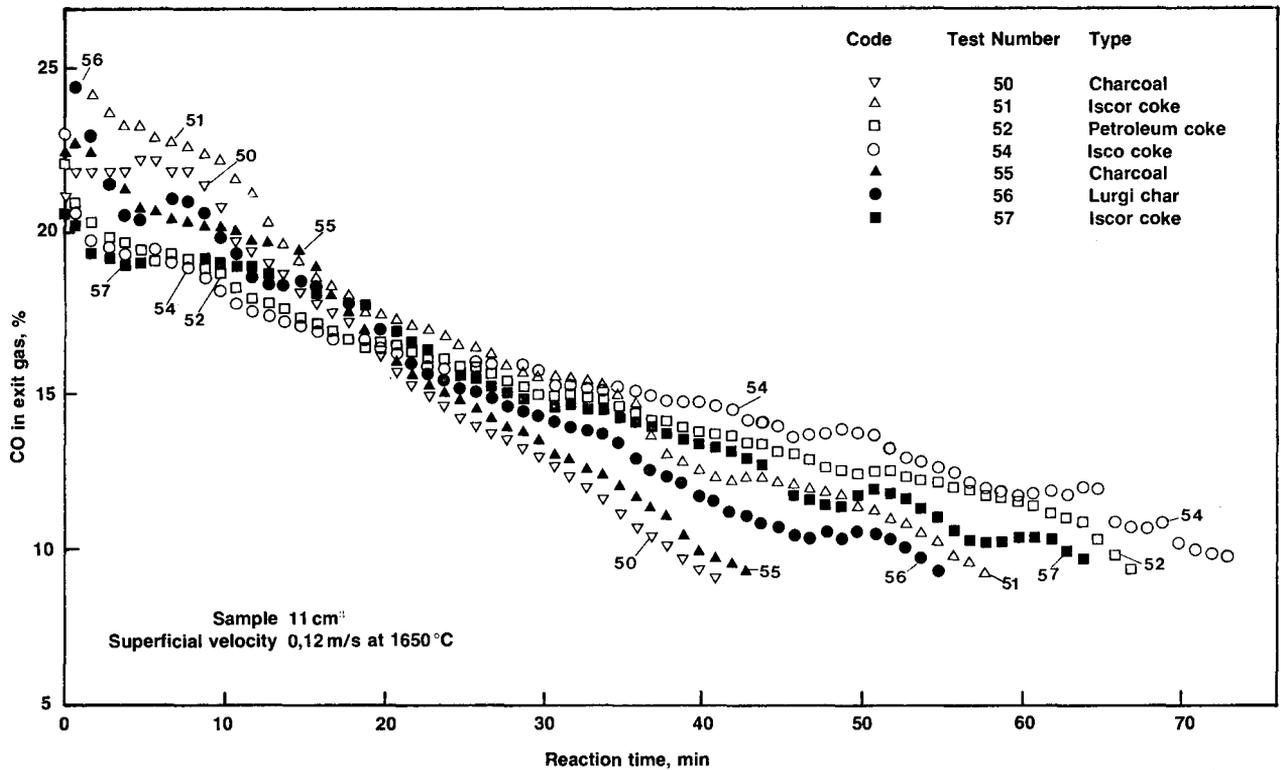


Fig. 5—Concentration of carbon monoxide (measured by infrared spectrometer) versus time for the reaction between selected reducing agents and silicon monoxide gas

Table 3 indicates the percentage of material that had a particle size smaller than 3,36 mm after each reducing agent had been reacted with silicon monoxide gas. It shows that charcoal could be unsuitable as a reducing agent for the production of silicon metal and ferrosilicon because of the relatively high proportion of fines generated (56 per cent being finer than 3,36 mm) and its complete loss of strength on conversion to silicon carbide. The generation of fines and loss of strength would have an adverse effect on the operation of the furnaces. Petroleum coke also generated a considerable quantity of fine material, 29 per cent being finer than 3,36 mm. Tuset and Raaness⁶ also reported that certain types of charcoals and form cokes lost their physical strength completely, and some types of petroleum cokes disintegrated, on being converted to silicon carbide.

Summary

- (1) A reactivity apparatus was tested to provide industry with additional information on the selection of carbonaceous reducing agents for the production of ferrosilicon and silicon metal. Further development of this apparatus is necessary.
- (2) A reactivity scale was proposed that is based on the amount of silicon monoxide gas required to give a 10 per cent content of carbon monoxide in the off-gas from an 11 cm³ sample of reducing agent.
- (3) The reactivities of the reducing agents towards silicon monoxide gas and carbon dioxide were shown to be similar at the extremes of the carbon dioxide reactivity scale. However, the carbon dioxide reactivity test did not indicate that charcoal

was an unsatisfactory choice for the manufacture of silicon alloys. Even though charcoal displayed the highest reactivity towards silicon monoxide gas and carbon dioxides, it could be unsuitable for the manufacture of silicon alloys because of its loss of strength and disintegration, resulting in the

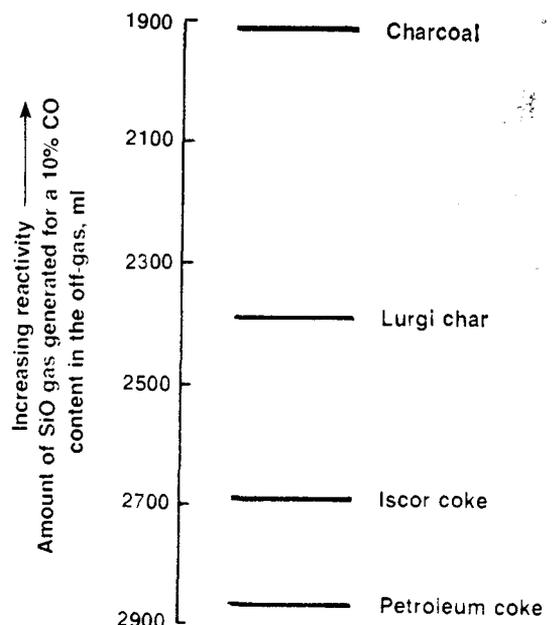


Fig. 6—The silicon monoxide reactivity scale based on the consumption of generation mixture that will give a 10 per cent carbon monoxide content in the off-gas

generation of fines on being converted to silicon carbide.

- (4) This test predicts that Lurgi char, among those studied, is the most suitable reducing agent for the production of ferrosilicon. Lurgi char has a high reactivity towards silicon monoxide gas and high strength on being converted to silicon carbide, but its high content of ash could be a disadvantage.

Acknowledgements

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References

1. FELDMANN, K. A., and FRANK, K.-D. Ferrosilicon. *METALLURGIE DER FERROLEGIERUNGEN*. Volkert, G., and Frank, K. D. (eds.) Berlin, Springer, 1972. pp. 529-569. (NIM Translation TR 452).
2. PAULL, J. M. The interaction of silicon monoxide with carbonaceous reducing agents. M.Sc. (Eng.) thesis, University of the Witwatersrand, Jan. 1978. 116 pp.
3. PAULL, J. M. The interaction of silicon monoxide gas with carbonaceous reducing agents. Randburg, National Institute for Metallurgy, Report no. 1961. 1978.
4. BLAYDEN, H. E. Reactivity of cokes and chars, a review. *RESIDENTIAL CONFERENCE ON SCIENCE IN THE USE OF COAL, PROCEEDINGS*. Sheffield Institute of Fuel, 1958. pp. 1-6.
5. TURKDOGAN, E. T., *et al.* Pore characteristics of carbons. *Carbon*, vol. 8. 1970. pp. 545-565.
6. TUSET, J. K., and RAANES, O. Reactivity of reduction materials for the production of silicon, silicon-rich ferroalloys and silicon carbide. *34th ELECTRIC FURNACE CONFERENCE, MISSOURI*. Dec. 1976. pp. 51-62.
7. RAO, Y. K. The kinetics of reduction of hematite by carbon. *Metall. Trans.*, vol. 2, no. 5. May 1971. pp. 1439-1447.
8. KOZHEVNIKOV, G. N., *et al.* Reactions between silicon monoxide and carbon. *Russian Metall.*, no. 4. 1972. pp. 51-54.
9. KOZHEVNIKOV, G. N., *et al.* Influence of oxides in the ash on the reaction between carbon and silicon monoxide. *Russian Metall.*, no. 5. 1973. pp. 24-27.
10. WILLAND, K., *et al.* An examination of the suitability of various reducing agents for the production of ferrochromium. Johannesburg, National Institute for Metallurgy, Report No. 1708. 27th Feb., 1975.

World mining congress

The Tenth World Mining Congress is to be held in Istanbul from 17th to 21st September, 1979. The main theme will be 'Mining and Mineral Raw Materials in the Service of Mankind'. The papers will be grouped into four general categories:

- (1) The utilisation of low-calorific solid resources (such as lignites, low-calorific hard coals, bituminous shales, tar-sands, asphaltites) for energy purposes.
- (2) Problems in the underground mining and utilization of small ore deposits — chromite, boron, manganese, lead-zinc, etc.
- (3) Progress in the mining of deposits under difficult conditions (offshore deposits, deep-sea deposits, deposits under high pressure, etc.).
- (4) Feasibility and profitability studies on mineral

deposits.

Round-table discussions will be held on the subjects 'New Outlooks on Mining Technology' and 'Mining Problems of the Developing Countries'.

The languages to be used in the Congress will be English, German, French, Russian, Spanish, and Turkish, and there will be simultaneous translation into all of these.

An International Mining Exhibition will be held, in conjunction with the congress, from 15th to 22nd September, 1979. Exhibits will cover all types of mining operations, with the emphasis on exploration and resource exploitation and including both deep and surface mining (open-cast mining).