SOLID-STATE REDUCTION OF COMPOSITE CHROMITE PELLETS IN AN EXTERNALLY HEATED MOVING-BED SHAFT FURNACE

by

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ABSTRACT

The advantages of the pre-heating and/or pre-reduction of chromite prior to smelting in electric-arc furnaces have long been recognized. The gaseous reduction of chromite by carbon monoxide and hydrogen is of no commercial importance, since low oxygen potentials must be maintained within the charge, even at temperatures as high as 1400°C, by the use of a composite feed, and because of problems associated with the transmission of large amounts of energy by the gas to the charge in the narrow temperature range of 1200 to 1400°C.

In recent years, Mintek has been active in the development of alternative routes for the pre-reduction of chromite. As part of this work, the authors have been involved in the development of a computer model for simulation of the pre-reduction of composite chromite pellets in an externally heated shaft furnace, and the verification of the predictions of that model by the use of a bench-scale shaft furnace.

This paper briefly describes the computer model and the results of the verification tests in an effort to assess the merits of further work towards the development of the process on an industrial scale.

1. INTRODUCTION

Electrical smelting of chromite is currently carried out in submerged-arc electric and transferred plasma-arc furnaces. The specific electrical energy consumption in these processes is about 4000 kW.h per ton of alloy produced.

At a few production plants, the feed is pre-heated and/or pre-reduced in rotary kilns prior to being charged into the electric furnace, with the result that considerable savings in specific electrical energy consumption are achieved.

In recent years great efforts have also been put into the development of potentially cost-effective, non-electrical routes for the production of ferrochromium, in which electrical energy is replaced by other energy sources.

Non-electrical processes essentially involve the use of coal and oxygen as the heat source in, for example, a converter-type vessel. Since the utilization of the energy from coal is low, and most of that energy leaves the vessel in the form of hot off-gas that is rich in hydrogen and carbon monoxide, these processes may be economically viable only if the energies of the off-gas can be utilized to the fullest extent.

The off-gas may be post-combusted in the converter in order to transfer some of its chemical energy back to the melt. Experiments in that regard have been carried out at Klöchner-CRA[1], and about 60 per cent of the energy released by about 20 to 30 per cent post-combustion of the off-gas in the vessel is stated to have been transferred to the melt. If the degree of post-combustion of the hot off-gas is not high (i.e. if the sum of the carbon dioxide and water vapour in the gas totals less than 5 per cent[2]), the gas may be used as a suitable reductant for the solid-state reduction of iron oxides in a shaft furnace. The COREX process of Iscor (Pretoria Works) is the first commercial process in the world that makes use of this principle.

The off-gas can also be used for other purposes, e.g. in an integrated plant it can be used as a fuel in the induration furnaces, reheating furnaces, steam boilers, etc.

Previous work conducted in a thermogravimetric analyzer (TGA) and in a vacuum resistance furnace showed that, although the carbonaceous reduction of chromite is indirect, i.e. the reducing agent is actually carbon monoxide gas, nevertheless the maintainence of the low oxygen potential - of the order of 10^{-12} atmospheres (at temperatures as high as 1400°C) - in the gaseous atmosphere that is needed for the reduction reaction to progress, remains a problem. Therefore the presence of finely divided carbon in close proximity to the chromite particles will be necessary so that the reduction potential of the gaseous phase can be restored quickly.

The transmission of large quantities of energy, in the order of 3 to 3,5 kW.h per kilogram of ferrochromium alloy, in the temperature range of the solid-state reduction reaction (1200 to 1400°C) is another problem encountered during reduction of chromite. A gas flowrate of some 20 m^3 (at standard temperature and pressure) per kilogram of ferrochromium is required[3].

These two problems that are associated with the gaseous reduction of chromite preclude the direct use of the off-gas from a down-stream smelter for the pre-reduction of chromite. However, composite chromite pellets can be pre-reduced in a cell of narrow rectangular cross-section (shaft) that is externally heated by the full combustion of the off-gas from a down-stream smelter.

A number of such reduction cells may be accommodated in a battery-type furnace for use on an industrial scale. The advantages of this type of furnace over the rotary kilns that are currently used for the pre-reduction of composite chromite pellets are as follows.

(a) There is no danger of contamination of the charge with deleterious substances (such as sulphur and phosphorus) in the fuel, nor of the contamination of the reduction atmosphere with the gaseous products of combustion.

(b) The reduction atmosphere can be controlled by the injection of various gases, such as nitrogen, methane, etc., into the reduction chamber.

(c) The fuel is essentially completely combusted, and after-combustion is therefore not necessary.

(d) Although the efficiency of heat transfer from the hot combustion gases to the charge is expected to be about half of that in a rotary kiln (owing to the muffle effect), this deficiency can be overcome, to a great extent, by the installation of a recuperator (or regenerator) on the exhaust for pre-heating the combustion air.

(e) The modular form of the furnace makes it flexible with regard to production rate, and its vertical stationary feature appears to offer a cost-effective process with regard to capital, operating, and maintenance costs.

A brief description is presented of a computer model that was developed for the simulation of pre-heating and pre-reduction of composite chromite pellets in an externally heated shaft, and of a bench-scale shaft furnace that was developed in order to be used for experimental verification of the simulation results. It will be shown that good agreement was found between the predicted and the experimental results.

2. THE COMPUTER MODEL

The impracticality of the gaseous reduction of chromite led to the search for other methods for the pre-reduction of chromite by the use of a hot off-gas, rich in carbon monoxide and hydrogen from a coal-oxygen smelter.

An externally heated shaft appeared to be a suitable option, despite concerns about its thermal efficiency. Therefore it was decided to develop first a computer simulation model of the proposed process, to carry out some test runs to define the optimum operational conditions, and then to verify the results of these runs by experimentation in an attempt to establish the basis for the future development of the process.

The 'EXHEAT' interactive computer program that was developed simulates the rise in the temperature and the degree of reduction as a function of time, within the charge of a moving-bed shaft furnace.

The fractional degree of reduction of chromite, R, at any process time, θ, is defined as:

$$R = \frac{\text{Mass of oxygen removed in the time period } \theta \text{ from start}}{\text{Mass of removable oxygen considered in the charge at start}}.$$

The shaft is assumed to have a narrow rectangular cross-section, and to be heated externally from the two wider sides. A transient unidirectional mode of heat conduction through a thin porous slab (the charge) at any temperature zone from the top to the bottom of the furnace may also be assumed to prevail.

The general equation for transient heat conduction in an isotropic body, i.e.

$$k_x = k_y = k_z = k,$$

with a heat source (or sink) of a uniform heat flux per unit volume is as follows.

$$\rho C_p \frac{\delta t}{\delta \theta} = k \nabla^2 t + \dot{q} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where ρ is the density of the body,

C_p is the heat capacity of the body,

k is the thermal conductivity of the body,

δt is the temperature increment,

$\delta \theta$ is the time increment,

$$\nabla^2 t = \frac{\delta^2 t}{\delta x^2} + \frac{\delta^2 t}{\delta y^2} + \frac{\delta^2 t}{\delta z^2}, \text{ and}$$

$\dot{q}$ is the heat flux per unit volume.

Continuous analytical solutions of some very simplified cases of equation (1) are often complex, and therefore numerical step-wise solutions, essentially based on the Dusinberre[4] generalization of the increment method, are often preferred.

In the program, discrete finite slices of equal thickness Δx, which together comprise the thickness x of a large thin slab with a uniform cross-sectional area, are employed (Figure 1).

Reduction is assumed to start and to progress uniformly in a slice once its face temperature reaches or exceeds 1200°C. The general equation for transient heat conduction is approximated and solved for the period of residence time of the charge in a particular hot zone by the use of a numerical method.

Since the rate of reduction for a specific charge is not only a function of temperature, but also a function of the degree of reduction, it is assumed that a charge at a certain degree of reduction, undergoing a rise in temperature, will continue to reduce at a rate equal to that of a similarly reduced charge at the higher temperature, up to the limit of the degree of reduction at that temperature.

The sensitivity of the reduction process to a number of variables was examined by simulation test runs of the 'EXHEAT' program. Two of these runs are described in the following sections.

2.1. Effect of Changes in the Height of the Furnace

Although an increase in the height of the pre-heating zones enhanced the thermal efficiency of the shaft, it did not cause an increase in the final degree of reduction of the charge. It was found that higher final degrees of reduction can be achieved in a shorter period of time if the length of the highest temperature zone is extended. This can be done by the installation of additional burners along the shaft.

2.2. Effect of Changes in the Width of the Furnace

Test runs showed that, for similar residence times of the charge in the furnace, higher final degrees of reduction can be achieved in narrower furnaces. This means that an increase in the width of the shaft modifies the furnace from a pre-reducer to a pre-heating reactor by increasing the ratio of the rate of energy consumed in heating to that used for the pre-reduction of the charge.

3. THE BENCH-SCALE SHAFT FURNACE

A schematic diagram of the bench-scale shaft furnace and its accessories is shown in Figure 2. The furnace is made of two halves, each consisting of a combustion chamber covered with a thin hot panel.

The furnace was assembled as follows. The two parts were installed parallel and opposite to each other on a steel structure. The distance between the two parallel hot panels was chosen as 120 mm in early experiments, but was changed to 160 mm in later experiments (owing to the softening of the hot panels). The two halves of the furnace were connected together by a number of long bolts, and the gaps in the sides were filled with refractory bricks. The dimensions of the reduction chamber thus formed were 250 by 120 by 960 mm.

The pedestal was made from castable alumina cement. Four B-type thermocouples (nos. 1, 2, 3 and 4) were installed on the pedestal at distances of 0, 20, 40 and 60 mm respectively from the left-hand wall of the reduction chamber. The pedestal was used to support the batches of feed material. The rise in the temperature within the charge was measured by means of these thermocouples.

Eight B-type thermocouples were installed in the hot panel on the left-hand wall of the furnace for measurement of the wall temperature along the height of the furnace.

The temperature of the flue gas was also measured by means of B-type thermocouples installed in each exhaust, close to the combustion chamber.

A stoichiometric mixture of air and liquid petroleum gas (LPG) was used for heating while industrial nitrogen, at a flowrate of 10 to 15 ℓ/min, was used to maintain an inert atmosphere in the reduction chamber.

A gas-tight vibratory feeder was also used for the charging of batches of about 11 kg of composite pellets into the furnace. The top-gas from the reduction chamber was flared.

3.1. Experimental Details

Commissioning of the facility was completed in September 1988, after which a number of blank tests were conducted. The blank tests were carried out by the use of graphite pellets in alumina crucibles, which were placed on the pedestal. No major problems were encountered in more than 150 hours of hot operation of the furnace.

In the reduction tests, batches of 11 kg (about 9,6 litres) of composite chromite pellets (5 to 15 mm in diameter) made from coal and LG-6 chromite fines (75 per cent passing 75 μm) were charged to the furnace after the wall temperature inside the reduction chamber, indicated by the thermocouple no. 1, had reached the desired value of 1200 to 1300°C. The readings of all the thermocouples were recorded every 5 or 15 minutes by the operator. The temperature of the shell was measured by means of a mercury thermometer after thermal stability had been reached. The heat loss was calculated from the maximum temperature of the shell, using an average coefficient of convective heat transfer of 10 $W/m^2.C^0$ for the furnace area (about 5 m^2). The calculated values of the heat loss were from 7,5 to 8,5 kW, which agree with estimates made from the overall energy balance.

3.2. Results of the Verification Tests

Figures 3 to 6 show the experimentally measured rise in the temperature within the charge of the furnace during four reduction tests, compared with the profiles predicted by the 'EXHEAT' model. Note that an appropriate step-wise curve is fitted to the readings of thermocouple no. 1 thus simulating a batch-type process with a model that is essentially developed for the simulation of a continuous process. The very limited data available on the effective thermal conductivity of a packed bed of composite chromite pellets[5], together with some extrapolations from these data, were used in the earlier test runs. However, more realistic values of the effective thermal conductivity of the bed, which are very close to the values given in the literature[4] for thermal conductivity of chromite, were used in the later runs of the program, which resulted in a good agreement between the results predicted by the program and those obtained by experimental work.

The calculated flowrates of LPG and air were found to be in excellent agreement with the measured values. This demonstrates the reliability and accuracy of the model in that regard.

Samples for analysis were taken from locations on the top of the thermocouples on the pedestal once the charge had cooled to ambient temperature. The samples from each run were ground, and then leached in 500 ml of diluted hydrochloric acid (made up from 250 ml of 37 per cent hydrochloric acid diluted with 250 ml of distilled water) at about 100°C for about 12 hours. The liquors and residues were analysed for Cr^0, Cr^{3+}, Fe^0 and Fe^{2+}. The analytical results are shown in Table 1.

The degree of reduction of the samples was calculated from these results by the use of a curve that was developed, which relates the degree of reduction to the degree of metallization of a sample. The degree of metallization is defined as

$$\frac{Cr^0 + Fe^0}{Cr^0+Cr^{3+}+Fe^0+Fe^{2+}+Fe^{3+}} \times 100, \text{ \% by mass}$$

Table 2 compares the overall degrees of reduction of the charge predicted by the program with the values calculated from the assay results. Although the predicted values for runs no. 1 and 4 are 20 to 30 per cent lower than the values from the analytical results, the data from runs no. 2 and 5 are in excellent agreement.

The reason for the discrepancy between the results in runs no.

1 and 4 may be attributed to the shorter residence time (4 hours) of the charge in the furnace in those runs, and hence the more pronounced effect of reduction at temperatures below 1200°C, which is not considered in the program.

4. SUMMARY AND CONCLUSION

The Computer Model

The EXHEAT interactive program successfully simulated the reduction of composite chromite pellets at various wall temperatures and different charge-residence times in an externally heated shaft furnace. The data from the program were in good agreement with those gained experimentally, which shows that the assumptions underlying the model are justifiable.

It is to be appreciated that experimentally determined values of the effective thermal conductivity (ETC) of a packed bed of composite (carbon plus oxide) material at temperatures above 500 to 600°C may not be accurate. If the experiments are conducted in an inert atmosphere, some reduction of the charge may take place, and if an oxidizing atmosphere is employed, some oxidation of the charge will take place. In both these cases, the temperature readings will be erroneous, and therefore the caluclated value of the ETC will be in error. It is worth mentioning that the model and the shaft together may be used for the accurate estimation of the ETC of a packed bed of composite materials, provided that other physical parameters of the charge, such as bulk density and heat capacity at various temperatures, as well as data on its reduction kinetics, are available.

The Bench-scale Shaft Furnace

The technological feasibility of the process was demonstrated by the bench-scale shaft furnace that was developed. The operation of the shaft was proved to be safe, simple and easily controllable during hot operation for more than 150 hours.

Further improvements to the apparatus, such as modification of the charge-discharge system to enable continuous operation, and the installation of a recuperator on the exhaust for pre-heating of the combustion air to 600 to 700°C, are possible if appropriate motivation and support can be obtained from industry.

5. ACKNOWLEDGEMENT

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6. REFERENCES

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TABLE 1

Degrees of metallization of chromium and iron obtained in the experimental runs
(all values are expressed in per cent)

Run no.	Distance of pellets from hot face, mm								Average	
	Zero		20		40		60			
	Cr	Fe	Cr	Fe	Cr	Fe	Cr	Fe	Cr	Fe
1	60	90,5	75	98,5	73	98,7	53	96,3	66	96
2	71,75	95,56	91,19	98,62	87,06	97,26	78,43	97,41	82	97
4	55,90	87,5	72	94,94	64,6	86,97	59,96	84,30	63	88
5	81,21	96,70	92,71	96,07	85,65	95,51	80,33	89,31	85	94

TABLE 2

Predicted and experimental values of the overall degree of reduction of the charge

Run no.	Degree of reduction, %	
	Experimental	Predicted
1	72	58
2	86	86
4	67	45
5	92	96

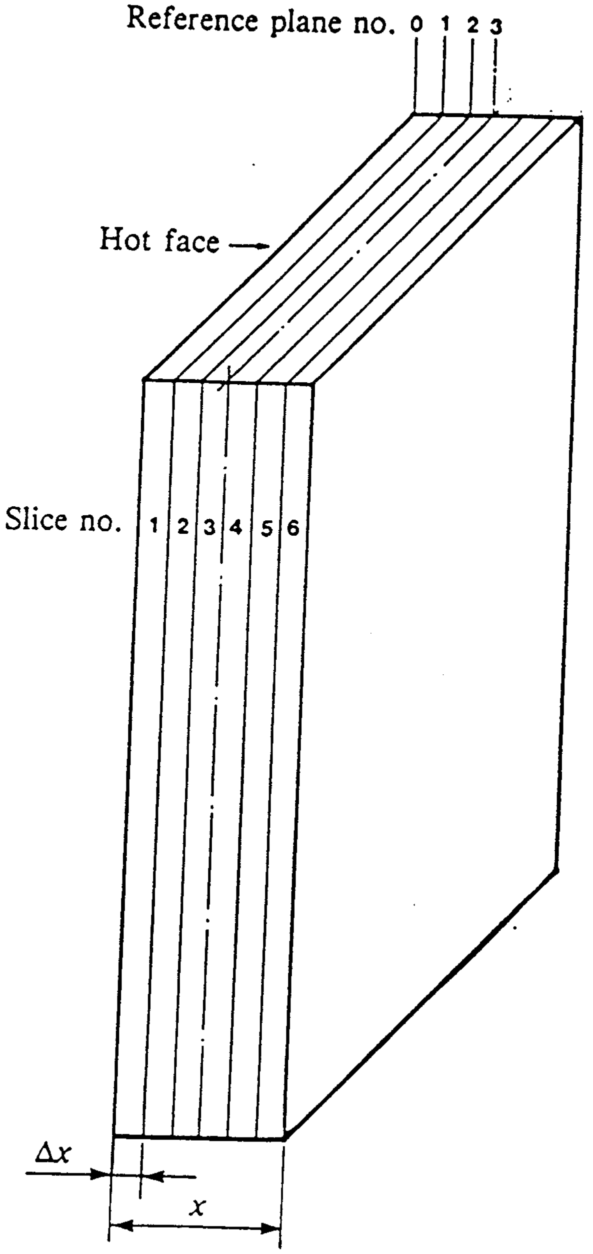

FIGURE 1. Schematic diagram of the slab-type charge, divided into six thin slices

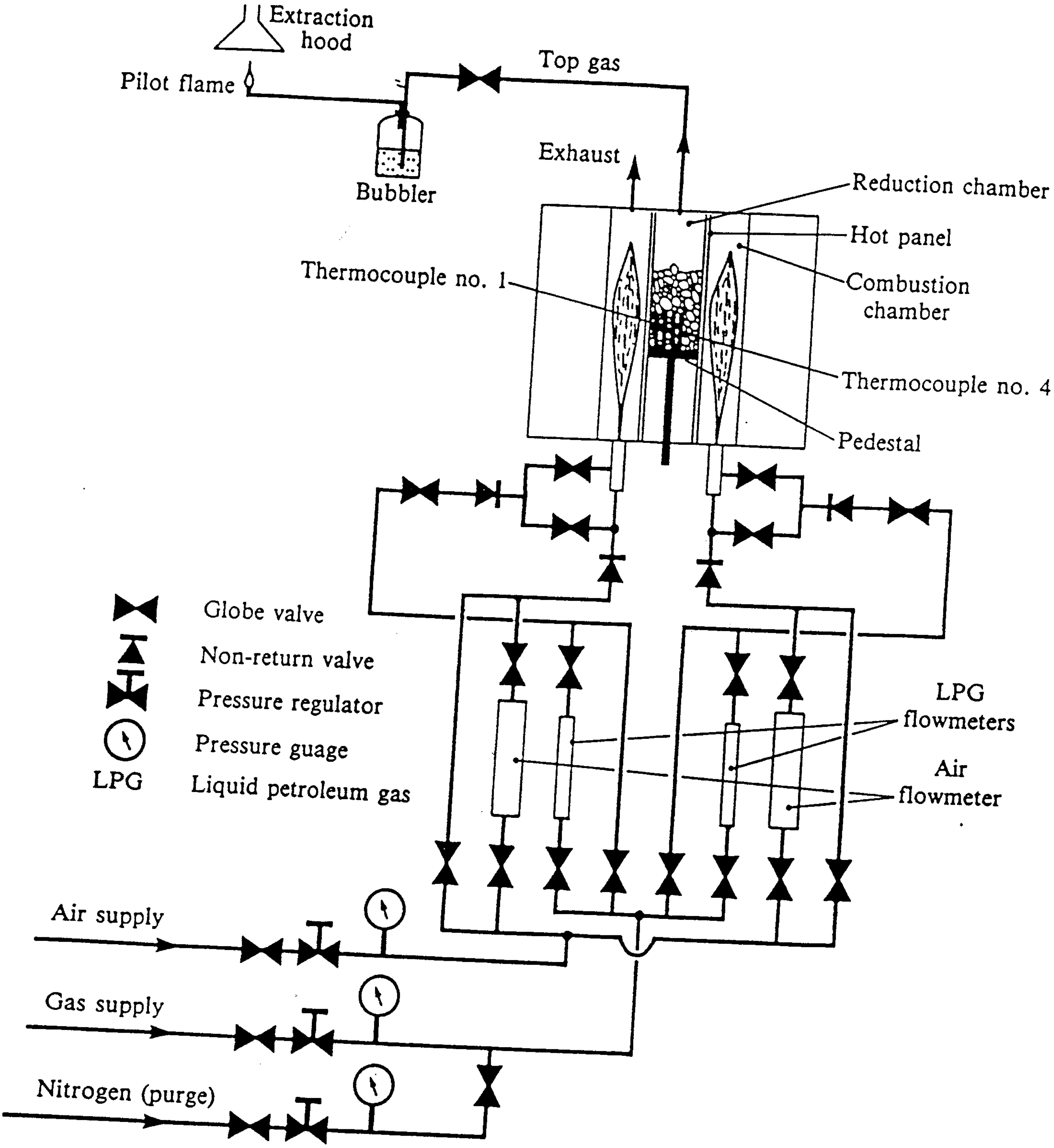

FIGURE 2. The bench-scale shaft furnace (not to scale)

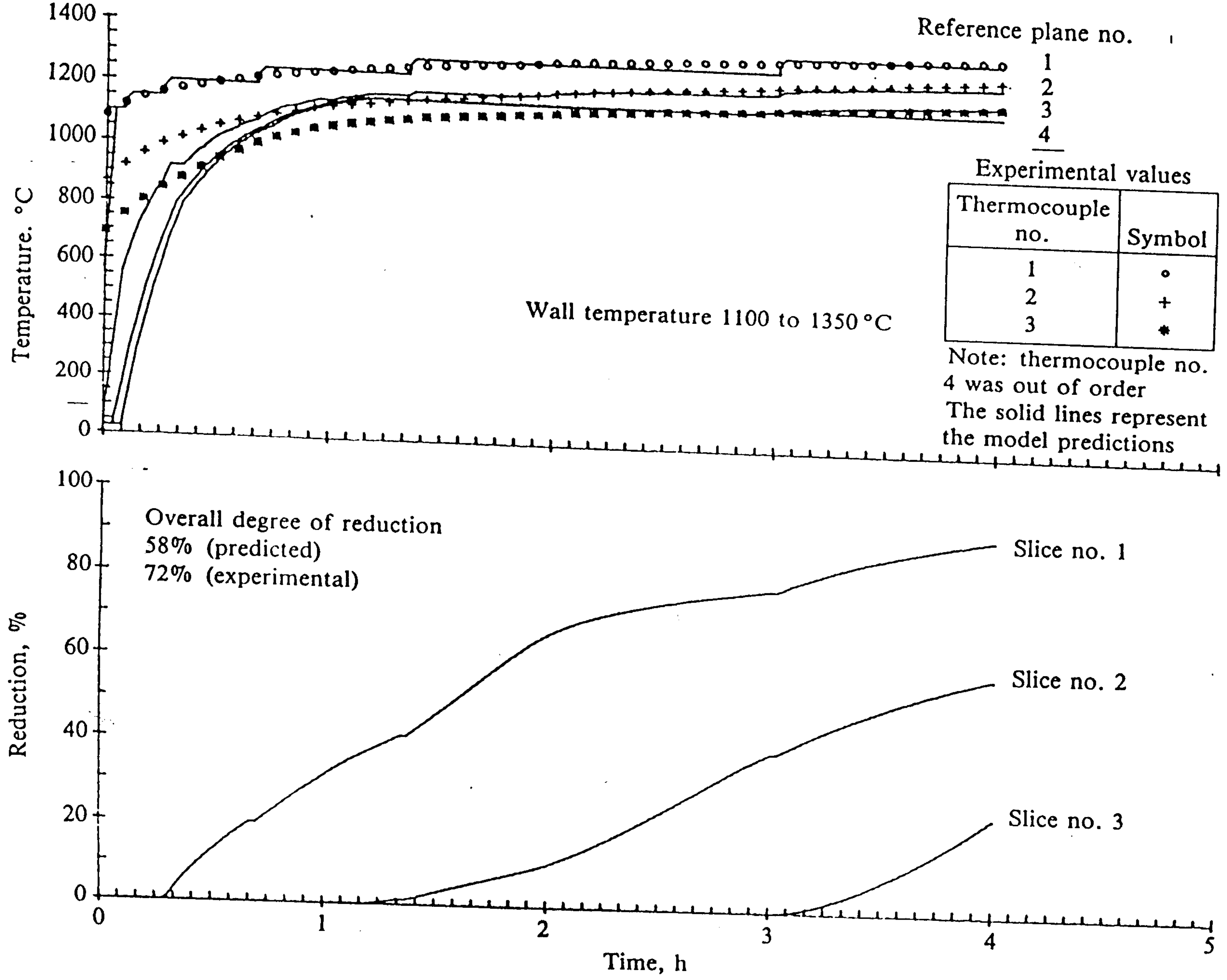

FIGURE 3. Predicted and experimental results—run 1

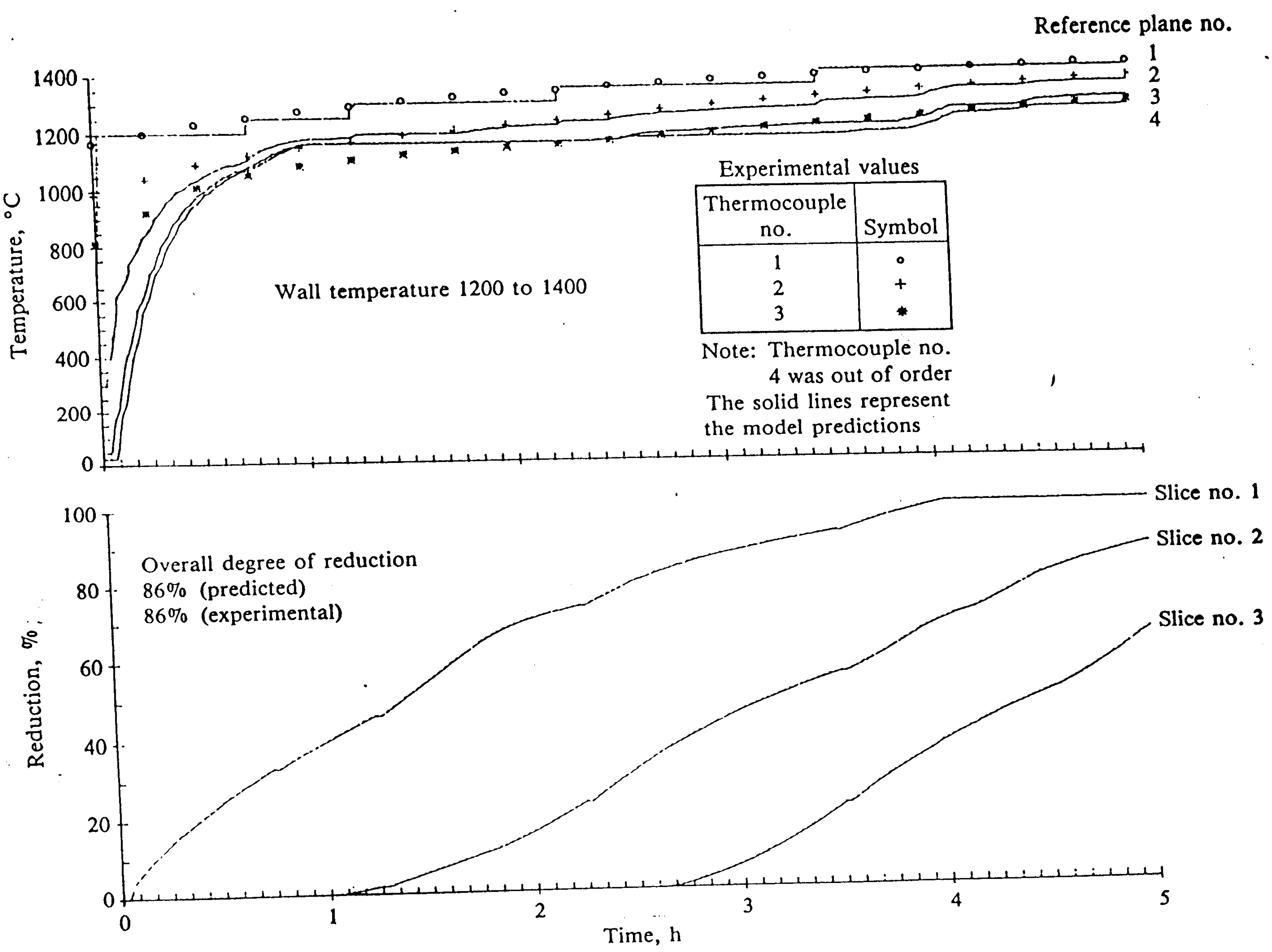

FIGURE 4. Predicted and experimental results—run 2

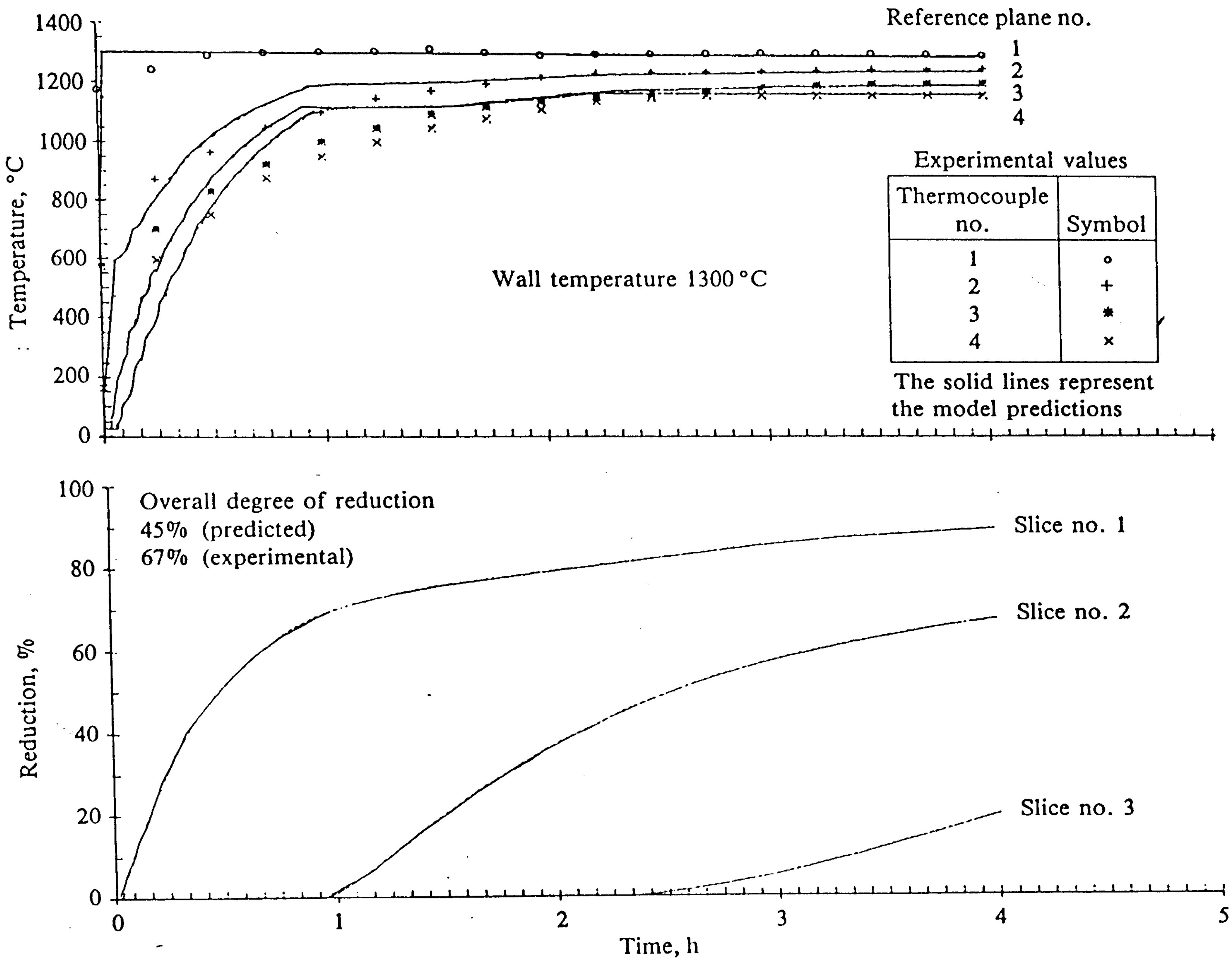

FIGURE 5. Predicted and experimental results—run 4

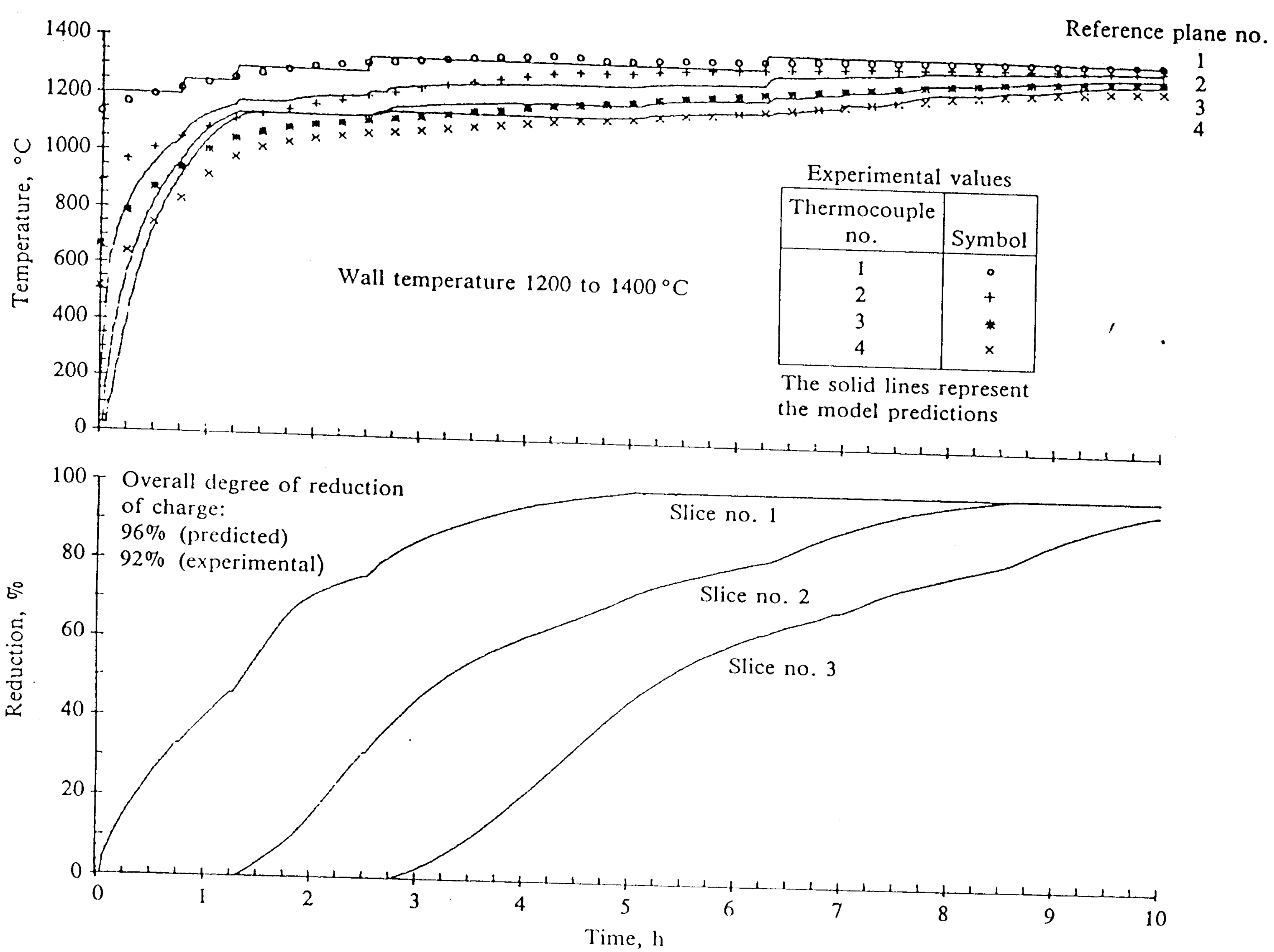

FIGURE 6. Predicted and experimental results—run 5