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THE FREE SWELLING BEHAVIOUR OF IRON OXIDE PELLETS

by

J.T. Price*and D.A. Reeve**

ABSTRACT

In recent years interest in the free swelling behaviour of iron oxide agglomerates has increased because increased amounts of pellets have replaced sinters and lump ores in blast furnace burdens. This paper describes a study of the free swelling behaviour of iron oxide pellets and details the investigations of workers from other countries. The Canadian data were discussed a a Working Group meeting of ISO/TC102/SC3 held earlier this year in Philadelphia.

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INTRODUCTION

The apparent volume increases that occur during gaseous reduction of iron oxides are related to the nature of the materials used. Sinters and lump ores generally exhibit small amounts of swelling while pellets may exhibit larger swelling properties. Pellets that swell more than 20 per cent are thought to cause operational problems in the blast furnace. The results in this report describe the free swelling behaviour of a Canadian iron ore pellet. The objective of the work was to determine a standard set of conditions to produce the largest degree of swelling. The method used in this study was similar to the method suggested to the Working Group of ISO/TC102/SC3 by Sweden[1] and uses a test sample consisting of 18 pellets. The temperature, time of reduction and flow rate of the reducing gases were varied.

Other test methods have also been used in the past to measure the free swelling behaviour of iron oxide pellets during reduction. Workers in the USSR[2] report a method for measuring the swelling effect based on an evaluation of the linear expansion of the sample during reduction. The Japanese Industrial Standard for free swelling[3] measures the volume increase of three pellets when reduced by carbon monoxide at 900 ^{o}C. An Italian study[4] suggests that the swelling behaviour of pellets can only be reliably assessed if a minimum of 75 pellets are used in the reduction.

METHOD

Eighteen pellets were chosen at random from the physical sample (10.0 - 12.5 mm in size) and were dried to a constant weight at 105 ± 5 °C. The volume of the pellets were determined in a mercury volumenometer. The pellets were placed in the ISO reducibility retort[5] using a three-tiered basket to hold the pellets. Six pellets were placed on each tier. The reduction tube was closed, placed in the furnace and heated to the desired temperature with a flow of 20 l/min (NTP) of nitrogen passing through the tube. Temperatures of 800, 900, 1000, and 1050 °C were used. After the desired temperature had been reached, the reducing gas mixture (60:40 N_2:CO) was introduced in the retort. Flows of 15, 20, and 30 l/min were used. Reduction, was allowed to proceed for 15, 40, 75, and 120 minutes. After reduction, the pellets were cooled under a flow of nitrogen gas.

RESULTS AND DISCUSSION

The pellet type chosen in this study was a Canadian commercial-grade pellet. It was chosen for the free swelling study because of its somewhat poor low-temperature disintegration properties. Chemical analyses of the pellet type are listed in Table 1. The pellet type exhibited good (small) swelling behaviour under all conditions tested. The swelling and per cent reduction are reported in Table 2 along with the temperature, flow rate and reduction time. Figures 1 and 2 indicate the maximum swelling (about 16 per cent) occurs when the pellet is 30 - 40 per cent reduced at a reduction temperature of 900 °C and a gas flow of 30 l/min. The degree of reduction was calculated and expressed as the percentage of oxygen removed from the sample:

$$R = \frac{Wi - Wf}{W_o} \times 100$$

where Wi, Wf, and Wo were the initial weight of sample, final weight of sample, and the total weight of oxygen combined with iron in the sample. The swelling values are reported as the percentage increase in volume (ΔV) and is calculated as:

$$\Delta V = \frac{Vf - Vi}{Vi} \times 100$$

where Vi and Vf are the initial and final volumes of the test sample.

The swelling behaviour of iron oxide pellets can be attributed to two causes: swelling caused by the nature of the reduction and swelling caused by the inherent properties of the pellet.

(a) Swelling due to the conditions of reduction

This study was concerned only with the swelling caused by the reduction conditions. It was hoped that a standard method could be determined to optimize the swelling behaviour. By varying the temperature, gas composition, gas flows, and the time of reaction it was possible to alter the degree of swelling.

(i) Time of reaction or degree of reduction

Figures 1 and 2 plot the degree of reduction of pellets used in this study against their per cent swelling. For all temperatures and flow rates, maximum swelling occurred when the test sample was 30 to 40 per cent reduced. Similar results have been observed in other investigations[6,7,8] and are characteristic of pellets said to have normal swelling behaviour. After a hematite pellet has been reduced by 40 per cent it consists mainly of wustite. Therefore, swelling occurs during the first two stages of reduction (Fe_2O_3 to Fe_3O_4, and Fe_3O_4 to FeO). The swelling in the first step is thought to be associated with a rearrangement of structure from the hexagonal hematite to the cubic magnetite. The wustite (FeO) to iron stage of reduction is generally accompanied by shrinkage of the pellet and is thought to be caused by a softening and sintering of the metallic iron. Edstrom[6] found that the stepwise reduction of hematite (by CO at 1000 ^{o}C) to iron via magnetite and wustite was accompanied by relative expansions of $1.00 \rightarrow 1.25 \rightarrow 1.37 \rightarrow 1.27$. Other workers[9,10,11] have observed a large swelling (as much as 300 per cent) for some pellets during the wustite to iron stage of reduction. Pellets that have these swelling characteristics are said to swell "abnormally" or "catastrophically". Such behaviour can be attributed to the chemical or physical properties of the pellets. The presence of certain metallic impurities in the reducing gas can also increase swelling.[21] Catastrophic swelling has been found to be associated with filamentary iron growth[12], which has been ascribed to the formation of iron from a limited number of nucleation sites.

These studies indicate that normal pellets have optimum (largest) swellings after 40 minutes of reduction for most temperatures and flow rates. This reduction time is probably adequate for determining the free-swelling index of most normal pellets. If the pellets are expected to swell catastrophically, or to have a low reducibility then a longer reduction time may be more suitable.

(ii) Gas composition

Although a gas composition of 60 per cent nitrogen and 40 per cent carbon monoxide was maintained throughout this study, preliminary results from samples reduced in a counter-current reactor[13] suggest that the swelling is lessened if the reducing potential of the gas and temperature are slowly increased throughout the reduction. Such behaviour has been confirmed by Walker and Moon[14]. Studies in France[15] suggest this behaviour can be attributed to the reducing potential of CO_2:CO:N_2 mixtures. Samples reduced by gas mixtures having a high reducing potential (40:60 CO:N_2) for one hour at 950 ^oC showed swelling in the order of 72 to 73 per cent while a similar sample reduced by a gas mixture having a lower reducing potential (17:25:58 CO_2:CO:N_2) showed little or no swelling. The degree of reduction, however, was not indicated.

(iii) Temperature and flow rate

From Figures 1 and 2 it can be seen that maximum swelling occurred at a flow of 30 l/min for the reducing gas at a temperature of 900 ^oC. The maximum swelling for all temperatures and flow rates is within the range of 13 $\pm$ 3 per cent. It is not known if the small differences between the curves is significant since measurements were not made in duplicate. Nevertheless, German investigators[16] found that a Venezuelan pellet had maximum swelling at a reduction temperature of 900 ^oC. The Japanese Industrial Standard[3] also suggests a reduction temperature of 900 ^oC. Swedish workers[8] found maximum swelling of pellets occurs at reduction temperatures of 1000 ^oC. Kortman et al.[17] has found that maximum swelling can occur anywhere between 900 and 1100 ^{o}C depending upon the hardening temperature of the test samples. Iron oxide materials fired at 1300 ^{o}C showed maximum swelling at 1100 ^{o}C while those fired at lower temperatures had maximum swelling at 900 ^{o}C. Therefore, it appears that the thermal history of a pellet significantly affects its swelling behaviour.

(b) Swelling caused by the properties of the pellet

(i) Physical properties

Observation of pure hematite pellets by microscope indicates these samples consist primarily of a large number of single hematite grains. A few of these grains are joined to each other through hematite bridges which hold the entire sample together. The more bridges in a pellet the stronger it becomes and swelling during reduction is expected to decrease. The technology devised to make pellets involves having a suitable particle size, a balling procedure and a high firing temperature. These procedures are important to the formation of hematite bridges which improve the strength of non-reduced pellets. Unfortunately, during the reduction of hematite to magnetite and the magnetite to wustite structural changes occur in the lattice which cause the pellet to disintegrate and swell. Pellets that have large swelling during the $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$ stages of reduction generally have swelling during the wustite to iron step[18]. If lime and silica are present in an iron oxide material (as is usually the case) the pellet strength can be increased through the formation of slag bonds which serve as bridges to the hematite grains and gives the pellet additional strength. These bonds are not attacked during reduction from hematite to wustite and maintain pellet strength throughout the reduction. Grebe et al[18] suggest that the presence of gangue materials can not possibly contribute to an increase in the swelling behaviour of a pellet provided that the gangue material has been fused. He suggests that the homogeneity (or distribution of the gangue components) in the pellet and an adequate hardening treatment are of prime importance.

(ii) Chemical composition of the pellet

Studies by other workers suggest that chemical impurities in iron oxide pellets can be a cause of swelling. Alkalies[19,20], calcium[12], and zinc[21] have been found to cause whisker growth and swelling under certain reduction conditions. The presence of even 0.1 per cent alkalies in the pellets (or in the gas vapour) is extremely detrimental to the swelling behaviour of pellets. The combined presence of carbon and alkalies in pellets has been found to accelerate the swelling phenomenon[20]. Bleifuss[12] found that uncombined lime contributes to the swelling in underfired pellets during the wustite to iron step in reduction. He suggested that during reduction the limited solubility of CaO in FeO can produce a wustite surface saturated with CaO. Nucleation on this surface is difficult and leads to whisker formation and swelling. Other studies[14] indicate that increased amounts of CaO decrease the amount of swelling provided the pellet has been subjected to a high firing temperature. To ensure small amounts of swelling, the firing temperature of the pellet must be such to ensure the formation of calcium diferrite (mpt 1226 ^{o}C) which bonds and bridges the iron oxide grains.

If silica is present in the ore concentrate the $CaO:SiO_2$ ratio can be adjusted to limit the swelling of the pellets. Moon and Walker[14] found pellets with basicities of 0.7 exhibit maximum swelling. In contrast, Kortman et al[17] found the lower the basicity the larger was the swelling with pellets that contain less than two per cent gangue. Pellets with higher basicities have less tendency to swell provided they have been subjected to a high firing temperature for an extended period of time. An increase in the amount of gangue (CaO and SiO_2) over 0.8 per cent decreased the swelling for all basicities.

The effect of zinc on the swelling behaviour of pellets is not so well understood. Results[13] showed that pellets containing one per cent zinc and reduced in a counter-current reactor had no tendency to swell abnormally provided the zinc is homogeneously distributed throughout the pellet and the pellet has been subjected to a high firing temperature. The presence of zinc can cause swelling and whisker growth under certain conditions[21]. Possibly, the presence of uncombined ZnO unevenly distributed on a wüstite surface behaves similarly to CaO and prevents nucleation. This causes whisker growth and promotes the swelling behaviour of pellets.

CONCLUSION

The nature of the iron oxide pellet as well as the reduction conditons are critical to the swelling of the pellet during reduction. Greater swelling occurs if reduction proceeds from hematite to iron rather than from magnetite or wustite to iron. Increasing the basicity (>1.0) and amount of gangue (>0.8) per cent) in a pellet will decrease the amount of free swelling. The gangue material should be homogeneously distributed throughout the pellet and exist in a vitreous state (a result of a high firing temperature) to minimize swelling. Any alkalies present in the pellets will drastically increase a pellet's swelling behaviour.

The commercial pellet used in this study exhibited normal free-swelling behaviour and showed a maximum when the reduction was carried out isothermally at 900 ^{o}C and a flow of 30 l/min. To improve the reliability of the test, it is felt more pellets (about 35) will be required. A decrease in the reducing potential of the reducing gas will decrease the swelling behaviour of a pellet. Maximum swelling occurred when the sample was 30 to 40 per cent reduced. For most cases a reduction time of 40 minutes would be suitable. If catastrophic swelling is expected then a reduction time of 60 or 75 minutes may be preferable. More experimentation is desirable with pellets that exhibit catastrophic swelling to define clearly the reducing conditions that maximize the swelling behaviour for this type of pellet.

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TABLE 1.

CHEMICAL COMPOSITION OF PELLET

Fe total	Fe	Fe^{o}	Ca	Si	CaO/SiO_2	Al	Mg
65.32	0.99	0.13	0.31	2.62	0.08	0.14	0.17

TABLE 2.

TEMPERATURE °C	FLOW RATE (l/min)	TIME (min)	% REDUCED	% SWELLING
800	15	120	51.0	13.9
800	20	40	30.1	14.7
800	20	75	42.5	14.6
800	20	90	52.0	13.7
800	20	120	67.9	9.5
800	30	40	35.1	13.1
800	30	75	42.0	13.1
800	30	120	67.6	10.7
900	15	120	65.4	13.0
900	20	15	20.1	14.4
900	20	40	39.3	13.5
900	20	75	50.2	11.9
900	20	120	64.6	7.9
900	30	15	25.1	15.1
900	30	40	38.6	15.4
900	30	75	52.7	12.9
900	30	120	68.7	11.8
925	20	75	53.2	10.6
1000	15	120	75.9	1.1
1000	20	15	23.0	12.7
1000	20	40	42.1	12.2
1000	20	40	44,2	12.1
1000	20	120	72.9	5.1
1000	30	40	41.9	11.5
990	30	75	57.7	9.9
1000	30	120	80.8	1.7
1050	20	15	22.6	13.8
1050	20	40	45.7	14.0
1040	20	75	74.0	6.7
1045	20	120	81.4	6.2
1050	30	15	26.1	13.2
1050	30	40	45.9	12.6
1050	30	75	62.9	7.6

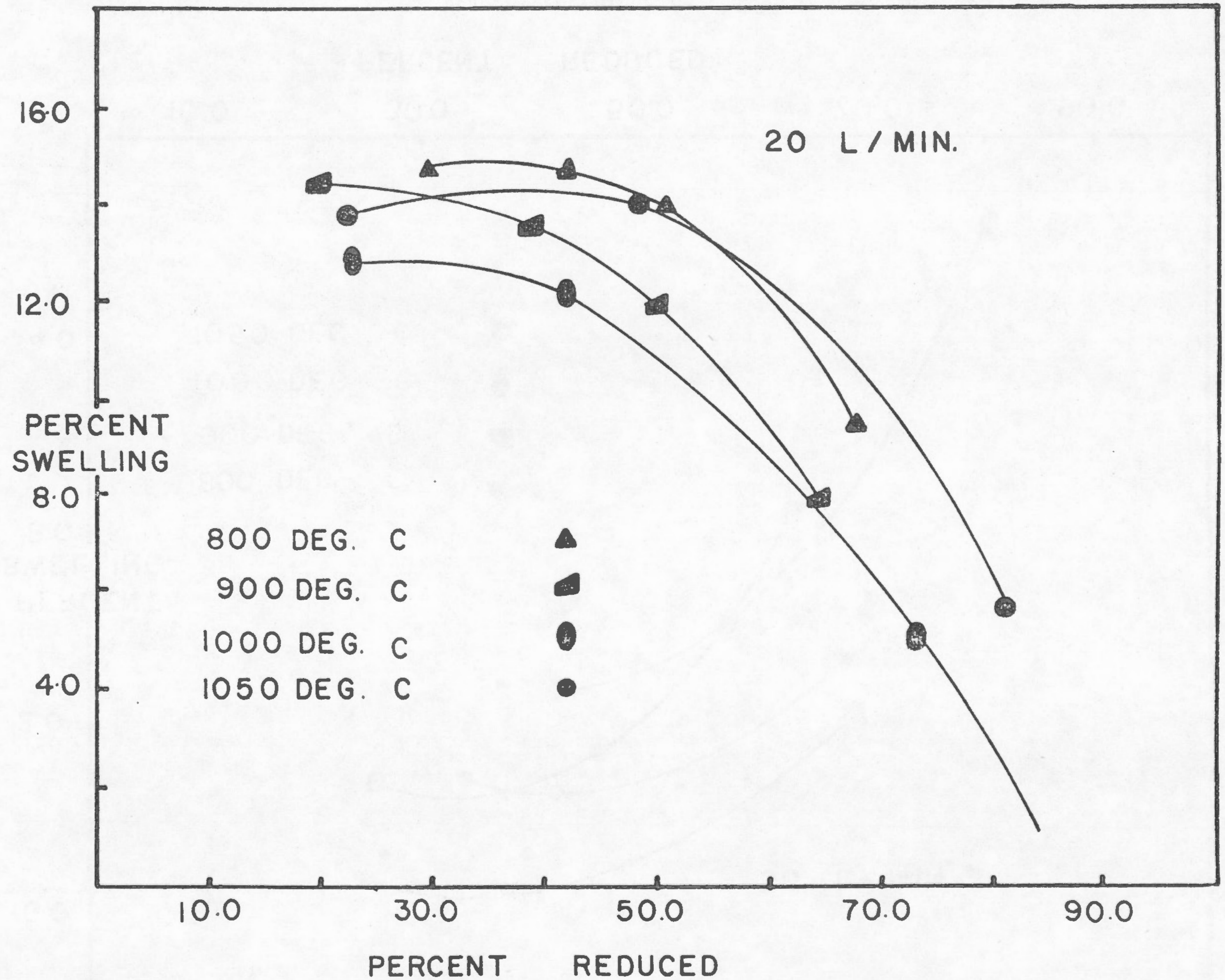

FIGURE 1. PERCENT SWELLINGS AT A FLOW RATE OF 20 l/MIN.

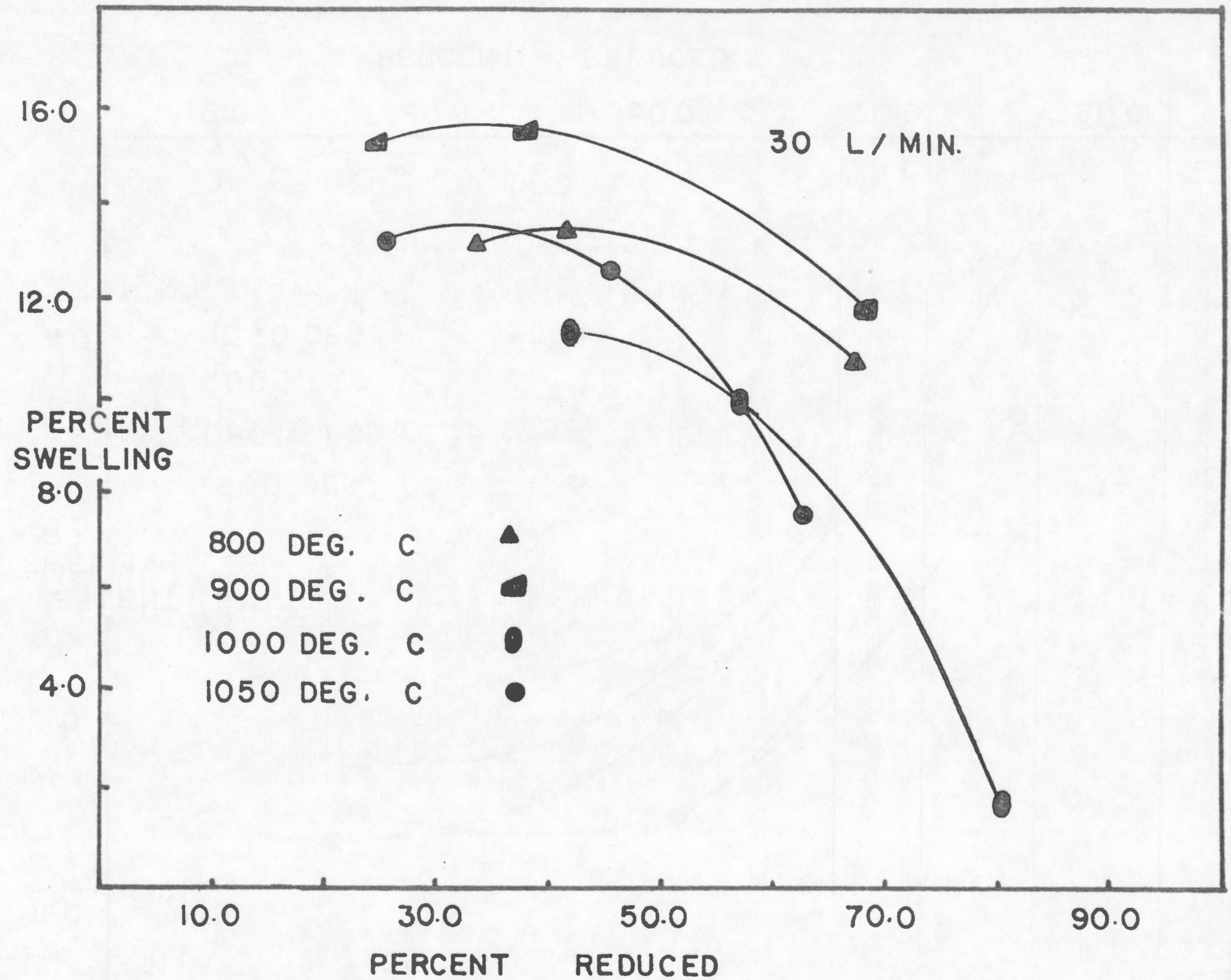

FIGURE 2. PERCENT SWELLINGS AT A FLOW RATE OF 30 1/MIN.