Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

CANADIAN INVESTIGATIONS INTO THE DETERMINATIONS OF THE REDUCTION DISINTEGRATION OF IRON ORE MATERIALS AND THE FREE SWELLING OF IRON OXIDE PELLETS

J. T. Price
Combustion and Carbonization Research Laboratory

AUGUST 1982

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
DIVISION REPORT 82-30 (TR)

CANADIAN INVESTIGATIONS INTO THE DETERMINATIONS OF THE REDUCTION DISINTEGRATION OF IRON ORE MATERIALS AND THE FREE-SWELLING OF IRON OXIDE PELLETS

by

J.T. Price

ABSTRACT

Over the past decade CANMET has established facilities to conduct physical testing of coke and iron ore materials under simulated blast furnace conditions. The success of the CANMET program in testing iron materials according to ISO TC 102 proposed methods has encouraged two Canadian steel companies and one iron ore company to develop similar facilities. This report presents results from three Canadian Laboratories participating in International Round Robin testing of the free-swelling and reduction disintegration (RDI) of iron ore materials. Standard deviations and precisions of the RDI test vary with the degree of ore degradation. Canadian results also indicate that RDI indices of iron oxide pellets and sinters deteriorate severely if small amounts of H_2 are included in the reducing gas. Small changes in temperature near 500°C had little effect on the RDI indices of one poor quality iron ore pellet.

INTRODUCTION

Coke and iron ore materials must meet increasingly stringent specifications to improve productivities and coking rates of today's modern blast furnaces. For evaluating the quality of iron ores, pellets, and sinters it is becoming increasingly important to evaluate these materials using temperatures and reaction conditions that exist in blast furnaces. It is generally accepted that poor reducibility, excessive swelling, early softening and high disintegration of iron ore materials have negative effects on blast furnace operation.

Standard test procedures to evaluate iron-oxide materials are being developed within the forum of the International Organization for Standardization (ISO)*. Investigations for the development of tests simulating blast furnace conditions are planned by CANMET and the Canadian Advisory Committee (CAC) to ISO Technical Committee 102 Sub-Committee (SC)-3 with members from the major Canadian iron ore and steel companies. The international body of ISO TC 102/SC 3 meets biannually and established at its most recent meeting in Pretoria, S.A., several working groups to develop test procedures. Specifications from such standardized tests will be included in contracts for the buying and selling of lump, iron ore, sinters and pellets.

In Canada, facilities to develop test procedures that simulate blast furnace reductions were established at CANMET in the early 1970's. The usefulness of CANMET facilities for evaluating the quality of iron ore burdens has recently prompted two Canadian steel companies and a Canadian mining company to set up similar facilities in their laboratories. One steel company has indicated at a recent CAC meeting that results from the reduction disintegration test appeared to relate to blast furnace performance and that they were planning to use this test for quality and process control at their plant and mines.

---

*The Member Body for Canada is the Standards Council of Canada (SCC). The Canadian National Committee on ISO(CNC/ISO), acting on behalf of the SCC in work relating to ISO, has Canadian advisory committees reporting to it which provide the necessary expertise and representation of Canadian interests related to specific technical committees.

This report describes work done by three Canadian laboratories for Working Groups 2 (Reduction Disintegration Test) and 3 (Free-swelling Test) of ISO TC 102/SC 3.

REDUCTION DISINTEGRATION TEST (WG-2)

In the blast furnace, the reduction of iron ore to iron takes place through intermediate stages of magnetite and wustite. The reduction disintegration test measures the degradation of iron ore materials during the transformation of hematite to magnetite. The procedure of DP-4696 involves passing 20 L/min of reducing gas (20% CO, 20% CO_2, 60% N_2) preheated to 500°C through a 500 g of iron oxide sample for 1 h. After weighing, then tumbling the product for 10 min at 30 rpm, the percentage of material greater than 6.3, 3.15 and 0.5 mm is reported (1). Although a great deal of work has been done by WG 2 to develop procedures for this test, results indicated that tolerances on gas composition, gas purity and test temperatures with iron oxide pellets needed further investigation. It was also agreed that international round robin testing would be done to measure the deviation of results between laboratories. Canada agreed to participate in round robin testing, and to investigate the effects of small additions of hydrogen and the effect of small changes in temperature on the reduction disintegration of iron oxide pellets. An earlier report (2) had shown that poor quality pellets were slightly effected by changing flow rates from 20 to 18 L/min but high quality pellets were not.

Small addition of hydrogen to reducing gas

Previous work on two lump ore and 3 sinters had shown that small additions of H_2 gas had little effect on the RDI indices of lump iron ores but caused a significant increase in reduction degradation for all sinters investigated. No similar investigations with pellets had been reported. Results of work done by CANMET on the effects of adding up to 5% H_2 on the RDI of an imported iron ore pellet (A_1) and Canadian pellet (B_1) are shown in Table 1.

Both pellets show increased reduction disintegration with small amounts of H_2 added to the reducing gas. Figure 1 shows maximum degradation occurs with about 1% H_2 added for pellet A_1; maximum degradation occurs at 2% H_2 addition for pellet B_1.

Table 2 compares results obtained by a Canadian steel company on North American pellets tested with 2% H_2 in the reducing gas and under standard test conditions. In all cases results indicate that greater degradation occurs when 2% H_2 is incorporated into the reducing gas. Figure 2 shows a comparison of the +6.3 mm RDI indices obtained from data in Tables 1, 2 and 3 and from previous investigations (3) for iron oxide pellets and sinters tested conventionally and with 2% H_2 in the reducing gas.

Small changes in temperature

According to Draft Proposal 4696 the test temperature is 500 ± 10°C. Previous work done on high quality iron oxide pellets, and a lump ore showed no significant variation in disintegration with small temperature changes near 500°C (3). However, a fluxed sinter showed maximum disintegration occurred at 500°C but with considerable variations between temperatures of 490 and 500°C. To investigate the effects of small changes in temperature on a low-grade pellet, a second sample of pellet A (A_2) was tested at the CANMET laboratory at 480, 490, 500, 510 and 520°C as indicated in Table 4. Results show very small changes in the degradation indices between the tolerance limits specified by the test, 490-510°C. Increased degradation may occur at higher temperatures but these conditions were not investigated because of a lack of sample.

Round robin testing

Three Canadian laboratories participated in the RDI testing of 2 lump ores supplied by Germany, 2 Swedish pellets, and 2 Australian sinters. Results for the 3 Canadian laboratories are given in Table 3 and generally appear to be quite comparable. A complete statistical evaluation will be done upon obtaining results from other countries.

Precision of RDI indices

Table 5 summarizes the mean RDI indices and standard deviations (σ) from static RDI tests published in a report by the WG 2 convenor (3). Standard deviations and mean RDI indices from the Canadian round robin study are also included; the standard deviations were calculated from the results in Table 4 as the square root of the average variances obtained by the three laboratories:

$$\sigma_M = \sqrt{\frac{\sigma_A^2 + \sigma_B^2 + \sigma_C^2}{3}}$$

Figure 3(a) shows a linear increase in the standard deviation of the -0.5 mm RDI index for ores, sinters and pellets as this index increases in value. Figure 3(b) plots the same results but shows for the existing data that sinters appear to have smaller standard deviations than do the lump ores and pellets. Figure 4 shows a similar type of plot for the +6.3 mm index. Results suggest the standard deviation increases markedly with increased pellet breakdown and may reach a maximum level at a +6.3 mm RDI index of 40-50% as shown by the best parabolic relationship in Fig. 3. Although conclusions should not be made before all results from the international round robin program have been received, the results presented here would indicate that no absolute tolerance values should be placed upon the RDI indices because precision varies with the degradation of the ore material.

INTERNATIONAL ROUND ROBIN TESTING OF THE FREE SWELLING OF IRON OXIDE PELLETS

ISO TC 102 Doc 3N 458 describes the current procedure for measuring the free-swelling properties of iron-oxide pellets (4). The method involves reacting 18 pellets at 900°C with a 15 L/min flow of reducing gas containing 30% Co and 70% N_2. Pellet swellings are measured using a mercury volumenometer and swellings greater than 20% are generally considered to cause operational difficulties in the blast furnace.

The WG-3 convenor from Sweden supplied duplicate samples (can 1 and can 2) of 3 types of iron oxide pellets labelled A, B and C for international round robin testing. Chemical analyses are given in Table 6. The testing program consisted of four steps.

1. Reproducibility test: This consisted of a duplicate test on both cans of the three samples and implies a test on sample homogeneity and the magnitude of the errors associated with dividing the samples.
2. Test temperature: On can 1 of each sample two additional tests were done using 1000°C instead of 900°C, leaving other parameters unchanged.
3. Gas flow rate: On can 2 of each sample two additional tests were done according to document 3N 458 but with a gas flow of 20 L/min.
4. Gas composition: On can 1 of each sample two additional tests were done with the CO/N_2 proportion changed from 30/70 to 40/60%.

CANMET results from the 4 tests methods are summarized in Table 7 and show that all three pellet types have quite similar swellings. The mean swelling results obtained for all 4 methods of testing showed the same relative order of swelling for the three types of pellets, B, C and A, with none of the methods appearing better. In all test methods pellet C has been reduced considerably more than the other pellets. Results from the reproducibility study are difficult to interpret but CANMET results show an average range of 1.3% in the swelling results from duplicate tests which is only slightly smaller than the 1.4% range obtained from the two divided samples (can 1 vs can 2). Detailed statistical analyses will be completed when test results from all laboratories are received.

Table 8 gives results on selected samples for an alternative method of measuring pellet swelling. This method calculates a mean particle diameter (and hence volume) by measuring the length of 18 pellets placed end to end upon a piece of angle iron before and after reduction. Table 8 suggests the reproducibility of the swelling determinations is much inferior to that obtained by using a mercury volumenometer.

REFERENCES

1. Iron Ores - Determination of low temperature disintegration - Cold tumbling after static reduction; DP 4696, ISO/TC 102 Doc. 290.

2. Price, J.T. "Assessment of current ISO physical and metallurgical methods for determining the quality of iron ore materials"; Energy Research Laboratories, CANMET; Report MRP/ERL 80-51 (TR).

3. Report of the work undertaken by ISO/TC 102/SC 3 - WG-2, in the period Nov. 1978 to Oct. 1980; ISO/TC 102/SC 3, Doc. 3N 509.

4. Iron Ore Pellets - Determination of relative free-swelling index; DP 4698, ISO/TC 102/SC 3 Doc. 3N 458.

Table 1 - Effect of adding small quantities of H_2 to reducing gas mixture (4 L/min CO, 4 L/min CO_2 and 12 L/min N_2) on the RDI indices of an acid iron ore pellet (A_1)

Sample A_1 (imported)

% Flow H_2 added	Wt. loss of iron ore (%)	6.3 mm	3.2 mm	-0.5 mm
0	2.9	74.8	97.0	1.81
0.3	3.1	44.6	87.3	3.28
0.6	3.1	42.4	83.1	3.42
1.0	3.1	37.5	78.3	5.37
2.0	3.1	41.7	81.4	4.26
3.0	3.4	48.8	84.2	4.35
5.0	3.0	50.1	79.1	5.60

All results are averages of duplicate tests with the exception of the test run with 5% H_2 added which was done with only one determination because of lack of sample.

Sample B_1

% Flow H_2 added	Wt. loss of iron ore (%)	6.3 mm	3.2 mm	-0.5 mm
0	3.05	99.7	99.7	0.26
0.5	3.08	98.4	98.8	1.12
1.0	3.04	97.1	97.9	1.92
2.0	3.03	95.9	97.3	2.58
3.0	3.04	97.1	97.8	1.92

Table 2 - I.S.O. RDI test results for North American pellets

Sample	Grade	Without H_2		With H_2	
		% wt. loss	+6.30 mm	% wt. loss	+6.30 mm
Pellet C	Magnetite	3.1	93.9	3.1	87.6
D	Magnetite	3.1	98.2	3.1	95.4
E	Magnetite	3.2	92.1	3.1	75.3
F	Hematite	3.1	95.1	3.2	87.2
G	Hematite	3.0	98.4	3.1	96.9
H	Hematite	3.1	98.3	3.2	90.0

Table 3 - Canadian Results from Reduction Disintegration Test for Ores, Sinters, and Pellets

		Lump Ores								Sinters								Pellets							
		Sample 2D				Sample 1D				Sample B				Sample A				Sample B				Sample A			
Parameter	Lab.	1	2	3	Avg.	1	2	3	Avg.	1	2	3	Avg.	1	2	3	Avg.	1	2	3	Avg.	1	2	3	Avg.
% wt. loss	A	6.17	4.58	5.07	5.27	1.04	1.16	1.02	1.07	0.67	0.72	0.62	0.67	0.50	0.51	0.50	0.50	2.99	2.97	2.97	2.98	2.98	2.99	2.96	2.98
	B	4.90	4.6	4.3	4.6	1.2	1.0	1.2	1.1	0.5	0.6	0.6	0.6	0.4	0.3	0.4	0.4	2.9	3.0	2.9	2.9	3.0	3.1	3.0	3.0
	C									0.58	0.67	0.65	0.63	0.38	0.43	0.45	0.42	2.96	2.98	3.04	2.99	2.96	2.97	3.03	2.99
RDI 6.3	A	68.0	68.9	68.1	68.3	80.8	80.4	84.5	81.9	13.3	13.4	17.0	14.6	36.8	38.6	35.5	37.0	94.8	95.3	94.7	94.9	98.6	98.6	99.0	98.7
	B	68.0	65.4	64.6	66.0	83.1	84.0	81.4	82.8	14.9	14.3	13.4	14.2	42.5	48.8	41.7	44.3	95.8	94.9	97.3	96.0	98.5	99.1	98.1	98.6
	C									9.72	6.39	7.64	7.92	35.8	31.9	30.5	32.7	95.1	93.6	95.4	94.7	98.4	98.4	98.7	98.5
RDI 3.15	A	79.1	80.6	79.7	79.8	87.3	88.9	89.1	88.4	49.7	48.8	52.1	50.2	68.3	71.0	69.7	69.7	98.4	98.2	96.7	97.8	98.9	98.9	99.0	98.9
	B	80.4	81.4	76.1	79.3	87.4	89.1	87.9	88.1	55.2	53.5	51.1	53.3	72.7	75.2	72.9	73.6	98.2	98.3	98.4	98.3	98.9	99.1	98.5	98.8
	C									44.9	39.9	47.1	44.0	69.9	66.5	66.7	67.7	97.9	97.5	98.2	97.8	98.8	98.7	98.8	98.8
RDI -0.5	A	11.0	9.38	10.3	10.2	4.47	4.04	3.89	4.13	10.8	12.1	10.6	11.2	7;99	7.25	7.51	7.58	1.35	1.45	1.72	1.51	1.01	0.99	0.87	0.96
	B	10.1	9.0	12.0	10.4	3.8	3.4	3.8	3.7	7.9	7.9	8.5	8.1	6.3	6.0	6.4	6.2	1.4	1.3	1.4	1.4	1.1	0.8	1.3	1.1
	C									9.06	10.2	8.86	9.37	6.60	7.30	7.67	7.19	1.69	2.00	1.58	1.76	1.12	1.23	1.01	1.12
% Wt. loss*	B									1.0	1.0	- -	1.0	0.8	0.8	- -	0.8	3.0	3.0	- -	3.0	3.0	3.1	- -	3.1
RDI 6.3*	B									3.2	3.3	- -	3.3	23.8	21.9	- -	22.9	87.8	87.8	- -	87.8	96.5	95.0	- -	95.8
RDI 3.15	B									35.0	32.6	- -	33.8	55.2	54.8	- -	55.0	92.8	92.9	- -	92.9	97.7	96.9	- -	97.3
RDI -0.50	B									9.0	8.9	- -	9.0	8.5	8.0	- -	8.3	5.0	5.4	- -	5.2	2.0	2.5	- -	2.3

*Experiments performed by Laboratory B on sinters and pellets using 20% CO, 20%CO_2, 58%N_2 and 2%H_2; all other tests use Standard conditions.

Table 4 - Effect of small changes in temperature on the RDI indices of a poor quality iron ore pellet (Sample A_2)

Temperature	% wt. loss	+6.3 mm	+3.15 mm	-0.5 mm
480°C	3.08	68.42	97.1	1.37
490	2.96	64.39	96.59	1.69
500	3.09	62.71	95.54	1.82
500	2.87	65.53	96.9	1.57
500	3.04	66.69	96.76	1.64
510	3.06	68.17	97.09	1.59
520	3.02	52.18	93.93	2.14

Table 5 - Summary of mean RDI indices and their standard deviations (σ) obtained by ISO test procedures

Ore material		RDI index				N	Ref
		+6.3 mm		-0.50 mm			
		$\bar{x}$	σ	$\bar{x}$	σ		
Pellets	-1	94.3	0.64	3.76	0.55	8	3
	-2	98.6	0.3	1.1	0.1	8	3
	-3	94.4	2.4	1.2	0.3	8	3
	-4	65.4	2.6	1.6	0.18	8	3
	-5	95.2	0.83	1.56	0.17	9	Table 3
	-6	98.6	0.33	1.06	0.16	9	Table 3
Sinters	-1	87.4	1.13	1.27	0.14	8	3
	-2	96.1	0.62	0.86	0.08	8	3
(16x10 mm)	-3	24.3	2.7	6.2	0.4	8	3
	-4	79.1	2.9	2.0	0.3	8	3
	-5	12.24	1.73	9.6	0.65	9	Table 3
	-6	38.0	2.88	7.0	0.40	9	Table 3
Lump ores	-1	88.0	1.5	3.6	0.5	8	3
(16x10 mm)	-2	64.8	2.1	6.4	0.8	8	3
	-3	67.2	1.29	10.3	1.35	6	Table 3
	-4	82.4	1.85	3.9	0.27	6	Table 3

N = no. of determinations to determine $\bar{x}$ and σ

Table 6 - Chemical analyses of pellet samples used for free-swelling determinations

Sample	A	B	C
Fe	66.5	65.85	62.2
Fe^{2+}	1.24	-	0.80
CaO	0.10	0.19	4.18
MgO	0.27	0.23	1.57
Al_2O_3	0.57	0.46	0.84
SiO_2	3.82	4.04	3.80

Table 7 - Canadian round robin test results on free swelling of iron oxide pellets - mercury volumenometer method

Item	Pellet sample no.	Can 1				Can 2			
		Det. no. 1		Det. no. 2		Det. no. 1		Det. no. 2	
		Sw(%)	Red(%)	Sw(%)	Red(%)	Sw(%)	Red(%)	Sw(%)	Red(%)
1	A	12.4	35.8	12.0	35.3	11.4	38.3	12.0	38.3
	B	13.1	38.5	13.9	37.8	14.3	35.7	15.9	39.6
	C	13.1	54.7	13.7	59.4	16.1	59.2	12.0	62.1
2	A	11.1	45.8	12.1	45.5				
	B	12.4	46.0	13.2	46.1				
	C	11.1	70.6	12.7	64.8				
3	A					11.3	36.0	9.7	35.7
	B					14.5	38.0	11.4	36.2
	C					13.3	61.7	9.8	54.0
4	A	8.2	41.0	9.9	41.8				
	B	11.9	44.8	10.1	46.7				
	C	10.7	63.4	10.8	66.1				

Item:

1 Reproducibility	900°C	15 l/min STP	30/70 % CO/N_2
2 Test temp	1000°C	15 l/min STP	30/70 % CO/N_2
3 Gas flow rate	900°C	20 l/min STP	30/70 % CO/N_2
4 Gas composition	900°C	15 l/min STP	40/60 % CO/N_2

Table 8 - Free swelling determinations based on the increase in the mean diameter of iron oxide pellets

Item	Pellet sample no.	Can 1				Can 2			
		Det. no. 1		Det. no. 2		Det. no. 1		Det. no. 2	
		Sw(%)/Red(%)		Sw(%)/Red(%)		Sw(%)/Red(%)		Sw(%)/Red(%)	
1	A	-	-	-	-	-	-	-	-
	B	-	-	-	-	21.4	-	10.6	-
	C	19.2	-	21.7	-	19.2	-	21.1	-
2	A	13.4	-	8.0	-				
	B	25.1	-	16.0	-				
	C	10.5	-	18.9	-				
3	A					14.5	-	8.0	-
	B					13.2	-	12.7	-
	C					10.3	-	16.6	-
4	A	7.7	-	10.8	-				
	B	21.9	-	15.9	-				
	C	18.9	-	13.0	-				

Item:

1	Reproducibility	900°C	15 l/min STP	30/70 % CO/N_2
2	Test temp	1000°C	15 l/min STP	30/70 % CO/N_2
3	Gas flow rate	900°C	20 l/min STP	30/70 % CO/N_2
4	Gas composition	900°C	15 l/min STP	40/60 % CO/N_2

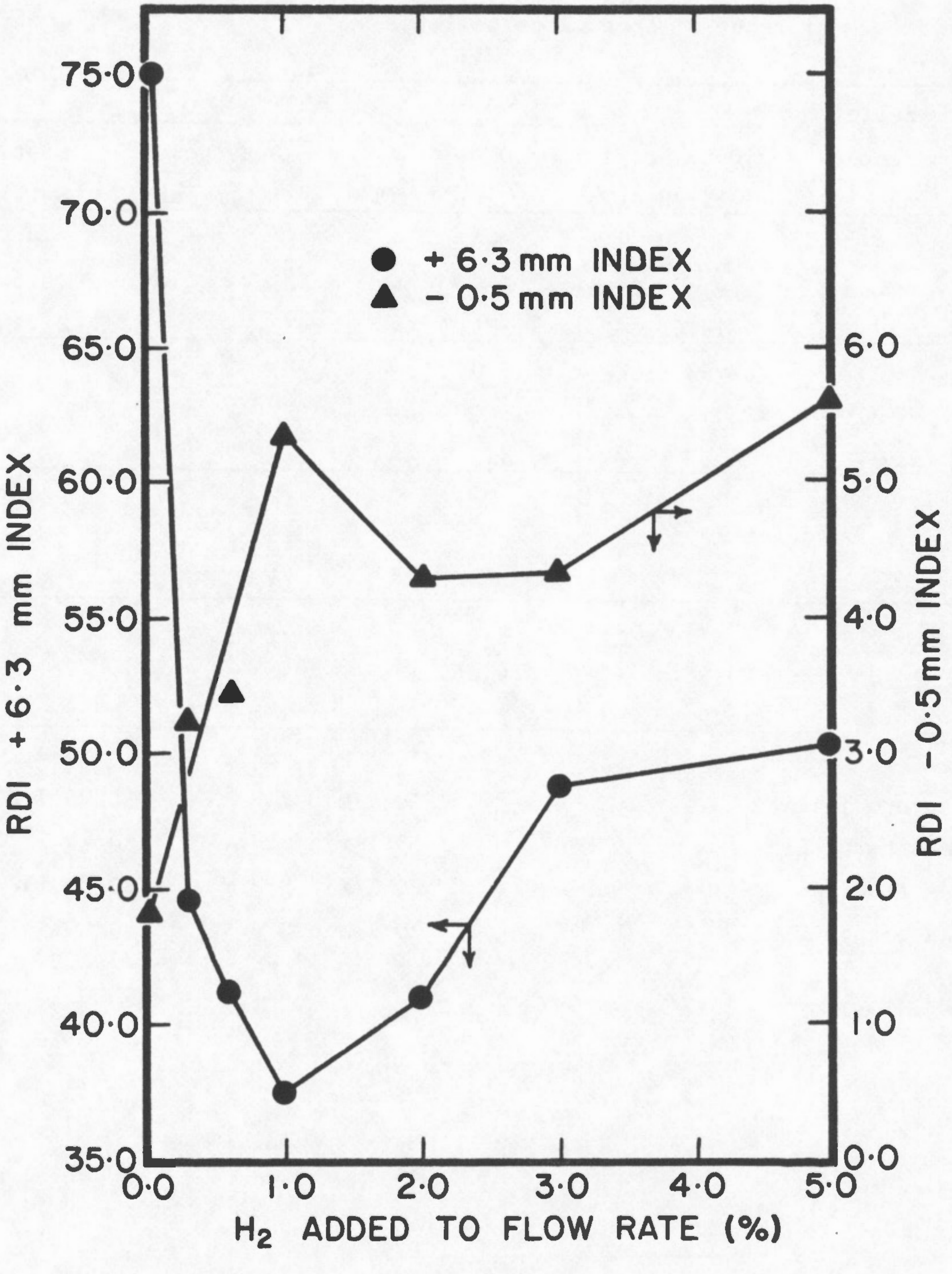

Fig.1 - Effect of hydrogen in reducing gas on RDI indices of pellet A.

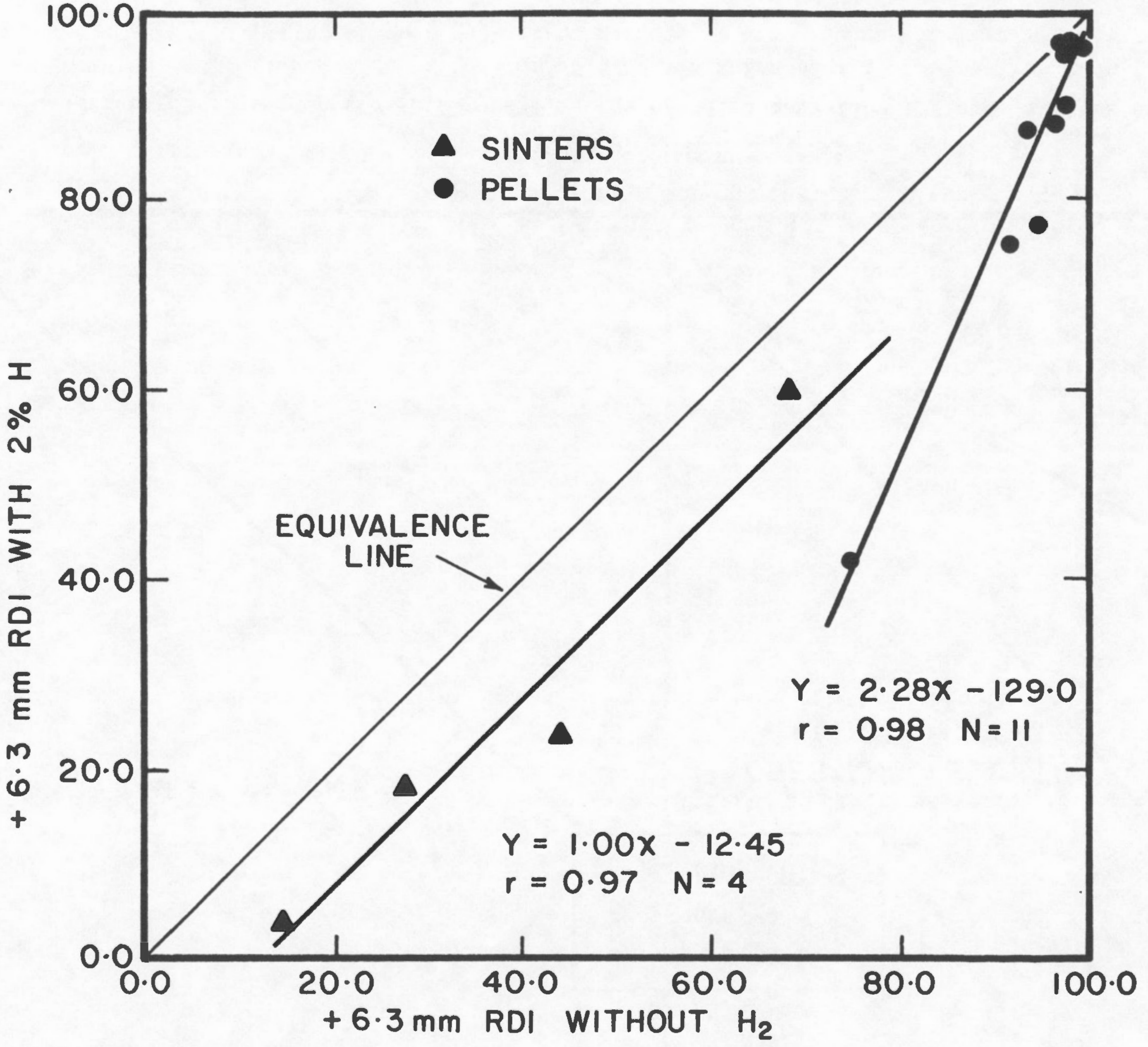

Fig. 2 - Comparison of plus 6.3 mm RDI with and without 2% H_2 included in reducing gas

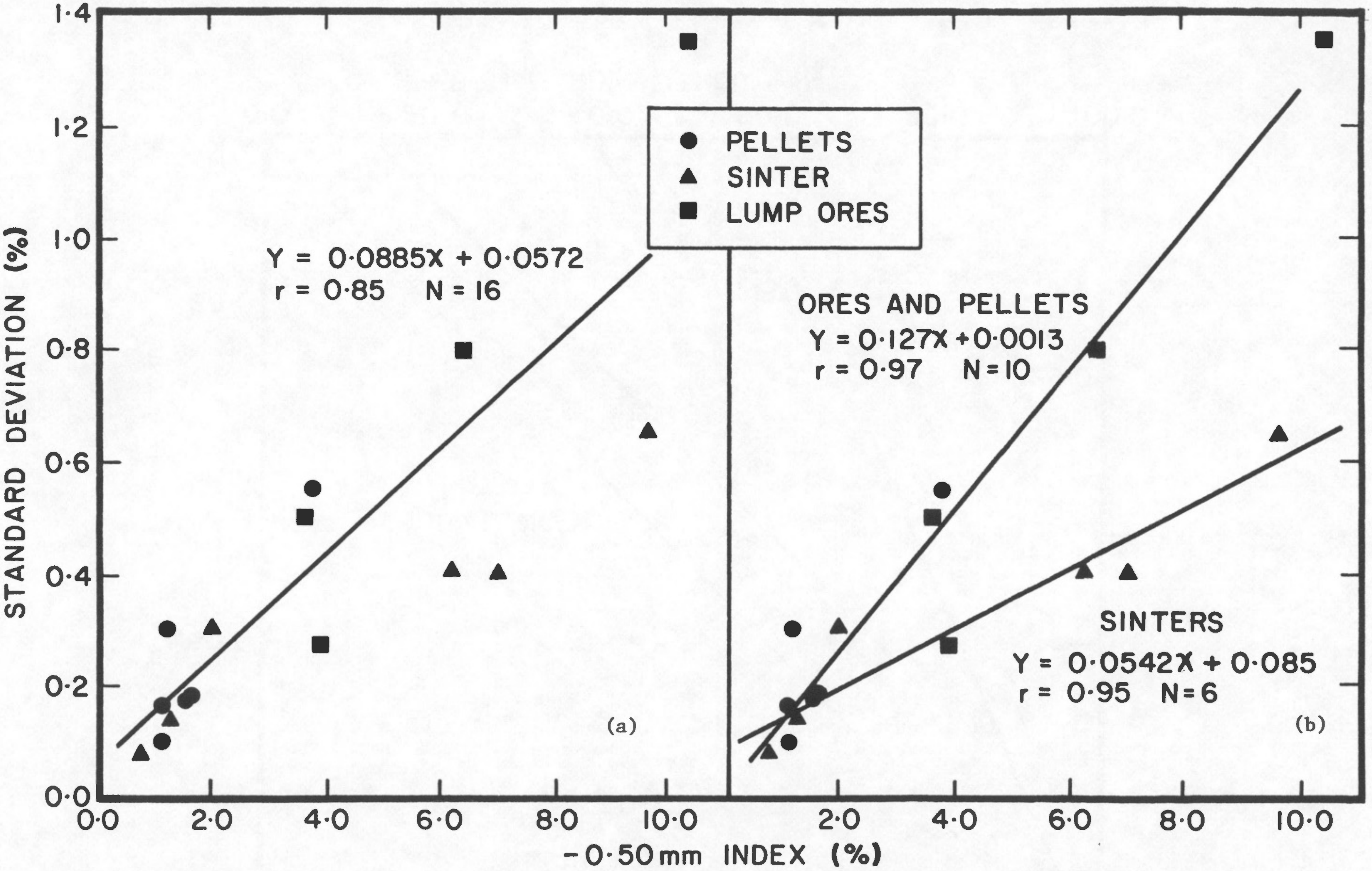

Fig. 3(a) - Effect of increases in the −0.5 mm RDI on the standard deviation for ore, sinters and pellets

(b) - Plot indicating standard deviations of −0.5 mm index for sinters may be less than for ores and pellets

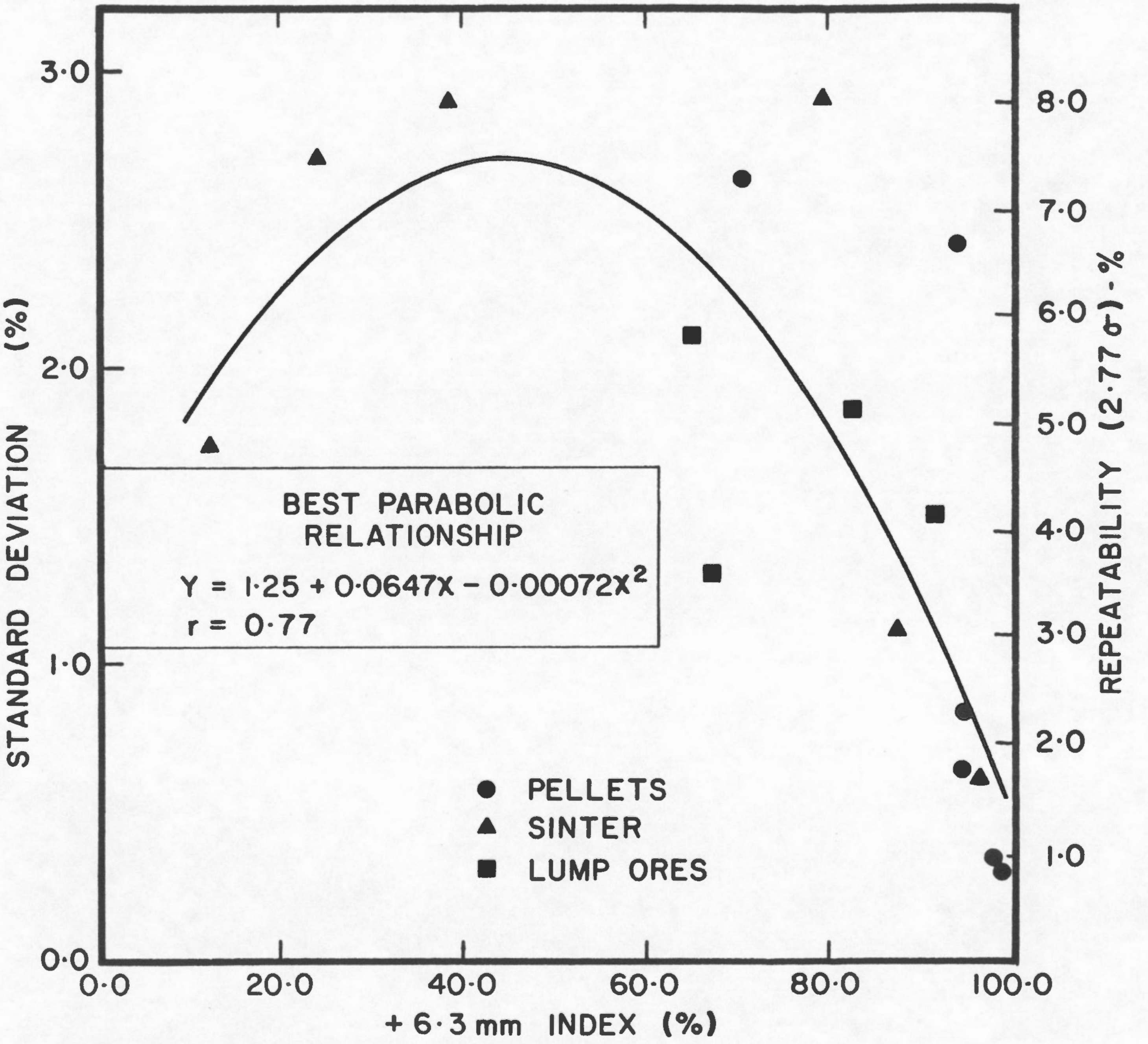

Fig. 4 - Effect of increases in the plus 6.3 mm RDI on the standard deviation and repeatability for ores, sinters and pellets.