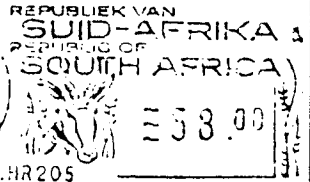
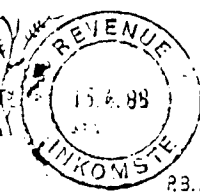


01-16-58

John & Kernick
FORM P1

7006

REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978
APPLICATION FOR A PATENT AND
ACKNOWLEDGEMENT OF RECEIPT
Section 30(1) - Regulation 39



The grant of a Patent is hereby requested by the undermentioned applicant(s) on the present application filed in duplicate

21	01	Official application No.	22	Lodging date	J&K Reference
		882581		13th April, 1988	P 10114 ZA/Mvs

71 Full Name(s) of applicants:
COUNCIL FOR MINERAL TECHNOLOGY . A legal body organised and existing under the laws of the Republic of South Africa.

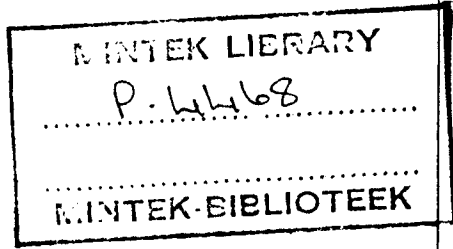
Address(es) of applicant(s)
200 Hans Strijdom Avenue, Randburg, Transvaal Province, Republic of South Africa

54 Title of Invention
THE THERMAL REDUCTION OF AGGLOMERATED METALLURGICAL FEED MATERIALS WITH OXIDE COATINGS

- The applicant claims priority as set out in the accompanying form P2
- This application is for a Patent of Addition to Patent/Application No.
- This application is a fresh application in terms of S 37 and based on application no.

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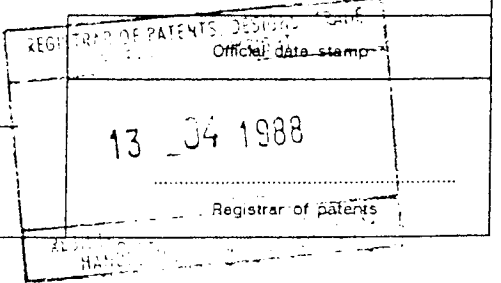
- This application is accompanied by:
- 1a A single copy of a provisional specification of _____ pages
 - 1b Two copies of a complete specification of **29** pages
 - 2a Informal drawings of _____ sheets
 - 2b Formal drawings of **5** sheets
 - 3. Publication particulars and abstract (form P8 in duplicate)
 - 4. A copy of Figure **1** of the drawings for the abstract
 - 5. Assignment of invention (from the inventors) or other evidence of title
 - 6. Certified priority documents (_____ documents)
 - 7. Translation of priority documents (_____ documents)
 - 8. Assignment of priority rights
 - 9. A copy of the form P2 and the specification of S.A Patent Application
 - 10. A declaration and power of attorney on form P3
 - 11. Request for ante-dating on form P4
 - 12. Request for classification on form P9
 - 13a Request for delay of acceptance on form P4
 - 13b



21	01	86/9654
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74 Address for Service: **JOHN & KERNICK, PRETORIA.**

Date **13th April, 1988**
Acrow
 For the Applicant



The duplicate will be returned to the applicant for service as proof of lodging but is not valid unless endorsed with official stamp.

COMPLETE SPECIFICATION

(Section 30(1) - Regulation 28)

21	01	Official application No.	22	Lodging date	J&K Reference
		882581		13th April, 1988	P 10114 ZA/MvS
51		International classification			
		C22B.			
71	Full Name(s) of Applicant(s)				
	COUNCIL FOR MINERAL TECHNOLOGY . A legal body organised and existing under the laws of the Republic of South Africa.				
72	Full name(s) of Inventor(s)				
	Robert Christopher NUNNINGTON, Robert Andrew FEATHERSTONE, Nicholas Adrian BARCZA				
54	Title of invention				
	THE THERMAL REDUCTION OF AGGLOMERATED METALLURGICAL FEED MATERIALS WITH OXIDE COATINGS				

- 1A -

"THE THERMAL REDUCTION OF AGGLOMERATED METALLURGICAL
FEED MATERIALS WITH OXIDE COATINGS"

FIELD OF THE INVENTION

THIS INVENTION relates to the solid state thermal reduction of agglomerated metallurgical feed materials under oxidising furnace conditions and, more particularly, relates to agglomerated metallurgical feed materials in which the material to be reduced is sub-divided and mixed with a solid reductant, and optionally any required fluxes or other additives, prior to agglomeration.

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More particularly, but not exclusively, the invention is concerned with the reduction of agglomerated feed materials comprising iron and chromium oxides such as chromites, iron oxides such as hematite, and mixtures thereof, manganese oxide, vanadium oxide, or any other carbothermically reducible oxide, using a carbonaceous reductant such as coal, preferably in the form of anthracite, char or other carbonaceous reductant in a step which is usually referred to as a pre-reduction step preparatory to effecting melting and slag/metal separation in a suitable furnace.

Still more particularly the invention relates to such reduction process which can be carried out in oxidising furnace atmospheres with a high content of CO₂ (carbon dioxide) or high CO₂ and oxygen or both.

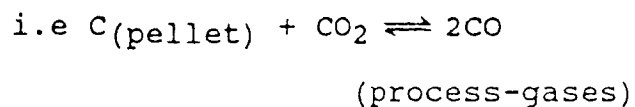
BACKGROUND TO THE INVENTION

In the solid state reduction of agglomerated finely

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sub-divided oxide material to be reduced together with a carbonaceous reductant, and any required fluxes or other additives, the agglomerated material is generally, after being prepared and cured, subjected to the action of off-gases from a combustion process in order to heat and/or reduce them. Such off-gases contain, in various different proportions, carbon-monoxide and carbon dioxide and can even contain free oxygen. Accordingly, the performance of the reduction reaction is seriously affected by such gas composition.

In particular, oxidation of carbon reductant in the pellet can occur as a result of reaction with carbon-dioxide contained in the process-gases to produce carbon monoxide by the so-called Boudouard reaction:



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The consequences of this reaction are two-fold. Firstly, removal of carbon from the pellet diminishes the amount of potential reductant available for prereduction and metallization of, for instance, chromium and iron species contained in the chromite or iron oxide present in the pellet. Secondly, an incompletely combusted gas (carbon monoxide) is generated which must be either rerouted elsewhere for combustion to realise the available sensible and thermochemical energy, or be flared off to waste.

In addition, reoxidation of the metallised Ferrochromium may occur as the conditions become less reducing within the pellet due to the carbon being oxidised. The oxidised ferrochromium is often identified microstructurally by the presence of sesquioxide laths ($\text{Al}_2\text{O}_3 \cdot \text{Cr}_2\text{O}_3$) adjacent to residual metallic blebs.

Presently used for the purpose of prereducing, for example hematite ore or chromite, are shaft and rotary furnaces which operate at CO_2 : CO ratios of about 1:10 and 2:1

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respectively. This represents a poor utilization of the fuel used for generating the necessary thermal energy for the process to take place.

It is the object of this invention to provide a process whereby the adverse effects of such Boudouard reaction between carbon and the CO₂ in the process gases which are in close contact with the agglomerated material can, at least to some noteworthy extent, be diminished with resultant more efficient use of thermal energy available from the heating fuel.

SUMMARY OF THE INVENTION

In accordance with this invention there is provided a process for the reduction of agglomerated metallurgical feed material composed of a sub-divided material to be reduced in admixture with a sub-divided solid carbonaceous reductant and wherein the units of agglomerated material are coated with a layer of oxide material chosen to

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inhibit at least contact between the components of the agglomerate and any component of heating gases employed for heating same which may react in a deleterious manner therewith, the reduction process being carried out in an atmosphere containing process gases in which the ratio of CO_2 to CO is at least 3 :1.

Further features of the invention provide for the reduction to be a prereduction step carried out at temperatures of from between 1200 to 1500°C, preferably at about 1300°C; for the agglomerate to be in any suitable form such as pellets, briquettes or the like; for the material to be reduced to be finely sub-divided oxides of chromium, iron or both, and in particular for such material to be a chromite ore; for the reductant to be a carbonaceous reductant, in particular anthracite, coal, coke, coal char or charcoal; for the agglomerate to optionally include any required flux additions; for the material coating the units of agglomerate to be either a coating of a specific oxide, or mixtures of suitable

/....

oxides; and for the heating to be carried out in process gases which have a CO₂:CO ratio of at least 5:1, and even more than 10:1 and up to 100:1 and which may contain additionally uncombined oxygen.

The material used for forming the coating is usually finely sub-divided and mixed with a suitable binder prior to formation of the layer thereof on the outside of the units of agglomerate. The formation of such a layer may conveniently be carried out by adding the coating material to a conventional pelletizing apparatus together with preformed pellets where the agglomerate is in the form of pellets.

The thickness of the coating layer is preferably of the order of up to 1,5mm. In any event, the quantity of the coating material will usually not be more than 50% by mass of the total weight of the coated pellet and will usually be of the order of 15% to 20% and preferably about 10%.

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Coatings may be obtained by any other convenient means for example dipping the agglomerate in a slurry or dusting the coating material onto the surface.

In the case of preformed agglomerates of chromite together with a carbonaceous reductant such as anthracite and fluxes, the preferred coating material based on research carried out to date is refractory grade andalusite employed together with a binder, which was preferably a bentonite clay binder, although other materials have been shown to be effective, although to a lesser extent.

Other oxide coating materials include tabular alumina, Portland cement, used alumino-silicate brick and refractory alumino-silicate cements (and mixtures thereof). Tests conducted to date have indicated that the coating materials must be chosen carefully as some materials operate better than others and some are difficult to form into an unbroken layer on the agglomerate units without excessive cracking or peeling,

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or otherwise without resulting in adverse effects during the processing of the agglomerate such as, fusion for example.

In order to demonstrate the operation of this invention, the results of a few selected tests will now be described with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings :-

FIGS. 1 & 2 are each graphs of the individual metallization of iron (Fe) and chromium (Cr) after 180 minutes treatment at 1300°C of a pelletized chromite feed material without a coating of this invention in a gaseous atmosphere composed of various ratios of carbon-dioxide and carbon-monoxide;

/.....

FIG. 3 is a similar graphical illustration wherein coated pellets were heated in a similar range of carbon monoxide to carbon dioxide ratios to those in Fig. 2 and in air;

FIG. 4 is a graphical illustration of metallizations wherein coated pellets were heated in an air at 1300°C, the graph being plotted as % metallization vs. time; and,

FIG. 5 is a graphical illustration of metallization achieved with different temperatures in respect of iron in a hematite anthracite pellet coated with andalusite.

DETAILED DESCRIPTION WITH REFERENCE TO THE DRAWINGS

Initially tests were carried out on two somewhat different

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recipes of a chromite ore with finely sub-divided anthracite as a reductant, the chromite, anthracite and fluxes having a particle size such that approximately 75% passed through a 74 μ m (ie. a 200 mesh) sieve.

The two recipes are detailed in Table 1 and it will be noted that they include granite and fluor \ddot{s} par fluxes which have been found to give enhanced reduction of chromite and have been described fully in our South African patent no. 87/5774 entitled "Process for enhanced reduction of Chromite". However, these pellets do not necessarily have to contain the fluxes for the coatings to work.

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TABLE 1

Pellet Compositions (Mass %)

	Recipe 1		Recipe 2	
	(proportions)		(proportions)	
Mooinooi chromite	65,4	(100)	56,6	(100)
Grinaker anthracite	19,6	(30)	28,3	(50)
Granite	9,8	} (20)	8,5	} (20)
Fluorspar	3,3		2,8	
Bentonite	<u>1,9</u>		<u>3,8</u>	
+ Moisture (%)	10,1		11,8	

NB. Figures in brackets relate proportions
of anthracite and total fluxes to chromite (100).

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The recipes were mixed in plastic drums with a light ball charge by tumbling them. Pellets were then formed in a disc pelletizer by the addition of a controlled amount of water followed by 8 - 12 hours air drying and oven drying at 110°C for approximately 12 hours.

The uncoated pellets were then heated isothermally in various different gas mixtures of carbon monoxide and carbon dioxide at 1300°C and the process was monitored with an on-line data logging facility. The various different gas mixtures that were used are as follows:-

Vol % CO	100	95	85	75	50	25	0
Vol % CO ₂	0	5	15	25	50	75	100

and the results are illustrated graphically in Figs. 1 and 2 for the two pellet compositions after heating for 180 minutes in the above gas atmospheres. It will be noted that, with both pellet recipes, the metallization of both iron and chromium were extremely low at gas compositions

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in which there was less than about 60% to 70% of carbon monoxide (ie. more than 30% to 40% carbon dioxide) when compared to the case in which a 100% carbon monoxide was employed.

Pellets of the recipe type 1 described above were then coated with different materials in order to test the operation of the present invention. The following materials were tested as coating layers:-

- (i) sodium silicate (50% solution);
- (ii) Portland cement;
- (iii) tabular alumina (75% - 74 μ m) and bentonite binder;
- (iv) calcined dolomite (75% - 74 μ m) and bentonite binder;
- (v) calcined dolomite (75% - 74 μ m) and sodium silicate binder;

/.....

- (vi) calcined dolomite (75% - 74 μ m) and granite fluorspar flux and bentonite binder;
- (vii) calcined dolomite (75% - 74 μ m) and granite fluorspar flux and sodium silicate binder;
- (viii) bentonite;
- (ix) andalusite treated concentrates;
- (x) used alumino-silicate brick;
- (xi) used alumino-silicate brick and FeCr fines combined;
- (xii) a dry setting alumino-silicate mortar;
- (xiii) a standard grade alumino-silicate mortar;
- (xiv) used alumino-silicate brick and mortar combined;

/.....

(xv) smelter slag from a Ferrometals Plant.

All the coated pellets were produced from one batch of standard recipe 1 pellets which were sized to approximately 9mm in size in order to minimize coating thickness variations.

The coating materials were premixed, where applicable, and gradually added to the sized pellets in the rotating pelletizing disc. A small amount of water (or sodium silicate) was added to re-wet the pellet surfaces before adding the coating material.

The coating additions were chosen to give a coating thickness of approximately 1mm. The pellets were then dried at 110°C for approximately 12 hours.

Some coating materials proved to be unsuccessful in that the coating tended to peel and crack excessively during

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the oven drying. These materials are those numbered (iv) to (viii) above which included dolomite and bentonite.

Of the remaining coating materials the andalusite layer was the most successful and the metallization of chromium and iron after heating the coated pellets in an identical manner to the uncoated pellets (ie. at 1300° C for 180 minutes) is shown for andalusite coatings in Fig. 3.

Calculations of % metallization for Cr and Fe were carried out as follows:-

Metallization and mass balance calculations

$$\text{Cr metallization (\%)} = \frac{\text{CL} \times \text{FM/LM}}{\text{IM} \times \text{A}} \times 100 \quad (\text{C})$$

$$\text{Fe metallization (\%)} = \frac{\text{FL} \times \text{FM/LM}}{\text{IM} \times \text{B}} \times 100 \quad (\text{D})$$

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$$\text{Total metallization (\%)} = \frac{(\text{CL} \times \text{FM}/\text{LM}) + (\text{FL} \times \text{FM}/\text{LM}) \times 100}{(\text{IM} \times \text{A}) + (\text{IM} \times \text{B})}$$

$$\text{Cr recovery in residue (\%)} = \frac{\text{CR} \times \text{RM} \times 0,01 \times \text{FM}/\text{LM} \times 100}{\text{IM} \times \text{A}} \quad (\text{E})$$

$$\text{Fe recovery in residue (\%)} = \frac{\text{IR} \times \text{RM} \times 0,01 \times \text{FM}/\text{LM} \times 100}{\text{IM} \times \text{B}} \quad (\text{F})$$

Deviation from closed mass balance

$$\text{Cr (\%)} = [\text{C} + \text{E}] - 100$$

$$\text{Fe (\%)} = [\text{D} + \text{F}] - 100$$

where CL = mass of dissolved Cr (metal) in leach
solution (g)

FL = mass of dissolved Fe (metal) in leach
solution (g)

FM = final mass of sample (g)

/.....

LM = mass of sample used for leaching (g)

IM = initial mass of sample (g)

RM = mass of leach residue (g)

CR = % Cr in residue

IR = % Fe in residue

A = mass of Cr from chromite in base pellet/g
coated pellet (g)

B = mass of Fe from chromite in base pellet/g
coated pellet (g)

For those pellets the coating amounted to about 26% by mass of dry coated pellets. It was observed that a coating of andalusite gave a suitable layer with respect to its physical integrity and with respect to the metallization of chromium and iron where approximately 97% of the iron and 57% of the chromium were metallized even in a 100% carbon dioxide atmosphere. In comparison with results for the uncoated pellets (Fig. 1) chromium metallization is significantly improved with andalusite coated pellets, even in a 100% carbon dioxide atmosphere,

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while iron metallization was found to be almost independent of gas composition.

It will, however, be noted that the extent of chromium metallization was still to some extent dependent on the gas composition. It appears that once the oxide coating has sintered sufficiently, metallization can proceed in the inner (core) pellet even with 100% carbon dioxide gas compositions. The carbon monoxide reaction product gas can, nevertheless, escape through the coating and can itself be combusted to CO_2 by introducing additional oxygen thereby increasing the energy available to the process.

Furthermore, experimental work has indicated that the nominal particle size for both base pellet and coating should not be finer than 75% to pass a $74\mu\text{m}$ screen, if the maximum reduction rates are to be achieved while preventing excessive sintering and shrinkage of the coating.

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The pellets which were coated with sodium silicate showed poor metallizations relative to the above. This apparently resulted from the sticking and consequent peeling of the pellets thereby exposing the carbon in the base pellet to the carbon dioxide in the gas atmosphere and, accordingly, resulting in the difficulty outlined at the preamble to this specification.

The cement coated pellets gave 60% chromium and 93% iron metallization in a 50% carbon dioxide / 50% carbon monoxide atmosphere but also suffered from significant fusion problems.

Accordingly it will be appreciated that extremely advantageous results can be achieved using the present invention but that the coating material must be chosen carefully as will be clear from the difficulties experienced in some cases outlined.

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When compared to the andalusite coatings, the other oxide coatings tended to show increased pellet core shrinkage, lower metallizations and somewhat higher sensitivity to the proportion of carbon dioxide in the gas composition. Nevertheless, highly advantageous results can be obtained using such oxide coatings when compared to the uncoated pellets.

Further experiments have shown that the andalusite coatings are effective even in the presence of free oxygen in the furnace atmosphere (Fig. 3) and even higher levels of chromium metallization are attained after 3 hours at 1300° C in air (approximately 79%) when compared with heating in 100% CO₂. Fig. 4 details the increase in metallization of chromium and iron with time for andalusite coated recipe 1 pellets under air at 1300° C. It can be seen that the final metallization levels of 95% iron and 79% chromium are essentially achieved after only 2 hours.

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With regard to iron oxide reduction, experiments have been conducted at temperatures between 800°C and 1000°C where hematite and anthracite based pellets were coated with andalusite and heated in a 100% CO₂ atmosphere. Pellet compositions are indicated in Table 2, while Fe (iron) metallizations are indicated in Fig. 5 which show that 100% Fe metallization was achieved after 180 minutes treatment under 100% CO₂ at 900°C.

TABLE 2

Andalusite coated hematite pellet composition

<u>Base Pellet</u>	<u>Mass %</u>	
Hematite	71,6	<u>N.B.</u>
Anthracite	26,4	1) All material sized to 75% - 74µm
Bentonite	2,0	2) Coating addition = 26% of dry coated pellets
 <u>Coating</u>		
Andalusite	98	
Bentonite	2	

The invention therefore provides a highly effective expedient for use in the reduction of pelletized feed materials mixed with a solid reductant and wherein contact between such solid reductant and the gases being used to heat same, in a solid state reduction process, is inhibited, at least to some measurable extent.

Furthermore the useful sensible energy in hot oxidising gases and the chemical energy in combustible gases which hitherto could not be used for heating and reducing oxide materials can now be employed and complete combustion of fuels (gaseous, liquid or solid) to the fully oxidised form can now be carried out thereby utilising all the available energy of combustion which can realise fuel (coal) savings of up to 36% by mass. Even the presence of free oxygen in the furnace atmosphere does not result in any loss of reduction with the protection of such oxide coatings. Thus such materials containing reducible

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oxides can be advantageously treated in for instance a shaft kiln, where the solid (or other) fuel requirement can be reduced, by combustion of, for instance, the CO present in smelter off gas (containing 60-70% by volume CO) to CO₂ thereby liberating the associated chemical (and sensible energy) contained therein.

A further advantage of such coatings is that they can inhibit pellet sticking and enhance the physical strength of the agglomerate (eg. up to a three-fold increase in the pellet drop number using a standard drop test).

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WHAT IS CLAIMED IS :-

1. A process for the reduction of agglomerated metallurgical feed material composed of a sub-divided material to be reduced in admixture with a sub-divided solid carbonaceous reductant and wherein the units of agglomerated material are coated with a layer of oxide material chosen to inhibit at least contact between the components of the agglomerate and any component of heating gases employed for heating same which may react in a deleterious manner therewith, the reduction process being carried out in an atmosphere containing

/.....

process gases in which the ratio of CO₂ to CO is at least 3 :1.

2. A process as claimed in claim 1 in which the ratio of CO₂ to CO is greater than 5:1.
3. A process as claimed in claim 2 in which the CO₂:CO ratio is greater than 10:1.
4. A process as claimed in claim 3 in which the CO₂:CO ratio is up to 100:1.
5. A process as claimed in any one of claims 1 to 4 in which uncombined oxygen is present in the process gases.
6. A process as claimed in any one of the preceding claims in which the agglomerate is in the form of pellets or briquettes.

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7. A process as claimed in any one of the preceding claims in which the material to be reduced is finely sub-divided oxides of chromium, iron or both.
8. A process as claimed in claim 7 in which the material to be reduced is a chromite ore.
9. A process as claimed in any one of the preceding claims in which the agglomerate includes flux additions.
10. A process as claimed in any one of the preceding claims in which the oxide material is a finely sub-divided material mixed with a binder therefor.
11. A process as claimed in claim 10 in which the oxide material is andalusite.
12. A process as claimed in any one of the preceding claims in which the coating constitutes no more

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than 50% by mass of the total mass of coated agglomerate.

13. A process as claimed in claim 12 in which the coating constitutes no more than 20% by mass of the total mass of coated agglomerate.
14. A process as claimed in claim 13 in which the coating constitutes from 10% to 15% by mass of the total mass of coated agglomerate.
15. A process as claimed in any one of the preceding claims in which the reduction is a prereduction step carried out at temperatures of from 1200°C to 1500°C in the case of chromium oxide containing material, or about 850°C in the case of hematite.
16. A process substantially as herein described with reference, where relevant to either of Figs. 3 and 5 of the accompanying drawings.

DATED this 14th day of APRIL, 1988


JOHN & KERNICK
For the Applicant

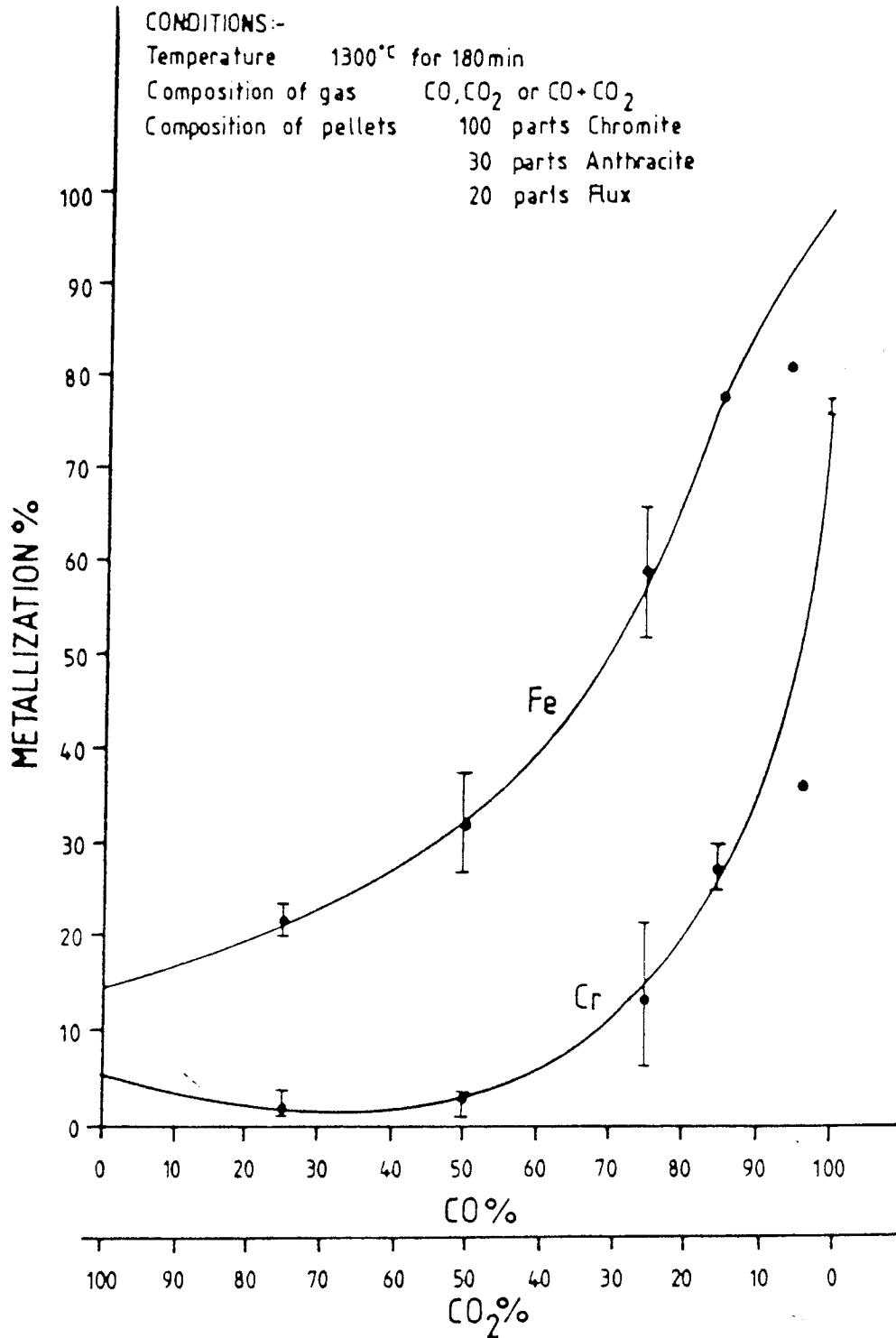


FIG 1: Metallization of Chromium and Iron in reduced pellets made according to recipe 1

[Signature]
 JOHN & KERNICK
 for the applicant

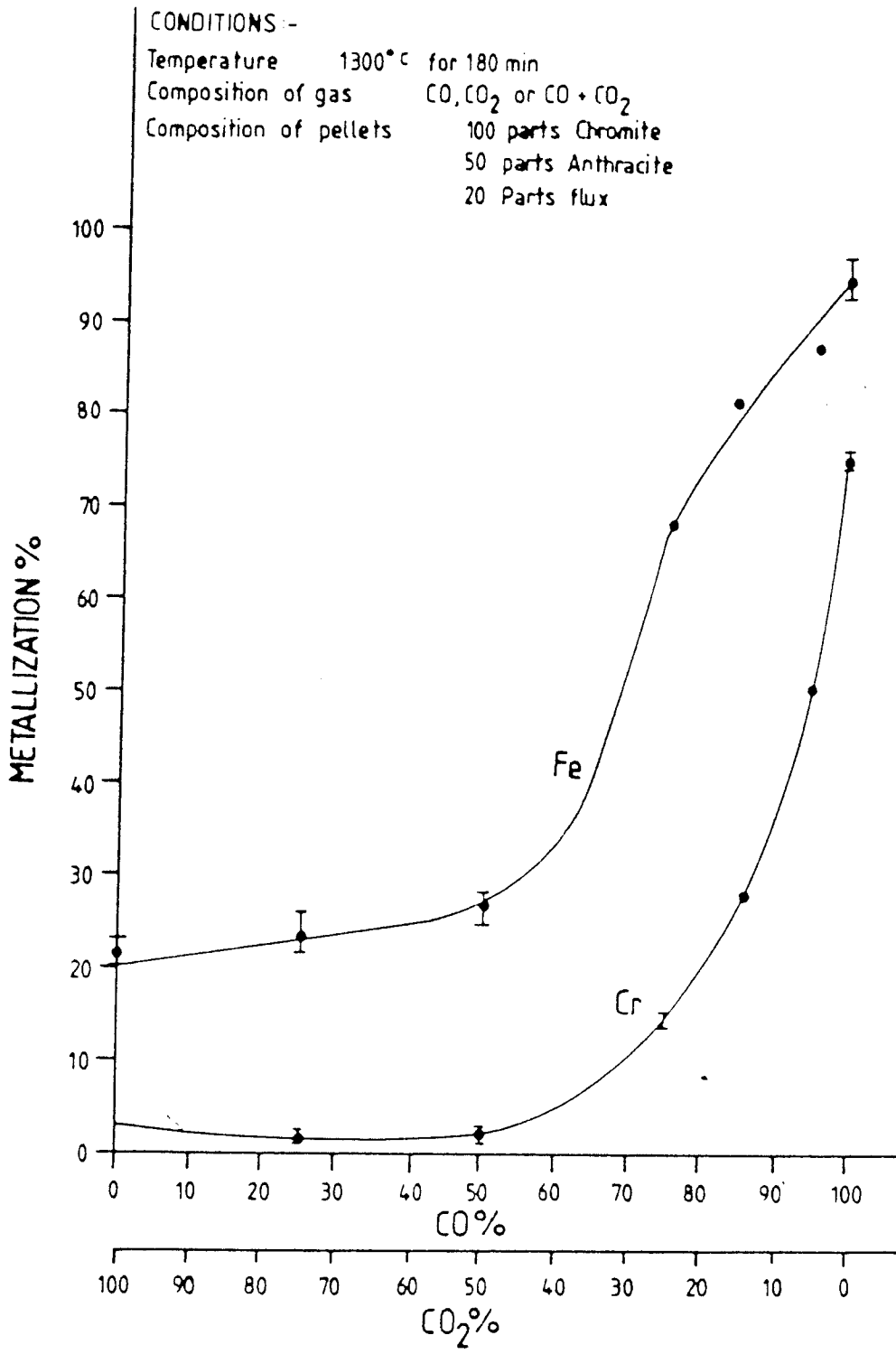


FIG2: Metallization of Chromium and Iron in reduced pellets made according to recipe 2

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 JOHN & KERNICK
 for the applicant

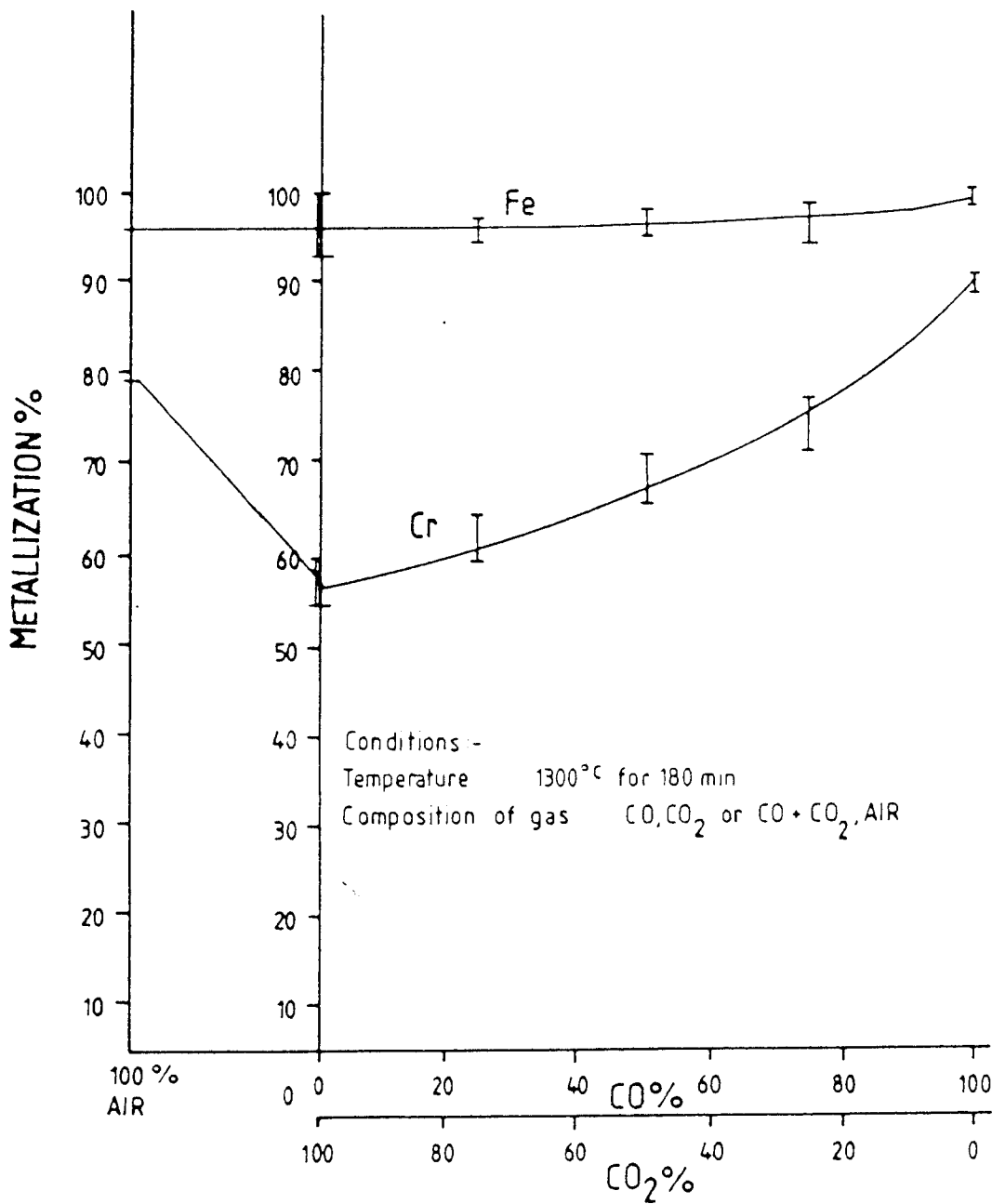
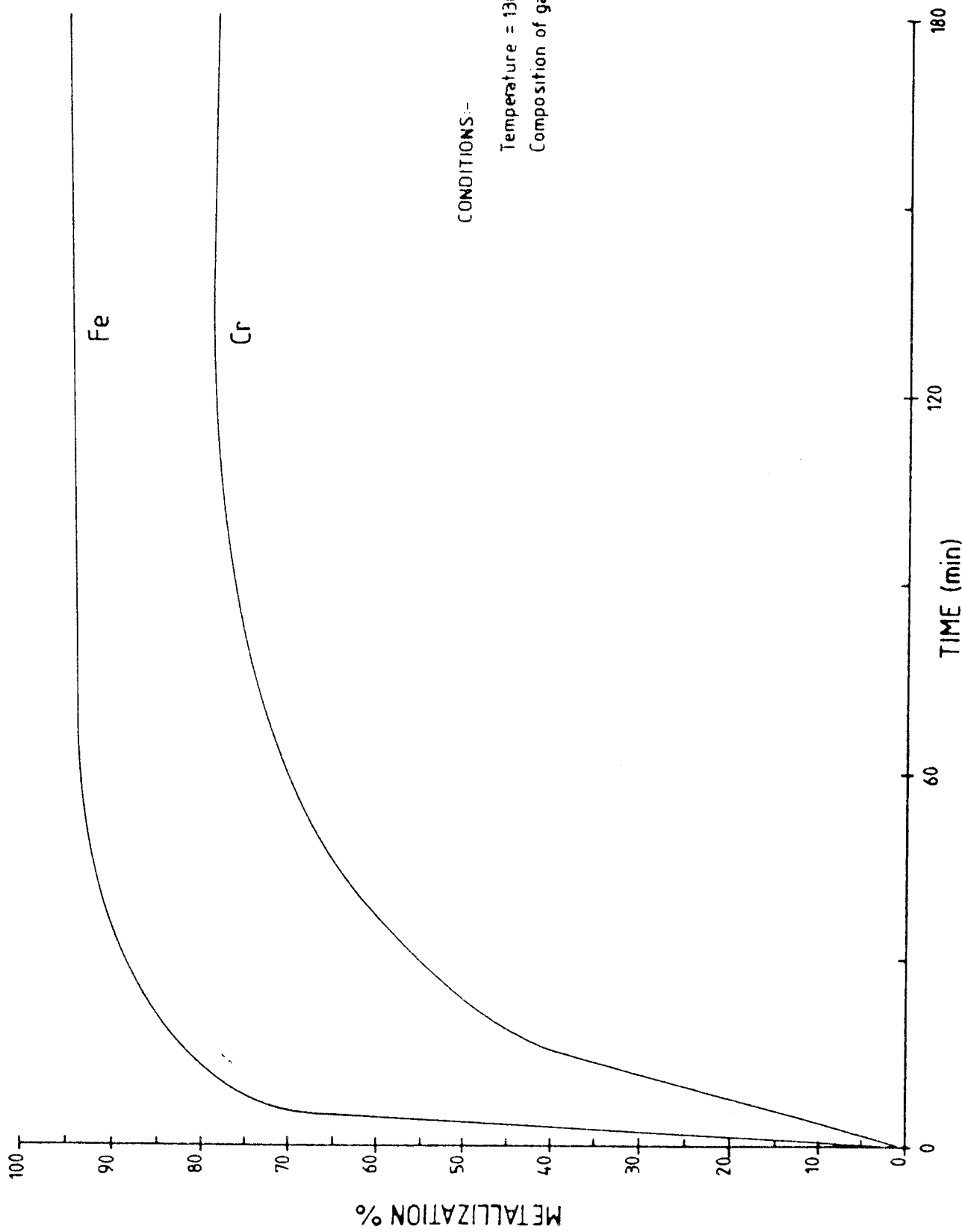


FIG3: Metallization of Chromium and Iron in reduced (Recipe 1) pellets coated with Andalusite

[Signature]
 JOHN & KERNICK
 for the applicant



CONDITIONS:-

Temperature = 1300°C

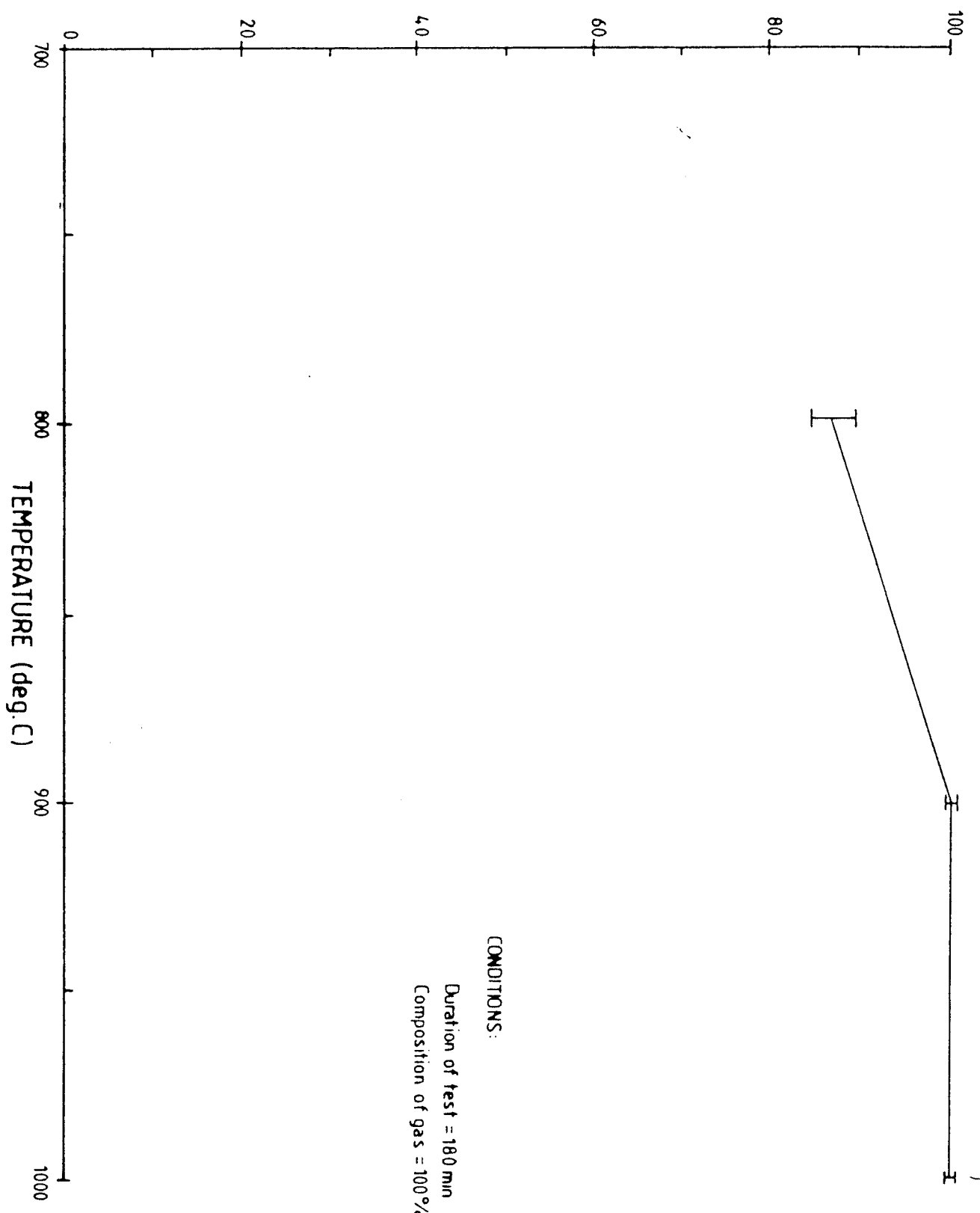
Composition of gas = 100 %

FIG 4. Metallisation of Chromium and Iron -VS- Time in reduced (Recipe 1) Pellets coated with Andalusite

John Kernick
 JOHN & KERNICK
 for the applicant

JOHN & KERNICK
for the applicant

Fe METALLIZATION %



CONDITIONS:

Duration of test = 180 min
Composition of gas = 100% CO

FIG 5. Metallisation of Fe in reduced Hematite - Anthracite pellets coated with Andalusite