

[54] **SEGREGATION PROCESS FOR BENEFICIATING NICKEL, COPPER, OR COBALT OXIDIC ORE**

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[51] Int. Cl.²..... **C22B 1/08**

[58] Field of Search..... 75/111-113,
75/82

[56] **References Cited**

UNITED STATES PATENTS

1,368,885 2/1921 Bradford..... 75/113

1,679,337	7/1928	Moulden et al.....	75/117 X
1,943,337	1/1934	Mitchell.....	75/111
2,085,114	6/1937	Mitchell.....	75/112 X
2,733,983	2/1956	Daubenspeck.....	75/82 X
3,453,101	7/1969	Takahashi et al.....	75/82 X
3,457,037	7/1969	Aramendia et al.....	75/1 X
3,466,169	9/1969	Nowak et al.....	75/113 X
3,725,043	4/1973	Kawai et al.....	75/72

FOREIGN PATENTS OR APPLICATIONS

18,763	1903	United Kingdom.....	75/112
377,705	7/1932	United Kingdom.....	75/112
301,342	11/1928	United Kingdom.....	75/112

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[57] **ABSTRACT**

An oxide ore or ore concentrate of nickel, cobalt or copper is beneficiated by means of a vapour phase process. The beneficiation is enhanced by increasing the level of the active iron oxide content to a level higher than that contained in the starting material.

4 Claims, 11 Drawing Figures

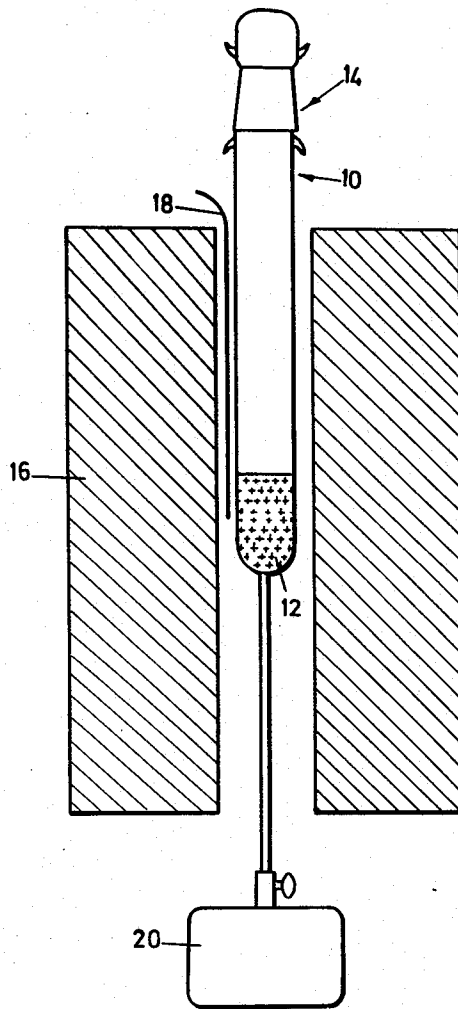


Fig. 1

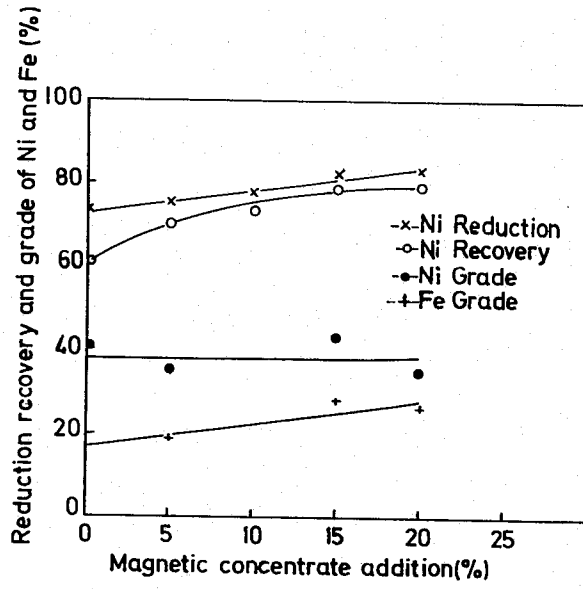


Fig. 2

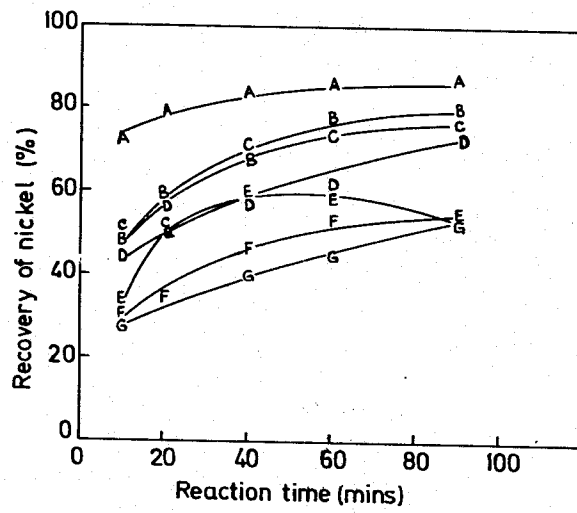


Fig. 3

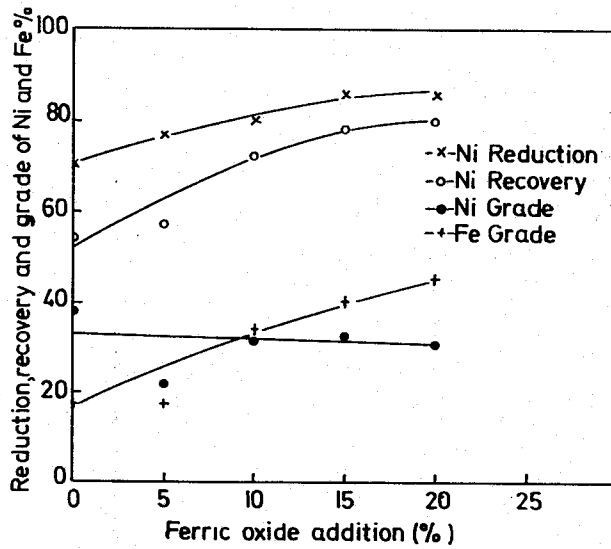


Fig. 4

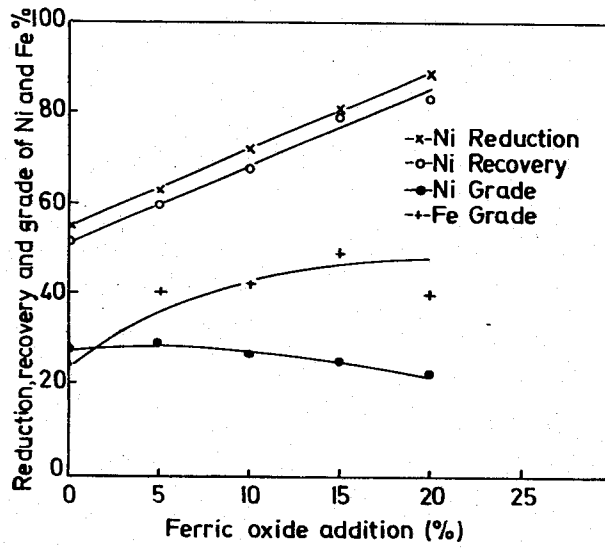


Fig. 5

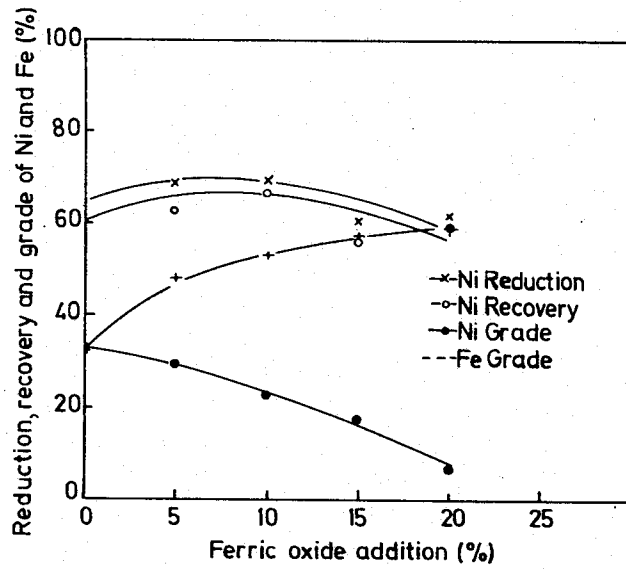


Fig. 6

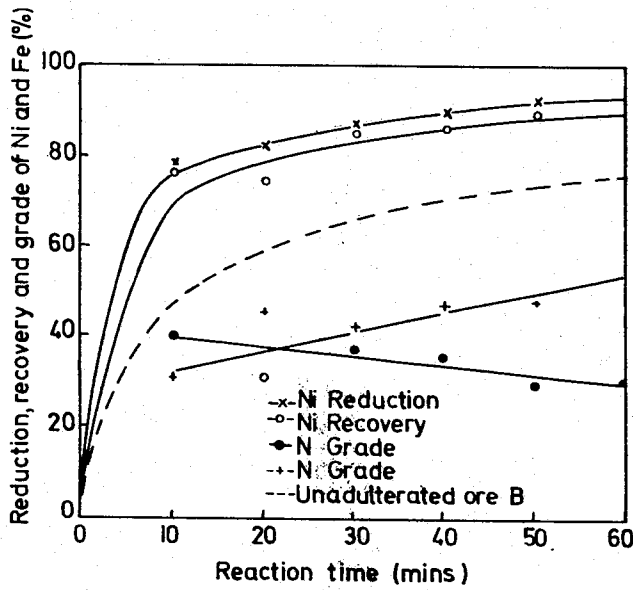


Fig. 7

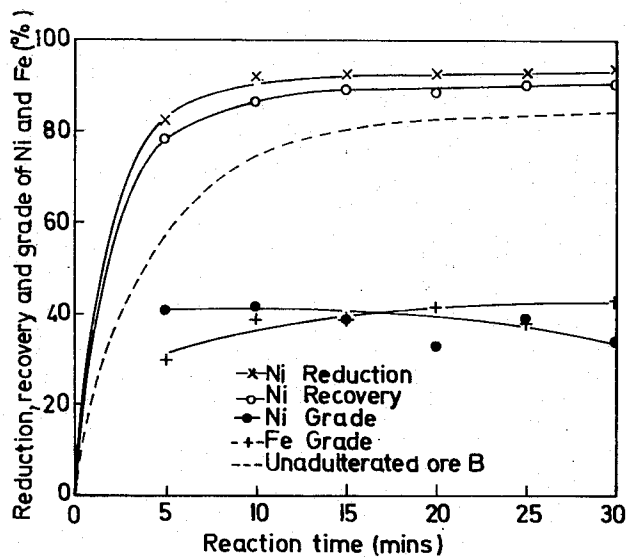


Fig. 8

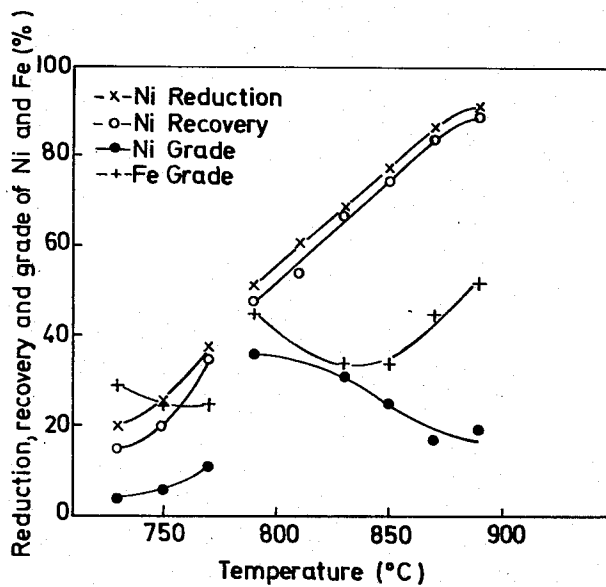


Fig. 9

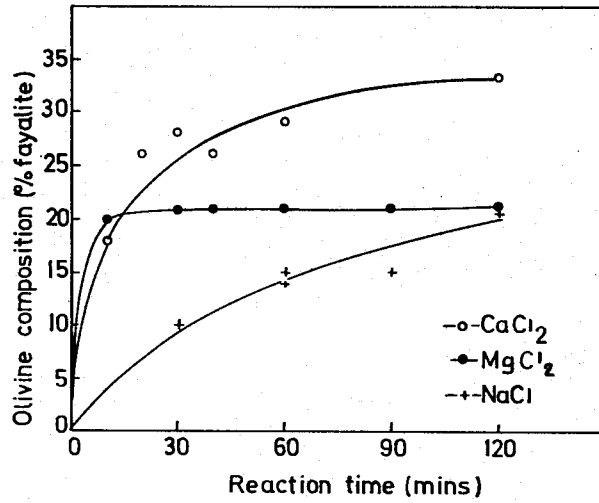


Fig. 10

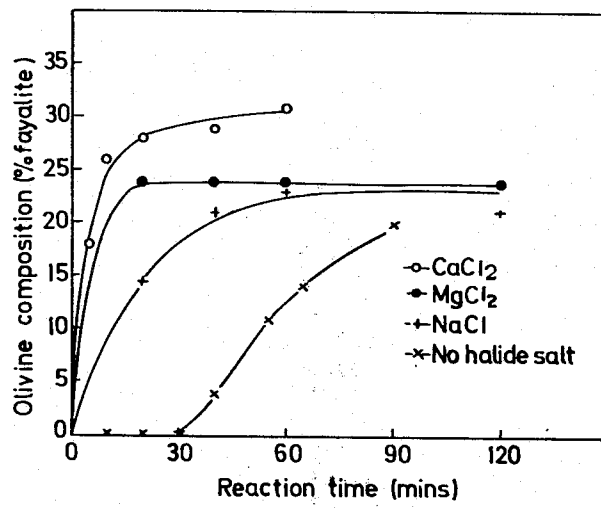


Fig. 11

SEGREGATION PROCESS FOR BENEFICIATING NICKEL, COPPER, OR COBALT OXIDIC ORE

The present invention relates to the beneficiation of oxidic materials containing nickel, cobalt, and copper, such oxidised ores of nickel cobalt or copper, by the segregation process.

The segregation process is disclosed in U.S. Pat. No. 1,679,337.

It is an object of the present invention to improve the beneficiation of such materials.

In a method of beneficiating an oxidic material containing nickel cobalt or copper, such as an oxide ore or ore concentrate of nickel, cobalt or copper, by the segregation process, comprising mixing the oxidic material with a halide salt and a suitable reductant while at an elevated temperature, the invention provides the improvement of increasing the active iron oxide content by adding ferrous or ferric oxide to the oxidic material.

The active iron oxide content can be increased by adding ferrous or ferric oxide per se or an ore containing ferrous or ferric oxide to the oxidic material.

The present invention is further discussed with reference to the following examples and accompanying drawings, in which:

FIG. 1 is a schematic illustration of a reactor for carrying out the invention.

FIG. 2 is a graph illustrating the effect of the addition of magnetic concentrate to ore B prior to segregation at 900°C: 5% CaCl₂/2% coke used as reagents, allowing 1 hour reaction time.

FIG. 3 is a graph illustrating the response of seven different garnierite-type ores to segregation at 900°C.

FIG. 4 is a graph illustrating the effect of the addition of ferric oxide to "demagnetized" ore B prior to segregation at 900°C for 1 hour.

FIG. 5 is a graph illustrating the effect of the addition of ferric oxide to ore G prior to segregation at 900°C for one hour.

FIG. 6 is a graph illustrating the effect of the addition of ferric oxide to ore F prior to segregation at 900°C for 1 hour.

FIG. 7 is a graph of reaction time data for segregation at 900°C of ore B blended with 20% of a nickeliferous laterite (1.6% Ni; 84% Fe₂O₃).

FIG. 8 is a graph of reaction time data for segregation at 1000°C of ore B blended with 20% of a nickeliferous laterite.

FIG. 9 is a graph showing nickel segregation as a function of temperature for ore B blended with 25% of a nickeliferous laterite.

FIG. 10 is a graph illustrating the effect of various halide salts on the reaction of "magnetized" ore D with 25% ferric oxide at 800°C in the presence of 3% coke.

FIG. 11 is a graph illustrating the effect of various halide salts on the reaction of "magnetized" ore D with 25% ferric oxide at 900°C in the presence of 3% coke.

The vapour phase recovery process used in the following examples was the segregation process which was carried out in the silica tube reactor illustrated schematically in FIG. 1. The reactor allowed for the addition of the segregation reagents at operational temperatures and in this reactor the ore samples were mechanically fluidised.

The reactor consists of a silica tube 10 into which the charge 12 is placed. The tube 10 is fitted with a Quick fit stopper 14 and heat is supplied by a tube furnace 16. A thermocouple 18 is provided to measure temperature. The tube 10 is vibrated by means of a vibro stirrer 20.

EXAMPLES 1 to 9

EXPERIMENTAL PROCEDURE

Seven garnierite-type ores, ground to pass a 65 mesh screen, were used. The relevant mineralogical and chemical compositions of the ores are shown in the table. The percentage fayalite in the olivine phase of the pre-roasted ore samples was determined using a Philips X-ray diffractometer, calibration being carried out according to the method of Yoder and Sahama. (Mineralogist 1957 Vol. 42 P. 473). The Ni/Fe ratios in the olivine phase of the pre-roasted ore samples were determined using an electronprobe X-ray microanalyzer.

TABLE

THE CHEMICAL AND MINERALOGICAL COMPOSITION OF SEVEN GARNIERITE-TYPE ORES							
	Ore sample (in order of segregation efficiency - see FIG. 3)						
	A	B	C	D	E	F	G
Chemical Composition:							
% Ni	1.43	1.50	1.02	0.70	0.85	1.00	1.07
% Fe ₂ O ₃	15.6	8.3	6.7	10.3	8.3	7.6	6.5
% MgO	22.3	29.7	22.9	30.8	29.3	35.6	32.5
Mineralogical Composition:							
% Lizardite		62	68	55	60	49	80
% Clino-Chrysotile		25	20	32	17		11
% Ortho-chrysotile				5	8		
% Quartz		8	15		5		
% Olivine			1		1	50	2
% Talc	70	1			2		
% Chlorite	10						
% Iron oxides	20	4	6	8	7	1	1
X-ray analysis on pre-roasted ore. (1 Hour at 900°C).							
% Fayalite in olivine	N.D.	0	0	0	0	5	2
Microprobe analysis on pre-roasted ore (1 Hour at 900°C).							
Ni/Fe X-ray intensity ratios in olivine	15	6.6	1.8	4.7	2.0	17	2.4

The ore samples were subjected to segregation in the tube reactor of FIG. 1. The vibration amplitude of the reactor was controlled by a variable transformer (0-220V), coupled to a 220V, vibro-stirrer vibrating at a frequency of 100 cycles per sec.

20gm of the ore was slowly added to the reactor (controlled at 50°C above the required operating temperature) over a period of 2 minutes, while applying 60V to the vibrator 20. This resulted in an initial lowering of the reactor temperature to the required value. The furnace controller was then reset to the desired temperature and the ore sample pre-roasted for 15 minutes while applying 100V to the vibrator. The Quickfit stopper 14 was left off during pre-roasting.

A pre-mixed calcium chloride/coke reagent (stored at 130°C) was then added to the reactor which was immediately stoppered with a well-greased Quickfit stopper, which was then secured in place. Vibration amplitude was increased by applying 180V for a further one minute in order to mix in the reagents, after which vibration was decreased by reducing the voltage to 100V. The reaction was allowed to continue for the desired time.

At the termination of the reaction, and before removing the reactor from the furnace, the stopper was securely seated so as to avoid any subsequent ingress of air. The reactor with its contents was then quenched in water and allowed to cool. The quenched product was wet-ground for 15 minutes in a mechanical mortar, and magnetic concentration of the segregated nickel-iron alloy produced carried out on the complete charge.

Unless otherwise stated, segregation was carried out using 5% C.P. calcium chloride and 3% minus 100 plus 200 mesh coke (4.2% volatile content).

EXAMPLE 1

A small magnetite/chromite fraction (6% by weight and containing 33% Fe and 8% Cr₂O₃) was removed magnetically from ore B prior to segregation in an attempt to effect higher nickel grades. However, this removal to the contrary resulted in nickel recoveries decreasing considerably on subsequent segregation at both 900°C and 1000°C. At 1000°C recoveries fell from 92 to 75%, while at 900°C a decrease from 64 to 61% was observed. Reduction to metallic nickel was likewise also adversely affected, although nickel grades were marginally better. Conversely, the addition of the same magnetic concentrate to ore B prior to segregation at 900°C resulted in nickel recoveries increasing from 61 to 79% (FIG. 2). Nickel reduction also appeared to increase substantially, but nickel grades were not affected to any great degree.

EXAMPLE 2

The seven sample ores were subjected to segregation at 900°C. The results are shown in FIG. 3 which illustrates their respective responses as a function of reaction time. It is immediately apparent that ore A with the highest free ferric-iron oxide content segregates most efficiently under the prescribed conditions, while ore G containing the lowest free iron oxide content displays the poorest segregation characteristics.

EXAMPLE 3

In order to confirm the above findings and to assess the part played by the mineralogical composition and more specifically the role played by iron oxide in nickel segregation, further investigation entailed the addition of ferric oxide to a selection of ores prior to segregation. In the first instance, three ores were selected on the basis of microprobe analysis in which the Ni/Fe ratios in the serpentine phase were widely divergent viz. high, medium and low. Ores F, B and G were thus chosen. Ore B, however, was demagnetized using a Jones Magnetic separator resulting in the total iron content decreasing from 8.3 to 4.7% Fe₂O₃. Secondly, chemical grade ferric oxide was used as a source of iron oxide rather than a magnetic concentrate to allow a better assessment of the subsequent response of the above ores to segregation.

The effect on segregation of the addition of ferric oxide to the above ores prior to segregation at 900°C is shown in FIGS. 4, 5 and 6. In the case of "demagnetized" ore B (FIG. 4) an almost linear increase in nickel recovery from 54 to 80% may be noted as the iron oxide concentration in the system is increased. The response of ore G to similar additions of ferric oxide (FIG. 5) is even more marked with nickel recoveries increasing from 51 to 84%. A corresponding increase in reduction to metallic nickel may also be noted in each case.

The response of ore F to iron oxide additions (FIG. 6.) illustrates a marked difference when compared with the above findings. Not only are the relative increases in nickel recoveries and reductions very much smaller on adding up to 10% ferric oxide, but further additions of ferric oxide actually result in decreased recoveries and reductions. While nickel grades are not adversely affected by high ferric oxide additions in the case of ores B and G (FIGS. 4 and 5), nickel grades are seriously affected by such additions in the case of ore F. This poor response of ore F to ferric oxide additions may be attributed to the unreactive nature of the large primary olivine phase already containing 5% fayalite found to be present in the original ore. The above results adequately demonstrate that iron oxide additions result in increased nickel recoveries at 900°C.

EXAMPLE 4

The effect of iron oxides on the kinetics of the segregation reaction was also examined. FIGS. 7 and 8 illustrate the segregation of ore B blended with 20% of a nickeliferous laterite (1.6% Ni; 84% Fe₂O₃), as a function of reaction time. Segregation was carried out at 900° and 1000°C respectively. When these data are compared with the segregation of the unadulterated ore B under similar reaction conditions (see dotted lines in FIGS. 7 and 8), a very significant increase in reaction rates is observed.

EXAMPLE 5

The recovery of nickel, as a function of temperature, from a garnierite-type ore containing optimum additions of iron oxide was investigated between 730° and 890°C (FIG. 9). Here ore B has been blended with 25% of a nickeliferous laterite (1.6% Ni; 84% Fe₂O₃). Segregation was carried out for 90 minutes using 5% coke

and 5% of a fusion mixture of calcium chloride and sodium chloride (80 mole % CaCl_2 ; m.p. 660°C). In the light of experience gained a higher coke addition was indicated in this case, because of the lower segregation temperatures employed. Likewise a lower melting point halide salt was used so as not to confuse the resulting data with any melting point effects (CaCl_2 m.p. 772°C).

The results shown in FIG. 9 show nickel recoveries increasing from 15% at 730°C to 89% at 890°C with a marked break in the overall data trends between 770° and 790°C .

EXAMPLE 6

FIGS. 10 and 11 show the effect of reacting demagnetized ore D (6.0% Fe_2O_3 ; 37.3% MgO ; 39.7% SiO_2) with 25% ferric oxide at 800° and 900°C respectively in the presence of 3% coke using various other chloridizing agents (the concentration of the halide salt was maintained at 5%). From the resulting kinetics, it is immediately apparent that calcium chloride is far more efficient in promoting the formation of fayalite than either sodium or magnesium chloride under the prescribed reaction conditions. Similar findings were also observed at 1000°C .

It may be also noted that whereas calcium chloride effects a fayalite content of up to 33% which corresponds approximately with the complete reaction of the added ferric oxide, both magnesium and sodium chloride are not capable of promoting the reaction beyond 24% fayalite.

EXAMPLE 7

The blending of a nickeliferous laterite with ore B prior to segregation has already been described in Example 4 and significant increases in reaction rates were observed when compared with the unadulterated ore B. Subsequent experiments in which ore B was blended with (a) a pre-roasted nickeliferous magnetite (1.0% Ni; 92% Fe_3O_4) and (b) a pre-roasted pyrrhotite concentrate (2.0% Ni; 45% Fe) also yielded similar improvements in nickel recoveries after segregation. The pre-roasting of the ores was found to be necessary in each instance in order to convert the iron present into a readily active oxide.

EXAMPLE 8

When Malagasy laterite was added to Wedza ore it was found that the recovery of nickel in the segregation process at 950°C increased from 81 to 91%. The optimum proportions for the mixture seem to be 20% Malagasy laterite to 80% Wedza ore.

It would also seem that the use of iron oxide enables lower temperatures to be used in the segregation process. At 850°C the normal recovery of nickel is very poor, about 47%. However, with the addition of 20% of Malagasy laterite the nickel recovery was increased from 47 to 81%.

EXAMPLE 9

In an experiment a Bechtel magnetite concentrate containing 1% nickel from asbestos tailings, was pre-roasted for 16 hours at 1100°C to oxidise to hematite i.e., a conversion from Fe_3O_4 to Fe_2O_3 .

This pretreated Bechtel ore was then added to demagnetised Wedza I ore, containing about 1.57% Ni.

and the mixture segregated at 1000°C for 60 mins. using the segregation process.

The results obtained are set forth in the following table:

% Bechtel Ore Added	Overall % Ni Recovery	Ni Grade
5	81.5	28
10	87.6	10.3
15	81.0	20.5
20	92.2	14.6

The above table shows that an increase in the amount of pretreated Bechtel ore concentrate added results in a corresponding increase in the nickel recovery for the range covered. However this improvement was not observed using Bechtel which was not pretreated.

It has also now been found that if a pre-roasted sample of a sulphide type ore, e.g. pyrrhite is added to a garnierite type ore, an improvement in the overall recovery of nickel is obtained.

EXAMPLE 10

In an example Tati rougher concentrate was roasted in the presence of air up to 900° in order to remove sulphur. The composition of the roasted ore was as follows:

45% Fe; 2.04% Ni; 0.34% Cu and 0.09% S.

The roasted Tati concentrate was blended with Wedza I (30% Tati concentrate) and segregated at 1000°C in a vibrating tube reactor for 60 mins., using 5% CaCl_2 and 3% coke.

Following magnetic concentration of the segregated charge, the following recoveries were recorded:

91% overall recovery of nickel at a grade of 33%
88% overall recovery of copper at a grade of 1.8%
14% overall recovery of iron at a grade of 53%.

EXAMPLE 11

Tenke Fungurume ore was segregated at 900°C for 1 hour in a one stage process using 3% CaCl_2 and 5% coke.

The cobalt recovery was 54% and the copper recovery 96%. The addition of 10% Fe_2O_3 and the subsequent segregation under identical conditions yielded a cobalt recovery of 79% and a copper recovery of 97%.

Thus the addition of Fe_2O_3 led to an increase in both cobalt and copper recoveries.

EXAMPLE 12

Tenke Fungurume ore was segregated at 950°C for 1 hour using 5% CaCl_2 and 5% coke, with various additions of Fe_2O_3 . The results are tabulated below.

% Fe_2O_3	% Co. recovery	% Cu recovery
0	60	69
½	68	76
1	69	79
2	69	80
3	71	78
3¼	77	74
5	79	70

The results show an increase of both cobalt and copper recoveries with additions of Fe_2O_3 .

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I claim:

1. In a method of beneficiating an oxidic ore or ore concentrate material containing silicate minerals and nickel, copper or cobalt by the segregation process comprising mixing the oxidic material with a halide salt and a reducing agent while at an elevated temperature; the improvement comprising adding ferrous or ferric oxide to the oxidic material to increase the active iron content of thereof and to form fayalite.

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2. A method as claimed in claim 1, in which said ferrous or ferric oxide which is added is contained in an ore.

3. A method as claimed in claim 1, in which said oxidic material is an oxidized ore of nickel.

4. A method as claimed in claim 1, in which said halide salt is calcium chloride.

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