(12) UK Patent Application (19) GB (11) 2 199 573 (13) A

(43) Application published 13 Jul 1988

(21) Application No 8729592

(22) Date of filing 18 Dec 1987

(30) Priority data
(31) 9567/86 (32) 18 Dec 1986 (33) AU

(71) Applicant
CRA Services Limited

(Incorporated in Australia-Victoria)

55 Collins Street, Melbourne, Victoria, Australia

(72) Inventors
Philip Hannaker
Kenneth Crichton Hamilton
Alan Stuart Buchanan
Keith Bowdler

(74) Agent and/or Address for Service
Gill Jennings & Every
53/64 Chancery Lane, London, WC2A 1HN

(51) INT CL⁴
C01F 5/30 C01G 23/02 25/04 C22B 26/22 34/12 34/14

(52) Domestic classification (Edition J):
C1A D10 G34 G34D10 G40 G40D10 G48 G48D10 P10

(56) Documents cited
GB 1127079 US 4442076

(58) Field of search
C1A
Selected US specifications from IPC sub-classes
C01F C01G

(54) Chlorination of metallurgical composites

(57) Metal values are recovered as chlorides from minerals containing titanium, zirconium and/or magnesium, for example ilmenite, rutile, zircon and magnesite, by forming a composite mixture of a said mineral and a moist plastic mass produced by subjecting brown coal to predominantly shearing forces; compacting the composite mixture to produce a compacted mass, drying the compacted mass, and heating the dried compacted mass to produce a carbonised mass; and heating the carbonised mass in the presence of chlorine to produce chlorides of titanium, zirconium and/or magnesium. The mineral may be mixed with the brown coal before, during or after the shearing treatment.

GB 2 199 573 A

CHLORINATION OF METALLURGICAL COMPOSITES

This invention relates to recovery of metal values as chlorides from minerals containing titanium, zirconium and/or magnesium.

The invention utilises upgraded carbonaceous material of the kind disclosed in our Australian patent applications AU-24294/84 (PF 8078), AU 52590/86 (PG 9283), and AU 52422/86 (PG 9107).

Australian patent application AU-24294/84 relates to a process for treatment of brown coal which comprises subjecting the said coal to shearing forces to produce a

plastic mass which is capable of conversion by subsequent compaction and drying into a fuel of increased density and enhanced calorific value.

AU-52590/86 relates to improvements in the process of 24294/84 characterised in that the water content of the coal is more than 54% and the shearing forces are applied for less than one hour, shorter times being preferred, for example less than 30 seconds. A preferred embodiment provides a continuous process in which the coal is treated in a machine that subjects it to sequential steps of shearing and extrusion in a continuous manner. The extruded product after drying provides the fuel of increased density and enhanced calorific value. The desired effect may also be obtained by treating part of a quantity of brown coal and blending the treated portion with the untreated remainder of the said quantity.

In AU-52422/86, densified coal pellets of improved physical properties and enhanced calorific value are produced by a process which includes subjecting coal to a shearing-attritioning step followed by extrusion and drying steps, characterised by incorporating an additive into the coal that is subject to the said shearing-attritioning step, said additive being chosen from one or more of the group consisting of: alkali metal hydroxides, alkaline earth metal hydroxides, ammonium hydroxide, alkali metal carbonates, alkaline earth carbonates, oxides of base metals, oxides of transition metals, and small molecule carbonyl compounds.

Our co-pending patent application AU-54395/86 (PG 9776) relates to a process for the production of metallurgical composites for use in bath smelting from finely divided ores and concentrates, particularly iron-, chrome- and zinc ores or concentrates, and upgraded brown coal. The upgraded brown coal referred to is brown coal upgraded by a process(es) in accordance with our co-pending patent application(s) AU-24294/84, AU-52590/86, AU-52422/86 and GB2172586.

Existing processes for direct chlorination of ores for the recovery of specific elements tend to be difficult technologically involving elevated temperatures (often in the range 1000-1200°C) with consequent severe materials of construction problems. Some involve introducing externally produced carbon monoxide as reductant which may be expensive because of major gas purification procedures being required. In such systems the ore must be in a sufficiently coarse form to resist carry over of fines to the product collection vessels. In consequence there are restraints on preliminary purification of the ore.

Other existing processes use separate coke and ore phases in a reactor with consequent penalties with respect to the rates of reaction likely to be achieved unless very high temperatures are used.

Yet further processes use finely divided ore mixed with fine coke, char or activated carbon and an aqueous binder (sulphite liquor, starch, magnesium chloride etc.) compressed into small briquettes. These processes are advantageous in providing a close association of ore and reductant and also benefit by utilisation of a reactive high surface area carbon. Nevertheless, in general high temperatures are required to effect rapid and complete chlorination of the ore in said briquettes. In addition the activated carbon or the separately prepared char are expensive components of the composites and so is the binder.

The process of the invention comprises recovery of metal values from minerals containing titanium, zirconium and/or magnesium by forming a composite mixture including a said mineral and a moist plastic mass resulting from subjecting brown coal to predominently shearing forces; compacting the composite mixture to produce a composite mass; heating to produce a carbonised mass; and heating

the carbonised mass in the presence of chlorine to produce chlorides of titanium, zirconium and/or magnesium.

Preferred minerals for the process are ilmenite, nitile, zircon or magnesite, producing titanium or zirconium tetrachlorides or magnesium chloride respectively.

Thus the process of the invention uses inexpensive upgraded brown coal both as binder to form fine ore into an agglomerate suitable for subsequent chlorination, and as a highly reactive reductant to play a cooperative role in the chlorination. The process of attritioning the brown coal converts it to a finely divided densified plastic form which is thoroughly smeared over the surfaces of the ore grains during the mixing of the moist mass. Association of the two phases is thus very close and efficient. The mineral may be mixed with the brown coal before, during or after the shearing treatment.

The moist mass formed from the mineral sand and finely divided, densified brown coal is dried at ambient temperatures followed by carbonisation. Carbonisation of the upgraded brown coal in the composite together with in-situ cracking of evolved organic volatiles by heating to temperatures of between 500 and 900°C. This generates a carbon matrix of extremely high reactivity in very close association with the ore particles. Moreover, this carbonised phase will continue to evolve for some considerable time both carbon monoxide and hydrogen, both of which are highly effective as reductants. The strong binding provided by the densified brown coal ensures that fines carry-over during chlorination is minimal.

The very favourable reaction conditions prevailing in the carbonised densifed brown coal composites lead to rapid chlorination reactions under temperature regimes substantially below those common in other chlorination

processes. Temperatures in the range of 500-1000°C may be employed, a principal determining factor being the volatility or mobility of the chlorides to be transported. For titanium minerals, preferred chlorination temperatures are 500-650°C, and for zirconium and/or magnesium minerals preferred chlorination temperatures are 960-980°C.

When considered in a little more detail the pyrometallurgical application of composites of metal ore and upgraded brown coal or plant material is seen to have the following significant advantages -

Attritioning to produce the moist plastic mass of coal provides a very effective medium for incorporation of finely divided metal ores or concentrates to give an agglomerate of any convenient shape or size.

Spontaneous evaporative water loss occurs from the composites during the densification reaction of the coal so producing hardened, dried, materials

which have proved to be particularly amenable to relatively rapid heating (without degradation) for metallurgical purposes.

The fine state of subdivision of the attritioned material is conducive to very close physical association of particles of metal ore with coal thus giving very favourable reaction conditions.

On heating the composites an initial evolution of water and low molecular weight organic volatiles takes place but above about 500°C this is replaced by a free evolution of a strongly reducing gas mixture consisting chiefly of hydrogen, carbon monoxide, carbon dioxide and methane.

The char produced by carbonisation temperatures of up to 900°C is particularly reactive. When the standard reaction $CO_2+C \rightleftharpoons 2CO$ is used for comparative purposes, the reactivities manifested are believed to be at least 2 orders of magnitude greater than those displayed by metallurgical coke. For metallurgical purposes the very high partial pressure of carbon monoxide which is maintained within the char composites is of particular value.

The low ash contents of many brown coals offer considerable advantages in providing clean reducing systems. The densified composites share in this advantage.

Although the hardened carbonised composites are generally strong and of vitreous appearance they still remain permeable to gases and vapours. This permeability has various useful consequences, for example,

Gas and vapour evolution can occur freely when the composites are heated rapidly thus avoiding explosive degradation which commonly occurs when higher ranking coals are so heated.

Other reactant gases can be readily introduced into the composites and will penetrate freely through the porous mass and product species will also diffuse out freely.

An eroding gas such as carbon dioxide or low oxygen partial pressure may be used to progressively destroy the char and eliminate it from the reaction zone. At the same time a high reducing potential of carbon monoxide is maintained.

It has been found that carbonised composites of the type of ores mentioned are particularly suitable for the direct production of metal chlorides by introduction of elemental chlorine with the system maintained at a suitable temperature. It is apparent that the metal oxides are being maintained in a strongly reducing environment which considerably assists in the replacement of oxygen by chlorine according to the reaction

$$MO+CO+Cl_2 \rightarrow MCl_2+CO_2$$

Such reactions are frequently exothermic with consequent rapid temperature increases and fast kinetics. The reaction equation indicates the significance of maintaining a sufficient supply of chlorine to take full advantage, in kinetic terms, of the high reducing power of the system.

The metal chloride generated by the chlorination reaction must be sufficiently volatile or mobile at the reaction temperature to be effectively eliminated from the porous composite pellet and to leave the reaction zone either as a vapour or as a free-flowing liquid.

The process of the invention will be more clearly understood by reference to the examples below -

Example 1 (Production of Titanium Tetrachloride)

Two kinds of fine mineral sand concentrates were used. One concentrate consisted principally of ilmenite ($FeO.TiO_2$) and the other of rutile (TiO_2).

To produce composites, brown coal ex Morwell, Victoria, was attritioned for 15 minutes in a sigma kneader (Janke and Kunkel HKS 50) to yield a moist plastic mass. The dry sand concentrates were then added and operation of the kneader continued for a further 5 minutes to ensure thorough mixing and close association of all mineral grains with coal particles. The composite plastic mass was then extruded with a hand operated screw extruder fitted with either a 10 mm or a 3 mm diameter nozzle to provide cylindrical pellets of these diameters and average length 10 mm. The pellets were subsequently dried in a still laboratory atmosphere at 20°C for 7 days. The dry and hardened pellets were then subjected to carbonisation to remove residual water, and low molecular weight organic volatiles (principally phenols). Carbonisation entailed heating the pellets in a tube furnace to several selected temperatures up to 900°C for periods of 4 hours.

Heating was conducted either in a flowing nitrogen atmosphere to remove volatiles or in a tube with one closed end to ensure that carbonisation occurred in the reducing atmosphere created by cracking of evolved volatiles.

For ilmenite composites concentrations of ilmenite of 10, 20, 35 and 60% by weight relative to dry coal weight were used. For rutile 20% composites were prepared.

After carbonisation, which caused volatiles' losses of up to 40% of dry coal weight, the mineral proportion was appreciably higher relative to the residual char.

Chlorination tests on the ilmenite and rutile composites were conducted by placing two pellets in a silica boat which in turn was placed in a silica tube mounted in a resistance furnace able to be regulated at temperatures up to 900°C. When the chosen temperature had been established, cylinder chlorine was admitted to the reactor either alone or with a nitrogen carrier stream. Volatile products (principally titanium tetrachloride and iron chlorides) were trapped in two water cooled condensers mounted sequentially. For quantitative purposes analysis of the residual pellets was usually used to determined titanium and iron transport.

Chlorine flow through the reactor (as monitored with a sulphuric acid bubbler) was maintained at a rate to give an excess at all times.

The results in Table 1 below illustrate the efficiency which can be achieved in chlorinating both ilmenite and rutile in the composites. Comparatively low chlorination temperatures (in the vicinity of 600^{o}C) gave fast reaction rates through to completion which compare favourably with reaction temperatures in the vicinity of 1,000^{o}C in comparable existing commercial processes.

Table 1

Composite composition (dry weights)	Carbonisation temperature °C	Chlorination time and temperature	%Fe before treatment	%Fe after treatment	%Fe eliminated from composite	%Ti before treatment	%Ti after treatment	%Ti eliminated from composite
Ilmenite								
20% ilmenite	500	2 hrs. 650°C	10.20	4.72	53.8	19.28	0.22	99.0
35% ilmenite	500	2 hrs. 650°C	11.63	3.03	74.0	21.48	0.12	99.4
Rutile								
20% rutile	500	2 hrs. 550°C				27.73	3.46	87.5

Example 2

Larger scale tests were conducted on the chlorination of ilmenite concentrates in brown coal composites with the object of exploring reaction characteristics of greater masses of the composites and of obtaining substantial quantities of products for analysis.

Composites were prepared as described above using 20% and 35% by weight of concentrate. Kilogram quantities were made and dried in air either at ambient temperature or in a low-temperature oven. The dry composites were carbonised either at 750°C and 900°C for two hours in externally heated steel coking pots (130 x 300 mm) using batches of about 0.5 kg. Evolved volatiles were burnt at the exit end of a short stack, the arrangement minimising access of atmospheric oxygen to the pot and facilitating in-situ cracking of a proportion off the volatiles within the pores of the mass of composites.

It was shown that substantial conversion of the iron oxides of the ilmenite to metallic iron occurred during the course of the carbonisation process. Conversion was almost complete after 2 hours carbonisation at 900°C.

Chlorination of the carbonised composites was conducted in an Inconel reaction vessel of length 385 mm and 42 mm internal diameter. Incoming chlorine was pre-heated and the emergent gases were passed through successively a ferric chloride condenser (maintained at 7-10°C above the boiling point of $TiCl_4$) and a water cooled glass condenser to trap the $TiCl_4$.

Chlorination experiments were performed at 500°C and 600°C with charges of 122.5 g using either pure Cl_2 at a flow rate off 1 l/min. or à 1:1 mixture of Cl_2 and N_2 at the same flow rate. Initial introduction of chlorine caused very rapid temperature rises as exothermic reactions proceeded. Slow addition was therefore adopted for the first 20 minutes after which the temperature became controllable and product chlorides commenced to emerge from the reactor. Condensation of $TiCl_4$ was often observed within about 2 minutes of chlorine flow rate increase and highest production rates noted usually

within 5 minutes of the onset of condensation. Production usually continued for 60 or more minutes. The observations made in 19 experiments are presented in summary form in Table 2 where rates of appearance of $TiCl_4$ are recorded together with the total extents of transport of titanium from the composites.

Table 2

% Ilmenite in composite	Carbonisation temp. °C	Chlorination temp. °C	PCl_2 atm	Rate of appearance ml/min	Extent of transport Ti %
20	750	500	1	0.32	88.5
20	750	600	1	0.29	100
20	750	500	1	0.21	86.3
20	750	600	0.45	0.18	99.3
20	750	600	1	0.28	99.0
20	750	600	0.5	0.29	99.9
20	900	600	0.5	0.10	96.2
20	900	600	1	0.34	98.7
20	900	600	1	0.34	98.1
20	900	600	0.5	0.17	98.2
35	750	600	0.5	0.41	98.5
35	750	600	1	0.42	99.7
35	750	500	1	0.24	95.0
35	750	600	1	0.57	98.9
35	750	600	0.5	0.27	99.5
35	900	600	1	0.51	97.2
35	900	600	1	0.31	97.6
35	900	600	0.5	0.24	92.0
35	900	600	0.45	0.34	96.5

The process illustrated below offers the opportunity of producing zirconium tetrachloride (as a precursor to zirconium dioxide) quickly and economically at a reaction temperature significantly below that currently used (1100°C) in the existing process which utilises milled zircon and petroleum coke as reactants in a fluidised bed reactor.

Example 3 (Production of Zirconium Tetrachloride)

A fine mineral sand (-325 mesh) concentrate of zircon ($ZrSiO_3$) was used to prepare brown coal composite pellets with Morwell brown coal as described for Example 1. As will be seen from Table 3 the 3 mm diameter (at extrusion) cylindrical pellets contained either 29% or 45% by weight of zircon in terms of dry coal weight.

After drying for seven days under ambient conditions the composites were carbonised at 900°C for periods ranging from 5 to 9 hours although there is no evidence to indicate that the longer periods of carbonisation were beneficial in improving subsequent chlorination. Carbonisation was conducted in a closed-end furnace tube so that the atmosphere consisted principally of the pyrolysis gases from the coal (CO, H_2) together with a little N_2 derived from the nitrogen stream sweeping past the open end of the pyrolysis tube. The carbonisation atmosphere was thus inert or reducing and conducive to deposition of cracked volatiles in the pores of the composites.

In all of the experiments recorded in Table 3 chlorination was conducted by causing chlorine to flow for 45 minutes over carbonised composites maintained at either 960°C or 980°C. In some experiments 10% of cylinder nitrogen was mixed with the chlorine the total pressure being one atmosphere. The object was to maintain a sufficient flow of gas to act as carrier for evolving volatile chlorides. The above time and temperature range was found to be satisfactory following earlier exploratory experiments. Zirconium tetrachloride evolved rapidly soon after admission of Cl_2 and appeared as a white powder deposit (snow) in the downstream

condensing tubes. When exposed to air this white powder rapidly assumed a golden colour as partial hydrolysis to the oxychloride occurred.

Table 3 indicates that 29% zircon composites yield 60-66% of the zirconium as volatile chloride when chlorinated at 960-980°C. Prior calcination of the zircon at 1200°C in air did not appear to yield any useful effect on subsequent chlorination.

Further experiments with 45% zircon composites, chlorinated under the same conditions produced improved results with 84-85% of the zirconium being eliminated from the composites (see (3) and (4) in Table 3). The only important difference between (1), (2) and (3), (4) was that the latter displayed much higher percentage weight losses during chlorination than the former (80-89% compared with 33-48%). Weight loss from the composites during chlorination are due in part to the loss of volatile chlorides and also to erosion of carbonaceous material by oxygen in the chlorinating gas mixture. The oxygen is present as a minor component of the 10% of cylinder nitrogen used in making the gas mix.

The higher concentration of zircon in the composites used in (3) and (4) will results, as chlorination proceeds, in increased permeability of the residual pellet. Oxygen erosion will amplify this effect thus facilitating diffusion of product chlorides from the interior of the pellets. Hence the use of a small partial pressure of oxygen during chlorination is markedly beneficial in enhancing recovery of zirconium as the tetrachloride.

In some of the experiments recorded in Table 3 silicon tetrachloride was detected in small amounts in the downstream condensing tubes. In a commercial operation this very volatile compound would require an efficient condensing system for its recovery either as a desired by-product or for control of emission to the environment.

Table 3

Composite composition	Carbonisation conditions	Chlorination time temperature	% Zirconium eliminated from composites	
(1) 29% zircon	5 hr at 900°C in N_2	45 min at 960°C weight loss 33%	66.4	
(2) 29% zircon	7 hr at 900°C in N_2	45 min at 980°C 10% N_2 in Cl_2 weight loss 48%	60.3	zircon calcined 2 hr at 1200°C
(3) 45% zircon	7 hr at 900°C in N_2	45 min at 980°C 10% N_2 in Cl_2 weight loss 89%	85.5	zircon calcined
(4) 45% zircon	9 hr at 900°C in N_2	45 min at 980°C 10% N_2 in Cl_2 weight loss 79%	83.9	zircon calcined

Example 4 Production of Anhydrous Magnesium Chloride

Morwell (Victoria) brown coal of water content 62% was attritioned in a sigma kneader for 15 minutes to yield a smooth moist plastic mass to which was then added either fine reagent grade magnesium carbonate or refined magnesite (-100 mesh or -400 mesh) of Tasmanian origin. A further 10 minutes of mixing in the kneader yielded very well mixed plastic masses suitable for extrusion with a hand operated screw extruder to yield either 3 or 10 mm diameter pellets. The pellets were dried at 20°C in still air for one week before being carbonised, which in all cases was conducted at 900°C for various times either in a nitrogen atmosphere or in the reducing atmosphere created by evolution of volatiles from the pyrolysing brown coal.

Table 4 shows the results obtained in a series of chlorination tests which were conducted in a vertical tube furnace in gas streams consisting of either chlorine alone or where indicated with chlorine followed by carbon dioxide. The evolved anhydrous magnesium chloride was carried to collector flasks at laboratory temperature. The product appeared as a white 'snow'.

In experimental series (1) (Table 4) carbonisation time in nitrogen gas was progressively increased from 1 to 4 hours at 900°C. The purpose of carbonisation was both to effect decomposition of the magnesium carbonate and to pyrolyse the coal to yield a char no longer evolving volatiles (other than CO and H_2). This first series indicated that 2.5 hours of carbonisation was required to enable complete chlorination and transport of magnesium to occur provided that the chlorination time (in chlorine gas alone) was extended to about 30 minutes at 960°C.

In (2) and (3) 40% magnesite (both -100 and -400 mesh) composites were used. In both series carbonisation times were extended to 5 hours at 900°C and chlorination times to 30 minutes (in Cl_2 alone) at 960°C. While magnesium

chloride formation and transport occurred it was less than complete. There was no beneficial effect of the finer -400 mesh particle size.

Since the experiments of series (1) had indicated that the times and temperatures used in (2) and (3) should have been sufficient for complete formation and transport of magnesium chloride it seemed probable that slow diffusion of $MgCl_2$ from the porous char was limiting the extent of transport in the latter experiments. Note that the composites in (2) and (3) contained twice as much magnesium. Accordingly experiment (4) was conducted with a period of flow of carbon dioxide (at 960°C) following the chlorination. This was sufficient to erode away residual char (by way of the reaction $C + CO_2 = 2CO$). Transport of the magnesium as anhydrous chloride was complete. A second experiment in series (4) with chlorination time reduced to 15 minutes at 960°C followed by CO_2 erosion of the char also gave essentially complete transport of magnesium.

Having established the benefits of char erosion by carbon dioxide a fifth experimental series was conducted with 60% (-100 mesh) magnesite in the composites. Chlorination time was further reduced to 7 minutes at 980°C. A carbon dioxide char erosion time of 30 minutes at 980°C was shown to be sufficient to give essentially complete magnesium transport. Furthermore it was also possible to reduce carbonisation time from 4 to 2.5 hours at 900°C while still achieving complete magnesium transport.

A further experiment (6) demonstrated that a similar result could be obtained with 40% magnesite in the composites (that is, using reduced carbonisation and chlorination times).

Table 4

Composite	Carbonisation time hr.	Carbonisation temp °C	Chlorination of 1 g samples time min.	Chlorination of 1 g samples temp °C	Other conditions	% $MgCl_2$ Produced
(1)						
20% mag.	1	900	15	960		49.3
carbonate	2	900	15	960		61.0
	4	900	15	960		61.9
	2.5	900	15	960		61.9
	2.5	900	25	960		88
	2.5	900	30	960		96
(2)						
40% (– 100 mesh) magnesite	5	900	30	960		77
(3)						
40% (– 400 mesh) magnesite	5	900	30	960		59

Table 4 (continued)

Composite	Carbonisation time hr.	Carbonisation temp °C	Chlorination of 1 g samples time min.	Chlorination of 1 g samples temp °C	Other conditions	% $MgCl_2$ Produced
(4)						
30% (- 100 mesh) magnesite	4	900	30	960	30 min. char erosion with CO_2 at 960°	100
	4	900	15	960	30 min. char erosion with CO_2 at 960°	94
(5)						
60% (-100 mesh) magnesite	4 carbonisation in presence of volatiles	900	7	980	30 min. char erosion with CO_2 at 980°	98.5

Table 4 (continued)

Composite	Carbonisation time hr.	Carbonisation temp °C	Chlorination of 1 g samples time min.	Chlorination of 1 g samples temp °C	Other conditions	% $MgCl_2$ Produced
(6) 60% (– 100 mesh) magnesite	4	900 carbonisation in presence of volatiles	7	980	45 min. erosion of char with CO_2 at 980°	93.5
	2.5	900 carbonisation in presence of volatiles	7	980	30 min. char erosion with CO_2	99.9
(7) 40% (–100 mesh) magnesite	2.5	900 carbonisation in presence of volatiles	7	980	30 min. CO_2 erosion	91

Note

. Unless otherwise indicated carbonisation was conducted with removal of evolved volatiles by a stream of N_2 gas.

. Where shown carbon dioxide was used to erode away the residual char of the composite pellets usually to completion thus facilitating displacement of all of the magnesium chloride.

It will be clearly understood that the invention in its general aspects is not limited to the specific details referred to hereinabove.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for recovery of metal values as chlorides from minerals containing titanium, zirconium and/or magnesium, characterised by forming a composite mixture including a said mineral and a moist plastic mass produced by subjecting brown coal to predominantly shearing forces; compacting the composite mixture to produce a compacted mass, drying the compacted mass, and heating the dried compacted mass to produce a carbonised mass; and heating the carbonised mass in the presence of chlorine to produce chlorides of titanium, zirconium and/or magnesium.

2. Process according to Claim 1, in which the composite mixture is formed by first mixing a finely divided said mineral with brown coal and then subjecting the mixture of mineral and brown coal to the said shearing forces.

3. Process according to Claim 1, in which the composite mixture is formed by adding a finely divided said mineral to brown coal while it is being subjected to the shearing forces.

4. Process according to Claim 1, in which brown coal is first subjected to predominantly shearing forces to form a moist plastic mass, and a finely divided said mineral is then mixed with the plastic mass to form the said composite mixture.

5. Process according to Claim 1, in which the said mineral is selected from ilmenite, rutile, zircon and magnesite.

6. Process according to Claim 1, in which the compacted mass is dried at ambient temperature.

7. Process according to Claim 1, in which the carbonised mass is produced by heating the dried compacted mass to a temperature in the range 500 to 900°C.

8. Process according to Claim 1, in which the mineral contains zirconium and/or magnesium and the carbonised mass is produced by heating the dried compacted mass at about 900°C.

9. Process according to Claim 1, in which the carbonised mass is heated in the presence of chlorine at temperatures in the range 500 to 1000°C.

10. Process according to Claim 1, in which the mineral contains titanium and the carbonised mass is heated in the presence of chlorine at temperatures in the range 500 to 650°C.

11. Process according to Claim 1, in which the mineral contains zirconium and/or magnesium and the carbonised mass is heated in the presence of chlorine at temperatures in the range 960 to 980°C.

Published 1988 at The Patent Office, State House, 66/71 High Holborn, London WC1R 4TP. Further copies may be obtained from The Patent Office, Sales Branch, St Mary Cray, Orpington, Kent BR5 3RD Printed by Multiplex techniques ltd. St Mary Cray, Kent. Con. 1/87.