United States Patent [19]

Vojkovic

[11] **3,753,681**

[45] **Aug. 21, 1973**

[54] **BENEFICIATION OF VANADIUM-CONTAINING MATERIALS**

[75] Inventor: **Milos Vojkovic,** Luxembourg, Luxembourg

[73] Assignee: **Continental Ore Corporation,** New York, N.Y.

[22] Filed: **Oct. 1, 1970**

[21] Appl. No.: **77,315**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 755,431, Aug. 26, 1968, abandoned.

[52] **U.S. Cl.** **75/1,** 75/24, 75/84

[51] **Int. Cl.** **C22b 1/00,** C22b 7/04, C22b 55/00

[58] **Field of Search** 75/1, 21, 24, 84, 75/27, 29, 63, 96, 3, 7, 59

[56] **References Cited**

UNITED STATES PATENTS

1,970,467	8/1934	Mayr	75/27
3,163,523	12/1964	Porter	75/65
2,242,759	5/1941	Schlecht	75/84
3,425,826	2/1969	Schmidt	75/84
3,305,355	2/1967	Darrow	75/1
2,369,349	2/1945	Hatherell	75/1
3,428,427	2/1969	Raicevic	75/1
3,118,757	1/1964	Peras	75/1
2,867,529	1/1959	Forward	75/7
2,864,689	12/1958	Perrin	75/59
3,295,952	1/1967	Johnson	75/3
2,867,529	1/1959	Carpenter	75/7

FOREIGN PATENTS OR APPLICATIONS

127,026	0/1960	U.S.S.R.	75/24

Primary Examiner—L. Dewayne Rutledge
Assistant Examiner—Peter D. Rosenberg
Attorney—C. R. Hoffman, G. Levy, D. S. Kane, J. C. Sullivan, J. T. Salerno, Jr., C. P. Bauer, D. H. Kane, P. T. Dalsimer, J. Kurucz, M. E. Goldstein, P. Saxon and P. C. Van Der Sluys

[57] **ABSTRACT**

A process for the beneficiation of vanadium-containing materials comprising preheating the material in the absence of oxygen and then reacting the hot material with oxygen to yield soluble vanadium compounds.

13 Claims, No Drawings

BENEFICIATION OF VANADIUM-CONTAINING MATERIALS

This Application for a patent is a continuation-in-part of my earlier U.S. Pat. application Ser. No. 755,431 filed on Aug. 26, 1968, and now abandoned.

This invention relates to the beneficiation of vanadium-containing material, the vanadium component of which can be oxidised to form soluble vanadium compounds.

There are no known naturally occurring materials that are rich in vanadium, and the metal is commonly obtained as a by-product in the production of other metals. In particular, it is known to obtain vanadium from slags (that is to say, solid materials that separate from the main, liquid component during smelting operations) obtained by the smelting of ores, especially slags formed in the manufacture of steel. In such slags, the vanadium is in a complex form in a spinel-type structure and is thus largely or completely in the trivalent state.

Vanadium can be extracted from such slags by oxidising the vanadium to the pentavalent state in the presence of salts of alkali metals. This breaks up the spinel-type structure and leads to the formation of soluble vanadates, which can be leached out in a conventional manner.

The oxidation of such slags for this purpose, however, presents a number of difficulties. First, the slag granules become coated with an oxide layer that inhibits further reaction and thus necessitates a long retention time for the slag in the reactor (so that the throughput/size ratio is low) and results in a low thermal efficiency. Further, both the temperature and the concentration of salts of alkali and/or alkaline earth metals have to be carefully controlled if the slag is not to soften and adhere to the walls of the reactor.

This invention provides a process for the beneficiation of vanadium-containing material, the vanadium component of which can be oxidised to form vanadium compounds that are soluble in an aqueous medium, which comprises preheating the material under inert conditions and then contacting the resulting hot material with oxygen to effect the formation of soluble vanadium compounds, the temperature of the preheated material when it is initially contacted with oxygen being such that the material reacts with the oxygen in a strongly exothermic manner.

When the vanadium-containing material is vanadium-containing slag, the process comprises preheating the slag in particular form under inert conditions and then contacting the resulting hot slag with oxygen to effect the formation of soluble vanadium compounds, the temperature of the preheated slag when it is initially contacted with oxygen being at least 600° C and such that the slag reacts with the oxygen in a strongly exothermic manner, and the maximum temperature reached by the slag while it is in contact with the oxygen being within the range of from 680° C. to 1,050° C.

For vanadium-containing materials other than vanadium-containing slag, the process comprises preheating the material under inert conditions and then contacting the resulting hot material with oxygen to effect the formation of soluble vanadium compounds, the temperature of the preheated material when it is initially contacted with oxygen being at least 400° C and such that the material reacts with oxygen in a strongly exothermic manner, and the maximum temperature reached by the material while it is in contact with the oxygen being within the range of from 600° C. to 1,200° C.

With the process of the invention, it is possible to reduce considerably the reaction period of vanadium-containing material with oxygen and at the same time to increase the percentage extraction of the vanadium component of the material over that obtained by the conventional extraction processes used with such materials. The throughput/size ratio of the plant in which the process is performed can be increased and the material can be oxidised in smaller batches allowing easier temperature control.

The process of the invention can be used irrespective of the vanadium content of the starting material. Further, the process of the invention makes it practicable to extract vanadium from materials from which extraction was previously impracticable for economic reasons. Of the materials other than slags, the process of the invention is especially important when the starting material is titaniferous ore, for example, titaniferous magnetite or fly ash, which is a product of crude oil combustion, or ferrophosphorus.

The temperature to which the material is preheated should be sufficiently high to ensure that, when the material is contacted with oxygen, the material reacts rapidly with the oxygen in a strongly exothermic manner. Thus, if the preheat temperature is sufficiently high, the temperature of the material will rise sharply, usually by at least 50° C. and advantageously by at least 100° C., when it is contacted with oxygen. The minimum satisfactory preheat temperature for a particular material can only be determined by trial and error but it depends upon the chemical composition and degree of physical sudivision of the material (the minimum satisfactory preheat temperature decreasing as the degree of the physical subdivision of the material becomes finer) the presence of any additives and the chemical composition and the concentration of the additives, if any.

Depending on the above mentioned factors, it will generally be found advantageous to preheat, for example, vanadium-containing titaniferous ores to a temperature within the range of from 800° to 1,000° C. and, preferably, within the range of from 850° to 950° C. Fly ash is advantageously preheated to a temperature within the range of from 400° to 750° C.

With regard to the chemical composition of vanadium-containing slags, there is a broad distinction between, on the one hand, slags that have a relatively high vanadium content (say, at least 10 percent by weight calculated as V_2O_5) and based on the total weight of the slag and, on the other hand, slags that have a relatively low vanadium content and a high content of calcium and/or magnesium, and possibly a substantial content of titanium. The slags in the first of these two broad categories, that is to say, those that have a relatively high vanadium content, normally have incorporated with them prior to roasting (as is described in greater detail hereinafter) a salt or salts of an alkali metal to serve as a fluxing agent, and require a relatively low pre-heat temperature. The slags in the second of these categories, on the other hand, require a relatively high preheat temperature. Also, it has been found that the minimum satisfactory preheat temperature is a decreasing function of the quantity

$$Fe + Si/Ca + Mg$$

where Fe, Si, Ca and Mg stand for the proportions by weight of these elements in the slag.

The minimum satisfactory preheat temperature decreases as the degree of physical subdivision of the slag becomes finer. Thus, for example, it was found that a batch of slag required a preheat temperature of 850° C. when ground to pass a 44 mesh (B.S.S.) screen, which corresponds to a maximum particle diameter of approximately 350 microns, whereas a preheat temperature of 750° C. sufficed when slag from the same batch was ground to pass a 200 mesh (B.S.S.) screen, which corresponds to a maximum particle diameter of approximately 75 microns.

It is usually advantageous to preheat slag to a temperature of at least 630° C., and it will generally be found preferable not to preheat it to a temperature exceeding 800° C.

The requirement that the material should be preheated under inert condition implies primarily that it should be preheated in the absence of oxygen. The purpose of preheating the material is simply to ensure that it is at a desired elevated temperature when it is contacted with oxygen, and not to effect any chemical change in the material. Thus, in addition to excluding oxygen, the material will be preheated in the absence of any substance with which it would react to any substantial extent during the preheating.

The material may be preheated in an inert atmosphere, for example, an atmosphere of nitrogen, or it may be preheated while confined within a region that is substantially completely filled by the material, and said region preferably being the interior of a conduit through which the material is supplied to a zone wherein it is contacted with the oxygen. The feasibility of preheating slag in a conduit that communicates with the oxidation zone arises in part from the fact that, during preheating, vanadium-containing slags evolve some water vapour and also, in the case of basic slags, a mixture of carbon monoxide and carbon dioxide, and in part from the fact that it is possible to feed the slag through the conduit in the form of a relatively tightly packed "plug."

The material is advantageously preheated by means of radiant heaters, but, when the material is preheated in an atmosphere of an inert gas, it may be preheated by heating the gas and fluidising or agitating a bed of material in particular form by passing the hot inert gas upwardly through it.

Since the purpose of preheating the material is that the material should be hot when it is contacted with oxygen, care should naturally be taken to prevent any substantial cooling of the material after it has been preheated and before it is contacted with oxygen.

The preheated material is advantageously contacted with substantially pure oxygen, but, if it is found that this results in the material reaching too high a temperature, the oxygen may be diluted with an inert gas. Thus, the preheated material may be contacted with oxygen-enriched air or even with air. The use of air, however, will usually result in the maximum temperature reached by the material being too low unless the air is also preheated. Further, it may be found that, in order to supply oxygen at the rate required for the reaction, the rate of supply of air has to be so high as to cause dusting losses.

The oxidation reaction that takes place when the preheated material is contacted with oxygen is exothermic and the maximum temperature reached by the material depends upon the rate of reaction (which in turn depends upon the concentration of the oxygen, the rate of diffusion of the oxygen to the material, the composition of the material including any additives, and the fineness of the particles of the material), on the rate of loss of heat from the reaction mixture, and on the temperature to which the material is preheated. Thus, there are a number of different parameters that can be controlled to ensure that the material remains within the desired temperature range during the oxidation reaction.

The maximum temperature reached by the material while it is in contact with the oxygen should not be so high that there is formed such a large liquid-phase component that the extraction efficiency is seriously reduced. Also, the said maximum temperature should not be so high that excessive sintering of the material occurs. As a rough guide, any sintering of the material should not be sufficiently severe to prevent the material after quenching, from being crumbled. It may be added that the maximum temperature reached by the material while it is in contact with the oxygen is always substantially below the temperature at which vanadium metal becomes incandescent.

In the case of slag, in general, and especially when (as is described hereinafter) a salt or salts of an alkali metal or metals is or are incorporated with the slag prior to its being contacted with oxygen, the maximum temperature reached by the slag while it is in contact with the oxygen advantageously does not exceed 840° C. and preferably does not exceed 820° C., because there is a tendency for a serious reduction in extraction efficiency to occur if the temperature is allowed to rise sufficiently high for alkali vanadates for other alkali or alkaline earth salts to fuse. Fortunately, however, those slags that require a high preheat temperature, say, over 800° C., are also relatively refractory, that is to say, they can be allowed to reach a relatively high temperature while in contact with oxygen, but it will generally be found advantageous not to allow the temperature of the slag to exceed 950° C. while it is in contact with the oxygen.

When (as is described hereinafter) oxidised slag is subsequently treated by leaching with acid, it is found that the quantity of acid required to extract a given quantity of soluble vanadium decreases as the maximum temperature reached by the slag while in contact with the oxygen increases. Thus, if the maximum temperature reached by the slag while in contact with the oxygen slightly exceeds the temperature, or the upper end of the temperature range, that gives the maximum oxidation of the vanadium component, the decreased consumption of acid in the subsequent leaching stage will tend to offset the economic disadvantage of the lower oxidation of the vanadium component. Also, the improved oxidation of constituents of the slag other than the vanadium component that results from operating with a higher maximum temperature of the slag while it is in contact with the oxygen prevents or lessens the loss of vanadium through reduction during the subsequent extraction stages. Indeed, it may in some cases be economically advantageous to operate in this way at a slightly lower extent of oxidation of the vanadium component, because it is possible, in economic terms,

for the lower oxidation of the vanadium component to be more than offset by the resulting lower acid consumption and the avoidance or lessening of vanadium . . . reduction during the extraction stages.

At least when the preheated slag is contacted with substantially pure oxygen, it will usually be found that the preferred upper limit of 820° C. (referred to hereinbefore) for the maximum temperature reached by certain slags during the oxidation reaction implies an upper limit of 680° C. for the temperature to which the slag is preheated.

Grinding the material more finely improves the extraction efficiency, but against this there has to be offset the greater cost of finer grinding. For a given extraction efficiency, finer grinding generally enables the preheating temperature and/or the exposure time to oxygen to be correspondingly reduced. Slag is advantageously ground to −36 mesh (B.S.S.), which corresponds to a maximum particle diameter of approximately 420 microns, and it may be ground to as fine as −85 mesh (B.S.S.), which corresponds to a maximum particle diameter of approximately 175 microns, or even finer if desired. Other materials are advantageously ground to −100 mesh (B.S.S.) or even finer. When the material is titaniferous ore, it is advantageously ground to as fine as −200 mesh (B.S.S.) or −400 mesh (B.S.S.).

Advantageously, a salt of an alkali metal, or a mixture of more than one of such salts, preferably, sodium chloride or sodium carbonate or a mixture of sodium and potassium chlorides, or a mixture of sodium chloride and sodium sulphate, is incorporated with the material prior to its oxidation. The salts serve as fluxing agents and their addition improves the yield of soluble vanadium by providing cat-ions for the formation of alakali vanadates. Because the salt or mixture of salts undergoes an endothermic reaction when the oxidation takes place, the addition of such salts provides a further method of achieving the desired temperature control. In the case of sodium carbonate, the liberation of carbon dioxide tends further to reduce the rate of the reaction, so that the incorporation of sodium carbonate with the material before it is contacted with the oxygen can provide a very substantial degree of temperature control.

The selection of the salt or mixture of salts to be added for the optimum results depends upon the chemical composition of the material. It will generally be found that the salt or mixture of salts to be added should be one which forms sodium oxide readily on exposure to oxygen. Advantageously, when titaniferous ore or fly ash is used as the starting material, the salt of an alkali metal incorporated with the material is sodium carbonate.

The quantity of the selected salt or salts to be added will depend on the proportion of alkali metals or alkaline earth metals present in the material originally, a smaller addition (or no addition) being required if the original content is higher. In general with slags, it will be found that the addition of such salts is most beneficial when incorporated with slags that have a relatively high vanadium content.

Preferably, the quantity of sodium carbonate incorporated in titaniferous ore is such that it comprises at least 10 percent of the total weight of the material and the quantity of sodium carbonate incorporated in fly ash is such that it comprises at least 25 percent of the total weight of the material.

In addition to, or instead of, the incorporation of a salt or a mixture of salts, to obtain the desired temperature control it may be found advantageous in the extraction of vanadium from some materials to incorporate with the material prior to its oxidation one or more other vanadium-containing materials, the vanadium component of which can be oxidised to form vanadium compounds that are soluble in an aqueous medium, of differing chemical composition. For example, the starting material may comprise a mixture of vanadium-containing slag and another material. If the material to be oxidised reacts violently on exposure to oxygen it is preferably mixed with a material that reacts slowly on exposure to oxygen. This can result in the average percentage of vanadium extracted from the roasted mixture after oxidation being increased over the percentage extraction obtained when each of the materials is roasted separately. For example, ferrophosphorus is advantageously mixed with a basic vanadium-containing slag.

With some materials it may be found, after roasting in accordance with the invention (primary roasting), advantageous to perform a secondary roasting operation, the material being ground or otherwise comminuted between the primary and secondary roasting operations. If the material is allowed to cool after the primary roasting operation, it may either be preheated again under inert conditions before being contacted at an elevated temperature with oxygen for a second time or the secondary roasting operation may be carried out in a conventional manner. This secondary roasting generally increases the average extraction of vanadium for a given starting material and enables more reliable and consistent results to be obtained. The salt of an alkali metal or mixture of salts and/or the one or more other vanadium-containing materials may be added at the primary roasting stage or at the secondary roasting stage or at both stages.

When ferrophosphorus is used as the starting material, it is advantageously roasted in accordance with the invention in the absence of additives, ground, mixed with basic vanadium-containing slag, and, preferably, also with sodium carbonate, and re-roasted by again preheating under inert conditions and contacting it at an elevated temperatre with oxygen.

After roasting, the material is advantageously quenched. It may then be treated, for example, in a conventional manner, to yield vanadium oxide. As compared with allowing the material to cool slowly, quenching gives a small improvement in extraction efficiency.

The liquid medium in which the vanadium compounds, that are formed as a result of the process of the invention, are soluble may be water, or an alkali medium, or an acid medium. It will generally be found that the vanadium compounds are soluble in water or an alkali medium but it may in some cases be necessary to use an acid medium.

In the case of slags that are rich in vanadium (for example, containing from 8 to 15 percent by weight of vanadium based on the total weight of the slag, corresponding to from approximately 14.3 to 26.8 percent of vanadium calculated as V_2O_5) and free from phosphorus and to which sodium carbonate has been added before roasting, the hot slag that has been contacted

with oxygen may be quenched with water, wet-milled and hot digested. After filtering, the strongly alkaline filtrate is neutralised to precipitate dissolved silica which is coagulated with a flocculating agent and removed by filtering. The silica-free liquor is then either treated to give ammonium metavanadate by direct salting with ammonium chloride at a pH of about 7 or treated to precipitate a hydrated acid polyvanadate. The metavanadate or polyvanadate is decomposed thermally to give flake of vanadium pentoxide.

In the case of slags that have a low vanadium content (for example, containing less than 10 percent by weight of vanadium calculated as V_2O_5) and based on the total weight of the slag and that contain phosphorus, the hot slag that has been contacted with oxygen may be quenched with water, wet-milled, and then leached with dilute acid, for example, dilute sulphuric acid, or quenched and leached with a dilute acid. The dilute acid is suitably added until a steady pH of 1 is reached at 50° C. The impure liquor may then be treated, for example, by passing gaseous chlorine through the liquor until an e.m.f. of −750 mV is reached, to ensure that any iron present is oxidised and the liquor is then subjected to a solvent-extraction process that extracts vanadium preferentially, the solvent used in the extraction being an organic liquid, which may comprise a tertiary amine in admixture with one or more organic solvents. The organic phase obtained in the extraction is stripped of vanadium by the use, for example, of an aqueous solution of sodium carbonate, and recycled for futher use. The vanadium is obtained as ammonium metavanadate by treating the sodium vanadate solution with ammonium sulphate. Alternatively, ammonium metavanadate may be obtained without the use of sodium carbonate by adding ammonium chloride directly to the organic phase containing the vanadium. In each case the product is heated to give fused vanadium pentoxide flake.

The process is advantageously carried out continuously, a mass of the material being carried in turn through a preheating zone and an oxidation zone. After leaving the oxidation zone, the material is preferably carried to a quenching zone. When it is desired to perform a two-stage roasting process, the mass of material, after leaving the oxidation zone, is preferably carried through a grinding zone, where aggregates are mechanically broken down, to a further preheating zone and a further oxidation zone before being carried through the quenching zone. The material is preferably carried, at least through the oxidation zone or zones, in the form of a shallow static bed supported on a conveyor, which may be a rotary hearth or a moving belt or grate. When the starting material is slag, the depth of the bed is preferably within the range of from 1 to 10 centimetres.

Several series of experiments were carried out with different starting materials to compare the process of the invention with the conventional method and to investigate the effects of different inert atmospheres for the preheating, and changes in preheating temperature, the rate of diffusion of oxygen to the preheated charge, length of time of exposure to oxygen, particle size, layer thickness of the charge, oxygen concentration, and the addition of other substances as well as the effects of secondary roasting on the extraction of vanadium from the material.

An experiment was carried out to investigate, whether the nature of the inert atmosphere (the term "inert atmosphere" being used throughout the specification to denote an atmosphere that does not undergo any substantial chemical reaction with the material during the preheating) in which the material is preheated affects the extent to which the material is oxidised when it is contacted with oxygen. Thus, samples of the same batch of slag were preheated to the same temperature in atmospheres that consisted, respectively, (to the extent of more than 99 percent by volume in each case) of nitrogen, helium, carbon dioxide and a mixture of nitrogen, carbon dioxide and steam. The preheat temperature and all other relevant conditions were maintained the same and it was found that, to within the limits of experimental error, the extent of oxidation of the slag that is to say, the change in weight of the slag as a result of the oxidation step, was the same in each case. On the other hand, when, contrary to the invention, further samples from the same batch of slag were preheated to the same temperature in an atmosphere that contained an appreciable proportion of oxygen, all other relevant conditions being maintained the same as before, it was found that the extent of oxidation of the hot slag was materially reduced. Thus, taking the extent of oxidation when the slag was preheated in an inert atmosphere as being 100 percent, it was found that the presence of 11 percent by volume of oxygen in the atmosphere in which the slag was preheated reduced the extent of oxidation to 68.8 percent, while 20 percent by volume of oxygen reduced the extent of oxidation to 45.0 percent and 33 percent by volume of oxygen reduced it to 17.1 percent, the balance being nitrogen in each case.

A series of experiments was performed with, as the starting material, vanadium-containing titaniferous magnetite a chemical analysis of which ore revealed that its composition was as follows, the percentages being by weight based on the total weight of the material:

Fe_2O_3	62.3%
TiO_2	13.3%
Cr_2O_3	1.16%
SiO_2	7.52%
MnO	0.37%
V_2O_5	1.79%

The ore, which was in the form of lumps of up to 3 inches in diameter, was crushed by passing through a 4 inch jawcrusher to reduce the size of the lumps to one-fourth inch in diameter and under. The ore was then reduced in size further either by a dry ballmill until the particles all passed through 60 mesh (B.S.S.) screen or by a "shatter box" using a single pass and a residence time of 3 minutes to reduce the size of the particles to less than 150 microns.

The ore that had been ground in the shatter box was blended with sodium chloride until the proportion of sodium chloride in the mixture was 28.6 percent by weight based on the total weight of the mixture. A sample of this charge was then roasted, not in accordance with the invention, at 800° C. in an electrically heated muffle furnace in a conventional manner. It was found that the percentage by weight of the total vanadium content of the charge extracted from the charge after it had been roasted for 1 hour was 44.4 percent and after 2 hours was 47.3 percent.

A further sample of the same charge was then roasted in accordance with the invention and the percentage by weight of vanadium extracted based on the total vana-

dium content of the charge was measured for different inert preheating temperatures and, in each case, an exposure time to oxygen of 10 minutes. It was found that the percentage vanadium extraction for a preheating temperature of 700° C. was 37.3 percent but that this rose to 59.7 percent for a preheating temperature of 800° C. Thus, when the charge was preheated to 800° C. in an inert atmosphere before exposure to oxygen for 10 minutes the percentage vanadium extraction obtained was greater than that obtained by roasting the charge at 800° C. for 2 hours in the conventional manner.

The ground titaniferous magnetite was blended with sodium carbonate until the proportion of sodium carbonate in the mixture was 28.6 percent by weight based on the total weight of the mixture and the experiments were repeated. For conventional roasting at 800° C. the percentage vanadium extraction after a roasting time of 1 hour was 77.0 percent by weight and this rose to 82.2 percent by weight after 2 hours. When the same charge was roasted in accordance with the invention the results shown in Table I were obtained.

TABLE I

Preheating temp. in °C.	Length of period of exposure to oxygen, in minutes	Percentage Vanadium Extraction
600	10	34.0
700	10	81.2
800	10	94.7
850	10	97.6

Thus, by using preheating temperatures above 700° C., the percentage vanadium extraction was increased over that obtained by using the conventional method with a much longer roasting period.

When titaniferous magnetite was preheated to a temperature of 600° C. a higher percentage vanadium extraction was obtained when sodium chloride was incorporated with the material prior to roasting than when sodium carbonate was used but, for preheating temperatures of 700° C. and above, considerably higher extraction percentages were obtained when sodium carbonate was incorporated with the material. The effects of the addition of different materials on the extraction of vanadium are, however, described in more detail hereinafter.

To study the effect of different preheating temperatures on the recovery of vanadium, the titaniferous magnetite that had been ground in the shatter box was blended with a quantity of sodium carbonate equal to 23.05 percent by weight based on the total weight of the mixture. Samples of this charge in the form of layers of about 5 mm. in thickness in small alumina boats were then preheated in an atmosphere of nitrogen to different temperatures within the range of from 500° to 1,050° C. and each exposed to an atmosphere of pure oxygen for 10 minutes. Each sample was then wet-milled and digested in water at about 80° to 90° C. and the percentage extraction of vanadium was calculated by measuring the quantities of soluble and insoluble vanadium present. The high proportion of sodium carbonate, the relatively long residence time in oxygen and the layer thickness were chosen so as to ensure that the percentage recovery of vanadium did not depend sensitively upon the precise values of these parameters. The results obtained are given in Table II.

TABLE II

Preheating Temperature in °C.	Percentage Vanadium Extraction
500	5.1
550	12.1
600	19.3
650	31.6
700	42.8
750	53.0
800	88.4
850	89.6
900	92.9
950	95.5
1,000	98.3
1,050	90.2

For preheating temperatures above 1,000° C. the formation of a liquid phase during exposure to oxygen caused the percentage vanadium extraction to decrease. It is thought, however, that the residence time of the charge in the oxygen was too short for greater fusion of the charge, and hence the formation of water-insoluble or alkali-insoluble vanadium compounds, to take place. For preheating temperatures below 800° C. it is thought that the formation of soluble vanadium compounds is caused by the effects of exothermal heat given out when the preheated charge is exposed to oxygen.

A further series of experiments was carried out in which the titaniferous magnetite that had been ground in the shatter box was mixed with a quantity of sodium carbonate equal to 28.6 percent by weight based on the total weight of the mixture. Samples of the charge were then preheated in an inert atmosphere to different temperatures before being exposed to pure oxygen for 10 minutes. The samples were on open-ended trays in layers of 5 to 10 mm. in thickness which were suspended horizontally so that they were in the middle of the path of flow of the oxygen. These measures were taken to increase the rate of diffusion of the oxygen to the charge. The results of the experiments are shown in Table III.

TABLE III

Preheating Temperature in °C.	Percentage Vanadium Extraction
600±25	34.0
700±25	81.2
800±25	94.7
850±25	97.6

Thus, as the rate of diffusion of oxygen to the charge is increased for the same preheating temperature the vanadium extraction efficiency is also increased.

Fly ash, recovered from flue gases in the burning of crude oil and in the form of a dark brown powder, gave the results shown in Table IV when subjected to a sieve analysis and the results shown in Table V when subjected to a chemical analysis.

TABLE IV

Sieve Mesh (B.S.S.)	Approximate Maximum Particle size in microns	Percentage of total weight	Percentage Cumulative weight
+40	—	0.05	0.05
−40+60	420	0.05	0.1
−60+80	250	0.1	0.2
−80+100	177	0.3	0.5
−100+140	149	3.2	3.7
−140+200	105	5.8	9.5
−200+230	74	8.4	17.9
−230+270	63	14.1	32.0
−270+400	53	10.8	42.8

−400	37	57.2	100.0

TABLE V

	Percentage of total weight
SiO_2	14.94
Fe	2.80
Mn	0.09
P	0.067
Al_2O_3	8.50
CaO	4.50
MgO	0.23
Cr	0
V	1.58
Cu	0
Ni	0.63
TiO_2	1.18
Na_2O	0.29
K_2O	0.50
C	55.70
S	2.60
Mo	0.04
Zn	0.05
Sr	0

Roasting the fly ash in accordance with the invention in the absence of any additives proved to be about 60% more efficient in reducing the carbon content of the fly ash than roasting in a conventional manner in a muffle furnace at 950° C. for a prolonged period. After reduction of the carbon content, a chemical analysis of the fly ash was calculated on the basis of the analysis obtained before roasting. This analysis is shown in Table VI.

TABLE VI

	Percentage of total weight
SiO_2	33.65
Fe	6.32
Mn	0.20
P	0.15
Al_2O_3	19.16
CaO	10.10
MgO	0.52
Cr	0
V	3.56
Cu	0
Ni	1.42
TiO_2	2.66
Na_2O	0.65
K_2O	1.13
C	trace
S	trace
Mo	0.09
Zn	0.10
Sr	0

A series of experiments was then carried out to investigate the effects of different inert preheating temperatures when using the fly ash as the starting material.

The fly ash was mixed with a quantity of anhydrous sodium carbonate equal to 28.6 percent by weight based on the total weight of the mixture and samples were placed on metal plates, each sample being in a layer of about 1 cm. in thickness. The samples were then each preheated to a different temperature in an atmosphere of nitrogen which was then replaced by pure oxygen. After an interval of 5 minutes, each sample was either rapidly withdrawn from the oxygen and quenched in water, the results being shown in Table VII, or allowed to cool in nitrogen, broken down and then re-roasted, the results being shown in Table VIII. In the secondary roasting process, each sample was preheated in inert atmosphere to the same temperature as in its primary roasting process and was again exposed to oxygen for 5 minutes.

TABLE VII

Preheating Temperature in °C.	Time in Oxygen, in minutes	Percentage Extraction of Vanadium
500	5	87.0
525	5	91.5
550	5	91.9
575	5	89.0
600	5	90.7
625	5	93.3
650	5	90.5
700	5	87.7
750	5	82.8
800	5	73.3
850	5	72.3

TABLE VIII

Preheating Temperature in both primary and secondary roasting, in °C.	Total Time in Oxygen, in minutes	Percentage Extraction of Vanadium after secondary roasting
300	10	12.14
400	10	92.70
450	10	95.00
500	10	96.0
525	10	96.5
550	10	96.6
575	10	96.9
600	10	96.9
625	10	97.1
650	10	96.9
675	10	97.3
700	10	97.3
725	10	96.85
750	10	95.60

When the results shown in Table VII are compared with those in Table II (noting that the preheating temperature of 300° C. is not within the scope of the invention), it will be seen that very much higher vanadium extraction values for the same preheating temperatures and shorter periods of exposure to oxygen are obtained for fly ash than for titaniferous magnetite. It is thought that the presence of a considerable quantity of carbon dust by its combustion helped propagate the oxidation reaction of the samples of fly ash preheated to only a relatively low temperature. Above preheating temperatures of 750° C., considerable liquid-phase formation occurred and it is thought that this accounted for the reduction in the extraction of vanadium from samples of fly ash preheated to these temperatures.

It will be seen from a comparison of the results obtained in Tables VII and VIII that the extraction of vanadium from fly ash is increased by secondary roasting comprising preheating in an inert atmosphere and exposure to oxygen.

A further experiment was carried out in order to investigate the way in which the temperature of slag varied with time while it was in contact with the oxygen after being preheated. Thus, a batch of slag containing 7.01 percent V_2O_5, 3.82 percent P_2O_5, 41.80 percent Fe, 15.08 percent SiO_2, 1.66 percent Al_2O_3, 18.07 percent CaO and 6.14 percent MgO (the percentages being by weight and based on the total weight of the slag) was ground to −200 mesh (B.S.S.), which corresponds to a maximum particle diameter of approximately 75 microns, and a layer of the ground slag 1.25 centimetres deep was preheated in an atmosphere of nitrogen to a temperature of 685° C. and then exposed to an atmosphere consisting substantially of oxygen. The temperature of the layer of slag was measured, by means of a thermocouple buried in it, at intervals of 6 seconds starting from when the preheated slag was first contacted with the oxygen. The results, which are set out in Table IX herein, suggest that the rate of oxida-

tion of the slag reached a maximum within the first 30 seconds.

TABLE IX

Duration of exposure to oxygen in seconds	Slag temperature °C.
0	685
6	705
12	790
18	815
24	910
30	970
36	960
42	900
48	840

To study the effects of different oxidation times on the extraction of vanadium, the titaniferous magnetite, that had been reduced in size by the shatter box, was blended with sodium carbonate until the proportion of sodium carbonate in the charge was 23.05 percent by weight. Samples of the material were then placed on open-ended trays, each sample being in a layer of about 10 mm. in thickness, and were preheated in an inert atmosphere to a temperature of 800° C. before being exposed to an atmosphere of oxygen, each sample being exposed for a different length of time. Each sample was then rapidly withdrawn and quenched in water.

The percentage vanadium extraction obtained after an exposure time of 10 secs. was 80.3 percent by weight based on the total weight of the vanadium content of the charge sample and this rose to over 90 percent for exposure times of from 20 secs. to 2 minutes. The oxidation reaction of the titaniferous magnetite is very fast, the charge being seen to glow on exposure to oxygen. This glow dies away very quickly.

Samples of the fly ash, blended with sodium carbonate in a proportion equal to 28.6 percent of the total weight of the mixture, were preheated in an atmosphere of nitrogen to 650° C. and then exposed to oxygen for different periods of time. The results obtained are shown in Table X.

TABLE X

Time in oxygen, in minutes	Percentage Vanadium Extraction
0	16.7
2.5	58.7
5	78.5
10	83.7
15	91.7
20	95.9
30	96.5

When the roasting was performed in two stages, the charge being milled prior to the secondary roasting, the results obtained were as shown in Table XI. In the secondary roasting process each sample of the charge was exposed to oxygen for the same time as in its primary roasting process.

TABLE XI

Total time in oxygen, in min.	Percentage Vanadium Extraction
5	67.4
10	91.7
20	95.5
30	97.0

The oxidation reaction of fly ash is very much slower than that of titaniferous magnetite, but when a two-stage roasting operation is performed on the fly ash the results show that vanadium extraction in excess of 90 percent by weight is obtained for a total exposure time to oxygen of 10 minutes or more.

An investigation of the effect of different particle sizes on the extraction of vanadium was carried out using titaniferous magnetite ground so that all the particles passed through a 60 mesh (B.S.S.) screen. The ore was then dry screened to obtain different particle size fractions and these fractions were preheated to 800° C. in an inert atmosphere, 28.6 percent by weight of the charge being sodium carbonate, and then exposed to oxygen for 5 minutes. The result obtained for the percentage vanadium extraction from each fraction is shown in Table XII.

TABLE XII

Screen fraction	Approximate Maximum particle size in microns	Percentage Vanadium Extraction
+80	250	52.1
−80+100	177	51.2
−100+140	149	67.1
−140+200	105	89.7
−200+400	74	92.4
−400	37	94.8

Although the above results suggest that it is desirable that the size of particles of titaniferous magnetite should be such that they all pass through a 200 mesh (B.S.S.) screen, it is thought that if the ore were only to be ground to pass through a 100 mesh (B.S.S.) screen the percentage vanadium extraction would be acceptable because the presence of a considerable amount of finer material promotes the oxidation of coarser material if they are roasted together. Titaniferous magnetite that has been ballmilled can easily be ground to this level.

In the case of fly ash, when similar experiments were performed, the fly ash of different particle size fractions being preheated to a temperature of 650° C. in an inert atmosphere, 28.6 percent by weight of the charge being sodium carbonate, and then exposed in a layer of 1 cm. in thickness to pure oxygen for 10 minutes, the percentage vanadium extraction for the plus 100 mesh (B.S.S.) fraction was 95.0 percent by weight and similar high results were obtained for the finer particle fractions. It is therefore concluded that, for the exposure times of 10 minutes, changes in the particle size within the range investigated have little effect on the percentage vanadium extraction from fly ash.

The effect of different layer thicknesses of charge was investigated using titaniferous magnetite that had been ground by the shatter box. The charge, of which 23.05 percent by weight was sodium carbonate, was spread in a layer over a given area, the layer thickness being increased by increasing the load per unit area. Layers of 5 mm., 10 mm., 15 mm., and 20 mm., in thickness were, in turn, preheated in an inert atmosphere to 800° C., the percentage vanadium extraction being determined for different exposure times for each layer thickness. Although for exposure times of 4 minutes and 8 minutes the percentage extraction increased slightly as the layer thickness was increased to 15 mm. and then decreased, the converse was true for exposure times of 16 minutes. Different layer thicknesses within the range of from 5 mm. to 20 mm. appear to have little effect on the extraction of vanadium from titaniferous magnetite.

A similar series of experiments but over a wider range of charge layer thicknesses was performed on fly

ash. For each layer thickness the charge, 28.6 percent by weight of which was sodium carbonate, was preheated in an inert atmosphere to 650° C. and then exposed to pure oxygen for 10 minutes. The size of the particles was such that they passed through a 20 mesh (B.S.S.) screen. The results obtained are shown in Table XIII below.

TABLE XIII

Layer thickness in cm.	Load in g. per unit area	Percentage Vanadium Extraction
0.1	0.14	92.8
0.2	0.35	94.9
0.3	0.70	97.7
0.5	1.05	97.7
0.75	1.40	98.7
1.00	1.75	91.6
1.30	2.10	90.6

From the above results it can be concluded that a surface loading of 1.5 grams/cm² would give high vanadium extraction. Greater loading would make it necessary to have longer exposure times to obtain similar results.

To study the effect of different oxygen concentrations in the atmosphere to which preheated charge is exposed, a series of experiments were carried out to investigate the effect on the extraction efficiency of diluting with nitrogen the oxygen with which preheated slag is contacted. Thus, samples taken from the same batch of slag were preheated to the same temperature in an inert atmosphere and were then contacted, respectively, with an atmosphere consisting (to the extent of more than 99% by volume) of oxygen and with atmospheres consisting of oxygen diluted with different proportions of nitrogen. With all other relevant conditions being maintained constant, it was found that the extraction efficiency fell as the proportion of nitrogen increased. The actual figures are set out in Table XIV herein, in which the percentages of oxygen and nitrogen are by volume and the extraction efficiency with an atmosphere consisting of oxygen is taken as 100 percent.

TABLE XIV

Percentage of oxygen	Percentage of nitrogen	Extraction efficiency per cent
20	80	30
33	67	30.5
43	57	38.0
50	50	62.2
57	43	86.9
67	33	90.0
80	20	94.5
>99	—	100.0

It will be seen from Table XIV that the efficiency of the extraction of vanadium from slag does not fall very rapidly with increasing dilution of the oxygen until the percentage of oxygen falls to about 60 percent by volume. Thus, while it is preferred to contact the preheated slag with substantially pure oxygen when that is possible, it is feasible to dilute the oxygen a little in order to reduce the maximum temperature reached by the slag while it is in contact with the oxygen if that maximum temperature would otherwise be too high.

A further series of experiments were peformed in which samples of titaniferous magnetite with which sodium carbonate was incorporated in a quantity equal to 23.1 percent by weight of the total weight of the mixture, were preheated to 800° C. in an inert atmosphere. The samples were then exposed to atmospheres composed of different proportions of oxygen and nitrogen, each sample being in a layer of 10 mm. in thickness and the maximum particle size being 150 microns. After 1 minutes, each sample was withdrawn and quenched in water. The concentration of oxygen in the gas to which each sample was exposed was always in excess of the minimum required for oxidation of the ore, the partial pressure of the oxygen being varied. For an atmosphere in which 10 percent by volume was oxygen, the extent of oxidation was 88.5 percent by weight of the total vanadium content. This rose to 94.5 percent by weight as the concentration of oxygen was increased to 20 percent by volume, and 100 percent by weight for concentrations over 40 percent by volume. Oxygen-enriched air would therefore give satisfactory results in the extraction of vanadium from titaniferous magnetite.

A similar series of experiments were performed on the fly ash. Samples of the fly ash, incorporated with sodium carbonate in a quantity equal to 28.6 percent by weight of the total weight of the mixture, were preheated to 650° C. in an inert atmosphere. The samples were then exposed to atmospheres of different proportions of oxygen and nitrogen for 10 minutes in layers of 1 cm. in thickness, the size of the particles being such that they all passed through a 20 mesh (B.S.S.) screen. When exposed to an atmosphere of pure nitrogen the percentage vanadium extraction, based on the percentage extraction obtained under the same conditions but using an atmosphere of pure oxygen, was 15.4 percent by weight. This value rose to 37.6 percent by weight in an atmosphere in which the proportion of oxygen was 10 percent by volume, 69.2 percent by weight as the proportion of oxygen was increased to 20 percent by volume and 92.3 percent by weight when the proportion of oxygen was 80 percent by volume. Thus, in the case of fly ash, a high concentration (at least in excess of 60 percent by volume) of oxygen in the atmosphere to which the preheated charge is exposed is desirable for efficient vanadium recovery.

To study the effects of the addition of salts of an alkali metal to the charge, a number of experiments were carried out to illustrate the effect of incorporating sodium carbonate with slag prior to contacting the preheated slag with oxygen. Thus, three slags A, B and C, respectively, were obtained from geographically different sources and treated in accordance with the invention.

Slag A had the following composition the percentages being by weight and based on the total weight of the slag:

V_2O_5	30.60%
SiO_2	14.80%
FeO	36.30%
MnO	5.18%
Cr_2O_3	6.15%
TiO_2	5.23%
CaO	1.87%
MgO	1.66%

Four samples of slag A were each preheated in an inert atmosphere to similar temperatures and then contacted with an atmosphere of substantially pure oxygen for a period of 5 minutes, the maximum temperature reached by the slag while it was in contact with the oxygen being measured. Each sample of the oxidised slag was quenched by introducing it into an aqueous solution of sodium carbonate of 5 percent strength and, after the oxidised slag had been hot-leached with this

solution, the insoluble residues were leached with dilute sulphuric acid and the vanadium extraction efficiency was determined. Sodium carbonate was incorporated with three of the samples of the slag before preheating and the results of the experiments, which are set out in Table XV herein, where the percentages of sodium carbonate are by weight and based on the weight of the mixture of slag and sodium carbonate, show that the incorporation of sodium carbonate both lowers the maximum temperature reached by the slag while it is in contact with the oxygen and improves the vanadium extraction efficiency.

TABLE XV

Experiment No.	Percentage of sodium carbonate	Preheat temperature °C	Maximum oxidation temperature °C	Percentage vanadium extraction efficiency
1	0.0	675	990	68.60
2	9.1	673	888	91.21
3	13.0	668	835	93.30
4	16.7	665	775	95.51

Slag B was subjected to four experiments in which the operating procedures followed exactly those of the experiments carried out on slag A and the results are set out in Table XVI herein. It will be seen from Table XVI that, as with slag A, the incorporation of sodium carbonate both decreases the maximum temperature reached by the slag while it is in contact with the oxygen and increases the vanadium extraction efficiency. On the other hand, the vanadium extraction efficiency when no sodium carbonate was added is not as low as with slag A despite the fact that the maximum oxidation temperature was very high. This was because slag B had a much lower vanadium content than slag A and so was more refractory than slag A, the composition of slag B being as follows the percentages being by weight and based on the total weight of the slag:

V_2O_5	11.78%
FeO	59.30%
Fe_2O_3	0.29%
MnO	1.70%
SiO_2	17.72%
Al_2O_3	1.60%
TiO_2	0.96%
Cr_2O_3	0.07%
CaO	3.79%
MgO	1.36%
P_2O_5	1.60%

TABLE XVI

Experiment No.	Percentage of sodium carbonate	Preheat temperature °C	Maximum oxidation temperature °C	Percentage vanadium extraction efficiency
1	0.0	690	1,005	82.15
2	9.1	680	923	88.42
3	13.0	680	880	91.20
4	16.7	680	835	94.60

Slag C had the following composition the percentages being by weight and based on the total weight of the slag:

V_2O_5	15.00%
SiO_2	15.90%
CaO	0.87%
P	0.06%
Fe	39.60%

Three samples of slag C were each mixed with 13.04 percent by weight of sodium carbonate, based on the weight of the mixture, and preheated in an inert atmosphere to different temperatures. Thereafter, the preheated slags were treated in the same manner as slags A and B were treated, and the results are set out in Table XVII herein. In each of the three experiments that were carried out on slag C, the maximum temperature reached by the slag while it was in contact with the oxygen was approximately 260° C. above the preheat temperature.

TABLE XVII

Experiment No.	Preheat temperature °C	Percentage vanadium extraction efficiency
1	620	94.95
2	650	96.14
3	700	96.74

Prior to being treated in accordance with the invention as described hereinbefore, each of slags A, B and C was ground to −60 mesh (B.S.S.), but the "feel" test carried out by crumbling the slag in the hand suggested that slag C was the most finely ground and that slag B was the coarsest.

To study the effects of the addition of salts to another vanadium-containing material, samples of titaniferous magnetite were fluxed with sodium chloride (that is to say, sodium chloride was incorporated with the samples) and further samples were fluxed with sodium carbonate, the proportion of fluxing agent in each sample being 28.6 percent of the total weight of the sample. The samples were then roasted in a conventional manner in a muffle furnace at 800° C. It was found that, after one hour, the extraction of vanadium from the titaniferous magnetite fluxed with sodium chloride was 44.4 percent by weight whereas that from the magnetite fluxed with sodium carbonate was 77.0 percent by weight. After 2 hours roasting at 800° C. in the muffle furnace, the values for the extraction of vanadium from two samples of titaniferous magnetite fluxed with sodium chloride were 33.0 percent and 41.6 percent by weight, and those for two samples of the material fluxed with sodium carbonate were 81.4 percent and 82.9 percent by weight. Thus, for titaniferous magnetite it is desirable that sodium carbonate should be used as the fluxing agent.

To investigate the effects of different proportions of fluxing agents in titaniferous ore roasted in accordance with the invention, a series of experiments were performed on samples of titaniferous magnetite mixed with different proportions of sodium carbonate. The samples, each being in a layer of 10 mm. in thickness, were preheated in an inert atmosphere to a temperature of 850° C. and then exposed to pure oxygen for a measured period of time. The results obtained for the percentage extraction of vanadium in each case are given in Table XVIII.

TABLE XVIII

Percentage concentration of fluxing agent	Exposure time to oxygen, in minutes	Percentage vanadium extraction
0	10	13.8
1.96	10	81.2
4.75	15	85.4
7.41	10	97.2
9.1	15	90.4
13.05	15	94.5
13.79	5	96.5
13.79	10	97.7
16.65	15	94.4
20.0	15	94.6
23.05	15	97.1
24.25	5	97.0
24.24	10	98.0

25.9	15	94.3
28.58	5	97.6
28.58	10	98.0
28.58	15	87.8

These results suggest that a concentration in the charge of between 10 and 15 percent by weight of sodium carbonate would be adequate for the recovery of over 90 percent by weight of the total vanadium content of titaniferous magnetite.

Similar series of experiments were performed on samples of fly ash. The samples were mixed with different proportions of either sodium carbonate, or sodium chloride or sodium sulphate and were roasted in the form of layers of about 1 cm. in thickness for 1 hour at 800° C. in a muffle furnace in a conventional manner not in accordance with the invention. The samples were then leached using water or an alkaline solution and the quantity of vanadium recovered was measured. The results obtained are given in Table XIX.

TABLE XIX

Fluxing agent	Percentage concentration of fluxing agent in charge	Percentage Vanadium Extraction
Na_2CO_3	0	16.6
"	9.1	43.6
"	16.7	62.3
"	23.1	87.7
"	28.6	82.3
NaCl	0	31.1
"	9.1	26.3
"	16.7	21.5
"	23.1	9.3
"	28.6	3.3
Na_2SO_4	0	35.2
"	9.1	26.3
"	16.7	56.4
"	23.1	54.5
"	28.6	73.6

From the above results it can be seen that it is desirable to use sodium carbonate as the fluxing agent for fly ash. This was found to be the most stable and reliable fluxing agent out of the three with which experiments were performed.

To investigate the effects of different proportions of fluxing agent in fly ash roasted in accordance with the invention, samples of fly ash, three of which were not mixed with sodium carbonate and the rest of which were mixed with sodium carbonate in proportions ranging from 2.4 percent by weight of the charge to 28.6 percent by weight, were each preheated in an inert atmosphere to a temperature within the range of from 600° to 680° C. and then exposed in a layer of 1 cm. in thickness to pure oxygen for 10 minutes. The results obtained are given in Table XX.

TABLE XX

Proportion of sodium carbonate in charge, in percent by weight	Percentage Vanadium Extraction
0	39.9
0	31.4
0	36.1
2.4	52.2
4.8	41.7
4.8	33.5
4.8	32.0
6.9	22.1
9.1	24.7
9.1	11.4
9.1	21.6
13.1	42.1
13.1	23.8
13.1	41.2
16.7	63.0
16.7	61.3
16.7	30.1
20.0	74.6
20.0	81.1
23.1	84.3
23.1	85.9
23.1	86.7
25.9	90.4
25.9	86.5
28.6	90.9
28.6	93.3
28.6	92.6

For a percentage extraction of vanadium of at least 90 percent by weight, the concentration of flux in the charge should be in excess of 25 percent by weight of the total weight of the charge.

In addition to the above experiments a further series of experiments were performed in which samples of the fly ash, mixed with different proportions of sodium carbonate, were preheated in an inert atmosphere to a temperature of 680° C. and exposed to oxygen. The samples were then cooled, milled slightly to break down aggregates and re-roasted by again being preheated in an inert atmosphere to a temperature of 680° C. and exposed to oxygen. The percentage vanadium extraction obtained on quenching the charge is given in Table XXI.

TABLE XXI

Proportion of sodium carbonate in charge, in percent by weight	Percentage Vanadium Extraction
0	47.7
4.8	31.3
9.1	12.5
13.1	43.4
16.7	64.4
20.0	71.1
23.1	94.4
25.9	96.7
28.6	96.5

It will be seen that for sodium carbonate concentrations of 23.1 percent by weight and over, the percentage extraction of vanadium from fly ash is higher than that obtained when it is subjected to only a single roasting operation.

Ferrophosphorus, which generally proves very difficult to process in a conventional manner, was ground in a shatter box and a sample was subjected to a chemical analysis which showed that it contained 17.78 percent by weight of vanadium pentoxide.

To compare the roasting process of the invention with the conventional roasting process, the ground ferrophosphorus was blended with anhydrous sodium carbonate to the extent that the mixture was composed of 23.1 percent by weight of sodium carbonate. One sample of the mixture was then roasted in a conventional manner in an electric muffle furnace at 600° C. for 24 hours and a second sample was preheated to a temperature of 600° C. in an inert atmosphere and then exposed to an oxygen-rich atmosphere for 24 minutes. Both samples were cooled and then leached with dilute sulphuric acid solution. The percentage of the total vanadium content of the charge extracted from the first sample was 34.5 percent by weight and from the second sample was 53.7 percent by weight. The conventionally roasted sample was found to have sintered considerably. It was thought that the fact that the extraction of vanadium was only 53.7 percent from ferrophosphorus roasted in accordance with the invention, even though this is a considerable improvement over that obtained from ferrophosphorus when roasted in a conventional manner, was because the ferrophospho-

rus reacted violently with the oxygen after being preheated in an inert atmosphere, a large liquid phase component being formed.

A series of experiments were performed to determine the effect of mixing with the ferrophosphorus different proportions of a basic, refractory, phosphorus-and vanadium-containing slag that had been found to react slowly when exposed to oxygen after being preheated in an inert atmosphere. Such slag had to be preheated to a temperature within the range of from 900° to 950° C. for an acceptable extraction value to be obtained and it was found that the highest percentage extraction that could be obtained was 85 percent to 86 percent by weight. The slag was subjected to a chemical analysis which showed that it contained 5.99 percent by weight of vanadium oxide and about 37 percent by weight of calcium and magnesium oxides.

Samples composed of different proportions of ferrophosphorus and basic slag were preheated to 600° C. in an inert atmosphere and then exposed to pure oxygen for 10 minutes. The results obtained for the percentage vanadium extraction are shown in Table XXII.

TABLE XXII

Proportion of ferrophosphorus in charge in percent by weight	Proportion of slag in charge in percent by weight	Preheat Temperature in °C.	Time in oxygen, in minutes.	Percentage extraction of Vanadium
20	80	600	10	50.7
15	85	600	10	56.4
10	90	600	10	71.0
5	95	600	10	67.7

From these results it was deduced that the ferrophosphorus, even when diluted with basic slag, still reacts too violently for a high extraction percentage to be obtained.

In a further series of experiments, the ferrophosphorus was first roasted in accordance with the invention in the absence of any additives, it being preheated in an inert atmosphere to a temperature of 600° C. and then exposed to only oxygen-enriched air. The roasted material was cooled down, broken and blended with the basic slag, the proportion of slag in the mixture being 90 percent by weight based on the total weight of the mixture. Sodium carbonate was then added to the mixture in a quantity such that the charge was composed of 28.6 percent by weight of sodium carbonate to control the reaction further and to help prevent the formation of liquid phase. Samples, preheated to different temperatures in an inert atmosphere, were exposed to oxygen for 5 minutes. The results obtained for the percentage extraction of vanadium obtained by acid leaching are shown in Table XXIII.

TABLE XXIII

Proportion of Ferrophosphorus in mixture in percent by weight	Proportion of slag in Mixture in percent by weight	Preheating temperature in °C.	Percentage Vanadium Extraction
10	90	600	85.8
10	90	650	89.0
10	90	700	91.6
10	90	750	97.4
10	90	800	99.0

The extraction of vanadium from the mixture, when the mixture is preheated to a temperature of at least 650° C. in an inert atmosphere, was greater than that obtained from the slag when roasted alone.

The following Example illustrates the invention, the percentages being by weight:

A slag, which contained 8.3 percent of vanadium, 18.7 percent of SiO_2 and 39.3 percent of FeO (the percentages being by weight and based on the weight of the slag) and also chromium, manganese and aluminium, but which was low in alkali metals, alkaline earth metals and phosphorus, was ground to −36 mesh (B.S.S.) which corresponds to a maximum particle diameter of approximately 420 microns.

Anhydrous sodium carbonate was blended with the ground slag, the proportions being such that the concentration of anhydrous sodium carbonate in the resulting mixture was 28.6 percent by weight.

The mixture was divided into a number of different samples and each sample was introduced into a flat container to form a layer 1 centimetre thick, and the container was inserted into a tube furnace which was purged with nitrogen and maintained at a temperature of 680° C. (as indicated by a thermocouple embedded in the sample), the flow of nitrogen was stopped and replaced by a flow of oxygen. After the oxygen flow had been maintained for a measured time, which was different for each sample, the oxygen flow was stopped and the flow of nitrogen was restarted. The sample was then withdrawn into the cold zone of the furnace and allowed to cool down.

Each resulting cold sample was slurried with water, stirred, heated to a temperature of approximately 80° C. and filtered. The resulting filtrate and any sample residue were assayed for vanadium and the percentage extraction was calculated using the following formula:

$$\frac{\text{vanadium in filtrate (grams)}}{\text{total vanadium in filtrate and residue (grams)}} \times 100 = \text{percentage of vanadium extracted}$$

The percentages of vanadium extracted after different periods of exposure to oxygen are shown in Table XXIV herein and it will be seen that very little improvement in extraction efficiency was obtained by prolonging the exposure to oxygen beyond 2.5 minutes. The extraction efficiency of 2.0 percent when the time of exposure to oxygen was nil is explained by the fact that the original slag contained some soluble vanadium and in fact the figure of 2.0 percent was identical with that obtained when the untreated slag was leached with hot alkaline solution.

TABLE XXIV

Oxygen exposure time	Percentage extraction of vanadium
nil	2.0
25 sec	50.0
50 sec	80.0
75 sec	87.0
100 sec	89.0
2.5 min	91.25
3.3 min	91.25
5.0 min	91.25
6.6 min	91.25
8.3 min	91.50
10.0 min	91.75

I claim:

1. In a process for the beneficiation of a vanadium-containing material, wherein the reaction period of vanadium-containing material with oxygen is considerably reduced and at the same time the percentage extraction of the vanadium component of the material is increased over that obtained by the conventional ex-

traction processes used with such materials, the steps of preheating the material under inert conditions in the absence of oxygen and free of any reducing effects so as to not effect any chemical change in the material and in the absence of any substance that would react to any substantial extent and then contacting the resulting hot material with oxygen to effect the formation of soluble vanadium compounds, the preheating of the material being effected to raise the temperature of the material to such an extent that it is at a temperature of at least 400° C. when it is initially contacted with oxygen and that it reacts with the oxygen in a strongly exothermic manner, the maximum temperature reached by the material while it is in contact with the oxygen being within the range of from 600° to 1,200° C. and below that at which excessive sintering of the material occurs and at which a large liquid-phase component is produced which would materially reduce extraction efficiency and below the temperature at which vanadium metal becomes incandescent the resulting material being soluble in aqueous medium.

2. The process of claim **1**, wherein the maximum temperature reached by the slag while it is in contact with the oxygen being within the range of from 680° to 1,050° C.

3. The process of claim **2**, wherein the maximum temperature reached by the slag while it is in contact with the oxygen does not exceed 950° C.

4. The process of claim **2**, wherein the temperature to which the ground slag is preheated under inert conditions is at least 630° C.

5. The process of claim **1**, wherein sodium carbonate is incorporated with the material prior to its being contacted with oxygen.

6. The process of claim **1**, wherein the slag is ground to −36 mesh (B.S.S.), corresponding to a maximum particle diameter of approximately 420 microns.

7. The process of claim **1**, wherein the vanadium-containing material is vanadium-containing titaniferous ore and the temperature to which the material is preheated under inert conditions is within the range of from 800° to 1,000° C.

8. The process of claim **1**, wherein the vanadium-containing material is fly ash and the temperature to which the material is preheated under inert conditions is within the range of from 400° to 700° C.

9. The process of claim **1**, wherein the material is ground to −100 mesh (B.S.S.).

10. The process of claim **1**, wherein, after the vanadium-containing material has been contacted with oxygen to effect the formation of soluble vanadium compounds, the vanadium-containing material is ground and then reacted with oxygen for a second time at an elevated temperature to effect the formation of a further quantity of soluble vanadium compounds.

11. The process of claim **10**, wherein, after the vanadium-containing material has been ground, it is preheated under inert conditions to a temperature of at least 400° C. prior to its being contacted with oxygen for a second time the temperature of the preheated material when it is initially contacted with oxygen for the second time being at least 400° C.

12. The process of claim **1**, wherein the vanadium-containing material is ferrophosphorus and, after the ferrophosphorus has been contacted with oxygen to effect the formation of soluble vanadium compounds, it is ground, basic vanadium-containing slag is incorporated with it, it is preheated under inert conditions, and then it is contacted with oxygen for a second time to effect the formation of a further quantity of soluble vanadium compounds the temperature of the preheated material when it is initially contacted with oxygen for the second time being at least 400° C.

13. The process of claim **1**, wherein, after the material has been contacted with oxygen for the first time, or, when the material is contacted with oxygen for a second time, after the material has been contacted with oxygen for the second time, the material is quenched.

* * * * *