United States Patent

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[54] **PROCESS OF EXTRACTING VANADIUM**
6 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **23/16,** 23/21, 23/140, 23/202
[51] **Int. Cl.** **C22b 59/00,** C01g 31/00
[50] **Field of Search** 23/16, 19.1, 17, 21, 140

[56] **References Cited**

UNITED STATES PATENTS

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OTHER REFERENCES

Glemser et al., " Zeitschrift fur anorganische und allgemeine chemie," Band 316, 1962, pp. 168–181.

Millner et al., " Nature," Vol. 163, No. 4146, April 16, 1949, pp. 601–602

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ABSTRACT: To separate vanadium from vanadium-bearing material such as slag heated to a temperature at least 600° C. by forming a volatile hydroxide in contact with water vapor and air, and to separate vanadium oxide by cooling the vanadium-containing gas thus formed.

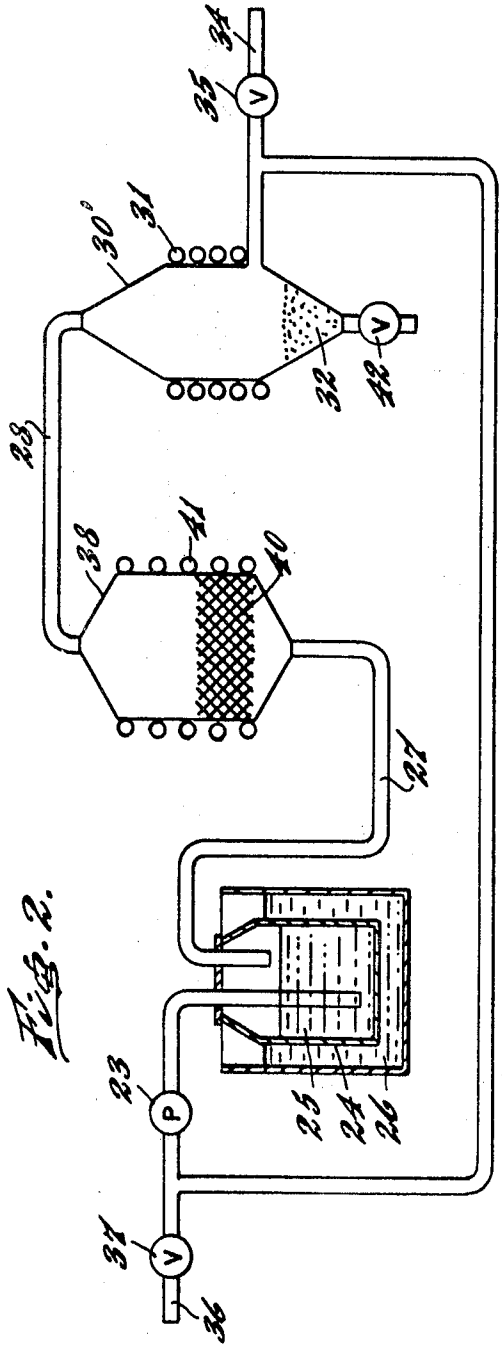


Fig. 2.

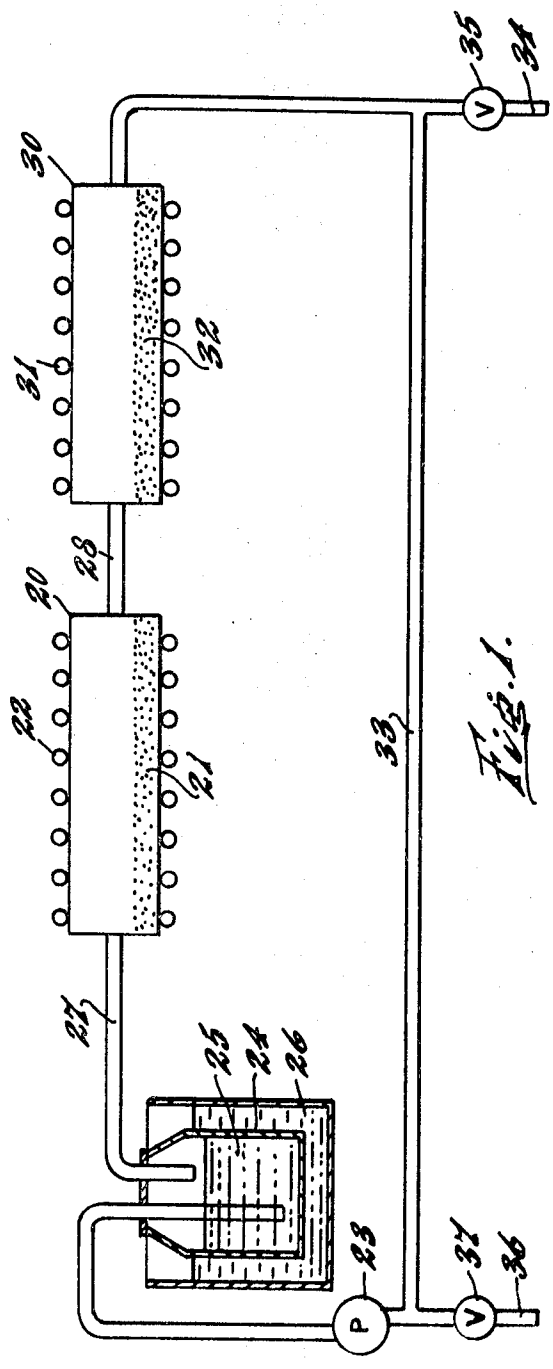


Fig. 1.

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PROCESS OF EXTRACTING VANADIUM

DESCRIPTION OF INVENTION

The present invention relates to a process of extracting vanadium as vanadium hydroxide from a solid vanadium-bearing material such as a slag or similar material.

A purpose of the invention is to heat a solid vanadium-bearing material such as a slag or the like to a temperature above 600° C., desirably in the range of 600° C. to 1,000° C., and most desirably in a range of 700° to 900°° C. and to pass in contact with the vanadium-bearing material a gas comprising water vapor and oxygen.

A further purpose is to maintain the gas at atmospheric pressure.

A further purpose is to maintain the gas at superatmospheric pressure.

A further purpose is to blow the gas through a bed of vanadium-bearing particles.

A further purpose is to deposit vanadium oxide from the vanadium-bearing gas by cooling it, suitably to a temperature below 500° C.

A further purpose is to maintain gas in contact with the vanadium-bearing material for a time of at least 1 hour.

A further purpose is to reduce the coloring content of solid titanium material by extracting vanadium as the hydroxide by a gas comprising water vapor and oxygen.

A further purpose is to selectively extract vanadium in the presence of one or more of iron, titanium, silicon, aluminum, calcium, magnesium, chromium, manganese, sodium, potassium, and sulfur by removing the vanadium heated to elevated temperature by a gas containing water vapor and oxygen and then deposit vanadium oxide by cooling the gas.

Further purposes appear in the specification and in the claims.

The drawings illustrate diagrammatically apparatus which may be used to carry on the process of the invention.

FIG. 1 is a diagrammatic view of a muffle apparatus which may be employed in the invention.

FIG. 2 is a diagrammatic view of a fluidized bed employed in the invention.

The invention relates to a process of removing vanadium from certain vanadium-bearing materials such as slags and the like, including alloy scrap, dross, cinder and matte. When removal of vanadium is referred to, it is intended to indicate that at least some of the vanadium is taken out, and not necessarily that all of the vanadium is removed.

One application of the invention is in removing much of the vanadium which contaminates certain titanium-bearing slags, and which is particularly objectionable where it is intended to produce titanium pigments for coating applications, in which vanadium may impart an undesirable color.

One of the virtues of the process is that when carried out within a proper temperature range it will normally deposit pure vanadium oxide in a single step. It is, therefore, to be preferred to intricate wet methods.

In accordance with the invention the vanadium material such as a slag is first crushed to a granular or powder form. This has the advantage of exposing present surface and reduces the reaction time. Experiments by the present inventor indicate that the particle size is not critical. Successful removal of vanadium by the process of the invention has been accomplished using granules through 10 mesh per linear inch (Tyler standard) and also with fine powder, either loose or compressed into pellets.

The present inventor has discovered that the extraction of vanadium from heated vanadium-bearing materials is greatly promoted by adding to the gas circulated in contact with the vanadium-bearing material oxygen as well as water vapor.

There is indirect evidence that the vanadium volatilizes in the form of the hydroxide and that this hydroxide decomposes upon cooling to a mixture of water vapor and vanadium oxide. The product on the cooled surface of the exit chamber is the oxide, not the hydroxide.

Without limiting to a particular theory, it appears from the experiments of the present inventor that vanadium hydroxide of higher valence is substantially more volatile at a moderate temperature range than vanadium hydroxide of lower valence. It is thus possible to remove a substantial proportion of the vanadium present without correspondingly volatilizing hydroxides of other materials which are likely to be present, such as iron, titanium, silicon, aluminum, calcium, magnesium, chromium, manganese, sodium and potassium. Furthermore, although sulfur will volatilize, it forms a fixed gas (not readily liquified or solidified) whereas vanadium will separate from a mixture of water vapor and oxygen as solid vanadium oxide at lower temperatures.

In order to obtain best results in the process of the present invention, the vanadium-bearing materials should be heated to a temperature of at least 600° C. In order to avoid volatilization of other metals which are likely to be present in a vanadium-bearing slag or the like, the temperature of treatment should not go as high as 1,300° C. and desirably should not be above 1,000° C. For best results the vanadium-bearing material from which the vanadium is being volatilized should be maintained at a temperature of 700° C. to 900° C.

The time of treatment will depend upon the extent of vanadium removal desired, the physical form of the vanadium-bearing material and the nature of the compound in which the vanadium is present in the material. Substantial vanadium removal from a slag or the like can ordinarily be obtained in 1 hour and often 4 hours exposure to the gas is sufficient to remove a considerable part of the vanadium. Also, recirculation of the gas over or through the vanadium-bearing material is preferred and much more prolonged treatment can be used if required.

One unique feature of the present invention is that it removes vanadium from vanadium-bearing titanium and iron slags and the like at moderate treatment temperatures without the need to fuse and dissolve the material for the vanadium extraction.

Following the contact operation by which the mixture of water vapor and air becomes charged with volatile vanadium compound, it is very easy to precipitate commercially pure vanadium oxide by simply cooling the gas suitably to a temperature below 600° C., preferably below 500° C., and permissibly to any desired lower temperature.

As previously mentioned, it is believed that a high valence vanadium hydroxide volatilizes but this form of vanadium is unstable at lower temperatures and appears to decompose to water vapor and solid vanadium oxide.

The process may be carried out in a laboratory transpiration apparatus of the character described by G. R. Belton nd F. D. Richardson, "58 Transactions of the Faraday Society 1562" (1962). In this apparatus an alumina reaction tube is used, conveniently with an inside diameter of 0.5 cm. The vanadium-bearing material is conveniently placed in a refractory boat of approximately 5 cm. length and inserted in the tube. As an alternative a stainless steel autoclave may be used instead of the alumina reaction tube.

FIG. 1 illustrates diagrammatically a device of this general character having an autoclave **20** containing vanadium material at **21** and heated to the desired temperature, conveniently by electric heating means **22**. An oxygen-bearing gas is circulated by a pump **23** through a wash bottle **24** containing water **25** held at a suitable temperature, say 95° C., by a constant temperature bath **26**. Thus the gas, suitably air, becomes saturated with water vapor at this temperature and is introduced through a tube **27** and passes over the vanadium-bearing material at elevated temperature. From the autoclave **20** the gas passes by a tube **28** to a condenser **30** which is suitably cooled or heated by means **31** to lower the gas temperature to below 600° C. and preferably below 500° C. As a consequence, vanadium oxide deposits at **32**. The gas is then recirculated through a tube **33**, there being a discharge connection **34** controlled by a valve **35** to release air and water vapor and there being an inlet connection **36** controlled by a

valve 37 to introduce fresh air or oxygen when desired. Thus in the apparatus of FIG. 1 the gas containing oxygen and water vapor recirculates repeatedly in contact with the vanadium bearing material 21 and removes vanadium and deposits it as vanadium oxide at 32.

FIG 2 illustrates a modified device which can be employed in the invention. A retort 38 containing a fluidized bed 40 in heated to the reaction temperature by a suitable heating means 41. In this case a gas containing a mixture of oxygen and water vapor is obtained as previously described, passes from below through the fluidized bed 40 and is introduced into a vertical condenser 30' heated or cooled by means 31 and discharging vanadium oxide 32 at 42, the gas being recirculated as above described.

It will be evident that recirculation of the gas conserves heat and avoids loss of vanadium, oxygen and water Also, a higher concentration of water vapor can be employed in the recirculating stream if desired.

The literature contains several references to the enhanced volatility of certain metals in the presence of water vapor at elevated temperatures. However, there appears to be nothing in the literature to describe the volatilization of vanadium hydroxide from solid vanadium-bearing materials such as glassy slags. Belton and Richardson, A volatile Iron Hydroxide, 58 Transactions of the Faraday Society 1562–1572 (1962) described the enhanced volatility of iron at elevated temperatures in a gas stream containing water vapor and hydrogen and ascribe this volatility of the gaseous compound $Fe(OH)_2$. Belton and Jordan, The Gaseous Hydroxides of Cobalt and Nickel, 71 Journal of Physical Chemistry 4114 (1967), measured the volatility of cobalt and nickel in mixtures of water vapor, hydrogen and argon. These experiments were made with samples of pure iron wire, nickel wire and cobalt wire. In these cases a reducing atmosphere was necessary in order to volatilize the hydroxides of these metals.

Vanadium has an enhanced volatility in the presence of a high water vapor pressure like these iron group elements, but contrary to the behavior of these iron group elements, it has been found by the present inventor that the volatility of vanadium hydroxide occurs at lower temperature and vanadium hydroxide is more volatile in the presence of an oxidizing atmosphere.

Vanadium appears to be similar to molybdenum in the volatility of the hydroxides in mixtures of water vapor and oxygen at temperature of 600° to 1,000° C. The behavior of molybdenum is described by Belton and Jordan, The Volatilization of Molybdenum in the Presence of Water Vapor, 68 Journal of Physical Chemistry 2065 (1965) Fortunately, vanadium and molybdenum rarely occur in he same raw material so that vanadium can be extracted from most materials as pure vanadium oxide without contamination with molybdenum.

The experiments of the present invention indicate that there is a linear relationship between the percentage of water vapor in contact with the vanadium-bearing material and the amount of vanadium volatilized in a given time at a given temperature and pressure. Furthermore, increase of the vapor pressure above atmospheric pressure speeds up the reaction probably because it brings more water vapor into contact with the vanadium. The process thus can be more effectively carried out at pressure of several atmospheres or more.

The temperatures of the vanadium-bearing material is not critical so long as it is above 600° C and preferably above 700° C. at atmospheric pressure. It will be evident that lower temperatures can be used with higher vapor pressures. The flow rate of the gas over the vanadium-containing material is not important. In some of the tests flow rates of 300 ml. and 1 liter per minute were used but in other tests the flow rates varied widely without serious effect on the results.

Tests were carried out over a temperature range of 500° to 1,300° C. The best results were obtained when the temperature of the vanadium-bearing material was in the range between 700° and 900° C At both the higher and lower limits of 500° to 1,300° C., the reaction rate slowed down, and at the higher range the hydroxides of other elements became volatile and appeared to contaminate the vanadium oxide.

Various gases were used in the test program. Among those tried were oxygen plus water vapor. air plus water vapor, hydrogen plus nitrogen plus water vapor. and air plus oxygen plus water vapor. The best results were obtained using air plus water vapor or a synthetic mixture of nitrogen plus oxygen enriched beyond the ratio present in air, plus water vapor.

Test periods ranged from 1 hour to 4 hours and it is evident that longer periods can be used if desired.

Comparisons were made with gases having no water vapor, gases saturated with water vapor at 80°, 90°, 95° C. at atmospheric pressure and gases saturated with water vapor at superatmospheric pressures.

Vanadium is present in recoverable quantities in titanium minerals and magnetites and apatites from many parts of the world, and in slags and the like derived therefrom. Vanadium is recovered on a commercial scale from such minerals at present but the processes are complicated and costly. Vanadium has a substantial market at relatively high prices and there is a distinct advantage in the present process of direct recovery of vanadium at high purity

One of the distinct virtues of the invention is that vanadium is a powerful and objectionable colorant in white titanium dioxide pigments and in titanium dioxide used as an opacifier in ceramic glasses, glasses and enamels It is very difficult to remove vanadium from titanium slags and the like which are to be used to produce titanium dioxide pigments and opacifiers. It is therefore evident that the invention may be employed to reduce the cost of obtaining titanium dioxide in white form and make available additional raw materials.

The following table shows typical analyses for several vanadium-bearing titanium-iron raw materials It is decidedly preferable in the present invention to employ the slags as raw materials, since high vanadium recovery is obtained more reliably and with less difficulty and delay

	African vanadium slag, percent	Canadian titanium slag, percent	Quebec Ilmenite-hermatite mineral, percent	Australian rutile, percent	Finland Ilmentiet, percent
V_2O_5	23.50	0.57	0.27	0.70	0.30
TiO_2	12.00	71.0	34.3	97.3	44.30
FeO	35.00	13.0	27.5	0.43	*36.60
Fe_2O_3			25.2		
SiO_2	4.00	6.3	4.3		
Al_2O_3		5.0	3.5		
CaO	7.00	0.23	0.9		
MgO		4.8	3.1		
Cr_2O_3	4.00	0.16	0.1	0.18	
MnO		0.10	0.16		
C		0.07			
S		0.06	0.30		
P_2O_5		0.03	0.02		
Na_2O+K_2O			0.35		

* Fe.

EXAMPLE 1

Canadian titanium slag (Quebec) of the type listed in the table containing 0.57 percent V_2O_5 was heated for 2 hours in a

muffle as in FIG. 1 at 745° C. A stream of air was circulated over it, the air having been saturated with water vapor in a vessel maintained at 95° C. After the test the analysis showed that the vanadium content of the slag had been reduced to 0.25 percent V_2O_5, or 56.4 percent of the vanadium had been extracted.

EXAMPLE 2

The procedure of example 1 was carried out heating the vanadium slag to 900° C. At atmospheric pressure 60 percent of the vanadium was extracted under these conditions.

EXAMPLE 3

The procedure of example 1 was carried out using a gas consisting of 10 percent hydrogen, 90 percent nitrogen, saturated with water vapor at 95° C. In this reducing atmosphere only 37 percent of the vanadium was extracted instead of 56.4 percent in example 1.

EXAMPLE 4

The procedure of example 1 was repeated using a gas mixture consisting of pure oxygen saturated with water vapor at 95° C. The vanadium extraction was only slightly better than that of example 1.

EXAMPLE 5

A series of experiments were carried out in which the vanadium slag was heated in a stainless steel autoclave and the gas was maintained at various pressures in the superatmospheric pressure range. Despite inability to circulate the gas freely around the vanadium-bearing slag, the quantity of vanadium extracted was increased by about 30 percent over that extracted at atmospheric pressure. These tests gave indirect evidence that the vanadium extraction can be increased to the order of 75 to 80 percent in comparison with 56 percent to 60 percent at atmospheric pressure when using apparatus which more effectively provides contact with the vanadium-bearing material.

In view of my invention and disclosure, variations and modifications to meet individual whim or particular need, particularly in the choice of raw material, will doubtless become evident to others skilled in the art to obtain all or part of the benefits of my invention without copying the process shown, and I, therefore, claim all such insofar as they fall within the reasonable spirit and scope of my claims.

Having thus described my invention what I claim as new and desire to secure by Letters Patent is:

1. The selective method of extracting vanadium from a complex solid vanadium-bearing mineral and slags derived therefrom containing one or more of titanium, chromium, and iron, which consists of reducing the mineral to articles through 10 mesh per linear inch, maintaining the mineral at a temperature of 600° to 1,300° C. in contact with a as comprising water vapor and oxygen until the gas picks up vanadium hydroxide, removing the vanadium-bearing gas from the vanadium mineral and cooling the gas to a temperature below 600° C. to deposit vanadium oxide selectively to oxides of titanium, chromium or iron.

2. The process of claim 1, which comprises maintaining the gas at atmospheric pressure.

3. The process of claim 1, which comprises maintaining the gas at superatmospheric pressure.

4. The process of claim 1, which comprises passing the gas in contact with the vanadium-bearing mineral by blowing the gas through a bed of vanadium-bearing mineral particles.

5. The process of claim 1, in which the temperature of the gas is between 600° and 1,000° C.

6. The process of removing at least some of the vanadium present in solid titanium mineral or slags derived therefrom, and thereby reducing the tendency of vanadium to discolor the mineral, which comprises reducing the mineral to particles through 10 per linear per linear inch, flowing in contact with the mineral a gas comprising water vapor and oxygen while maintaining the mineral at a temperature of at least 600° C. and below 1,300° C., removing the vanadium-bearing gas from the titanium mineral, and then cooling the gas below 600° C. to separate the vanadium.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. U.S. 3,607,005 Dated Sept. 21, 1971

Inventor(s) Gordon H. Chambers

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 60, the word "present" should be --more--.

Column 3, line 7, the last word in the line should be --is-- instead of "in".

Column 3, line 25, the word "volatile" should be capitalized --Volatile--.

Column 3, line 41, the word --a-- should be inserted before the word "lower".

Column 3, line 46, the word "temperature" should be --temperatures--.

Column 4, line 4, the word "pressure" should be --pressures--.

Column 6, line 13, the word "articles" should be --particles--.
Column 6, line 15, the word "as" should be --gas--.

Column 6, line 34, the words "per linear" appear twice and one duplication should be omitted and the word --mesh-- should be inserted after the numeral "10".

Signed and sealed this 25th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents