Title: PRODUCTION METHOD OF VANADIUM OXIDE USING ION-EXCHANGE TO REALIZE WASTEWATER CIRCULATION

Abstract: Provided is a production method of vanadium oxide using ion-exchange to realize wastewater circulation, which belongs to the technical field of vanadium oxide extraction, and can not only obtain high quality vanadium product but also circulate and reuse vanadium extraction wastewater. The method comprises preparing raw material to be roasted, calcining roasting, leaching, solid-liquid separating, ion-exchanging, vanadium precipitating, and removing ammonia by calcination or reducing to prepare vanadium oxide; where vanadium extraction wastewater is returned to the system for circulation and reuse after neutralization treatment with lime milk, and no wastewater discharge is realized. Vanadium recovery rate is improved, and production cost is reduced. By combining with other techniques, the method can also convert waste resulted from extraction into secondary resource for reuse, so as to realize clean production.
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(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report (Art. 21(3))
— with amended claims and statement (Art. 19(1))
A production method of vanadium oxide using ion-exchange to realize waste water circulation

Technical field

The present invention relates to production method of vanadium oxide using ion-exchange to realize waste water circulation, and belongs to the technical field of vanadium oxide extraction.

Technical background

Conventional vanadium extraction process using sodium salt comprises: adopting common sodium salts, such as Na₂CO₃, Na₂SO₄, or NaCl, as additives, and roasting the sodium salt with vanadium-containing raw material at high temperature, wherein vanadium in the raw material is oxidized to V⁵⁺ by oxygen in air, and then V⁵⁺ bonds with sodium salt to generate sodium vanadate easily dissolvable in water; leaching the roasted product with water to dissolve sodium vanadate into solution, carrying out solid-liquid separation, removing major impurities such as P, Si and so on from the solution by using CaCl₂, adding ammonium salts such as (NH₄)₂SO₄, NH₄Cl, (NH₄)₂CO₃, or NH₄NO₃ etc. thereto, regulating pH of the solution to 1.5-2.5, heating the solution to above 90°C, and holding at the temperature for 40-90min to separate out ammonium polyvanadate precipitate from the solution; removing impurities such as sodium salts carried in the ammonium polyvanadate precipitate by washing with water after filtering, drying, and calcining the precipitate to remove ammonia to give V₂O₅, or reducing the precipitate at high temperature with reducing gas such as coal gas or natural gas to give V₂O₃. Presently, most manufacturers in the world adopt this process to produce vanadium products.

This process has the advantages of high product quality, stable process, and easy control. However, ammonium salt has to be used in an amount much higher than theoretical amount during vanadium precipitation to give high quality vanadium product, such that wastewater after vanadium precipitation has high concentration of ammonia nitrogen and sodium salt and is most difficult to be treated, e.g., NH₄⁺ concentration usually is as high as 2,000-8,000 mg/L or even higher, and Na⁺ concentration can be above 20g/L. Therefore, wastewater treatment is the most difficult problem to be handled in the vanadium extraction process using sodium salt. If the wastewater is directly returned to leaching step for circulation, as sodium vanadate in roasted material (also referred to as "roasted product") is continuously dissolved
in water while sodium salt can not be discharged from the solution, sodium salt concentration in the solution becomes increasingly high, the ammonium salt amount required by vanadium precipitation becomes increasingly large, the solution quickly becomes viscous, it is difficult to carry out filtration or vanadium precipitation, and actually the circulation can not be continued after 1-2 cycles; therefore the wastewater can not be directly circulated and reused. Presently, there are mainly two schemes for solving pollution problems of wastewater from vanadium extraction process using sodium salt. One scheme is to remove heavy metals, carry out ammonia removal and sodium removal treatments, and then discharge wherein the ammonia removal technique mainly comprises air stripping method, membrane separation method, magnesium ammonium phosphate precipitation method, chemical oxidation method, zeolite adsorption method, and biological nitrogen removal method, and the sodium removal method mainly adopts concentration crystallization method. The disadvantages of this scheme comprise that cost of ammonia removal treatment and sodium removal treatment is too high to be accepted by manufacturing plants, new pollution is likely to occur during the treatment, and the recovered sodium salt is sodium sulfate containing many impurities, which will release SO₂ to pollute environment upon roasting and thus is not suitable as roasting additive. The other scheme is to remove heavy metals, carry out ammonia removal and sodium removal treatments, and return condensation water for circulation. The difference from the first scheme is that the water of the first scheme does not circulate, but has to meet national industrial wastewater discharge standard (≤ 15mg/L for ammonia nitrogen wastewater), so it is very difficult to meet the standard, and high cost is required; although the second scheme does not discharge wastewater, a large amount of energy has to be consumed to evaporate wastewater, which also has the disadvantage of high cost, and evaporated gaseous ammonia is usually not recovered.

Therefore, treatment and utilization of wastewater having high ammonia nitrogen and high sodium salt resulted from vanadium extraction process using sodium salt is urgently to be solved in the field.

Since 1960s and 1970s, vanadium extraction process using lime or limestone as roasting additive, usually called vanadium extraction process using calcium salt or calcifying roasting vanadium extraction process, has been studied, which targets at some inherit shortcomings of vanadium extraction process using sodium salt, including (1) strict restriction on CaO content (less than 1.5%) in vanadium slag, because vanadium recovery yield drops A.J-9% as CaO content in the slag increases 1%; (2) high cost due to large consumption amount of sodium salt and ammonium salt; and (3) environment pollution caused by large amount of sodium salt.
and ammonium salt in wastewater. The roasted material of vanadium extraction process using calcium salt can be leached with sulfuric acid, or with carbonate or bicarbonate. Germany Patent Application No. 2324737 and British Patent Application No. 1394024 reported a method for leaching calcified roasted material with sodium carbonate solution. US Patent No. 3853985 reported a method for leaching calcified roasted material with ammonium carbonate or ammonium bicarbonate. Thermodynamics and kinetics of vanadium slag calcium salt roasting-carbonate leaching" (Vanadium titanium, 1997, No. 6: 1-6) reported thermodynamics and kinetics of leaching the calcified roasted material using carbonate and bicarbonate. Due to use of sodium salt and ammonium slat, the above methods in the literatures also have the problem of ammonia nitrogen wastewater treatment. British Patent Application No. 1394024 also reported a method including leaching roasted material with sulfuric acid or hydrochloric acid, regulating pH of the acidic leachateto 1.6-1.9, heating to hydrolyze and precipitate vanadium, and drying and calcining the precipitate to give vanadium oxide product containing about 93.5% of V2O5 and considerable amount of impurities. "Study of V2O5 extraction process by vanadium slag lime roasting method" (Iron Steel Vanadium Titanium, 1992, 13(6): 1-9) reported the study on V2O5 production by subjecting atomized vanadium slag to calcifying roasting and sulfuric acid leaching, in which the obtained acidic leachate is added with sulfuric acid to regulate pH to 2, and then heated to hydrolyze and precipitate vanadium to give product with purity of 93.6-93.92%. "Study of V2O5 extraction by vanadium slag calcium salt roasting-sulfuric acid leaching" reported study of calcifying roasting and sulfuric acid leaching of vanadium slag. Tula Vanadium Plant of former Soviet Union constructed the world first (also the only one) vanadium manufacture plant adopting calcifying roasting-sulfuric acid leaching-vanadium hydrolysis precipitation process, which can give V2O5 product with purity of 88-94% (92% on average) and containing main impurities of Mn, Mg, and Ca, and then V2O5 product is smelted into vanadium iron also containing many impurities; therefore the manufacturer is non-competitive on international market, and mainly supplies product to domestic market, that is the main reason that other vanadium plants do not adopt this process. To improve product competitiveness on market, Russian patent application Nos. 2001127026/02 and 96106854/02 disclosed method for producing high quality vanadium oxide from hydrolysis precipitate containing Mn, Ca, and Mg impurities. The method comprises adopting NaOH to dissolve hydrolysis precipitate, then adding ammonium salt like ammonium sulfate while heating, precipitating ammonium polyvanadate, and calcining to give high quality vanadium oxide with V2O5 content higher than 98%. The method reduces total amount of
ammonia-containing wastewater, but still requires wastewater treatment including ammonia removal and sodium removal; therefore the technical and economic difficulties of high cost and difficult ammonia nitrogen wastewater treatment still exist, additionally, vanadium recovery rate is lowered to some extent due to long treatment process and complicated procedures.

Until now, there’s no relevant report regarding process which can not only give high quality vanadium product, but also completely solve the problem of vanadium extraction wastewater treatment and reuse.

**Summary of the invention**

The object of the present invention is to provide a vanadium oxide production method which can not only obtain high quality vanadium product but also circulate and reuse vanadium extraction wastewater. The vanadium oxide production method in the present invention comprises following steps including:

a. mixing vanadium-containing material with additive to give mixed material, wherein the additive is CaO or limestone, and the amount of the additive makes the CaCVV₂O₅ weight ratio in the mixed material be 0.5-1.4 : 1;

b. roasting the mixed material at 860°C-950°C in oxidizing atmosphere for 60-240min to give roasted material;

c. adding water into the roasted material to give slurry, stirring, and slowly adding sulfuric acid solution to leach the slurry while controlling pH at 2.5-3.5;

d. removing residue after leaching to give leachate, subjecting the leachate to P-removal treatment and Ca-removal treatment to make weight ratio of total V to P in the leachate >1000 and [Ca²⁺] in the leachate <0.05g/L, washing the residue with circulation water to give washing water useful for preparing slurry in next leaching;

e. subjecting the P-removed and Ca-removed leachate to ion exchange with a strong acid cation resin which is previously transformed by ammonia or ammonium salt so as to obtain a exchanged solution in which the weight ratio of NH₄/Mn is 0.6-2000 : 1, the strong acid cation resin being the resin which can be used to exchange ion at pH of 2-5 to absorb Mn³⁺, Mg²⁺ and Fe³⁺;

f. regulating pH of the exchanged solution with sulfuric acid to 1.5-2.5, heating to a temperature between 90°C and boiling temperature, holding at the temperature for 30-120min, filtering, and washing and drying the precipitate to give ammonium polyvanadate,
subjecting the ammonium polyvanadate to calcination to remove ammonia to give V2O5, or reducing the ammonium polyvanadate to give V2O3; and

g. removing P, Mn, and Mg impurities in the wastewater generated in step f to make Mn^{2+} and Mg^{2+} concentrations lower than 5g/L respectively, and P concentration lower than 0.005g/L to give circulation water, and returning the circulation water to step c for preparing slurry and to step d for washing the residue,

wherein the solid raw material used in the above steps has total alkali metal amount not more than 0.3wt%, and total amount of Cl^- and NO_3^- not more than 0.1wt%; and the liquid raw material used in the above steps has total alkali metal amount not more than 0.1g/L, and total amount of Cl^- and NO_3^- not more than 0.1g/L.

According to the present invention, wastewater can be circulated and reused; and in addition, as the inventive method adopts calcifying roasting and sulfuric acid leaching to give vanadium solution substantially free of alkali metal ions, and various raw materials (including supplement water) are substantially free of easily soluble ions of alkali metal, halogen, and nitrate, balance of the easily soluble ions can be maintained during circulation process, wastewater can be circulated and reused after treatment, and thus problems of wastewater treatment of conventional vanadium extraction process using sodium salt are avoided.

In step a, the vanadium-containing material can be various vanadium-containing raw materials useful for preparing vanadium oxide, such as vanadium slag or other vanadium-containing raw materials (such as vanadium-containing magnetite, and vanadium lead zinc ore, etc.), preferably vanadium slag.

Preferably, in step a, the mixed material is pulverized to particle size of 0.1mm or less, to make vanadium be easily oxidized into V^{5+} to generate vanadate.

In step b, the oxidizing atmosphere can be pure oxygen, air, or mixture of oxygen and inert gas. The inert gas is preferably nitrogen gas. During roasting, appropriate roasting temperature and time can be selected within the range in the present invention, for example when the roasting temperature is high (such as 950°C), the roasting time can be shortened (such as 60min), and when the roasting temperature is low (such as 860°C), the roasting time can be prolonged (about 240min).

Preferably, in step c, the roasted material is cooled and pulverized to 0.18mm or less to facilitate leaching before being prepared into slurry.
Preferably, in step c, the slurry is prepared by stirring the roasted material with water 1.5-4 times by weight. The adopted water is the washing water resulted from the residue washing, and if the washing water is insufficient, circulation water is adopted for supplement. The sulfuric acid solution for leaching has concentration of 10-75%, the leaching temperature is between room temperature and 58°C, and the leaching time is 30-90min. More preferably, pH of the slurry is regulated to 2.8-3.3 with 32-65wt% sulfuric acid solution.

During washing the residue, the washing times are preferably 5-7, the amount of water used for each washing is preferably 20-35wt% of the residue on dry basis, to maintain water balance in circulation process.

P-removal reagent can be adopted for P-removal treatment, as long as TWP ≥ 1000 is satisfied. Ca-removal reagent can be adopted for Ca-removal treatment, as long as [Ca^{2+}]<0.05g/L is satisfied.

In step e, strong acid cation resin is previously transformed by ammonia or ammonium salt to convert most exchangeable groups in the resin into NH₄⁺ while the remaining keeps to be H⁺. The strong acid cation resin is preferably polystyrene sulfonate resin or polypropylene sulfonate resin. Preferably, the strong acid cation resin is previously transformed by ammonia or ammonium salt such that the wash water resulted from the transformation has pH of 2.8-3.8. Alkaline of alkali metals such as sodium hydroxide or potassium hydroxide can not be used for transformation.

Furthermore, in step e, after ion exchange, the strong acid cation resin containing Mn²⁺,Mg²⁺ and Fe³⁺ can be desorbed by 4-6wt% sulfuric acid solution to remove the Mn²⁺,Mg²⁺ impurity such that the resin is regenerated and can be reused, and the solution resulted from the desorption can be used for desorption again and can be used for Mn recovery Mn with wastewater neutralization residue after the desorption ability decreases.

In step g, the wastewater can be treated according to various routine methods to remove P, Mn, and Mg, for example, lime milk is adopted to neutralize wastewater to pH 9-11, the wastewater is filtered to remove main impurities such as Mn, P, and Mg while obtaining wastewater neutralization residue useful as raw material for Mn recovery; or Mn can be individually recovered with other reagents, and then impurities like Mn, P and Mg are removed.
As the returned circulation water may contain a certain amount of NH$_4^+$, if the weight ratio of NH$_3$/Mn in the P-removed and Ca-removed leachate already satisfies above requirement, ion exchange is not added, and vanadium precipitation is directly carried out. The present invention has following beneficial effects:

1. The inventive method adopts calcifying roasting and sulfuric acid leaching technique to give vanadium solution substantially free of alkali metal ions, and various raw materials (including supplement water) are substantially free of easily soluble ions of alkali metal, halogen, and nitrate, so that balance of the easily soluble ions can be maintained during circulation, and problems of wastewater treatment of conventional vanadium extraction process using sodium salt are avoided.

2. Ion exchange resin is adopted to substitute impurities like Mn, P and Mg with NH$_4^+$ to refine the vanadium-containing solution so as to prepare high quality vanadium oxide product, so that technical problem that conventional calcifying roasting-sulfuric acid leaching process cannot produce high quality vanadium product is solved.

3. Weight ratio of NH$_3$/Mn of the solution before vanadium precipitation is controlled to control the extent of the ion exchange, when the ratio in the exchanged solution is lower than the value specified in the present invention, ion exchange is performed to regulate the ratio to the specified value, and then the vanadium precipitation is carried out; when the ratio in the leachate has already reached the specified value in the present invention, ion exchange is not needed, and vanadium precipitation is directly carried out, and part of NH$_4^+$ is discharged along with ammonium polyvanadate precipitate, so that NH$_4^+$ concentration in the system will not continuously increase to enable circulation and reuse.

4. The circulation water containing sulfate salt such as (NH$_4$)$_2$SO$_4$ is adopted for leaching; within the leaching condition range in the present invention, NH$_4^+$ will not cause adverse influence, and SO$_4^{2-}$ is beneficial for increasing leaching rate of calcified roasted material, so that water circulation and reuse can be finally realized.

5. The inventive method can greatly increase total recovery rate (up to 83-85%) of vanadium oxide from vanadium slag, while the recovery rate of the conventional vanadium extraction process using sodium salt is about 80%; therefore the inventive method has increased the recovery rate by 3-5% on average compared with conventional vanadium extraction process using sodium salt, and the obtained vanadium product has good quality, and meets Chinese National Standard No. GB3283-87.

6. The inexpensive lime material is adopted to replace expensive sodium carbonate, the
consumption amount of sulfuric acid is similar to that in the vanadium extraction process using sodium salt, and consumption and cost of other auxiliary materials are low; therefore, consumption and cost of various auxiliary and raw materials are significantly decreased.

5 Brief Description of Drawings
Fig. 1 shows flow chart of one preferred embodiment of the method in the present invention.

Preferred Embodiments
The present invention will be further described through following examples.
The following examples all adopt the flow as shown in the Fig. 1. The preferred examples are briefly described in combination with Fig. 1.
Firstly, vanadium slag and lime is mixed to give mixed material (equivalent to step a);
The mixed material is calcified and roasted (equivalent to step b);
Sulfuric acid solution is adopted to leach the roasted material at constant pH (equivalent to step c);
After leaching, residue and leachate are separated out, the residue is washed with diluted sulfuric acid solution of pH 3-6, and the washing water is collected for preparing slurry (equivalent to step d);
The leachate is subjected to ion exchange to remove impurity (equivalent to step e);
Vanadium precipitation is performed, and ammonium polyvanadate obtained from vanadium precipitation is calcined or reduced to give high quality vanadium oxide (equivalent to step f);
The wastewater obtained from vanadium precipitation is added with lime milk for neutralization, the obtained circulation water is returned to prepare slurry or wash residue, and Mn is recovered from the neutralization residue (equivalent to step g).

Example 1
Roasted material prepared according to step (1) is adopted, 51 cycles of wastewater circulation test are carried out according to the inventive method, and each cycle includes steps (2)-(6).
(1) Preparation of roasted material:
Common vanadium slag with composition shown in Table 1 is ground to less than 0.098mm, 28kg of ground vanadium slag powder is mixed with 1.96kg of lime (ground to below 0.1mm)
containing CaO>98%, and then the mixture is roasted at 860 °C in air for 240min, cooled, and ground to less than 0.18mm.

Table 1  Main components of vanadium slag (%)  

<table>
<thead>
<tr>
<th></th>
<th>V2O5</th>
<th>CaO</th>
<th>MnO</th>
<th>P</th>
<th>K + Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.67</td>
<td>3.54</td>
<td>9.14</td>
<td>0.04</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>

(2) Leaching of roasted material

2,000ml of water resulted from residue washing of last cycle (clear water is used for the first cycle) is added to 500g of the ground roasted material to prepare slurry, 10-32wt% sulfuric acid solution is slowly added continuously while stirring, pH is controlled at 2.8-3.3 during leaching process while the slurry temperature is held at a temperature between room temperature and 58°C, the reaction is carried out for 60min. The resultant is filtered to give leachate, the residue is washed with circulation water (clear water is used for the first cycle) for 6-7 times, water used for each time is 120ml, the washing water is combined for preparing slurry for leaching of next cycle, and the residue is dried and weighed to determine TV (total vanadium) content and calculate vanadium leaching rate. The leachate is subjected to P-removal treatment and Ca-removal treatment to make P satisfy TV/P>1000 and [Ca<sup>2+</sup>]<0.05g/L, and then ion exchange is carried out.

(3) Ion exchange

The P-removed and Ca-removed leachate is subjected to ion exchange with a polystyrene sulfonate cation resin which is previously transformed by ammonia. The exchanged solution is used for vanadium precipitation. The weight ratio of NEb/Mn in the exchanged solution is controlled to be 0.6-50 : 1 by controlling the weight ratio of the leachate to the resin.

(4)  Vanadium precipitation and V2O5 production by calcination

A small amount of sulfuric acid is used to regulate pH of the exchanged solution to 1.5-2.5, then the resultant is heated to above 90°C, held for 60-120min, and filtered, the precipitate is washed with tap water containing [Na+K]<0.1g/L for 3 times and water used for each time is 30ml, and the washing wastewater is combined with supernatant of vanadium precipitation to give wastewater of vanadium precipitation.

Ammonium polyvanadate precipitate is dried, calcined and melted at 500°C-800°C to give V2O5, and the composition of the obtained V2O5 is analyzed.

(5) Wastewater treatment

Lime milk with low water content is prepared, added into the wastewater of vanadium precipitation to regulate pH of the solution to 9.0-10.0, and filtered. The filtrate is regulated to pH of 5-7 with diluted sulfuric acid to give circulation water as residue washing water for
leaching in the next cycle. The neutralization residue obtained from the filtration is used as raw material for Mn recovery.

(6) Regeneration of the resin

The resin containing cation such as Mn$^{2+}$ (carried resin) is reused after being desorbed by 4-6wt% sulfuric acid solution. The solution resulted from the desorption is used for desorption again and used for Mn recovery Mn with wastewater neutralization residue after the desorption ability decreases.

The above steps (2)-(6) are repeated, 500g of roasted material is used for each cycle, liquid solid ratio for each cycle is 4:1, vanadium precipitation is not carried out after leaching in the first cycle, the leachate is used for slurry preparation of the second cycle to increase vanadium concentration of the leachate; then during leaching in each of the rest cycles, residue washing water of last cycle is used in step (2), and the insufficient part is supplemented by circulation water; circulation water is used for washing the residue, and the insufficient part is supplemented by clear water. 51 cycles are carried out, and no wastewater containing ammonia nitrogen is discharged from the system.

Except the first cycle without vanadium precipitation, the maximum value, the minimum value, and the average value of the recovery rate of the rest cycles are shown in Table 2; the maximum value, the minimum value, and the average value of the chemical compositions of the V$_2$O$_5$ product of the rest cycles are shown in Table 3, and the Table 3 also shows compositions of the metallurgical No. 98 and No. 99 of Chinese National Standard No. GB3283-87; and the maximum value, the minimum value, and the average value of the composition of the circulation water after circulation treatment for the rest cycles are shown in Table 4.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Raw material pretreatment</th>
<th>Leaching</th>
<th>Ion exchange</th>
<th>Vanadium precipitation</th>
<th>Ammonia removal by calcination</th>
<th>Total recovery rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>98.50</td>
<td>89.93</td>
<td>97.81</td>
<td>98.43</td>
<td></td>
<td>97.00</td>
</tr>
<tr>
<td>max</td>
<td>93.64</td>
<td>98.66</td>
<td>99.29</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>91.86</td>
<td>98.25</td>
<td>98.88</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The recovery rates of the raw material pretreatment and ammonia removal by calcination in the above Table 2 are obtained from long term industrial production data.

Note: The procedure of raw material pretreatment includes pulverization of bulk coarse
vanadium slag, grinding, and iron removal, and a small amount of vanadium is lost in this process.

It can be observed from Table 2 that the total average recovery rate of $V_2O_5$ from vanadium slag reaches 85.26% by the inventive method.

<table>
<thead>
<tr>
<th>Items</th>
<th>$V_2O_5$</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>TFe</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Na$_2$O+K$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>98.41</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>Max</td>
<td>99.77</td>
<td>0.04</td>
<td>0.03</td>
<td>0.10</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>99.06</td>
<td>0.03</td>
<td>0.02</td>
<td>0.06</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>GB3283-87 metallurgical 98</td>
<td>&gt;98</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.25 &gt;1.5</td>
<td></td>
</tr>
<tr>
<td>GB3283-87 metallurgical 99</td>
<td>&gt;99</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.15 &gt;1.0</td>
<td></td>
</tr>
</tbody>
</table>

The table 3 shows that the vanadium product obtained by the process has good product quality, and meets Chinese National Standard No. GB3283-87.

<table>
<thead>
<tr>
<th>Items</th>
<th>Mn</th>
<th>Mg</th>
<th>NH$_4^+$</th>
<th>Na+K</th>
<th>Ca</th>
<th>SO$_4^{2-}$</th>
<th>P</th>
<th>Al</th>
<th>Si</th>
<th>TFe</th>
<th>TCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>0.79</td>
<td>1.31</td>
<td>1.22</td>
<td>0.21</td>
<td>0.71</td>
<td>15.41</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>2.85</td>
<td>3.82</td>
<td>2.91</td>
<td>0.40</td>
<td>1.19</td>
<td>27.14</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>1.90</td>
<td>2.67</td>
<td>2.13</td>
<td>0.31</td>
<td>0.97</td>
<td>21.74</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be observed from Table 4 that, after 51 cycles of wastewater circulation, various impurity ions have no enrichment tendency, and circulation and reuse of vanadium extraction wastewater in low cost is realized, wherein K and Na are mainly from vanadium slag raw material, and sum of K+Na in the circulation water is stabilized within 0.2-0.4g/L and does not increase after 51 cycles.

**Example 2**

Roasted material prepared according to step (1) is adopted, 51 cycles of wastewater circulation test are carried out according to the inventive method, and each cycle includes steps (2)-(6).

(1) **Preparation of roasted material:**

The vanadium slag shown in Table 5 is ground to less than 0.098mm.

<table>
<thead>
<tr>
<th>V$_2$O$_5$</th>
<th>CaO</th>
<th>Mn</th>
<th>P</th>
<th>K + Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.75</td>
<td>4.93</td>
<td>6.56</td>
<td>0.049</td>
<td>0.19</td>
</tr>
</tbody>
</table>

28kg of ground vanadium slag powder is mixed with 1.82kg of lime (ground to below 0.1mm) containing 98% CaO, and then the mixture is roasted at 950°C in air for 60min, cooled, and ground to less than 0.18mm.
(2) Leaching of roasted material

1250ml of water resulted from residue washing of last cycle (clear water is used for the first cycle) is added to 500g of the ground roasted material to prepare slurry, 32-65wt% sulfuric acid solution is slowly added continuously while stirring, pH is controlled at 2.8-3.3 during leaching process while the slurry temperature is held at a temperature between room temperature-58°C, the reaction is carried out for 60min. The resultant is filtered to give leachate, the residue is washed with circulation water (clear water is used for the first cycle) for 6 times, water used for each time is 120ml, the washing water is combined for preparing slurry for leaching of next cycle, and the residue is dried and weighed to determine TV (total vanadium) content and calculate vanadium leaching rate. The leachate is subjected to P-removal treatment and Ca-removal treatment to make P satisfy TVVP≥1000 and [Ca^{2+}]<0.05g/L, and then ion exchange is carried out.

(3) Ion exchange

The P-removed and Ca-removed leachate is subjected to ion exchange with a polystyrene sulfonate cation resin which is previously transformed by ammonia. The exchanged solution is used for vanadium precipitation. The weight ratio of NEb/Mn in the exchanged solution is controlled to be 2-10 : 1 by controlling the weight ratio of the leachate to the resin.

(4) Vanadium precipitation and V_2O_5 production by calcination

A small amount of sulfuric acid is used to regulate pH of the exchanged solution to 1.5-2.5, then the resultant is heated to above 90°C, held for 60-120min, and filtered, the precipitate is washed with tap water containing [Na+K]<0.1g/L for 3 times and water used for each time is 30ml, and the washing wastewater is combined with supernatant of vanadium precipitation to give wastewater of vanadium precipitation.

Ammonium polyvanadate precipitate is dried, calcined and melted at 500°C-800°C to give V_2O_5, and the composition of the obtained V_2O_5 is analyzed.

(5) Wastewater treatment

Lime milk with low water content is prepared, added into the wastewater of vanadium precipitation to regulate pH of the solution to 9.0-9.5, and filtered. The filtrate is regulated to pH of 5-7 with diluted sulfuric acid to give circulation water as residue washing water for leaching in the next cycle. The neutralization residue obtained from the filtration is used as raw material for Mn recovery.

(6) Regeneration of the resin

The resin containing cation such as Mn^{2+} is reused after being desorbed by 4-6wt% sulfuric acid solution. The solution resulted from the desorption is used for desorption again and
used for Mn recovery Mn with wastewater neutralization residue after the desorption ability decreases.

The above steps (2)-(6) are repeated, 500g of roasted material is used for each cycle, liquid solid ratio for each cycle is 4:1, vanadium precipitation is not carried out after leaching in the first cycle, the leachate is used for slurry preparation of the second cycle to increase vanadium concentration of the leachate; then during leaching in each of the rest cycles, residue washing water of last cycle is used in step (2), and the insufficient part is supplemented by circulation water; circulation water is used for washing the residue, and the insufficient part is supplemented by clear water. 51 cycles are carried out, and no wastewater containing ammonia nitrogen is discharged from the system.

Except the first cycle without vanadium precipitation, the maximum value, the minimum value, and the average value of the recovery rate of the rest cycles are shown in Table 6; the maximum value, the minimum value, and the average value of the chemical compositions of the V2O5 product of the rest cycles are shown in Table 7; and the maximum value, the minimum value, and the average value of the composition of the circulation water after circulation treatment for the rest cycles are shown in Table 8.

### Table 6 Vanadium recovery rate in circulation process (%)

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Raw material pretreatment</th>
<th>Leaching</th>
<th>Ion exchange</th>
<th>Vanadium precipitation</th>
<th>Ammonia removal by calcination</th>
<th>Total recovery rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>98.50</td>
<td>89.59</td>
<td>97.33</td>
<td>98.36</td>
<td>97.00</td>
<td>84.16</td>
</tr>
<tr>
<td>max</td>
<td></td>
<td>92.37</td>
<td>98.18</td>
<td>99.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
<td></td>
<td>91.09</td>
<td>97.79</td>
<td>98.88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The recovery rates of the raw material pretreatment and ammonia removal by calcination in the above Table 6 are obtained from long term industrial production data.

It can be observed from Table 6 that the total average recovery rate of V$_2$O$_5$ from vanadium slag reaches 84.16% by the inventive method.

### Table 7 Main components of V2O5 product obtained by the circulation process (%)

<table>
<thead>
<tr>
<th>Items</th>
<th>V$_2$O$_5$</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
<th>TFe</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Na$_2$O+K$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>98.66</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.06</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.22</td>
</tr>
<tr>
<td>max</td>
<td>99.34</td>
<td>0.20</td>
<td>0.03</td>
<td>0.18</td>
<td>0.11</td>
<td>0.03</td>
<td>0.03</td>
<td>0.02</td>
<td>0.38</td>
</tr>
<tr>
<td>Average</td>
<td>99.10</td>
<td>0.12</td>
<td>0.02</td>
<td>0.13</td>
<td>0.07</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.31</td>
</tr>
</tbody>
</table>
The table 7 shows that the vanadium product obtained by the process has good product quality, and meets Chinese National Standard No. GB3283-87.

Table 8 Main components of circulation water (g/L)

<table>
<thead>
<tr>
<th>Items</th>
<th>Mn</th>
<th>Mg</th>
<th>NH₄⁺</th>
<th>Na⁺+</th>
<th>Ca</th>
<th>SO₄²⁻</th>
<th>P</th>
<th>Si</th>
<th>Al</th>
<th>TFe</th>
<th>TCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>0.36</td>
<td>0.25</td>
<td>1.94</td>
<td>0.20</td>
<td>0.43</td>
<td>12.58</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>1.88</td>
<td>1.49</td>
<td>3.11</td>
<td>0.37</td>
<td>0.68</td>
<td>16.23</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>1.15</td>
<td>0.88</td>
<td>2.55</td>
<td>0.29</td>
<td>0.56</td>
<td>14.48</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be observed from Table 8 that, after 51 cycles of wastewater circulation, various impurity ions have no enrichment tendency, and circulation and reuse of vanadium extraction wastewater in low cost is realized, wherein K and Na are mainly from vanadium slag raw material, and sum of K+Na in the circulation water is stabilized within 0.2-0.4g/L and does not increase after 51 cycles.

**Example 3**

Roasted material prepared according to step (1) is adopted, 100 cycles of wastewater circulation test are carried out according to the inventive method, and each cycle includes steps (2)-(6).

1. Preparation of roasted material:

110kg of vanadium slag with composition shown in Table 9 is ground to less than 0.098mm, the ground vanadium slag powder is mixed with 7.7kg of lime (ground to below 0.1mm) containing 98% CaO, and then the mixture is roasted at 920°C in air for 150min, cooled, and ground to less than 0.18mm.

Table 9 Main components of vanadium slag (%)

<table>
<thead>
<tr>
<th>V₂O₅</th>
<th>CaO</th>
<th>Mn</th>
<th>P</th>
<th>K + Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.68</td>
<td>2.15</td>
<td>5.98</td>
<td>0.147</td>
<td>0.18</td>
</tr>
</tbody>
</table>

2. Leaching of roasted material

2,000ml of water resulted from residue washing of last cycle (clear water is used for the first cycle) is added to 1,000g of ground roasted material to prepare slurry, 50-75wt% sulfuric acid solution is slowly added continuously while stirring, pH is controlled at 2.8-3.3 during leaching process while the slurry temperature is held at a temperature between room temperature and 58°C, the reaction is carried out for 60min. The resultant is filtered to give leachate, the residue is washed with circulation water (clear water is used for the first cycle) for 5-6 times, water used for each time is 250ml, the washing water is combined for preparing slurry for leaching of next cycle, and the residue is dried and weighed to determine TV (total vanadium) content and calculate vanadium leaching rate. The leachate is subjected to P-removal treatment and Ca-removal treatment to make P satisfy TVVP≥1000 and [Ca²⁺]<0.05g/L, and then ion exchange is carried out.
(3) Ion exchange
The P-removed and Ca-removed leachate is subjected to ion exchange with a polystyrene sulfonate cation resin which is previously transformed by ammonia. The exchanged solution is used for vanadium precipitation. The weight ratio of NH3/Mn in the exchanged solution is controlled to be 10-2000 : 1 by controlling the weight ratio of the leachate to the resin.

(4) Vanadium precipitation and V₂O₅ production by calcination
A small amount of sulfuric acid is used to regulate pH of the exchanged solution to 1.5-2.5, then the resultant is heated to above 90°C, held for 60-120min, and filtered, the precipitate is washed with tap water containing [Na+K]<0.1g/L for 3 times and water used for each time is 30ml, and the washing wastewater is combined with supernatant of vanadium precipitation to give wastewater of vanadium precipitation.

Ammonium polyvanadate precipitate is dried, calcined and melted at 500°C-800°C to give V₂O₅, and the composition of the obtained V₂O₅ is analyzed.

(5) Wastewater treatment
Lime milk with low water content is prepared, added into the wastewater of vanadium precipitation to regulate pH of the solution to 10-11, and filtered. The filtrate is regulated to pH of 5-7 with diluted sulfuric acid to give circulation water as residue washing water for leaching in the next cycle. The neutralization residue obtained from the filtration is used as raw material for Mn recovery.

(6) Regeneration of the resin
The resin containing cation such as Mn²⁺ is reused after being desorbed by 4-6wt% sulfuric acid solution. The solution resulted from the desorption is used for desorption again and used for Mn recovery Mn with wastewater neutralization residue after the desorption ability decreases.

The above steps (2)-(6) are repeated, 1000g of roasted material is used for each cycle, liquid solid ratio for each cycle is 2:1, vanadium precipitation is not carried out after leaching in the first cycle, the leachate is used for slurry preparation of the second cycle to increase vanadium concentration of the leachate; then during leaching in each of the rest cycles, residue washing water of last cycle is used in step (2), and the insufficient part is supplemented by circulation water; circulation water is used for washing the residue, and the insufficient part is supplemented by clear water. 51 cycles are carried out, and no wastewater containing ammonia nitrogen is discharged from the system.

Except the first cycle without vanadium precipitation, the maximum value, the minimum value, and the average value of the recovery rate of the rest cycles are shown in Table 10; the
maximum value, the minimum value, and the average value of the chemical compositions of the V₂O₅ product of the rest cycles are shown in Table 11; and the maximum value, the minimum value, and the average value of the composition of the circulation water after circulation treatment for the rest cycles are shown in Table 12.

### Table 10 Vanadium recovery rate in circulation process (%)

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Raw material pretreatment</th>
<th>Leaching</th>
<th>Ion exchange</th>
<th>Vanadium precipitation</th>
<th>Ammonia removal by calcination</th>
<th>Total recovery rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>98.50</td>
<td>88.43</td>
<td>97.38</td>
<td>98.68</td>
<td>97.00</td>
<td>83.18</td>
</tr>
<tr>
<td>max</td>
<td>91.78</td>
<td>98.14</td>
<td>99.41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>average</td>
<td>89.97</td>
<td>97.73</td>
<td>99.02</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The recovery rates of the raw material pretreatment and ammonia removal by calcination in the above Table are obtained from long term industrial production data. It can be observed from Table 10 that the total average recovery rate of ViOs from vanadium slag reaches 83.18% by the inventive method.

### Table 11 Main components of V₂O₅ product obtained by the circulation process (%)

<table>
<thead>
<tr>
<th>Items</th>
<th>V₂O₅</th>
<th>Mn</th>
<th>Mg</th>
<th>Na⁺</th>
<th>Ca</th>
<th>TFe</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Na₂O+K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>99.06</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>0.06</td>
</tr>
<tr>
<td>max</td>
<td>99.97</td>
<td>0.03</td>
<td>0.01</td>
<td>0.03</td>
<td>0.01</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.01</td>
<td>0.23</td>
</tr>
<tr>
<td>average</td>
<td>99.48</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The Table 11 shows that the vanadium product obtained by the process has good product quality, and meets Chinese National Standard No. GB3283-87.

### Table 12 Main components of circulation water (g/L)

<table>
<thead>
<tr>
<th>Items</th>
<th>Mn</th>
<th>Mg</th>
<th>NH₄⁺</th>
<th>Na⁺+K⁺</th>
<th>Ca</th>
<th>SO₄²⁻</th>
<th>P</th>
<th>Si</th>
<th>Al</th>
<th>TFe</th>
<th>TCr</th>
</tr>
</thead>
<tbody>
<tr>
<td>min</td>
<td>0.17</td>
<td>0.12</td>
<td>2.31</td>
<td>0.17</td>
<td>0.38</td>
<td>10.28</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>max</td>
<td>0.54</td>
<td>0.49</td>
<td>4.65</td>
<td>0.47</td>
<td>0.52</td>
<td>15.63</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.34</td>
<td>0.29</td>
<td>3.39</td>
<td>0.31</td>
<td>0.44</td>
<td>12.74</td>
<td>&lt;0.005</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It can be observed from Table 12 that, after 51 cycles of wastewater circulation, various impurity ions have no enrichment tendency, and circulation and reuse of vanadium extraction wastewater in low cost is realized, wherein K and Na are mainly from vanadium slag raw material, and sum of K+Na in the circulation water is stabilized within 0.1-0.5g/L and does not increase after 51 cycles.
Claims

1. A production method of vanadium oxide, comprising the following steps:
   a. mixing vanadium-containing material with additive to give mixed material, wherein
   the additive is CaO or limestone, and the amount of the additive makes the CaO/V2O5's weight
   ratio in the mixed material be 0.5-1.4 : 1;
   b. roasting the mixed material at 860°C-950°C in oxidizing atmosphere for 60-240min
to give roasted material;
   c. adding water into the roasted material to give slurry, stirring, and slowly adding
   sulfuric acid solution to leach the slurry while controlling pH at 2.5-3.5;
   d. removing residue after leaching to give leachate, subjecting the leachate to P-removal
treatment and Ca-removal treatment to make weight ratio of total V to P in the leachate ≥1000
and [Ca2+] in the leachate <0.05g/L, washing the residue with circulation water to give
washing water useful for preparing slurry in next leaching;
   e. subjecting the P-removed and Ca-removed leachate to ion exchange with a strong
acid cation resin which is previously transformed by ammonia or ammonium salt so as to
obtain a exchanged solution in which the weight ratio of NH4/Mn is 0.6-2000 : 1, the strong
acid cation resin being the resin which can be used to exchange ion at pH of 2-5 to absorb
Mn2+, Mg2+ and Fe3+;
   f. regulating pH of the exchanged solution with sulfuric acid to 1.5-2.5, heating to a
temperature between 90°C and boiling temperature, holding at the temperature for 30-120min,
filtering, and washing and drying the precipitate to give ammonium polyvanadate,
   subjecting the ammonium polyvanadate to calcination to remove ammonia to give V2O5,
or reducing the ammonium polyvanadate to give V2O3; and
   g. removing P, Mn, and Mg impurities in the wastewater generated in step f to make
Mn2+ and Mg2+Concentrations lower than 5g/L respectively, and P concentration lower than
0.005g/L to give circulation water, and returning the circulation water to step c for preparing
slurry and to step d for washing the residue,
   wherein the solid raw material used in the above steps has total alkali metal amount not
more than 0.3wt%, and total amount of Cl− and NO3− not more than 0.1wt%; and the liquid
raw material used in the above steps has total alkali metal amount not more than 0.1g/L, and
total amount of Cl− and NO3− not more than 0.1g/L.
2. The production method of vanadium oxide according to claim 1, wherein the mixed material obtained in step a has particle size of 0.1mm or less.

3. The production method of vanadium oxide according to claim 1, wherein in step c, the roasted material is cooled and pulverized to 0.18mm or less before being prepared into slurry.

4. The production method of vanadium oxide according to claim 1, wherein in step c, the concentration of the sulfuric acid solution is 10-75wt%, the leaching temperature is 10-58°C, and the leaching time is 30-90min.

5. The production method of vanadium oxide according to claim 1, wherein the circulation water obtained in step g is returned to step d to wash the residue to obtain washing water, the washing water is returned to step c for leaching and preparing slurry, if the washing water is not sufficient, the circulation water is adopted for supplement.

6. The production method of vanadium oxide according to claim 1 or 5, wherein in step c, the weight ratio of total amount of water for slurry preparation to the roasted material is 1.5-4: 1.

7. The production method of vanadium oxide according to claim 1, wherein during washing of the residue, the washing times are 5-7, and the amount of water used for each washing is 20-35wt% of the residue on dry basis.

8. The production method of vanadium oxide according to claim 1, wherein in step e, the strong acid cation resin is polystyrene sulfonate resin or polypropylene sulfonate resin.
9. The production method of vanadium oxide according to claim 1, wherein in step e, the strong acid cation resin is previously transformed by ammonia or ammonium salt such that the wash water resulted from the transformation has pH of 2.8-3.8.

10. The production method of vanadium oxide according to claim 1, wherein in step e, the conditions of the ion exchange make weight ratio of NH₃/Mn in the exchanged solution within 2-10 : 1.

11. The production method of vanadium oxide according to claim 1, wherein in step e, the strong acid cation resin having been subjected to ion exchange is reused after being regenerated by 4-6wt% sulfuric acid solution and then transformed by ammonia or ammonium salt.
Claims

1. A production method of vanadium oxide, comprising the following steps:
   a. mixing vanadium-containing material with additive to give mixed material, wherein the additive is CaO or limestone, and the amount of the additive makes the CaO/V₂O₅ weight ratio in the mixed material be 0.5-1.4:1;
   b. roasting the mixed material at 860°C-950°C in oxidizing atmosphere for 60-240min to give roasted material;
   c. adding water into the roasted material to give slurry, stirring, and slowly adding sulfuric acid solution to leach the slurry while controlling pH at 2.5-3.5;
   d. removing residue after leaching to give leachate, subjecting the leachate to P-removal treatment and Ca-removal treatment to make weight ratio of total V to P in the leachate >1000 and [Ca²⁺] in the leachate <0.05g/L, washing the residue with circulation water to give washing water useful for preparing slurry in next leaching;
   e. subjecting the P-removed and Ca-removed leachate to ion exchange with a strong acid cation resin which is previously transformed by ammonia or ammonium salt so as to obtain an exchanged solution in which the weight ratio of NH₃/Mn is 0.6-2000:1, the strong acid cation resin being the resin which can be used to exchange ion at pH of 2-5 to absorb Mn²⁺, Mg²⁺ and Fe³⁺;
   f. regulating pH of the exchanged solution with sulfuric acid to 1.5-2.5, heating to a temperature between 90℃ and boiling temperature, holding at the temperature for 30-120min, filtering, and washing and drying the precipitate to give ammonium polyvanadate, subjecting the ammonium polyvanadate to calcination to remove ammonia to give V₅O₃, or reducing the ammonium polyvanadate to give V₂O₅; and
   g. removing P, Mn, and Mg impurities in the wastewater generated in step f to make Mn²⁺ and Mg²⁺ concentrations lower than 5g/L respectively, and P concentration lower than 0.005g/L to give circulation water, and returning the circulation water to step c for preparing slurry and to step d for washing the residue,

   wherein the solid raw material used in the above steps has total alkali metal amount not more than 0.3wt%, and total amount of Cl⁻ and NO₃⁻ not more than 0.1wt%; and the liquid raw material used in the above steps has total alkali metal amount not more than 0.1g/L, and total amount of Cl⁻ and NO₃⁻ not more than 0.05g/L.
2. The production method of vanadium oxide according to claim 1, wherein the mixed material obtained in step a has particle size of 0.1mm or less.

3. The production method of vanadium oxide according to claim 1, wherein in step c, the roasted material is cooled and pulverized to 0.18mm or less before being prepared into slurry.

4. (amended) The production method of vanadium oxide according to claim 1, wherein in step c, the concentration of the sulfuric acid solution is 10-75wt%, the leaching temperature is from room temperature to 58°C, and the leaching time is 30-90min.

5. The production method of vanadium oxide according to claim 1, wherein the circulation water obtained in step g is returned to step d to wash the residue to obtain washing water, the washing water is returned to step c for leaching and preparing slurry, if the washing water is not sufficient, the circulation water is adopted for supplement.

6. The production method of vanadium oxide according to claim 1 or 5, wherein in step c, the weight ratio of total amount of water for slurry preparation to the roasted material is 1.5-4:1.

7. The production method of vanadium oxide according to claim 1, wherein during washing of the residue, the washing times are 5-7, and the amount of water used for each washing is 20-35wt% of the residue on dry basis.

8. The production method of vanadium oxide according to claim 1, wherein in step e, the strong acid cation resin is polystyrene sulfonate resin or polypropylene
sulfonate resin.

9. The production method of vanadium oxide according to claim 1, wherein in step e, the strong acid cation resin is previously transformed by ammonia or ammonium salt such that the wash water resulted from the transformation has pH of 2.8-3.8.

10. The production method of vanadium oxide according to claim 1, wherein in step e, the conditions of the ion exchange make weight ratio of $\text{NH}_3/\text{Mn}$ in the exchanged solution within 2-10 : 1.

11. The production method of vanadium oxide according to claim 1, wherein in step e, the strong acid cation resin having been subjected to ion exchange is reused after being regenerated by 4-6wt% sulfuric acid solution and then transformed by ammonia or ammonium salt.
Statement under Article 19(1)

The claims as originally filed are amended under Article 19 as follow:

(1) Claim 4 is replaced by amended claim bearing the same number;

(2) Claims 1-3 and 5-11 are unchanged.

After the amendment, the leaching temperature in claim 4 is the same as the priority document, i.e., between room temperature and 58°C. Therefore, the priority claim shall be valid, and the document D2 (CN 101402470A) can not be considered as the prior art of the present application. Accordingly, claim 4 shall possess novelty under PCT Article 33(2) and involve an inventive step under PCT Article 33(3).
Fig. 1
**A. CLASSIFICATION OF SUBJECT MATTER**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC C01G31/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, CNKI, CNPAT, vanadium oxide, ammonium, polyvanadate, APV, CaO, calcium oxide, CaCO$_3$, limestone, Sulfuric, H2SO4, wastewater, waste

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
<thead>
<tr>
<th>Category</th>
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* Further documents are listed in the continuation of Box C

**Date of the actual completion of the international search**

09 Dec 2009(09 12 2009)

**Date of mailing of the international search report**

28 Jan. 2010 (28.01.2010)

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**Authorized officer**

SHI Weiliang
TelephoneNo (86-10)6208501 0
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