Article

The investigate of vanadium-containing slurry oxidation roasting process for vanadium extraction

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Abstract: Vanadium containing slurry is a by-product of vanadium pentoxide by hydrometallurgical methods from vanadium slag. It is promising technogenic raw material for vanadium production. The phase analysis of vanadium-containing slurry by X-ray diffraction method has shown that it contains vanadium in spinel form ($FeO{\cdot}V_2O_3$). The various oxidation roasting methods for slurry treatment have been studied for increasing vanadium extraction into the solution. It has shown that the most effective additive is 1% $CaCO_3$ at a roasting temperature of 1000 °C. The oxidation roasting of vanadium-containing slurry with the additive led to increase acid-soluble form of V_2O_5 from 1.5 to 3.7% and decrease the content of $FeO{\cdot}V_2O_3$ from 3 to 0.4%. These results have confirmed the efficiency of the application of oxidation roasting to convert vanadium compounds into acid-soluble forms. The conversion mechanism of spinel to acid-soluble phases during oxidation roasting with additives was investigated by thermogravimetric analysis and thermodynamic simulation. It has shown that the formation of acid-soluble calcium vanadates during oxidation roasting without additives occurs at temperatures above 800 °C, but $CaCO_3$ addition allows to reduce this temperature to 600 °C.

Keywords: vanadium; wastes; extraction; spinel; acid-soluble phases; vanadium-containing slurry; oxidation roasting

1. Introduction

Vanadium is one of the most important strategic metals. It is widely used in various industries such as metallurgy, chemical, aerospace, medicine, etc. [1–10].The main raw materials for vanadium extraction are titanomagnetite ore deposits. [11–15]. Vanadium can be recovered from coal, spent catalysts, thermal power plant ash, and other sources [16–21]. Russia is one of the world's leading producer of vanadium. Evraz Group S.A. (EVRAZ) is the main manufacturer of vanadium in Russia, which produces about 17 thousand tons of vanadium per year (in terms of vanadium in vanadium slag) [22].

The Evraz Group includes three plants for a manufacturer of vanadium production, namely EVRAZ KGOK, EVRAZ NTMK and EVRAZ Vanady Tula. EVRAZ KGOK produces vanadium concentrate from titanomagnetite ore. EVRAZ NTMK manufactures vanadium-containing slag according to the following flowsheet: pig iron with a high content of vanadium is produced by smelting in a blast furnace with subsequent treatment in basic oxygen furnace using oxygen blowing. EVRAZ Vanady Tula produces commercial vanadium pentoxide by hydrometallurgical treatment of vanadium slag, as well as ferrovanadium using pyrometallurgical processing of vanadium pentoxide.

The main phases of vanadium converter slag are spinel phase $(Ti,V,Fe,Cr,Mn)_3O_4$, fayalite (Fe_2SiO_4) and cristobalite (SiO_2). Vanadium in vanadium slag also can be contained in $CrVO_4$ and VO_2 form [23].

During hydrometallurgical conversion V^{3+} in spinel ($FeO \cdot V_2O_3$) is oxidized during roasting with limestone to V^{5+} in the form of acid-soluble compounds, which pass into solution during sulfuric acid leaching. Vanadium pentoxide is produced from vanadium solutions by hydrolysis at 95–98°C [24–25].

Extraction of vanadium from vanadium slags is 73.8% at the stage of hydrometallurgical processing [26]. The rest of the vanadium is lost with the waste slurry. Such slurries contain 1.5–4.5 wt. % V_2O_5, which exceeds the vanadium content in the initial titanomagnetites [23, 27–28]. EVRAZ Vanadiy Tula has accumulated more than 80 million tons of this waste [23]. Thus, vanadium-containing slurries can be considered a promising technogenic raw material for vanadium production.

The oxidation roasting of vanadium slag with sodium salts leads to formation of the different sodium vanadates such as Na_3VO_4, $Na_4V_2O_7$, $NaVO_3$. It has shown [24–25, 29–30] that these compounds have well solubility in acid solutions that improve extraction of vanadium by acid leaching. Despite their advantages, these methods have disadvantages. The oxidation roasting with sodium salts additions is accompanied by formation of the toxic gases, which have hurt the environment. Furthermore, the roasting process with sodium salts leads to the formation ofundesirable phases (silicates, ferrites, aluminates, etc.) that subsequently result in the obtaining of low-quality vanadium pentoxide. Another disadvantage of these methods is pollution by sodium of waste solutions and leach residue that complicates their recycling.

The other approach, which allows to forming well soluble vanadium compounds, is roasting with different calcium-containing additions, for example, limestone, lime, etc. [24–25, 31–32]. The oxidation roasting of vanadium slag with calcium-containing compounds leads to calcium vanadates formation such as calcium metavanadate ($Ca(VO_3)_2$), calcium pyrovanadate ($Ca_2V_2O_7$) and calcium orthovanadate ($Ca_3(VO_4)_2$). This method is more environmentally friendly compared with the sodium roasting because wastewater can be neutralized by lime milk addition and returned inprocess.

Calcium vanadates have specific dissolution characteristics for each compound in both the acidic and alkaline medium. $Ca(VO_3)_2$ is almost completely dissolved at pH = 0.5–1.8 at room temperature, while $Ca_2V_2O_7$ – at pH = 0.5–1.35. Dissolution degree of $Ca_3(VO_4)_2$ in acidic media is only 93–95 % at pH = 1–2. The highest extraction of vanadium from $Ca(VO_3)_2$ in alkaline medium is only 70 % at 80 °C and pH = 7–9, moreover, an increase of pH leads to a decreasing of the dissolution degree. The solubility of vanadium from $Ca_2V_2O_7$ in the alkaline medium is up to 20%.The highest dissolution degree up to 70% of $Ca_3(VO_4)_2$ can be achieved only at pH = 7, and it decreases with increasing of pH [26].

Investigation of vanadium slag oxidation roasting with MgO addition showed that during roasting process vanadium spinel is converted to magnesium metavanadate ($Mg(VO_3)_2$), magnesium pyrovanadate ($Mg_2V_2O_7$), and magnesium orthovanadate ($Mg_3(PO_4)_2$) [33]. It is well-known [26] that magnesium vanadates react most fully with sulfuric acid at pH < 1.0. The increasing of leaching temperature leads to an increase of dissolution degree of vanadium. In an alkaline medium at pH = 7–8 recovery reaches its maximum of 87.8% only from magnesium metavanadate at 80 °C. Extraction of vanadium from magnesium pyrovanadate does not exceed 60 % at 60 °C. Additionally, a non-salt roasting method exists, which lead to the conversion of vanadium from spinel form to $Ca(VO_3)_2$, $Mn(VO_3)_2$, $Mg(VO_3)_2$ forms [34–35].

Thus, vanadium from the vanadium compounds formed during the roasting process is favourable to extract in an acidic medium. Therefore, in this work, was used sulfuric acid leaching for treatment of slurry roasted. This method has the following advantages: the possibility of removal of sulfate ions from aqueous solutions with generally available reagents (hydrated lime, limestone) allows to reuse of water and create a closing water cycle; lower volatility and toxicity compared with hydrochloric and nitric acids; more accessible of reagent due to itis using for current processing of vanadium slag.

The aim of this work is an investigation of methods for oxidation roasting of vanadium-containing slurry to develop its recycling technology.

2. Materials and Methods

2.1 Materials

The original vanadium-containing slurry was taken from EVRAZ Vanadii Tula plant (Russia, Tula). The chemical analysis was performed using an X-ray fluorescence spectrometer AXIOSmax Advanced (PANalytical, Almelo, Netherlands) by the method described in [36–37]. Table 1 shows the chemical composition of slurry.

Table 1. Chemical composition of vanadium-containing slurry samples, %wt.

No.	V_2O_5	$V_2O_{5a.s}$	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	SO_3
1	3,59	1,4	1,04	1,56	11,8	0,03	0,11	12,1	7,3	3,35	6,52	36,7	15,9
2	3,79	1,5	1,33	1,5	11,82	0,03	0,14	11,9	7,4	3,25	6,54	36,6	15,7
3	3,67	1,4	0,84	1,42	11,6	0,03	0,11	12	7,6	3,35	6,68	36,5	16,2

$V_2O_{5a.s}$ – acid-soluble form of V_2O_5

The X-ray phase analysis results in an earlier work [37] showed, that the main phases of sample 3 are spinel $FeO{\cdot}V_2O_3$ (3.0%), hematite Fe_2O_3 (30.6%), bassanite $CaSO_4{\cdot}0{,}5H_2O$ (17.3%). The silicate part is represented by quartz SiO_2 (4.5%), manganese is present as ramsdellite MnO_2 (0.8%) form. The sample also contains rutile TiO_2 (1.2%) and armolcolite Fe_2TiO_5 (13.5%). It should be noted that the composition of individual phases can be unstable. Iron and vanadium are partially replaced in spinel composition by chromium, titanium, and manganese [23].

2.2 Methods

2.2.1 Oxidation roasting

The oxidation roasting of the vanadium-containing slurry was carried out in a muffle furnace at the temperature range of 600–1000 °C during 2 hours. Before roasting the slurry and additives were dried and mixed. The additives were used chemically pure reagents such as Na_2CO_3 (99.5 %), MgO (97%), $CaCO_3$ (95.7%).The 50 g of slurry with additions were added into a ceramic boat and placed in a furnace for roasting.

The roasting efficiency was evaluated by the V_2O_5 acid-soluble form content of the roasted samples, the V_2O_5 extraction degree into the solution (η_{V2O5}) and the content of spinel.

The contents of V_2O_5 acid-soluble form in the original and roasted samples were determined by redox titration. A sample of 20 g in weight was dissolved in a solution of 7% H_2SO_4 at solid/liquid (S/L) relation = 1:10 with mixing through of an upper-drive stirrer during 30 min. The solution was filtered under vacuum and the precipitate was washed with 50 ml of water. The volume of the obtained filtrate was determined by a measuring cylinder and an aliquot was selected from this solution for titration [27].

The V_2O_5 extraction degree into the solution was calculated as follows:

$$\eta_{V2O5} = V_2O_{5a.s.} / V_2O_5, \tag{1}$$

where $V_2O_{5a.s.}$ is the acid-soluble form of V_2O_5content in the roasted sample, %wt.; V_2O_5 is the total content of V_2O_5 of the roasted sample, %wt.

2.2.2 X-ray Diffraction Analysis

X-ray diffraction analysis (XRD) of samples was performed on the analytical installation ARL 9900 Workstation (Thermo Fisher Scientific, Waltham, MA, USA) combining a XRF spectrometer with an upper tube and a θ–θ diffractometer. Samples for XRD analysis were prepared by the pressing of powder onto the surfaceof a boric acid substrate.

2.2.3 Thermogravimetric analysis

Thermogravimetric analysis was carried out on the device STA 449 F3 Jupiter (Netzsch, Selb, Germany) at the temperature range 25–1200 °C with the heating rate 10 $°C·min^{-1}$. The analysis was performed in an argon atmosphere using closed alund crucibles. Samples of 10–13 mg in weight were placed into the crucible to evenly cover the bottom to ensure maximum contact with the crucible material.

2.2.4 Thermodynamic modeling

Thermodynamic modelling was performed using HSC Chemistry 9.9software (Outotec, Pori, Finland) at 500–1200 ºC in at atmospheric pressure. The species with small fractions were excluded from the calculation. Based on the chemical and phase analysis data was calculated the following rational composition of the slurry which was used for thermodynamic modelling: %wt.: 26.94 $CaSO_4$; 25.91 Fe_2O_3; 17.95 Fe_2TiO_5; 4.78 FeV_2O_4; 11.76 SiO_2; 2.04 TiO_2; 8.70 MnO_2; 0.76 $Cr_2(SO_4)_3$; 1.15 Cr_2O_3. The composition of the slurry is partly simplified for calculations since the program does not consider the formation of solid solutions and phases of variable composition.

3. Results and Discussion

3.1 The oxidation roasting efficiency

Consistent with our previous work [37], vanadium in the slurry presents in $FeO·V_2O_3$ (V^{3+}) form. However, the samples contain 1.4-1.5 wt.% $V_2O_{5a.s}$ (see Figure 1), i.e. vanadium can be partly presents in the form of acid-soluble phases ($Ca(VO_3)_2$, $Ca_2V_2O_7$, $Ca_3(VO_4)_2$, etc.), which couldn't be found by this method of analysis. Based on the results of our previous works [23, 37], we can assume that there are also other soluble vanadium compounds such as $Mn_2V_2O_7$ and $Ca_3Fe_{3,5}V_{1,5}O_{12}$. They were found in roasted vanadium slags with the additive of lime. It should be mentioned that vanadium slurries are an insoluble residue after leaching of the roasted vanadium slag. Forms of vanadium such as VO_2 and $CrVO_4$ were also found in the original slags.

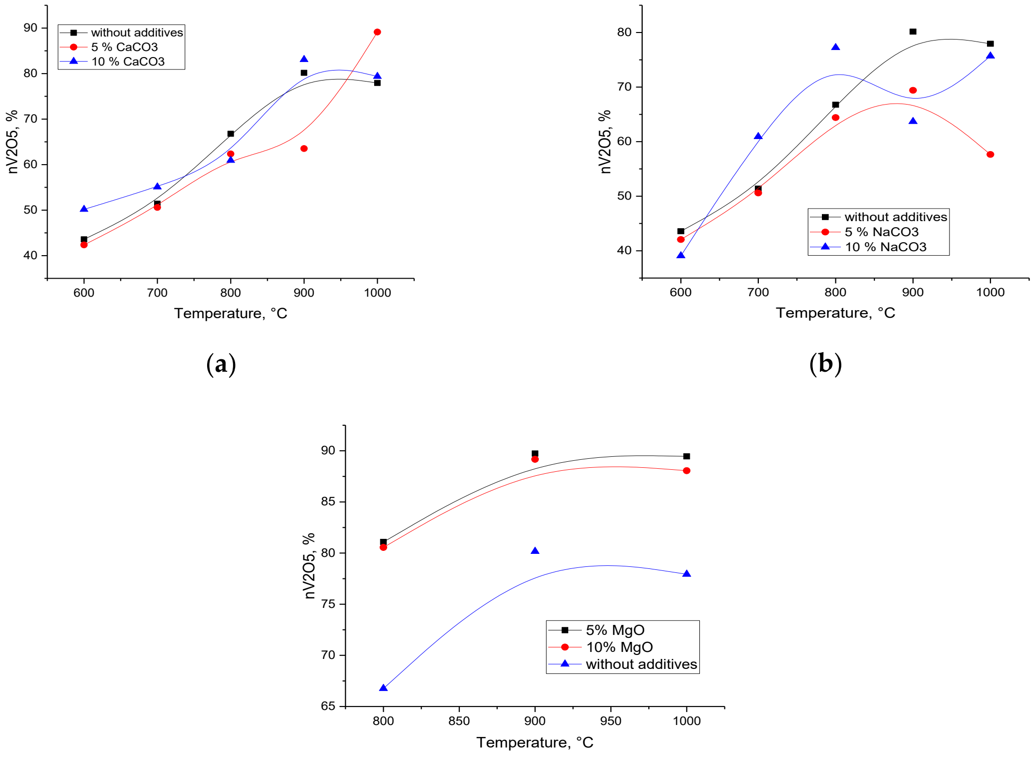
The oxidation roasting of the original slurry was carried out without additives and with 5-10% amount of $CaCO_3$, Na_2CO_3 and MgO additives. It was shown that an increase of roasting temperature with $CaCO_3$ and Na_2CO_3 addition led to the growth of the $V_2O_{5a.s.}$ values, therefore roasting with MgO addition was performed at 800–1000 °C. Table 2 and figure 1 show the amount of $V_2O_{5a.s}$ and η_{V2O5} in samples after roasting, respectively.

The data showed in figure 1 points out that there are a maximum amount of η_{V2O5} in samples with additives of 5% $CaCO_3$ (89.1%) at roasting temperature 1000 °C and 5% MgO (89.7%) at 900 °C.

Table2. Effect of the roasting temperature and addition amount on the V_2O_5 acid-soluble form content, %wt.

Roasting temperature, ºC	**$V_2O_{5a.s.}$**						
	Without additive	**$CaCO_3$**		**Na_2CO_3**		**MgO**	
		5%	**10%**	**5%**	**10%**	**5%**	**10%**

600	1,56	1,44	1,63	1,43	1,27	–	–
700	1,84	1,72	1,79	1,72	1,98	–	–
800	2,39	2,12	1,98	2,19	2,51	3	2,9
900	2,87	2,16	2,70	2,36	2,07	3,32	3,21
1000	2,79	3,03	2,58	1,96	2,46	3,31	3,17



(**a**) (**b**)

(**c**)

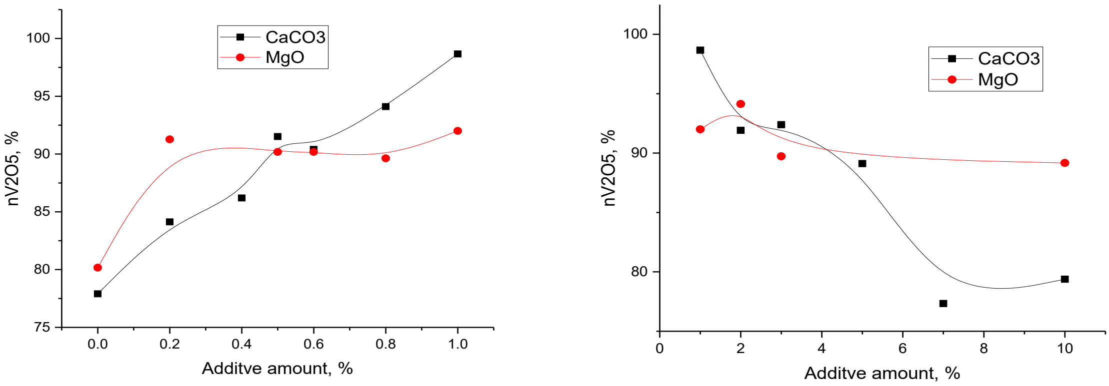
Figure 1. Effect of roasting temperature and additive amount on V_2O_5 extraction degree with additives $CaCO_3$ **(a)**, Na_2CO_3 **(b)** and MgO **(c)**.

To unambiguously determine the optimal consumption of these additives the additional experiments were carried out. Table 3 shows that the addition of 1% $CaCO_3$ and 2% MgO during the roasting led to a maximum η_{V2O5} which were 98.7% and 94.1%, respectively (Figure 2).

Table 3. Effect of additive different amount on $V_2O_{5a.s.}$content in roasted slurry, %

Content of additive, %	Additive	
	$CaCO_3$	MgO
0	2.79	2,87
0.2	3.18	3,45
0.4	3.25	-
0.5	3.45	3,40
0.6	3.40	3,40
0.8	3.54	3,37
1.0	3.70	3.45
2.0	3.41	3.53
3.0	3.40	-

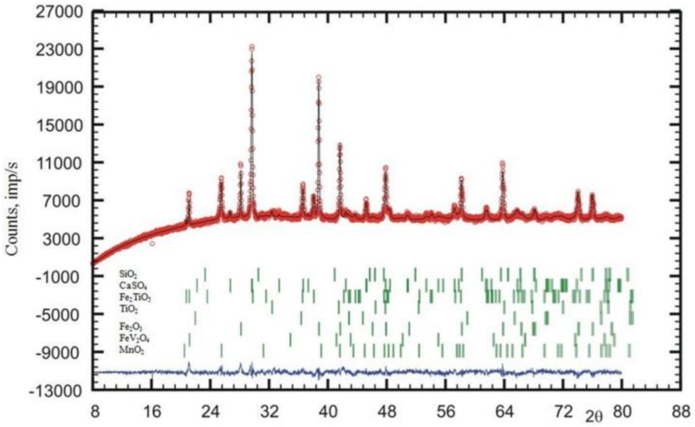
5.0	3.03	3.32
7.0	2.90	-
10.0	2.58	3.21



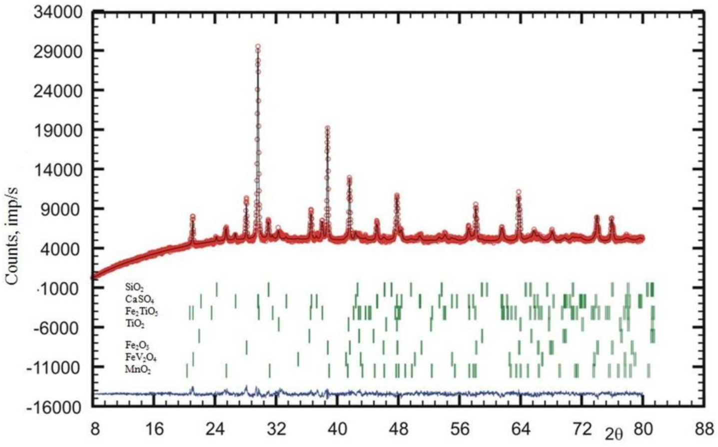
(**a**) (**b**)

Figure 2. Effects of $CaCO_3$ and MgO addition on η_{V2O5} in the roasted slurry at optimal roasting temperature (1000 °C for $CaCO_3$ and 900 °C for MgO): **(a)** – addition amount of 0-1%; **(b)** – addition amount of 1-10%.

Figure 3 and Table 4 demonstrate XRD patterns and quantitative phase distribution for the roasted samples with 1% $CaCO_3$ and 2% MgO additives. The shown data point out that using oxidation roasting did not lead to complete the decomposition of spinel. However, its content significantly decreased from 3 up to 0.4% for roasting with 1% $CaCO_3$ addition and up to 0.8% for 2% MgO addition.



(**a**)



(b)

Figure 3. Experimental (red), theoretical (black), and differential (blue) diffractograms acquired from samples of roasted slurry with 1% $CaCO_3$ (a) и 2% MgO (b) additives. Green dashes correspond to the positions of reference diffraction peaks of correspondent phases.

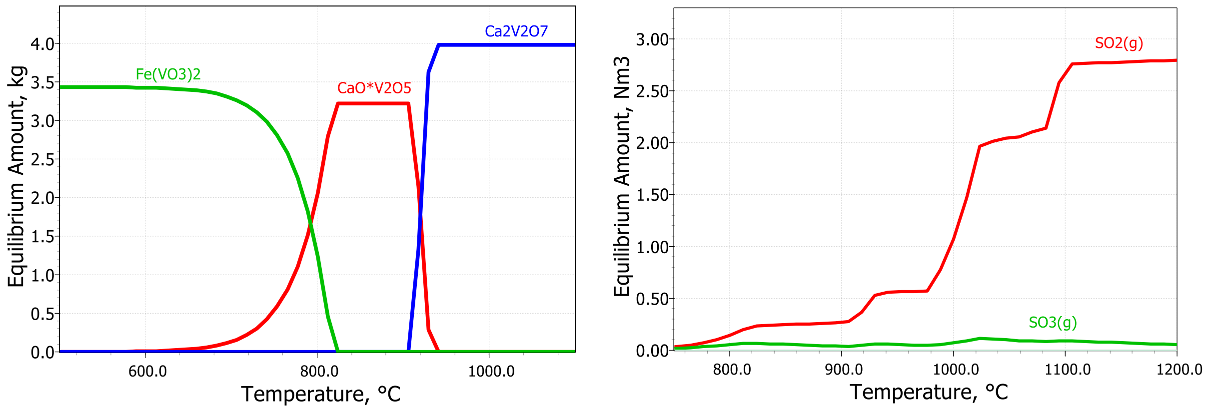
Table 4. The quantitative phase composition of original and roasted vanadium slurries, %wt.

Phases	Original slurry	Roasted slurry with different additives	
		1% $CaCO_3$	2% MgO
Gypsum ($CaSO_4 \cdot 2H_2O$)	-	<0.1	<0.1
Bassanite ($CaSO_4 \cdot 0.5H_2O$)	17.3	<0.1	<0.1
Anhydride ($CaSO_4$)	-	30.2	34.2
Spinel ($FeO \cdot V_2O_3$)	3.0	0.4	0.8
Hematite (Fe_2O_3)	30.6	33.0	32.9
Armalcolite (Fe_2TiO_5)	13.5	12.2	19.7
Rutile (TiO_2)	1.2	1.4	2.5
Ramsdellite (MnO_2)	0.8	11.8	3.4
Quartz (SiO_2)	4.5	<0.1	4.4
Grossular ($Ca_3Al_2Si_3O_{12}$)	-	<0.1	<0.1
Calcite ($CaCO_3$)	-	<0.1	<0.1
Periclase (MgO)	-	<0.1	<0.1
Amorphous phase		11.1	2.1

Thus, the cumulative evidence suggests that the optimal conditions of slurry treatment are roasting with the 1% $CaCO_3$ additive at a 1000 °C. At these conditions, the most complete decomposition of spinel can be achieved, as well as the extraction of V_2O_5 in solution.

3.2 Thermodynamic modeling and thermogravimetric analysis

To study the mechanism of conversion spinel into acid-soluble phases during the roasting of slurries with an optimal additive 1% $CaCO_3$ thermogravimetric analysis and thermodynamic modelling were performed. Figure 4 show the equilibrium amounts of vanadium-containing compounds in a solid phase and equilibrium amounts of sulfur-containing compounds in a gas phase as a function of the roasting temperature during the oxidation roasting of the slurry without additions.



(**a**) (**b**)

Figure 4. Effect of roasting temperature on the equilibrium amount of vanadium-containing compounds in the solid phase **(a)** and sulfur-containing compounds in the gas phase **(b)**

Figure 5 (a) shows, that spinel ($FeO{\cdot}V_2O_3$) is probably oxidized to iron vanadate (II) by the reaction:

$$FeO{\cdot}V_2O_3 + O_2(g) = Fe(VO_3)_2 \quad (2)$$

The iron vanadate (II) can react with calcium sulfate that can lead to forming of $Ca(VO_3)_2$ at temperatures above 600 °C and with a further increase of temperature can to are formed $Ca_2V_2O_7$ (Figure 4, a). It can be seen with an increase of temperature above 950 °C only $Ca_2V_2O_7$ exists in the system. Thus, an increase of the vanadium extraction degree into the solution with an increase of temperature probably associated with a better solubility of calcium pyrovanadate in sulfuric acid [24].

The process can be described by summary reactions:

$$4CaSO_4 + 4Fe(VO_3)_2 = 4Ca(VO_3)_2 + 4SO_2(g) + 2Fe_2O_3 + O_2(g) \quad (3)$$

$$4CaSO_4 + 4Fe(VO_3)_2 + 2TiO_2 = 4Ca(VO_3)_2 + 4SO_2(g) + 2Fe_2TiO_5 + O_2(g) \quad (4)$$

$$4CaSO_4 + 2Fe(VO_3)_2 = 2Ca_2V_2O_7 + 4SO_2(g) + Fe_2O_3 + 1.5O_2(g) \quad (5)$$

$$4CaSO_4 + 2Fe(VO_3)_2 + TiO_2 = 2Ca_2V_2O_7 + 4SO_2(g) + Fe_2TiO_5 + 1.5O_2(g) \quad (6)$$

Figure 5 demonstrates the thermograms of a sample of vanadium slurry without additives and pure $CaSO_4$. It can be seen from this figure a significant decrease in the mass of the vanadium slurry begins at a temperature above 800 °C. This agrees well with thermodynamic calculations (see Figure 4). The thermogram of $CaSO_4$ shows that its decomposition doesn't occur at temperatures below 1000 °C. Thus, the formation of calcium vanadates during the roasting of vanadium slurry is possible only by the direct reaction of oxidized spinel (iron vanadate) $Fe(VO_3)_2$ and $CaSO_4$ according to reactions (3)–(6) at temperatures above 800 °C.

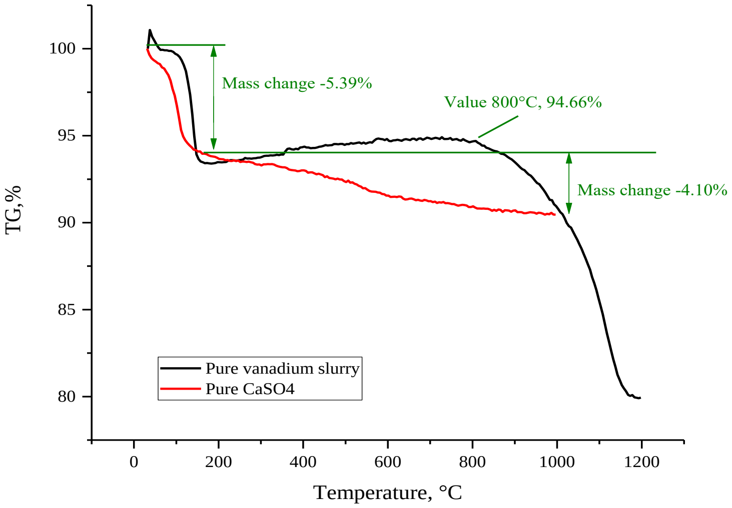


Figure5. TG curves of the vanadium slurry without additives and pure $CaSO_4$

Although the formation of acid-soluble vanadium compounds during oxidation roasting of slurry is possible without any additives, which is also confirmed by laboratory investigations (see Table 2 and Figure 1(a)), the additive $CaCO_3$ can reduce the temperature of their formation.

Figure 6 shows that $CaCO_3$ already decompositions at temperatures above 600°C with the formation of free CaO by reaction:

$$CaCO_3 = CaO + CO_2(g) \tag{7}$$

It can be seen from Figure 6 that the vanadium slurry thermogram with an additive 1% $CaCO_3$, in contrast to the thermogram of pure slurry, shows an additional decrease of slurry mass at the 600–800 °C temperature range, which indicates about the decomposition of limestone addition.

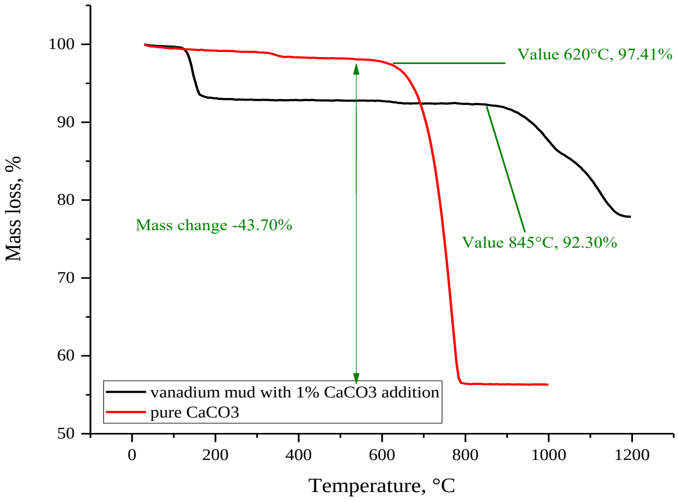


Figure 6.TG curves of the vanadium slurry with 1%$CaCO_3$ additive and pure $CaCO_3$

It is well known, that in the presence of CaO the formation of calcium vanadates during the roasting of vanadium slag is possible already at a temperature near 700°C [32] by the reaction[32,33]:

$$2FeO\cdot V_2O_3 + 2CaO + 2.5O_2(g) = 2Ca(VO_3)_2 + Fe_2O_3 \quad (8)$$

Therefore, $CaCO_3$ additives to the slurry during the oxidation roasting lead to reduces the temperature of well acid-soluble vanadates formation and increases the vanadium extraction degree.

4. Conclusions

1. Oxidation roasting of vanadium-containing slurries with and without additives such as $CaCO_3$, MgO, Na_2CO_3 was investigated. The optimal roasting conditions are 1% $CaCO_3$ additive and 1000 °C roasting temperature were determined. The most content of acid-soluble V_2O_5 and extraction degree were 3.7% and 98.7 % at these optimal conditions.
2. The results of X-ray phase analysis the roasted slurry with 1% $CaCO_3$ additive showed, that the content of spinel decreased from 3 to 0.4 wt.% after treatment.
3. The transformation mechanism of spinel into acid-soluble phases during the roasting process was studied. The formation of acid-soluble vanadium compounds during oxidation roasting is possible without any additives. Calcium vanadates are formed at temperatures above 800 °C by direct reaction of oxidized spinel (iron vanadate) and gypsum. An increase of the vanadium extraction degree into the solution with an increase of temperature probably associated with a better solubility of calcium pyrovanadatein sulfuric acid. Calcium carbonates addition to the slurry during the oxidation roasting led to reduces the temperature of well acid-soluble vanadates formation and increases the vanadium extraction degree.

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