

# Study of the process of oxidizing-sodium roasting of industrial vanadium-containing ferrophosphorus and vanadium slags

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Among the alloying metals used in the smelting of high-quality steels, vanadium occupies a special place. Its introduction into steel, even in very small amounts (tenths and hundredths of a percent), provides significant improvement in the service properties of metal structures made from it. Global demand for vanadium ferroalloys exceeds its production. Lack of vanadium raw materials is the limiting factor for increasing production of ferrovanadium. Siliceous-carbonaceous ores of Karatau in Kazakhstan, amounting to more than four billion tons, are among the world's largest vanadium reserves. Although these ores contain up to 1%  $V_2O_5$ , they cannot be enriched, and there are no technologies for the rational vanadium extraction from them. This article presents the results of studies on the extraction of vanadium from ferrophosphorus, obtained during the complex processing of these ores together with phosphorites in the process of obtaining yellow phosphorus. The processes of oxidizing-sodium roasting of industrial vanadium-containing ferrophosphorus (1.5 % V) and vanadium slag (10 %  $V_2O_5$ ) obtained during the converter processing of ferrophosphorus have been studied. It has been shown that water-soluble compound  $NaVO_3$  is forming during oxidizing roasting of ferrophosphorus or slag in mixed with  $Na_2CO_3$ . With aqueous acid leaching of ferrophosphorus roasting cinder, vanadium extraction into solution is achieved up to 81 %, and with leaching of slag cake with  $Na_2CO_3$  – more than 92 %. Total  $V_2O_5$  extraction is 75 %. Mastering of the technology for processing phosphate and vanadium-containing siliceous raw materials at Kazphosphate LLP will expand the raw material base of vanadium and will allow creating a production facility for smelting more than 200 tpy of 50 % ferrovanadium.

**Keywords:** vanadium-containing ferrophosphorus, vanadium slag, oxidation-sodium roasting, sodium vanadate, extraction of vanadium oxide (V).

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## Introduction

Vanadium occupies especial place among alloying metals which are used in melting of high-quality steels. Its introduction in steel, even with very small amounts (tenths and hundredths of a percent), provides significant improvement in the service properties of metal structures made from it.

The technology of steel microalloying by vanadium, which was mastered in China during recent years, allowed to obtain more light and strong reinforced bars with smaller diameter for constructions; it provides lowering of metal consumption and increasing of efficiency of industrial and civilian construction.

Although vanadium content in the Earth crust is rather high ( $10^{-2}$  -  $10^{-1}$  %), presence of ores with high vanadium content is very restricted. Vanadium compounds in raw materials are very spattered due to chemical mobility of vanadium atoms and slight solubility of its compounds in weak acid and alkali solutions, as well as in water solutions. Their content makes, as a rule, tenths and hundredths of

a percent. Thereby the global market meets lack of vanadium raw materials and, respectively, lack of ferrovanadium which is required for steel alloying.

Siliceous-carbonaceous ores of Karatau in Kazakhstan, amounting to more than four billion tons, are among the world's largest vanadium reserves [1-3]. Although these ores contain up to 1%  $V_2O_5$ , they cannot be enriched due to chemical mobility of vanadium atoms and slight solubility of its compounds in weak acid and alkali solutions, as well as in water solutions. Well-known technologies of vanadium extraction from these ores [4-8], including direct vanadium extraction via pyro- and hydrometallurgical methods [9-12] and production of silicon-vanadium alloying compositions (Fe-Si-V alloys) are not always efficient [13]. Use of these ores as fluxes in phosphorus production is prospective [14, 15]. Use of joint processing of phosphoritic sinter and vanadium siliceous-carbonaceous ores in electrothermic furnace leads to transition of 95 % V in forming ferrophosphorus, where its content increases by 4 times in comparison with vanadium content in siliceous-carbonaceous ores

and achieves 1.5 % [16]. This phosphorus is considered as a good raw material for vanadium extraction.

Different methods for vanadium extraction from vanadium-containing raw materials [17, 18], i.e. from ferrophosphorus [19], are known. This ferrophosphorus is produced at the phosphorus plant in the USA and contains more than 7 % of vanadium. Ferrophosphorus processing was carried out via soda roasting and hydrometallurgical extraction of  $V_2O_5$  from cinders. Vanadium extraction exceeded 80 %. This source provided 20 % of vanadium manufacturing in the USA.

This paper presents the research results of the processes of hydrometallurgical processing of ferrophosphorus (1.5 % V) and converter slag (10 %  $V_2O_5$ ) with obtaining of vanadium technical pentoxide, as well as recommendations for its use in melting of vanadium ferroalloys.

Actuality and expediency of this research are stipulated by lack of vanadium raw materials worldwide and presence of large reserves of vanadium-containing siliceous-carbonaceous ores in Kazakhstan, which are not used. Development of the methods for efficient vanadium extraction from these quartzites and creation of the grounds for starting production of vanadium ferroalloys are the aim of this work. Scientific novelty is concluded in establishment of possibility and determination of technological parameters of technological processes of vanadium extraction from high-phosphorus alloy (P : V = 15) to commercial low-phosphorus product (P : V = 0.002-0.05).

### The research methods

Pyro- and hydrometallurgical technology of vanadium extraction from ferrophosphorus includes vanadium transition in water-soluble form via oxidation-sodium roasting and consequent aqueous leaching of a cinder [20].

Vanadium-containing ferrophosphorus, which was manufactured at Kazphosphate LLP in industrial conditions, was used as initial products for experiments. It was produced in the RKZ-80 F furnace during joint melting of phosphoritic sinter and vanadium-containing siliceous-carbonaceous ores, it contains (weight %): 1.5 V; 19.8 P; 7.2 Si; 2.7 Mn; 1.7 Ti and residual Fe.

To determine the optimal conditions for oxidation-sodium roasting of the alloy and leaching of a cinder, the laboratorial investigations were conducted.

Initial charge was fed in the reactor made from stainless steel; this charge contained vanadium-containing

ferrophosphorus and sodium bicarbonate in different proportions. Introduction of oxidizing agent (air) was implemented through a pipe, under reactor net, and then gas passed through the charge layer. This reactor was located in the shaft furnace SShOL-8/11.

The experiments were conducted at the temperature 800 °C during 90 min, with air feeding speed 2-4 l/min (depending on charge amount located in the reactor). Air was introduced from a standard gas cylinder.

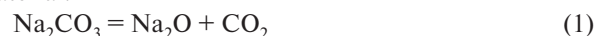
The mix containing of 100 g and 50 g of ferrophosphorus with addition of different amounts of sodium bicarbonate was prepared for experiments.

### Results and discussion

The experimental data from the stage of oxidation roasting are presented in the **Table 1**.

100 g of ferrophosphorus contain 7 g Si, 20 g P, 3 g Mn, 1.7 g Ti, 65 g Fe. 66 g of oxygen or 220 g of air are required for their oxidation up to higher dioxides.

The following decomposition reaction passes together with oxidizing processes, during thermal action on charge material:



Mass decrease by 4.1 g occurs per each 10 g of sodium carbonate, which was added to charge.

After furnace cooling to the room temperature, obtained cinder was extracted from the reactor, weighed, comminuted to the fraction < 0.2 mm and subjected to step-by-step leaching. Leaching of cakes was carried out consequently, with different liquid phase components and with different correlation between solid and liquid phases. Water (with solid/liquid phases relation S:L equal to 1:3), as well as aqueous solution of  $H_2SO_4$  with 3 % concentration was taken as liquid phase medium.

The relation between ferrophosphorus and sodium carbonate equal to 5:1 is considered as an optimal charge composition. Leaching was conducted during two stages. At the first stage of leaching, vanadium of higher oxidation degree  $V^{5+}$  transited in a cake solution, and at the second stage of leaching by acid solution, also vanadium oxidized to  $V^{3+}$ ,  $V^{4+}$  transited in solution.

The experiment, which is characterized by obtaining the best samples (**Table 2**), includes consequent cake leaching by water and then by sulfuric acid solution (with 3 % concentration and with S:L relation equal to 1:3). Totally 81 % vanadium of general amount was extracted.

Table 1. Oxidation roasting of ferrophosphorus by oxidizing agent

No. of experiment	Ferrophosphorus amount (with vanadium content 1.5 %), g	Amount of $Na_2CO_3$ , g	Air feeding speed, l/min	Cinder mass, g	Relative mass increase, %
1	100	5.0	4	63	20.5
2	100	10.0	4	62	13.4
3	100	20.0	4	68	12.5
4	50	7.5	2	39	35.4
5	50	10.0	2	41	37.9

The conducted experiments displayed that direct vanadium extraction from the Fe-P-V alloy is principally possible. However, this process will be low profitable for low vanadium content in this alloy (1.5 %), otherwise to the alloy with 7 % of vanadium [20]. Thus, further experiments will be directed on increase vanadium concentration in charge material, which is used in oxidation-sodium roasting. It is possible in production of vanadium slags containing 10–12 %  $V_2O_5$ , during converter processing of Fe-P-V alloy with 1.5 % of vanadium.

The researches on production of vanadium slags in the pilot converter were carried out. Bath volume of this converter was 50 kg of liquid ferrophosphorus containing (weight %): 19.8 P; 7 Si; 2.7 Mn; 1.5 V; 1.7 Ti and residual Fe.

Melting of vanadium-containing ferrophosphorus was carried out in the induction furnace with maximal charge of 250 kg of the alloy. Taking into account the increased titanium and silicon content, preliminary melt refining with silicon content up to 0.5 % (mass.) should be realized mandatorily. Fe oxide powder was used as a flux additive. The experiments with use of agglomerated Fe oxide in the amount of 15, 20 and 25 % of metal mass were conducted.

Consumption of a flux additive in the amount of 20 % of ferrophosphorus mass was chosen as the optimal variant allowing to decrease silicon content to the value  $< 0.5$  % (mass.); in this case total vanadium remains in metal, while phosphorus content lowered to 18.7 %. It is explained by reduction of Fe oxide and its transition in the alloy.

Vanadium extraction in slag achieved 72–73,5 %. Composition of the final converter slags is presented in the **Table 3**.

It was established via petrographic analysis [21] that vanadium is contained in slag mainly in spinelide and (in small amount) in metal inclusions, while it was not found in silicate and phosphate phases. Fe is mainly presented mainly in metal inclusions (metallic beads in sponge slag), in spinelide, in phosphate and silicate phases. Phosphorus is contained in slags, in phosphate and silicate phases, in metallic beads, while it was not found in spinelide. Silicon is practically completely presented in a vitreous phase. Manganese is uniformly distributed among all phases.

Thus, large-scale checking of the converter technology for processing of vanadium-containing ferrophosphorus in

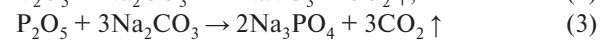
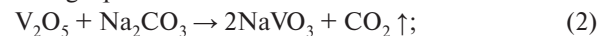
the unit with acidic (silica) lining and side oxygen blowing allows to achieve deep separate vanadium extraction from the alloy. Obtained converter slag contains up to 12 % (mass.)  $V_2O_5$ , it is suitable for hydrometallurgical processing with manufacture of vanadium technical oxide. Refined metal, which meets the requirements of blast furnace ferrophosphorus FF-19 in its composition, is a commercial product in casting and foundry production.

Preliminary industrial desiliconization should be carried out in a kind of electric steelmaking furnace, which allows to introduce iron and limestone fluxes in charge for slag processing of silicon and titanium.

Slags with increased phosphorus content will be formed in an industrial converter during deep alloy devanadation with 90 % and more vanadium extraction degree. Vanadium extraction from these slags is conducted expediently via pyro- and hydrometallurgical method.

Slag samples with  $V_2O_5$  content as large as 10.6 % were mixed (in the amount 50 g) with calculated amounts of sodium carbonate ( $Na_2CO_3$ ). Mixed thoroughly, the obtained mixtures were placed in alundum crucibles and were sintered in a muffle furnace SNOL-8.2/1200 at different temperature and during different time. The results of these experiments are presented in the **Table 4**.

The processes which are occurring during interaction between slag and sodium carbonate are described by the following equations of the chemical reactions:



Decomposition of sodium carbonate takes place during sintering, with emission of gaseous carbon dioxide; it causes decrease of cake mass relating to primary mass of sintered mixture.

Obtained cakes were comminuted to the fraction 0–0.2 mm and then subjected twice to consequent leaching (stages 1 and 2) by water and once by 3 % solution of sulfuric acid (stage 3). This process was conducted at the temperature 90 °C during 60 min. Correlation between solid substance and liquid phase (S:L) was equal to 1:3. Leaching process was carried out in a retort in water bath conditions with permanent stirring. The results of experiments are presented in the **Table 5**.

Table 2. The results of cinder leaching

No. of experiment	Cinder leaching at 90 °C during 60 min		Mass part of the elements in the solution, mg/l		Total vanadium extraction in the solution, %
	Cinder, g	Dry residue, g	$V_2O_5$	$P_2O_5$	
1	50	49	606	504	81.2
2	50	50	571	550	80.9

Table 3. Composition of converter slags

Name	Composition of the components, % (mass.)				
	$V_2O_5$	FeO	$P_2O_5$	$SiO_2$	MnO
Melt No. 1	9.8	18.5	17.8	20.5	20.5
Melt No. 2	10.6	20.1	20.6	19.9	19.7
Melt No. 3	11.9	20.1	20.5	20.0	19.9

Table 5. Averaged content of  $V_2O_5$  and  $P_2O_5$  in cakes, solutions and insoluble precipitates

No. of experiment	Initial content in 50 g of cakes, g		Transited into solution from 50 g of cakes, g		Extraction in solution, %		Content in insoluble precipitate, %		Losses and errors, %	
	$V_2O_5$	$P_2O_5$	$V_2O_5$	$P_2O_5$	$V_2O_5$	$P_2O_5$	$V_2O_5$	$P_2O_5$	$V_2O_5$	$P_2O_5$
1	4.34	10.42	2.30	4.49	53.07	43.14	41.97	47.93	4.96	8.93
2	4.32	10.38	1.91	4.37	44.20	42.14	49.98	49.11	5.82	8.75
3	4.33	10.40	3.12	4.17	72.10	40.13	24.72	56.02	3.18	3.85
4	4.34	10.42	2.96	4.49	68.30	43.14	24.69	51.44	7.02	5.42
5	3.53	8.47	2.89	5.19	81.93	61.20	9.61	29.99	8.47	8.81
6	3.53	8.46	2.94	5.35	83.56	63.21	11.65	31.71	4.79	5.08
7	3.50	8.40	2.82	5.56	80.58	66.22	12.75	27.01	6.67	6.77
8	3.53	8.47	2.96	5.18	84.00	61.20	7.59	30.19	8.41	8.61
9	3.88	9.30	3.03	6.16	78.32	66.22	16.13	26.09	5.55	7.69
10	3.89	9.32	3.41	5.80	87.79	62.21	7.35	32.30	4.85	5.49
11	3.89	9.33	3.60	5.62	92.78	60.20	4.59	30.08	2.63	9.72

Table 6. Material balance by vanadium in the process of its extraction from cake

Feed of $V_2O_5$ with 50 g of cake	Processing stages	$V_2O_5$ extraction in solution	
		g	%
3.89	1 <sup>st</sup> leaching by water	3.07	78.90
	2 <sup>nd</sup> leaching by water	0.27	6.94
	3 <sup>rd</sup> leaching by 3% solution of $H_2SO_4$	0.27	6.94
	Total extraction (3 stages)	3.61	92.78
	Insoluble precipitate	0.11	2.84
	Experimental losses and errors	0.17	4.38
Totally:		3.89	100.00

The experiment for obtaining maximal degree of  $V_2O_5$  extraction (more than 92 %) and maximal  $V_2O_5$  concentration in the solution (32,31 %) was carried out; it included consequent threefold cake leaching (twice by water and once by 3 % sulfuric acid solution). Correlation between slag and  $Na_2CO_3$  is 2:1, correlation between solid and liquid phases (S:L) was equal to 1:3. Leaching process was conducted at the temperature 90° C, during 60 min.

The balance of  $V_2O_5$  extraction was conducted based on the results of this experiment (see **Table 6**).

The conducted researches displayed that total  $V_2O_5$  extraction in the solution achieves 92.78 % for the optimal conditions of vanadium slag sintering with  $Na_2CO_3$  (with slag:  $Na_2CO_3$  relation =2:1, at the temperature 750° C during 90 min) and  $V_2O_5$  transition from cake to solution in the process of three-stage leaching (with S:L relation = 1:3, at the temperature 90° C, during 60 min). Concentration of  $V_2O_5$  in the solution makes 24 g/l. It testifies on high vanadium extraction degree in the solution during processing of vanadium slags and on high efficiency of the suggested technology.

Vanadium deposition from the solution in the process of cake leaching was carried out via dual-stage route.

At the first stage, solution was subjected to processing by sulfuric acid with obtaining sodium hexavanadate. pH of the solution was varied and corrected until it achieves neutral medium parameters. Then the solution was heated in water bath up to 90° C with holding during 4 hours.

At the second stage, the solution was processed and filtered by concentrated ammonia solution with deletion of  $Na_2H_2V_6O_{17}$  precipitate, and ammonium vanadate ( $NH_4VO_3$ ) was precipitated.

The balance of vanadium deposition from solutions after conducted cake leaching can be presented as follows:

Initial content of $V_2O_5$ in 1 l of solution:	- 32.31 g (100 %)
Precipitated $V_2O_5$ during acidic processing of the solution:	- 19.70 g (61.00 %)
Precipitated $V_2O_5$ during processing of the solution by ammonia:	- 6.65 g (21.51 %)
Residual content of $V_2O_5$ in the solution:	- 5.96 g (18.45 %)
Total amount of $V_2O_5$ (in the form of $NH_4VO_3$ ) makes:	- 26.35% g (81.55 %)

Thus, 75.66 % of  $V_2O_5$  and accompanying element  $P_2O_5$  (up to 3-5 %) are totally extracted in commercial product during hydrometallurgical processing of converter slag. Then dual-stage ammonium metavanadate recrystallization was carried out via the known technology, up to  $V_2O_5$  enrichment (not less than 77.5 %) and lowering of  $P_2O_5$  content down to 0.3 %. In such way the presented technology allows to obtain vanadium (V) oxide with correspondence to  $V_2O_5$  grades VNO-1 and VNO-2 (97-98.5 % and  $P_2O_5$  to 0.01-0.02 %).

The conducted researches were aimed on obtaining of complex vanadium alloying composition directly from

manufactured vanadium slag. Charge containing slag (with 10.6 % of  $V_2O_5$ ), 75 % ferrosilicon and lime in different proportions was subjected to melting in graphite crucibles at the temperature 1550–1600 °C. The obtained alloys, containing (weight %) 6–10 V; 15–25 Mn; 30–45 Si; 8–10 Ca; 0.2–0.8 P and residual Fe, can be used as alloying compositions in melting of several steel grades.


The technology vanadium pentoxide extraction from vanadium slags and melting of standard ferrovanadium on its base is recommended as the main one, due to restricted grade range of such steels.

Thus, the results of conducted investigations allow to expand vanadium raw material base owing to involvement of vanadium-containing siliceous-carbonaceous quartzites of Karatau.

### Conclusion

It was shown on the base of conducted investigations that vanadium processing in a converter with obtaining vanadium slag (containing 10 % of  $V_2O_5$ ) is the best variant of vanadium extraction from vanadium-containing ferrophosphorus. Optimal parameters of consequent oxidation-sodium slag roasting and aqueous acidic processing of obtained cake were established. Correlation between slag and  $Na_2CO_3$  is 2:1, at the sintering temperature 750 °C and holding time 90 min). Three-stage aqueous acidic leaching of  $V_2O_5$  from a cake is conducted at the temperature 90 °C during 60 min.  $V_2O_5$  extraction from the solution makes more than 92 %. Vanadium precipitation from the solution via its processing by sulfuric acid (at the first stage) and by ammonia (at the second stage) provides total  $V_2O_5$  extraction in the commercial product in the amount more than 77.5 %.

Possibility of direct obtaining of alloying compositions from vanadium slag is shown; these compositions contain 6–10 % of V and 0.2–0.8 % of P and are using for alloying of several steel grades. However, owing to restricted grade range of such steels, it is recommended to process slags with  $V_2O_5$  obtaining and consequent ferrovanadium melting on its base.

Taking into account lack of vanadium raw material base, involvement of vanadium-containing quartzites from Karatau deposit will allow to expand it and to make prerequisites for organization of the new ferrovanadium production as well as melting of steel which is alloyed by vanadium. 

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