Original Article

Pyro-Hydrometallurgical Processing Of Vanadium-Containing Ferrophosphorus

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Abstract

The process of oxidizing-smelting roasting of vanadium-containing ferrophosphorus, which has a composition close to that obtained by joint melting of phosphorite agglomerate and vanadium quartzite, has been studied. It has been shown that vanadium is oxidized to V2O5 and forms a water-soluble compound Na VO3 with sodium in the course of oxidative roasting of a mixture of ferrophosphorus powder and Na2CO3 in a ratio of 10:1 at 800°C. After water-acid leaching of vanadium from the roasting cinder and precipitation of V2O5, a through extraction of vanadium into a commercial product of more than 75% is achieved.

The practical development of this technology will expand the raw material base of vanadium and create a new production of vanadium ferroalloys.

Keywords: Vanadium-containing ferrophosphorus, oxidation-sodium roasting, sodium vanadate, extraction of vanadium oxide

INTRODUCTION

Taking into account the great demand for vanadium for the production of alloyed steels, the involvement in the production of one of the world's largest vanadium reserves of the Karatau siliceous ore deposit is very relevant. A promising method is the joint processing of these ores with phosphorites to obtain yellow ferrophosphorus [1–4]. In this case, vanadium will be 95% extracted into ferrophosphorus, where its content will be about 1.5%. The extraction of vanadium from this alloy into commercial vanadium pentoxide and the smelting of ferrovanadium will expand the raw material base of vanadium and reduce the shortage of ferrovanadium.

The relevance of research is due to the shortage of vanadium raw materials for the smelting of ferrovanadium and the presence in Kazakhstan of huge unused reserves of siliceous-carbonaceous vanadium ores.

The aim of the work is to develop an effective method for extracting vanadium from these ores to organize the production of ferrovanadium.

RESULTS AND DISCUSSION

Pyro-hydrometallurgical technology for the extraction of vanadium from ferrophosphorus provides for the conversion of vanadium into a water-soluble form by oxidizing-caustic roasting and subsequent aqueous-acid leaching of the cinder.

The initial product for the experiments was vanadium-containing ferrophosphorus containing: V - 1.52, Si - 6.5, P - 20.3, Mn - 3.0, Ti - 1.6, Fe - the rest.

To determine the optimal conditions for the oxidative-caustic roasting of the alloy and leaching of the cinder, studies were carried out in laboratory conditions.

The initial mixture consisting of vanadium-containing ferrophosphorus and sodium bicarbonate in various proportions was placed in a stainless steel reactor. The oxidizer (air) was supplied through a tube under the reactor grid, then the gas passed through the charge layer. For experiments, a fraction of ferrophosphorus less than 0.2 mm was used. Sodium bicarbonate introduced into the mixture was mixed with ferrophosphorus. The mixture was triturated and sieved through a 0.2 mm sieve and then loaded into the reactor. The reactor was placed in a shaft furnace SShOL-8/11.

The experiments were carried out at a temperature of 800°C for 90 minutes at an air supply rate of 2 to 4 liters per minute (depending on the amount of charge placed in the reactor). Air was supplied from a standard gas cylinder.

After the furnace was cooled to room temperature, the resulting sinter was removed from the reactor, weighed and ground to a fraction of less than 0.2 mm, and in an amount of 50 g it was subjected to phased leaching with water and 3% sulfuric acid solution in the ratio S:L = 1:3 for 60 minutes , at 90°C. At the end of each leaching step, the filter cake was dried and weighed.

Initially, a mixture containing 200 g of ferrophosphorus and 10, 20, 30, and 40 g of sodium bicarbonate was prepared for the experiment. But based on the results of the experiments, it was concluded that this amount of charge is too large, oxidation does not occur evenly, not in the entire volume, forming a “crust” on the surface of the reacted (oxidized) mass, and in deeper layers, oxidation does not occur.

Subsequently, the total mass of the load was reduced by half, and a mixture consisting of 100 g of ferrophosphorus and 5, 10, 15, and 20 g of sodium bicarbonate was prepared for experiments.

Mixtures consisting of 50 g of ferrophosphorus and 2.5, 5, 7.5 and 10 g of sodium bicarbonate were also prepared and subjected to oxidative roasting, that is, a thinner layer of charge was created on the reactor grid.

Experimental data on the stage of oxidative roasting are presented in table 1.

Table 1 - Data on the stage of oxidative roasting of ferrophosphorus with atmospheric oxygen

№ of experiment	*The amount of ferrophosphorus (with a vanadium content of 1.5%), g*	*Amount of Na_2CO_3, g*	*Air flow rate l/min*	*Weight of cinder, g*	*Relative increase in mass,%*
1	100	5.0	4	126.50	20.5
2	100	10.0	4	124.70	13.4
3	50	7.5	2	71.76	24.5
4	50	7.5	2	77.87	35.4
5	50	10.0	2	82.75	37.9
6	100	20.0	4	135.00	12.5
7	50	10.0	2	81.18	35.3

The amount of oxidizing agent sufficient to complete the oxidative roasting was determined based on the fact that the elements that make up the ferrophosphorus are in metallic form.

$[Me] + O_2 = Me_xO_y$ [1]

100 g of ferrophosphorus contains 6.5 g Si, 20 g P, 3 g Mn, 1.6 g Ti, 6.5 g Fe. For its oxidation to higher dioxides, 66 g of oxygen or 330 g of air are required.

$[P] + 502 = 2P_2O_5$ [2]

100 g of ferrophosphorus contains 20 g of phosphorus. For its oxidation to pentoxide, 5 x 32 x 20 / (4 x 31) = 26 g of oxygen is needed.

$[Mn] + O_2 = MnO_2$ [3]

100 g of ferrophosphorus contains 3 g of manganese. Oxidation to dioxide requires 3 x 32 / (4 x31) = 1.8 g of oxygen.

$[Ti] + 02 = TiO_2$ [4]

100 g of ferrophosphorus contains 1.7 g of titanium. To oxidize this amount to dioxide, 32 x 1.7 / 48 = 1.1 g of oxygen is needed.

$4[Fe] + 3O_2 = 2Fe_2O_3$ [5]

100 g of ferrophosphorus contains 6.5 g of iron. For its oxidation, 3x32x 65 / (4 x 56) = 28 g of oxygen is needed.

$4[V]+5O_2=2V_2O_5$ [6]

100 g of ferrophosphorus contains 1.5 g of vanadium. For its oxidation to pentoxide, 1.5 x 5 x 32 / (4 x 51) = 1.2 g of oxygen is needed.

In total, for the process of complete oxidation of the components that make up 100 g of ferrophosphorus, oxygen is needed in the amount of: 8 + 26 + 1.8 + 1.1 + 1.2 + 28 = 66.1 g.

The air contains 20% oxygen, therefore, it will need 5 times more: 66 × 5 = 330 g, or in terms of liters: 330 × 22.4 / 29 = 255 liters of air.

In real conditions, for the reaction to proceed, a supply of three times the volume of air is required, compared with the calculated one, which will be: 255 × 3 = 765 liters of air. The duration of the process is 90 minutes, and the air supply rate will be: 765 / 90 = 8.5 l/min.

Determination of the content of vanadium in solutions obtained as a result of leaching of the roasting cinder was carried out by a titrimetric method based on the reduction reaction of pentavalent vanadium to the oxidation state of +4 with Mohr's salt in the presence of phenylanthronilic acid as an indicator. Schematically, the reaction equation looks like this:

$V^{5+} + Fe^{2+} = V^{4+} + Fe^{3+}$ [7]

When analyzing the products of vanadium oxidation to the highest degree of oxidation, potassium permanganate ($KMnO_4$) found the presence in the samples of a certain amount of vanadium, with an oxidation state below 5+. This indicates that the vanadium oxidation process has not reached its completion. This may be the lack of an oxidizing agent and the impossibility of penetration of the oxidizing agent into the inner layers of the charge.

From the data of table 1 it can be seen that the relative increase in the mass of the resulting cinder to the total mass of the charge is at least 12.5%, and the maximum is 37.9%. This is due to the oxidation of the metal components of the charge to oxides.

Along with oxidative processes, under thermal action on the charge, a decomposition reaction occurs: $Na_2CO_3 = Na_2O + CO_2$. The weight loss is 4.1 g for every 10 g of sodium bicarbonate added to the mixture. Data on the staged leaching of cakes are presented in Table 2.

The leaching of cakes was carried out sequentially, with different liquid-phase components and with different ratios of solid and liquid phases.

As a liquid-phase medium, we took (in the ratios of the solid phase to the liquid S:L equal to 1: 1.25 and 1: 3) water, as well as an aqueous solution of H_2SO_4 with a concentration of 3% and 5%.

Leaching experiments were carried out in a stirred flask placed in a water bath, where the thermostat maintained the set temperature of 90°C.

The duration of the leaching process - 60 minutes.

From 50 g of cakes, from 12 to 23.5 g of vanadium passed into solutions, after sequential processing, which is from 24 to 47%.

The solutions obtained by successive leaching were analyzed separately after each stage and subsequently not mixed with each other.

It can be seen from the experimental results that when a large amount of charge was placed in the reactor, the oxidation did not proceed uniformly. More uniformly oxidized cakes were obtained as a result of the initial decrease in the amount of the initial charge in the reactor.

At the same time, up to 48% of phosphorus, which was originally contained in ferrophosphorus, passed into the solution. During leaching with water (in the ratio of solid phase to liquid S:L = 1:3, 14% of the phosphorus contained in the charge passed into the solution. The second and third stages of leaching with a 3% solution of sulfuric acid in the ratio S:L = 1: 3 increased the transition of phosphorus into solution up to 19%.

The optimal composition of the charge was the ratio of ferrophosphorus to sodium bicarbonate 5:1. Leaching was carried out in two and three stages. .

At the same time, 45% of vanadium, which was originally contained in ferrophosphorus, passed into the solution. Step by step it looks like this:

At the first stage of experiment 1, leaching with water in the ratio S:L=1:3, 24.08% of vanadium passed into the solution;

At the second stage of leaching with a 3% sulfuric acid solution in the ratio S:L=1:3, 14.32% vanadium passed into the solution;

At the third stage of leaching with a solution of sulfuric acid H_2SO_4, in the ratio S:L = 1:3, 6.52% of vanadium passed into the solution.

At the first stage of leaching, vanadium of the highest oxidation state V^{5+} passed into the solution from the sinter, and at the 2nd and 3rd stages of acid leaching, vanadium oxidized to V^{3+}, V^{4+} also passed into the solution. The transition of phosphorus into solution parallel to vanadium was maximum 76%.

In the case of two successive leachings with an aqueous solution of 3% sulfuric acid, in the ratio S:L=1:3, the amount of vanadium that passed into the solution increased to 63%. Moreover, the amount of vanadium that passed into solution at the first and second stages is almost the same (31.6% each).

Table 2 - Results of staged leaching of cinders obtained as a result of oxidative roasting of ferrophosphorus with sodium bicarbonate. Temperature 90°C, holding time 60 minutes

№ of experiment	*Staged leaching options*		*Weight of cinder taken for leaching, g*	*Mass of dry residue obtained after leaching, g*	*Indicators for the content of vanadium*				
	№ of stage	*Options*			*Concentration in solution during leaching, g/l*	*The amount passed into the solution during the leaching process, g*	*The amount in the dry residue that did not pass into solution, g*	*Extracted from ferrophosphorus in stages %*	*Total extracted from ferrophosphorus %*
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
1.1.	1	H_2O, S:L1:3	50	47.18	0.68	0.102		24.08	45
1.2.	2	3% p-p H_2SO_4, S:L1:3		40.32	0.40	0.061		14.32	
1.3.	3	3% p-p H_2SO_4, S:L1:3		34.92	0.18	0.028	0.23	6.52	
2.1.	1	3% p-p H_2SO_4, S:L1:3	50	33.64	1.09	0.164		31.60	63
2.2	2	3% p-p H2S		29.81	1.09	0.164	0.19	31.60	

.		O_4, S:L1/3							
3.1.	1	5% p-p H_2SO_4, S:L1:3	50	33.92	1.35	0.203		39.13	65
3.2.	2	5% p-p H_2SO_4, S:L1:3		29.03	0.88	0.133	0.18	25.58	
4.1.	1	H_2O, S:L1:3	25	24.51	1.04	0.078		30.10	81
4.2.	2	3% p-p H_2SO_4, S:L1:3		18.53	1.733	0.130	0.05	51.14	

In the third case, the cake was twice subjected to leaching with sulfuric acid, a concentration of 5% in the ratio S:L=1:3. The total amount of vanadium that passed into solution was 65%, which repeats the results of the previous experiment, and shows that an increase in the concentration of sulfuric acid from 3 to 5% has a minimal effect on the extraction process.

In the case of transition to a solution of 45% vanadium, phosphorus, 76% goes into solution.

The experiment during which the best results were obtained (experiment 4 with the smallest mass of cinder) is the successive leaching of the cake with water, and then with sulfuric acid, a concentration of 3%, % in the ratio S:L=1:3. A total of 81% of vanadium was extracted from the total amount. Based on the results of the last experiment, the calculation of the balance for the release of vanadium from ferrophosphorus during oxidative roasting with sodium bicarbonate was carried out.

In this case, the solution resulting from the first water leaching step contains 1.040 mg/l vanadium. 30.1% vanadium passes into it.

The solution obtained as a result of the second stage of leaching with a 3% sulfuric acid solution contains 1.733 g/l of vanadium, which corresponds to the transition to a solution of 50.14% vanadium.

The experiments performed have shown that it is fundamentally possible to directly extract vanadium from the Fe-P-V alloy. However, with a low content of vanadium in this alloy (1.5%), in contrast to an alloy with 7% V [5], the process will be unprofitable. Therefore, further experiments will be aimed at increasing the concentration of vanadium in the charge going to the oxidative-sodium calcination. This is possible when obtaining vanadium slags containing 10-12% V_2O_5, in the process of converter processing of Fe - P - V alloy with 1.5

CONCLUSION

With the direct extraction of vanadium from the Fe - P - V alloy, the pyro-hydrometallurgical processing of the smallest amount of sinter, which provides the best conditions for the oxidation of its components, is optimal. Alloy roasting with Na_2CO_3 at 750 °C. Water-acid leaching of the sinter at 90 °C with the ratio L:S=3:1. With further processing of the solution with sulfuric acid and ammonia, up to 72% of vanadium is extracted into commercial vanadium pentoxide.

To implement the technology in industrial conditions, it is recommended to increase the content of V_2O_5 in the material used for the extraction of vanadium. This can be ensured by obtaining slags during the converter processing of the alloy.

Thus, the introduction of this technology will expand the raw material base of vanadium and create a new production of ferrovanadium in Kazakhstan.

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