

Processing of Vanadium and Niobium Electrodeposited from Alkali Chloride Melts

M.V. Chernyshov,^a I.B. Polovov,^a O.I. Rebrin,^a V.A. Volkovich,^a
R.V. Kamalov^a and T.R. Griffiths^b

^a Department of Rare Metals and Nanomaterials, Ural Federal University, Ekaterinburg,
620002, Russia

^b Redston Trevor Consulting, Ltd., Leeds, LS17 8RF, UK

The methods of hydrometallurgical treatment of cathodic deposits obtained by electrorefining vanadium and niobium metals in chloride melts were studied. The effectiveness of employing nitric acid was demonstrated. The optimal conditions of leaching trapped salt were determined: HNO₃ concentration of 2.5 wt. % for vanadium and 5 wt. % for niobium; solid-to-liquid ratio 1:10 for both metals. The effect of increasing duration of a washing cycle on number of process stages was investigated. The methods of final washing and drying metallic powders were considered.

Introduction

Electrorefining in halide melts is one of the prospective methods of obtaining high-purity metals that cannot be electrodeposited from aqueous media. Alkali chloride based baths can be employed for producing electrolytic powders of VB-group metals. Developing an effective industrial-scale technology of electrorefining heavily depends on the feasible and reliable method of hydrometallurgical processing of the cathodic deposits including leaching trapped salt electrolyte, rinsing and subsequent drying metallic powders.

Available literature data concerning hydrometallurgical treatment of vanadium and niobium electrodeposited from alkali chloride baths are summarized in Table I. It is clear, that the information provided is deficient and often contradictory. It is also necessary to note that there is no data concerning the selection of conditions for processing of vanadium and niobium powders electrodeposited from alkali chloride melts.

The prime objective of the present work was determining the optimal conditions of the hydrometallurgical treatment of the cathodic deposits. This included selecting suitable acid, studying the effect of acid concentration and quantity, time of leaching, washing and drying and also temperature of drying on effectiveness and the rate of processing vanadium and niobium electrolytic powders.

Experimental

The cathodic deposits of vanadium and niobium were obtained by electrorefining corresponding compact metals in NaCl-KCl based electrolytes (16, 19). The conditions of electrorefining experiments (cathodic and anodic current density, temperature, specific quantity of electricity passed) for each metal were kept constant and therefore characteristics of the cathodic deposits (particle morphology and size distribution) were similar for all bathes of vanadium or niobium powders. The amount of the salt trapped in the deposits was around 72-76 wt. % for vanadium (having dendritic particles) and 65-70 wt. % for niobium (forming spheroidal particles).

Water and dilute solutions of hydrochloric (5 and 10 wt. %), nitric (0.5, 1.0, 2.5, 5 and 8 wt. %) and sulfuric acid (5 wt. %) were tested as salt leaching reagents. The solid-to-liquid ratios were set at 1:20, 1:10 and 1:5. The number of the leaching cycles was always kept at 4. Time of a leaching cycle (τ) was varied from 15 min to 4 h. After each cycle the liquid phase was decanted and analyzed to determine the amount of salts leached using the ICP AES technique (Optima 2100 DV, Perkin Elmer). The error of chemical analysis did not exceed 3 %.

TABLE I. Literature data concerning processing vanadium and niobium electrodeposited from alkali chloride melts

Electrolyte	Salt washing		Rinsing		Reference
	Reagent	Conditions	Reagent	Conditions	
NaCl-VCl ₂	dilute HCl	no data	no data	no data	(1)
NaCl-VCl ₂	2-3% HCl	no data	acetone	no data	(2)
LiCl-KCl-VCl ₂	2-3% HCl	no data	water	no data	(3)
NaCl-VCl ₂	HCl (1:20)	no data	water	no data	(4-7)
LiCl-KCl-VCl ₂					
LiCl-NaCl-VCl ₂					
CaCl ₂ -NaCl-VCl ₂					
BaCl ₂ -KCl-NaCl-VCl ₂					
NaCl-KCl-VCl ₂	no data	no data	no data	no data	(8,9)
NaCl-KCl-VCl ₂	no data	no data	no data	no data	(10,11)
NaCl-KCl-VCl ₂	3% HCl	no data	acetone or alcohol	no data	(12)
NaCl-KCl-VCl ₂	no data	no data	no data	no data	(13-15)
LiCl-KCl-VCl ₂					
CaCl ₂ -NaCl-VCl ₂					
NaCl-KCl-VCl ₂	10 % HCl	no data	water	until pH=5.8÷6.2	(16)
NaCl-KCl-NbCl ₃	hot water	no data	no data	no data	(17)
LiCl-KCl-NbCl ₃	no data	no data	no data	no data	(18)
NaCl-KCl-NbCl ₃					
NaCl-KCl-NbCl _n	no data	no data	no data	no data	(19)

The metallic particles were then rinsed with water to remove the leachate. At this stage the solid-to-liquid ratio was set at 1:10 and the time of rinsing cycle was 1 h. The effectiveness of washing was monitored by measuring pH of the solution.

Results and discussion

Leaching trapped electrolyte from cathodic deposits

In the preliminary set of experiments we found that removal trapped salts from electrolytic powders using water leaching was not possible due to formation of lower oxidation state metal chlorides and hydrated oxides having low solubility in water (20, 21).

When hydrochloric acid leaching was applied to niobium cathodic deposits the quantitative separation of the metal from the quenched trapped salt was not achieved. It is possible that lower oxidation state niobium chlorides were formed as colloids or precipitates. This can explain why in the subsequent rinsing niobium powders from hydrochloric acid solution even after 20 rinsing cycles the solutions had acidic reaction and contained chloride-ions. Thus, hydrochloric acid solution cannot be effectively used for washing electrorefined niobium particles from the salt. Taking into account relatively weak oxidation properties of dilute solutions of sulfuric acid we can assume that H₂SO₄ also will demonstrate low effectiveness for leaching salts from niobium powders.

Comparative study of various common mineral acids showed the advantage of using nitric acid leaching solutions (Fig. 1). When a 5 % solution of HNO₃ was employed, both for vanadium and niobium, over 95 and 99 % of the trapped electrolyte was leached after the 1st and 2nd stages, respectively.

The optimal concentration of nitric acid in the leaching solution was determined in a special series of experiments. The best results (2 cycles of leaching for vanadium and 3 for niobium) were obtained when the concentration of HNO_3 was 2.5 wt. % and higher for vanadium (Fig. 2) and 5 wt. % and higher for niobium (Fig. 3). It was also found that the optimal solid : liquid ratio was 1:10 for both metals (Fig. 4, 5).

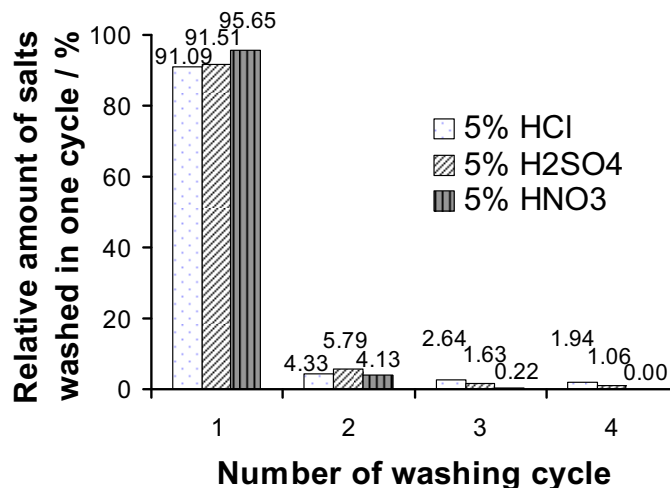


Figure 1. The effectiveness of leaching trapped salt from vanadium electrolytic powders using different acids (solid : liquid ratio of 1:10, $\tau = 1$ h).

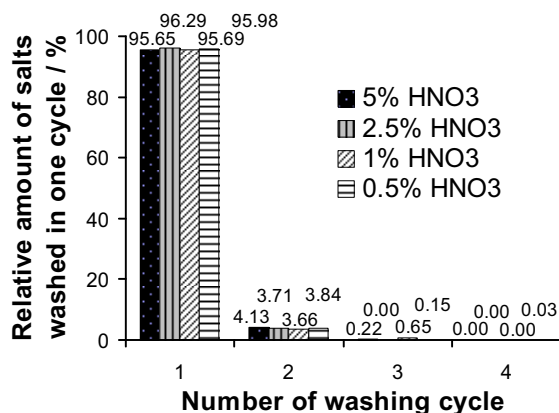


Figure 2. The effect of nitric acid concentration on effectiveness of washing trapped salt electrolyte from electrolytic vanadium powders ($\tau = 1$ h, solid-to-liquid ratio 1:10).

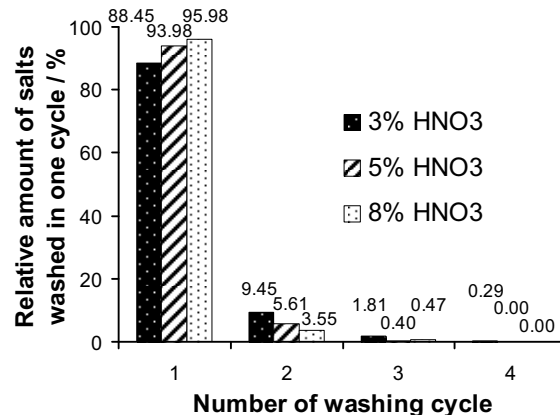


Figure 3. The effect of nitric acid concentration on effectiveness of washing trapped salt electrolyte from electrolytic vanadium powders ($\tau = 4$ h, solid-to-liquid ratio 1:10).

To determine the optimal regime of leaching the effect of washing cycle duration was analyzed. Time (τ) was varied from 15 min to 1 h in the case of vanadium, and from 2 to 4 h for niobium. Other parameters (nitric acid concentration, solid-to-liquid ratio) were kept constant. The results obtained showed that decreasing leaching time required increasing number of cycles; at least 1 h cycle was necessary for vanadium dendritic powders and 4 h for niobium spheroidal particles.

Therefore we can conclude that dilute nitric acid solution is most effective for leaching trapped salt electrolytes from electrodeposited vanadium and niobium. The optimal conditions of leaching are the following, HNO_3 concentration of 2.5 wt. % for vanadium and 5 wt. % for

niobium; solid : liquid ratio 1:10 for both metals. Under such conditions niobium powder is completely washed from salts in two four-hour stages, and vanadium can be washed in two stages lasting 1 h each. The countercurrent process can be used to reduce nitric acid consumption.

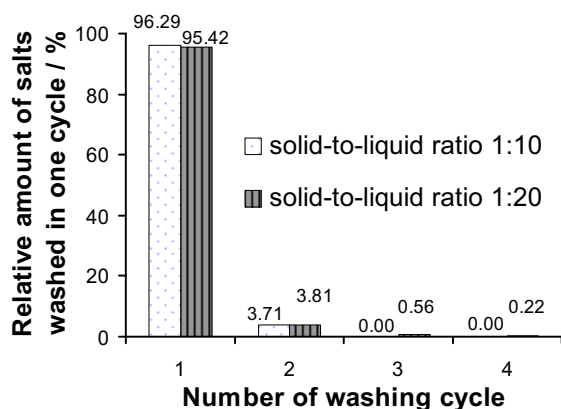


Figure 4. The effect of solid-to-liquid ratio on efficiency of washing vanadium cathodic deposit (2.5 % HNO₃ solution, 1 hour washing cycle)

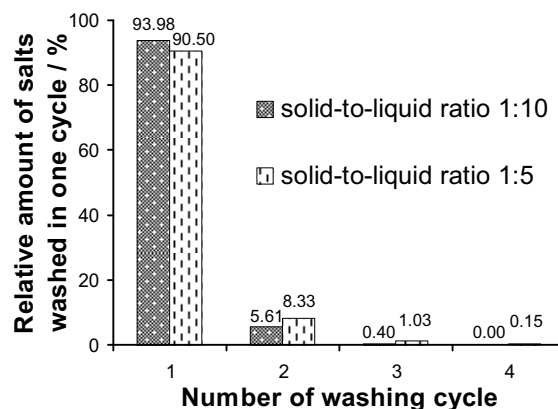


Figure 5. The effect of solid-to-liquid ratio on efficiency of washing vanadium cathodic deposit (5 % HNO₃ solution, $\tau = 4$ h)

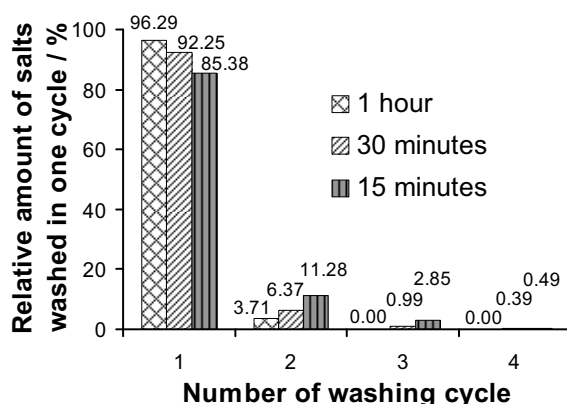


Figure 6. The effect of washing cycle duration on efficiency of washing vanadium cathodic deposit (2.5 % HNO₃ solution, solid-to-liquid ratio 1:10)

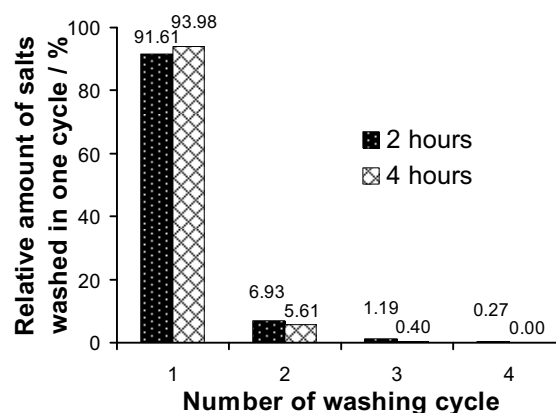


Figure 7. The effect of washing cycle duration on efficiency of washing vanadium cathodic deposit (2.5 % HNO₃ solution, solid-to-liquid ratio 1:10)

Rinsing from acid solutions

After acidic leaching the metallic powders were rinsed with distilled water to remove the leachate. The number of washing cycles was varied depending on the acid used, its concentration and solid-to-liquid ratio. The results of the experiments are presented in Tables II and III. Fig. 8 shows a typical example of how pH value of the solution changed during rinsing metallic powders from nitric acid solution.

The minimum number of rinsing cycles was required after the nitric acid based leaching; the pH value of the rinsing solution reached 5.0-5.5 after 3 cycles for vanadium or 7 cycles for niobium. This data also indicate that the morphology of the cathodic deposits also influences the

hydrometallurgical treatment. In multistage rinsing the countercurrent process can be used to reduce the distilled water consumption.

TABLE II. Number of rinsing stages used to remove leachate from electrodeposited vanadium

Reagent	HCl	HCl	H ₂ SO ₄	HNO ₃	HNO ₃	HNO ₃	HNO ₃	HNO ₃	HNO ₃
Concentration, wt %	5	10	5	5	5	2.5	2.5	1	0.5
Solid-to-liquid ratio	1:10	1:10	1:10	1:10	1:5	1:10	1:20	1:10	1:10
No. of washing cycles	4	4	4	3	3	3	3	3	3

TABLE III. Number of rinsing stages used to remove leachate from electrodeposited niobium

Reagent	HCl	HNO ₃	HNO ₃	HNO ₃	HNO ₃	HNO ₃
Concentration, wt %	5	8	5	5	5	3
Solid-to-liquid ratio	1:10	1:10	1:5	1:10	1:20	1:10
No. of washing cycles	>20	17	15	12	10	10

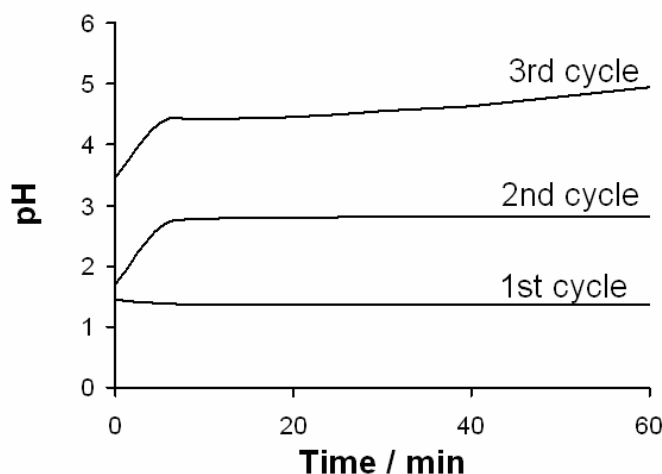


Figure 8. Time dependence of pH of washings during water treatment of vanadium cathodic deposits washed by 2.5 % solution of HNO₃ (solid-to-liquid ratio 1:10).

Drying metal powders

After water rinsing the metallic powders retained around 1.5 g H₂O / g V or 1.2 g H₂O / g Nb and required drying. Two methods of drying were tested: direct drying at 90–95 °C and washing the powders with acetone (*ca.* 1 ml per 1 g of the metal) with the subsequent drying at 40 °C. The drying process was monitored by measuring the weight of metallic powder.

Rinsing the powders with acetone allows to decrease the drying temperature and reduces the oxidation and chances of ignition of metallic powders. This method can be recommended for drying fine (below 0.74 mm) powders of electrolytic metals. Electrorefining normally yields more coarse powders that can be effectively dried at 90 °C without preliminary acetone washing.

Conclusions

Hydrometallurgical processing vanadium and niobium electrodeposited from alkali chloride melts was investigated. Of water and all common mineral acids (HCl, H₂SO₄, HNO₃) dilute nitric acid was the most effective. The optimal conditions of removing trapped salt electrolyte from the cathodic deposits were determined. The salts are best leached using HNO₃ solution (2.5 wt. % for vanadium or 5 wt. % for niobium) keeping the solid : liquid ratio at 1:10 for both metals. Under such conditions niobium can be washed from the salts in two stages (taking 4 h each), for vanadium two one-hour cycles are sufficient. It was shown, that distilled water can be

effectively used to rinse electrolytic powders from acidic solutions. It was found that the morphology of electrodeposited metals influences the number and duration of leaching and rinsing stages. The methods of metal drying were recommended for different types of vanadium and niobium electrolytic powders.

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