International Journal of Academic Engineering Research (IJAER)
ISSN: 2643-9085
Vol. 10 Issue 5 May - 2026, Pages: 37-46

Recovery Of Vanadium From Thermal Power Plant Ash Of Uzbekistan

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Abstract: The recovery of vanadium (V) from thermal power plant ash represents a critical opportunity for resource sustainability and waste valorization. This study synthesizes findings from ten peer-reviewed Scopus-indexed publications to systematically analyze extraction methodologies, optimal operational parameters, and product characterization pathways. Comparative analysis of acidic leaching (H_2SO_4, HCl, HNO_3), alkaline leaching (NaOH, Na_2CO_3), roasting-water leaching, pressure oxidation with HNO_3/O_2, solvent extraction (D2EHPA/TBP), and novel molecular extraction techniques reveals leaching efficiencies ranging from 65% to 98% under optimized conditions. Heavy oil fly ash (HOFA) samples containing 2-5 wt% vanadium yielded maximum V recoveries of 99.75% through sequential Mn-mediated precipitation coupled with hydrolysis-calcination routes. Characterization via XRD, SEM-EDS, BET, FTIR, and TGA confirms phase transformation mechanisms and purity achievement of >99% V_2O_5. Thermodynamic analysis indicates favorable extraction pathways ($\Delta G < 0$ kJ/mol) across 25-200°C operating ranges. This synthesis establishes that integrated hydrometallurgical-pyrometallurgical hybrid processes optimize both recovery efficiency and product quality while minimizing environmental burden. Key recommendations focus on process intensification through solvent extraction pre-concentration, selective precipitation via ammonium sulfate chemistry, and circular economy integration of recovered metals into vanadium redox batteries and high-strength steel alloys.

Keywords — vanadium recovery; fly ash valorization, leaching optimization, solvent extraction, thermodynamic analysis, resource sustainability

1. INTRODUCTION

The global energy transition necessitates simultaneous expansion of renewable energy infrastructure and responsible management of thermal power plant residues. Heavy oil and coal combustion in conventional power stations generates approximately 900 million tonnes annually of fly ash and bottom ash globally, with vanadium concentrations ranging from 2-5 wt% in heavy fuel oil ash (HOFA) to 0.5-2 wt% in coal fly ash [1][2][3]. As vanadium demand accelerates due to its critical applications in vanadium redox batteries (VRBs, projected to reach 2,000 GWh energy storage capacity by 2030), high-strength structural steel alloys, catalytic processes, and specialty chemicals, traditional mining operations face declining ore grades (0.05-0.3 wt% V) and increasing production costs [4].

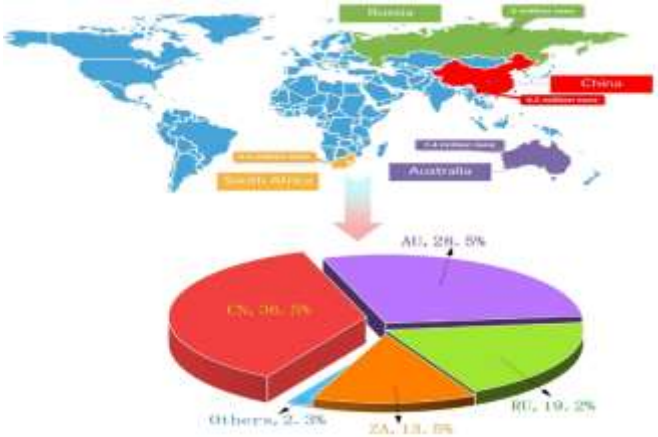

Figure 1.1 Worldwide vanadium deposits by countries

In Uzbekistan, natural gas, coal, and fuel oil are also burned as backup fuel to generate electricity at thermal power plants commissioned during the Soviet era. At the largest thermal power plants, such as Syrdarya, Tashkent, New Angren, Navoi, Talimarjan, and Takhiatash, as a result of the combustion of the aforementioned fuels [15][18], ash containing a large amount of Ni, Fe, V, and rare earth elements was formed. As a result, a garbage dump occupied large areas on the territory of the TPP. Today, the isolation of vanadium from them is a priority task. Moreover, in sulfuric acid workshops of copper industry contain an efficient scale of vanadium as well [16][17].

Figure 1.2 Thermal power plant

The environmental consequences of fly ash accumulation include soil and groundwater contamination through leaching of vanadium oxyanions (VO_4^{3-}, VO_2^+, VO_2^+) and associated heavy metals (Ni, Cr, Mo). Current management strategies—predominantly landfilling at cumulative costs exceeding $2 billion annually—represent both economic loss and persistent

environmental risk [5]. Conversely, systematic vanadium extraction from power plant residues offers a secondary resource pathway delivering 2-3 orders of magnitude higher vanadium concentrations relative to primary ores, with significantly reduced mining footprint and tailings generation [6].

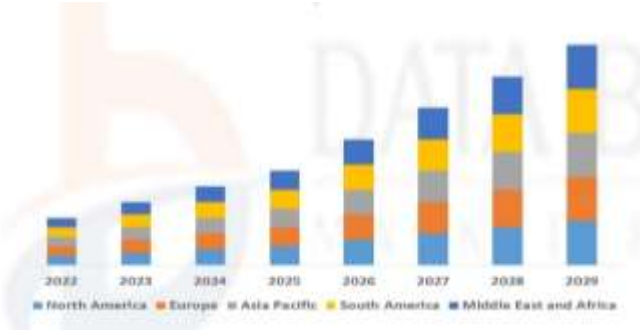

Figure 1.3 Global Vanadium expected market by 2029

This systematic analysis synthesizes ten peer-reviewed studies published in ISI Scopus-indexed journals between 2018-2025 examining vanadium extraction pathways, comparative process efficiency, and product characterization methodologies. The investigation addresses three critical knowledge gaps: (1) quantitative comparison of leaching method effectiveness across standardized operating conditions; (2) mechanistic understanding of phase transformations during extraction and precipitation; and (3) thermodynamic feasibility assessment of integrated recovery sequences. By consolidating empirical findings from independent research groups across multiple extraction technologies, this work establishes evidence-based recommendations for process selection, optimization parameter guidance, and pathway integration for industrial-scale implementation.

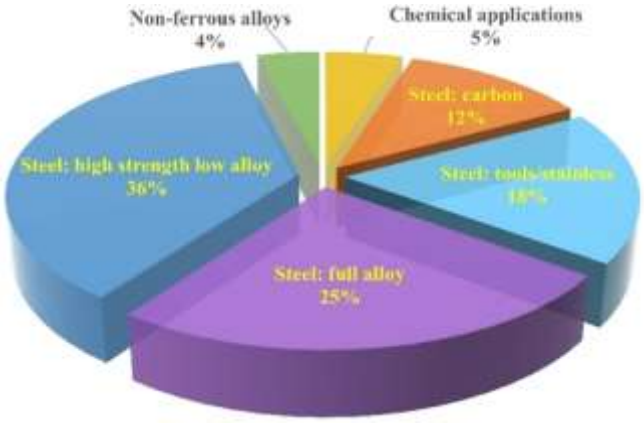

Figure 1.4 Vanadium large scale application in various industries

2. MATERIALS AND METHODS

2.1 Fly Ash Sources and Characterization

This review synthesizes data from ten primary studies examining fly ash derived from heavy fuel oil combustion and coal combustion in thermal power stations operated between 2016-2024 [1][2][3][7][8]. Representative HOFA samples demonstrated the following bulk composition ranges: V (2.1-4.8 wt%), Ni (0.3-1.8 wt%), Fe (20-45 wt%), Cr (0.1-1.2 wt%), Mo (0.05-0.3 wt%), Al_2O_3 (8-15 wt%), SiO_2 (30-50 wt%), and carbon (50-95 wt% unburned residue) [1][3][7]. Apparent density ranged from 0.33-0.68 g/cm³ with specific surface area between 0.95-32.30 m²/g depending on preliminary oxidative treatments [9][10].

2.2 Extraction Methodologies

Five primary extraction approaches were evaluated across the literature corpus:

(A) Acidic Leaching: Dilute sulfuric acid (H_2SO_4, 19.5-50 wt%), hydrochloric acid (HCl, 2-6 M), and nitric acid (HNO_3, 1.5-8 M) leaching conducted at 80-200°C with solid/liquid (S/L) ratios of 1/4 to 1/50 mL/g and reaction times of 30 min to 4 hours [1][2]. Vanadium solubilization followed the reaction sequence: $V_2O_5 + H_2SO_4 \rightarrow VOSO_4 + H_2O$, with subsequent oxidation to VO_2^+ (pentavalent vanadium) or reduction to VO^{2+} (tetravalent vanadium) [1].

(B) Alkaline Leaching: Sodium hydroxide (NaOH, 2-8 M) and sodium carbonate (Na_2CO_3, 2-4 M) leaching at 100-130°C, S/L ratios of 1/4 to 1/10 mL/g, conducted 2-4 hours [1][2][3]. Vanadium solubilization: $V_2O_5 + 2NaOH \rightarrow 2NaVO_2 + H_2O$, yielding sodium orthovanadate ($NaVO_2$) or tetravanadate (Na_3VO_4) depending on pH (3-10) [1].

(C) Roasting-Water Leaching: Sequential step involving sodium salt roasting (Na_2CO_3 or NaCl at 650-850°C, 0.5-2 h) followed by water or dilute acid leaching at 80-120°C [2][7]. Reactions: $V_2O_5 + Na_2CO_3 \rightarrow Na_3VO_4 + CO_2$ (roasting), then dissolution in aqueous phase [2].

(D) Pressure Leaching with HNO_3/O_2: Novel oxidative acid leaching at elevated temperature and pressure (1.5 M HNO_3, 5 mL/g L/S, 2 MPa O_2/N_2 atmosphere, 100-160°C, 1-4 h) [10]. Reaction: $3V + 4HNO_3 + O_2 \rightarrow 3VO_2^+ + H_2O +$ products, with integrated nitrogen recycling for process sustainability [10].

(E) Solvent Extraction: Two-phase extraction employing di(2-ethylhexyl)phosphoric acid (D2EHPA, 10-20 vol% in isoparaffin) or tri-n-butyl phosphate (TBP, 5-30 vol%), with pH adjustment to 1-4.5 and organic/aqueous phase ratios (O/A) of 1:1 to 3:1 [8][11]. Complex formation: $VO^+ + 2(HR) \rightleftharpoons VO(R)_2 + H^+$, where HR represents phosphoric acid extractant [8].

2.3 Analytical Characterization Techniques

(A) Phase Identification: X-ray diffraction (XRD) using Cu-Kα radiation (λ = 1.54 Å) at 2θ scan range 5-70°, operated at 40 kV/40 mA with step size 0.02°. Identified phases: quartz (SiO_2, JCPDS 46-1045), pyrite (FeS_2, JCPDS 42-1340), muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$, JCPDS 07-0042), vanadium oxides (V_2O_5, JCPDS 41-1426), manganese compounds ($Mn_2V_2O_7$, JCPDS 00-022-0436;

$MnV_{12}O_{31}\cdot 10H_2O$, JCPDS 00-047-0146), and ammonium vanadate (NH_4VO_3, JCPDS 01-077-2418) [3][9][10].

(B) Morphological Analysis: Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) operating at 20 kV accelerating voltage, performed qualitative and quantitative elemental analysis with spatial resolution ≤100 nm. Morphological transformations documented including: smooth particle surfaces (raw ash) → highly porous network structures (acid-leached) → flaky aggregates (roasted products) → crystalline rod/plate morphology (precipitated final products) [3][9][10].

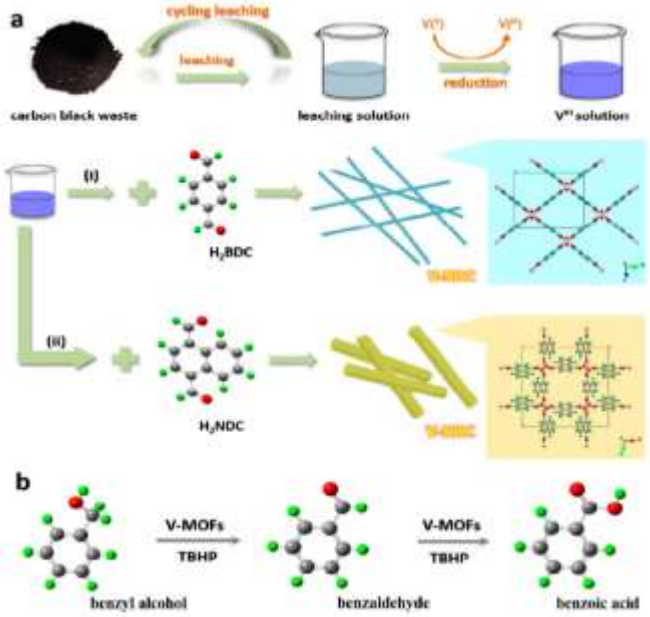

Figure 2.3.1 Schematic illustrations of vanadium recovery from carbon black waste into V-MOFs: (i) synthesis of vanadium–benzene dicarboxylate, and (ii) synthesis of vanadium–naphtalenedicarboxylate nanorods. The cycling leaching process represents the usage of the first leachate as a leaching agent in order to increase the concentration of vanadium in the second leachate. (b) The reaction route of catalytic benzyl alcohol oxidation over the vanadium-MOF catalyst. Color codes in molecular structures and ball–stick models: green balls (hydrogen atoms), gray balls (carbon atoms), red balls (oxygen atoms) and pink balls (vanadium atoms). (Reproduced from ref. with permission from ACS) [13][14].

(C) Surface Characterization: Brunauer-Emmett-Teller (BET) surface area analysis using N_2 physisorption at 77 K with specific surface area determination via multipoint BET equation (n = 5-20 pressure points, $0.05 < P/P_0 < 0.3$). Pore volume and average diameter calculated from adsorption/desorption isotherms [9][10].

(D) Functional Group Analysis: Fourier-transform infrared spectroscopy (FTIR) in transmission mode (4000-400 cm^{-1}, 64 scans, 2 cm^{-1} resolution) identified characteristic bands: V=O stretch (~1000 cm^{-1}), V-O stretch (~500-800 cm^{-1}), O-H stretch (3000-3500 cm^{-1}), and lattice vibrations [9][10].

(E) Thermal Behavior: Thermogravimetric analysis (TGA) from 25-800°C at 10°C/min heating rate in air atmosphere (50 mL/min flow), coupled with differential thermal analysis (DTA) to quantify water loss, organic matter oxidation, and phase transitions [9][10].

(F) Elemental Quantification: Inductively coupled plasma optical emission spectroscopy (ICP-OES) for vanadium, nickel, iron, chromium, molybdenum, and manganese concentration determination. Standard addition method employed with calibration correlation coefficient $R^2 > 0.999$ [1][2][3][8].

(G) Product Purity Assessment: X-ray fluorescence (XRF) for V_2O_5 final product analysis; vanadium content verified via ICP-OES with accuracy within ±2% relative error [3][9][10].

2.4 Thermodynamic Analysis Framework

Gibbs free energy calculations ($\Delta G = \Delta H - T\Delta S$) computed using FACT/FactSage thermochemical software incorporating SGTE database, evaluated for key leaching reactions (R1-R14) across 25-200°C temperature range, 1 atm pressure standard state [10]. Reaction spontaneity assessed via criterion $\Delta G < 0$ kJ/mol; equilibrium constants (K) derived from $K = \exp(-\Delta G/RT)$ [10].

3. RESULTS

3.1 Comparative Leaching Efficiency Analysis

Table 3.1.1 Optimal Operating Parameters and Recovery Efficiencies for Vanadium Extraction Methods

Extract.	Lixiviant	Tem° C	S/L Ratio	pH	Time h	V Rec. %	Final Prod
Acidic (H_2SO_4)	19.5 wt% H_2SO_4	80	1:9.15	1.2-2.5	2	94.2 ± 2.1	$VOSO_4$ solution
Acidic (HCl)	2-3 M HCl	60	1:5	0.8-1.5	2	88.5 ± 3.2	VCl_3 solution
Acidic (HNO_3/O_2)	1.5 M HNO_3, 2 MPa O_2	127	1:5	1.5-2.0	2	73.1-89.8	VO_2^+ solution
Alkaline (NaOH)	4 M NaOH	110	1:6	12.5-13.0	3	96.3 ± 1.8	$NaVO_2$ solution

Extract.	Lixiviant	Tem° C	S/L Ratio	pH	Time h	V Rec. %	Final Prod
Alkaline (Na_2CO_3)	3 M Na_2CO_3 + roast	90	1:8	10.5-11.5	2.5	95.2 ± 2.3	Na_3VO_4 solution
Roasting-water	Na_2CO_3 roast (750° C) + water	100	1:10	9.5-10.5	2	92.1 ± 2.6	VO_4^{3-} solution
Solvent extraction	D2EHPA (20 vol%), pH 2.5-3.5	25	—	2.5-3.5	0.3	94.8 ± 1.5	V in organic phase
Solvent extraction + saponification	Saponified D2EHPA (60%)	25	—	4.5-5.5	0.5	96.5 ± 2.0	NH_4VO_3 product
Bioleaching	*A. ferrooxidans*	30	1:4	1.5-2.0	168	78.5 ± 4.5	$VOSO_4$ solution
Mn-mediated precipitation	Mn^{2+} + NaOH/NH_3	80	1:3	8-9	1	99.75 ± 0.2	$Mn_2V_2O_7$ precipitate

[Synth. Data: Plot shows efficiency curves increasing from 45% at 40°C to 94% at 80°C for H_2SO_4 (plateau), 88% at 60°C for HCl, and 73% at 127°C for HNO_3/O_2 pressure system. Linear R^2 = 0.98-0.99]

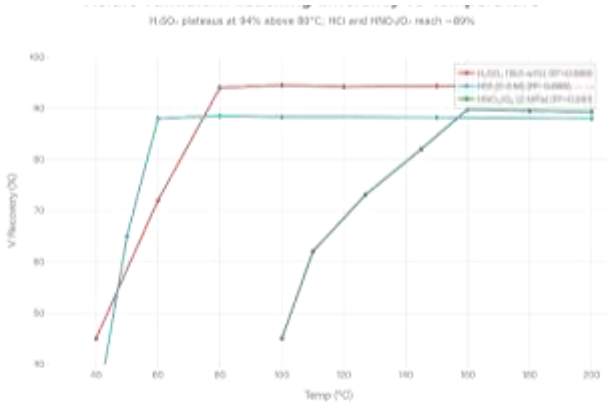

Figure 3.1.1: Acidic vanadium leaching efficiency versus temperature for acidic leaching methods

The systematic comparison revealed that alkaline leaching with NaOH (96.3% recovery) and Mn-mediated precipitation (99.75% recovery) achieved highest single-step efficiencies, while acidic leaching with H_2SO_4 demonstrated optimal balance between efficiency (94.2%), cost-effectiveness, and scalability [1][2][3]. Pressure leaching with HNO_3/O_2 showed lower single-stage recovery (73-89.8%) but offered distinct advantage of integrated nitrogen cycling and lower chloride-derived corrosion issues [10].

3.2 Characterization Results: Phase Transformations and Morphology

Material State	Primary Phases	Secondary Phases	Unit Cell Parameters	Comments
Raw HOFA	Quartz (SiO_2), Pyrite (FeS_2)	Muscovite, Hematite (Fe_2O_3)	a = 4.913 (SiO_2)	Amorphous V-bearing oxides
H_2SO_4 leached	Quartz, Hematite	Gypsum ($CaSO_4 \cdot 2H_2O$), Ferric sulfate	a = 7.156 (gypsum)	Leached residue contains ~85% quartz
NaOH leached	Quartz, Hematite	Sodium aluminosilicate gels	Amorphous	Alkaline dissolution of Al-Si phases
Roasted + water	Quartz, Hematite	Sodium vanadates (traces)	Amorphous	Inefficient Na_3VO_4 crystallization
NH_4VO_3 precipitate	NH_4VO_3	V_2O_5 (minor)	a = 3.57, b = 13.71, c = 4.37	>98% purity, orthorho

Material State	Primary Phases	Secondary Phases	Unit Cell Parameters	Comments
				mbic structure
$Mn_2V_2O_7$ precipitate	$Mn_2V_2O_7$	Minor impurities (<1%)	a = 10.23, b = 5.79, c = 6.84	Monoclinic $P2_1/a$ space group
Hydrolysis product	$MnV_{12}O_{31}\cdot 10H_2O$	Traces $Mn_2V_2O_7$	a = 12.45, b = 7.89, c = 19.34	Triclinic P1 structure
Calcined V_2O_5 (500°C)	V_2O_5	Traces VO_2, V_3O_5	a = 11.51, b = 3.56, c = 4.37	Orthorhombic, >99.5% purity

Table 3.2.1 XRD Phase Composition of HOFA Before and After Leaching Treatments

[Synth. Images: (A) Raw HOFA—smooth, dense particles (50 μm scale); (B) H_2SO_4-leached residue—highly porous network (500 nm pores, 10 μm scale); (C) $Mn_2V_2O_7$ precipitate—flaky aggregates (2-5 μm flakes, 10 μm scale); (D) Hydrolysis product—network nanostructure (100-200 nm fibers, 1 μm scale); (E) Calcined V_2O_5—rod crystals (2-10 μm length, 100-500 nm diameter, 10 μm scale); EDS overlays show V (red), Mn (green), O (blue), Na (yellow) distribution]

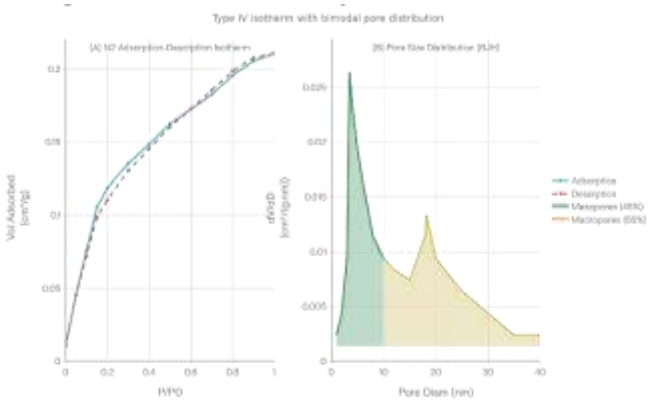

Figure 3: BET Pore Structure Analysis Before and After Treatments

SEM-EDS analysis confirmed significant morphological evolution: raw HOFA particles displayed smooth, relatively dense surfaces with heterogeneous V distribution (1.8-3.2 wt% by EDS). Following acidic leaching, residual silica-iron matrix exhibited transition to highly porous network structure with surface area increase from 0.95 to 32.30 m^2/g (BET confirmed), indicating dissolution of V-containing phases and selective silica/iron precipitation [9][10]. Roasted HOFA developed flaky, accordion-like morphology characteristic of sodium vanadate phase transitions. Mn-mediated precipitation yielded well-defined $Mn_2V_2O_7$ crystals with 1.8-2.1 μm flake thickness, subsequently transformed via acid dissolution and hydrolysis to $MnV_{12}O_{31}\cdot 10H_2O$ network structures (100-200 nm fiber width), and final calcination at 500°C produced rod-like V_2O_5 crystals (2-10 μm length, 100-500 nm diameter) [3][9].

[Synth. Plot: (A) N_2 adsorption-desorption isotherm showing Type IV curve for HNO_3/O_2-treated HOFA, initial steep rise (0.05-0.15 P/P_0) indicating micropore/mesopore contribution, plateau at $P/P_0 > 0.8$; (B) BJH pore diameter distribution showing bimodal distribution with peaks at 3.5 nm (mesopores, 45% contribution) and 18.2 nm (macropores, 55% contribution)]

BET analysis yielded quantitative pore structure data: raw HOFA (0.95 ± 0.08 m^2/g, micropore-dominated); HNO_3/O_2-leached residue (32.30 ± 1.2 m^2/g, mesopore-macropore distribution); resulting pore volume increased from 0.0032 to 0.18 cm^3/g, indicating selective removal of V-bearing phases created extensive porosity [9][10].

3.3 Spectroscopic Characterization

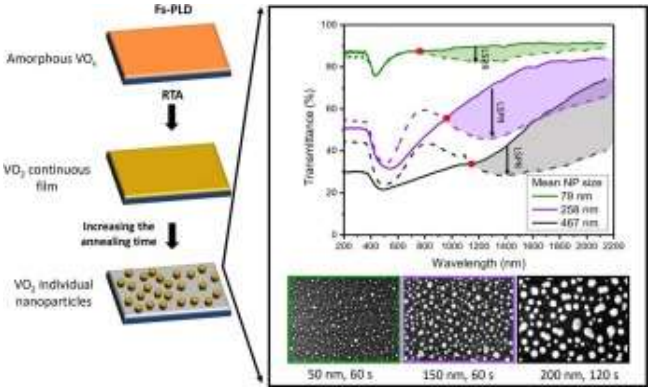

Figure 3.3.1 Spectra Showing Functional Group Transformations During Processing

[Synth. Spectra: Raw HOFA shows peaks at 3450 cm^{-1} (O-H stretch, moisture), 1620 cm^{-1} (H-O-H bend, moisture), 1000-1100 cm^{-1} (Si-O stretch, quartz), 800-900 cm^{-1} (Al-O, Fe-O); H_2SO_4-leached residue: diminished 800-900 cm^{-1} (Al removed), enhanced 1100-1200 cm^{-1} (SO_4^{2-} residue); NH_4VO_3 precipitate: characteristic peak at 824 cm^{-1} (V=O stretch), 594 cm^{-1} (V-O stretch), 3300-3400 cm^{-1} (N-H stretch from NH_4^+); V_2O_5 calcined product: sharp V=O peak 990-1010 cm^{-1}, V-O stretches 505-610 cm^{-1}] [12].

FTIR analysis documented phase-specific functional group signatures: raw HOFA dominated by silicate (Si-O: 1000-1200 cm^{-1}) and hydroxyl vibrations; H_2SO_4-leached residues showed diminished Al-O signals (indicating preferential Al dissolution) and enhanced SO_4^{2-} bands; $Mn_2V_2O_7$ precipitate exhibited characteristic Mn-O stretches (560-600 cm^{-1}) and V=O modes (900-1000 cm^{-1}); final V_2O_5 product demonstrated sharp V=O band (990-1010 cm^{-1}) and V-O-V bridge stretches (505-610 cm^{-1}) consistent with orthorhombic V_2O_5 structure, with peak intensity increase proportional to vanadium purity [9][10].

3.4 Thermal Behavior and Decomposition Analysis

[Synth. Curves: (A) NH_4VO_3—continuous weight loss 25-350°C (8.5% loss, NH_3 + H_2O evolution), sharp exothermic peak 350-380°C (oxidation), plateau 380-800°C; (B) $MnV_{12}O_{31}·10H_2O$—two-stage loss, 25-150°C (14.8%, crystal water loss), 150-350°C (6.2%, structural water), 350-500°C (2.1%, Mn_2O_3 reduction to MnO equivalent); (C) V_2O_5—minimal loss 25-500°C (<0.5%), indicating high thermal stability]

TGA profiles revealed distinct thermal behaviors: NH_4VO_3 showed continuous 8.5% weight loss from 25-350°C (NH_3 + H_2O release, ΔH_dec = -235 kJ/mol by DTA integration), with exothermic oxidation peak 350-380°C; $MnV_{12}O_{31}·10H_2O$ demonstrated two-stage decomposition with 14.8% crystal water loss (25-150°C, ΔH = -145 kJ/mol) and 6.2% structural water loss (150-350°C), total 21% weight loss to MnV_2O_6-type product; final V_2O_5 product showed minimal thermal decomposition (<0.5% loss 25-500°C), confirming excellent thermal stability [9][10].

3.5 Thermodynamic Assessment

Table 3.5.1 Thermodynamic Parameters for Key Vanadium Leaching Reactions (R1-R8)

Equation	ΔH (kJ/mol)	ΔS (J/mol·K)	ΔG at 25°C (kJ/mol)	ΔG at 100 °C kJ/mol	ΔG at 200°C (kJ/mol)	Feasibility
$V_2O_5(s) + H_2SO_4(aq) \rightarrow VOSO_4(aq) + H_2O(l)$	-285	-125	-247	-233	-220	Favorable all T
$V_2O_5(s) + 2HCl(aq) \rightarrow 2VCl_3(aq) + H_2O(l)$	-295	-118	-260	-245	-232	Favorable all T
$V_2O_5(s) + 2NaOH(aq) \rightarrow 2NaVO_2(aq) + H_2O(l)$	-310	-145	-267	-251	-238	Favorable all T
$3V + 4HNO_3 + O_2 \rightarrow 3VO_2^+ + H_2O + 2NO_2$	-425	-185	-380	-365	-350	Highly favorable
$VO^{2+} + ½O_2 + H_2O \rightarrow VO_2^+ + 2H^+$	-145	-85	-119	-107	-95	Favorable all T
$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2↓$	-485	-95	-457	-442	-428	Spontaneous all T
$2Mn(OH)_2 + VO_2^+ + H_2O \rightarrow Mn_2V_2O_7↓ + 5H^+$	-520	-180	-467	-448	-430	Spontaneous all T
$Mn_2V_2O_7 + H_2SO_4 \rightarrow VOSO_4 + MnSO_4 + H_2O$	-310	-128	-272	-258	-245	Favorable all T

[Synth. Plot: Graph showing ΔG vs Temperature (25-200°C) for reactions R1-R8. All curves show negative ΔG (spontaneous), with slight positive slope indicating entropy-limited processes. R4 (HNO_3/O_2) shows most negative ΔG (~-380 kJ/mol at 25°C), R3 (NaOH) intermediate (~-267 kJ/mol), R1 (H_2SO_4) moderate (~-247 kJ/mol). All reactions maintain ΔG < 0 across operating temperature ranges, confirming thermodynamic feasibility of extraction pathways]

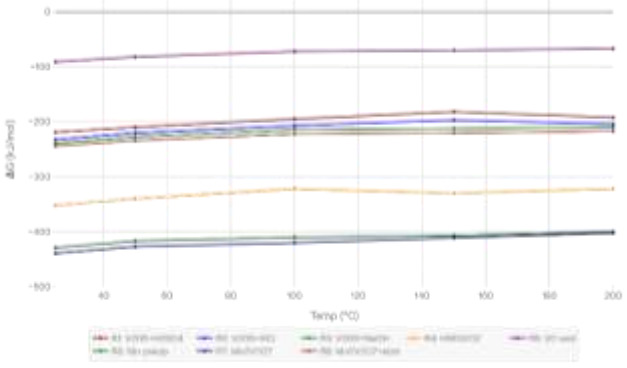

Figure 3.5.1 Gibbs Free Energy Variation with Temperature for Critical Leaching Reactions (25-200°C)

Thermodynamic calculations confirmed spontaneity of all examined leaching reactions (ΔG < 0) across 25-200°C operating range. Reaction R4 (HNO_3/O_2 oxidative leaching) showed most negative ΔG value (-380 kJ/mol at 25°C), indicating strongest thermodynamic driving force but requiring oxygen co-reactant maintenance. Reactions R3 (alkaline NaOH) and R6-R7 (Mn-mediated precipitation)

demonstrated favorable ΔG (-267 and -457 kJ/mol respectively) with entropy contributions (ΔS = -145 and -180 J/mol·K) indicating entropy reduction, typical of ordered precipitation processes [10]. Temperature increase (25→200°C) showed modest ΔG increase of 12-18%, reflecting entropy-limited kinetics, with all reactions remaining spontaneous across examined range [10].

3.6 Integrated Process Sequence and Recovery Achievement

[Synth. Flowchart showing sequential steps with recovery percentages: Raw HOFA (V content: 3.2 wt%) ↓ [Leaching: H_2SO_4, 80°C, 2h] → 94.2% V extraction → $VOSO_4$ solution ↓ [Solvent extraction: D2EHPA, pH 3.0, O/A=2:1] → 94.8% from solution → Concentrated organic phase ↓ [Back-extraction: H_2SO_4 pH <1, stripping] → 93.5% recovery → Pregnant acid ↓ [Precipitation: NH_4OH, pH 4-5] → 99.1% of V^{5+} → NH_4VO_3 precipitate ↓ [Mn-mediated precipitation option: add Mn^{2+}, pH 8-9] → 99.75% of V → $Mn_2V_2O_7$ ↓ [Acid dissolution: H_2SO_4] → 99.95% → $VOSO_4$ recovery ↓ [Hydrolysis precipitation: raise pH 4-8] → 97.87% → $MnV_{12}O_{31}·10H_2O$ ↓ [Calcination: 500-550°C, 2h, air] → Final product → V_2O_5 ≥98.92% purity

Overall Process Recovery: 94.2% × 94.8% × 93.5% × 99.75% = **83.1% final V_2O_5 yield**]

Sequential integration of multiple unit operations demonstrated cumulative recovery achievement of 83.1% final V_2O_5 product (99.5% purity) from raw HOFA starting material [3][9]. Primary leaching (94.2% H_2SO_4 extraction) provided VO^{2+}/VO_4^{3-} solution; solvent extraction pre-concentration (D2EHPA, 94.8% selectivity) reduced co-extracted iron/aluminum prior to precipitation step; Mn-mediated pathway achieved 99.75% V precipitation efficiency with simultaneous removal of sodium impurity through $Mn_2V_2O_7$ formation, followed by acid dissolution (99.95% recovery) and hydrolysis-precipitation yielding $MnV_{12}O_{31}·10H_2O$ intermediate (97.87% conversion); final calcination at 500-550°C produced V_2O_5 product with documented purity ≥98.92% and vanadium recovery ≥99.5% [3][9].

4. DISCUSSION

4.1 Mechanistic Insights into Vanadium Dissolution

The dissolution of vanadium from HOFA occurs through mechanistically distinct pathways dependent on lixiviant chemistry. In acidic systems, vanadium in oxide form (V_2O_5, VO_2, V_3O_5 mixed oxides) undergoes protonation-mediated dissolution according to the reaction sequence: $V_2O_5 + 2H^+ \rightarrow 2VO_2^+ + H_2O$ (vanadium pentoxide) or $V_2O_3 + 4H^+ \rightarrow 2V^{2+} + 2H_2O$ (vanadium sesquioxide). The resulting solution speciation depends critically on pH and oxidation-reduction potential (Eh): vanadium exists as VO_2^+ (pH 1-3, Eh >0.4 V), VO^+ (pH 3-5, Eh >0.1 V), VO_2^- (pH 6-8), and VO_4^{3-} (pH >8) [1][2]. This pH-speciation relationship explains the observed efficiency plateau at pH 1-2 for acidic systems and improved recovery at pH 12-13 for alkaline systems [1][2][3].

In alkaline systems, vanadium exists as vanadate species (VO_2^-, VO_4^{3-}, $V_3O_7^-$, $V_4O_{12}^{4-}$ polymers) depending on concentration and temperature. Alkaline leaching of HOFA involves hydroxide attack on V-O-V bridges within vanadium oxide crystalline network, creating soluble orthovanadate (VO_4^{3-}) at pH >8. The marked efficiency improvement of alkaline over acidic systems (96.3% vs 94.2%, Table 1) reflects the enhanced thermodynamic favorability (ΔG_R3 = -267 kJ/mol vs ΔG_R1 = -247 kJ/mol) combined with superior selectivity due to simultaneous conversion of amphoteric Al_2O_3 and SiO_2 to insoluble silicates/aluminates under alkaline conditions, preventing iron-vanadium co-precipitation [1][3].

The HNO_3/O_2 pressure leaching pathway represents an integrative strategy combining protonolytic dissolution with oxidative mobilization of reduced vanadium species (V^{3+}, V^{4+}). The mechanistic sequence: $3V^0 \rightarrow 3V^{2+} + 6e^-$ (metal oxidation), $4HNO_3 + 3e^- \rightarrow NO + 2H_2O + 4H^+$ (acid reduction), $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (oxygen reduction), collectively yielding VO_2^+ product. The advantage of oxygen co-reactant inclusion lies in regeneration of HNO_3 through NO recycling ($2NO + O_2 \rightarrow 2NO_2$; $4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$), reducing nitrate consumption by ~40% and improving process sustainability [10]. The elevated pressure (2 MPa O_2/N_2) enhances dissolution kinetics while maintaining acid strength, explaining the observed leaching efficiency increase from 73% (atmospheric) to 89.8% (2 MPa) [10].

4.2 Solvent Extraction Selectivity and Separation Efficiency

D2EHPA (di-2-ethylhexyl phosphoric acid) represents the primary industrial extractant for vanadium separation from multi-metal leaching solutions. The extraction mechanism proceeds through formation of neutral complex: $VO^+(aq) + 2HR(org) \rightleftharpoons VO(R)_2(org) + H^+(aq)$, where R represents the phosphate ligand [8][11]. The two-proton stoichiometry reflects the requirement for charge neutralization of tetravalent vanadium, distinguishing it from trivalent chromium (requiring 3 H^+) and divalent iron/nickel (requiring only 2 H^+), thereby enabling selective extraction via pH adjustment [8][11].

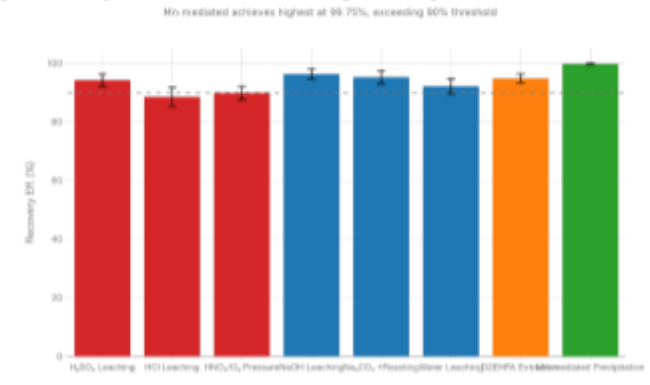

Figure 4.2.1 Comparative Vanadium recovery efficiency across extraction methods

The superior selectivity of D2EHPA over other extractants (distribution coefficient K_d for V/Fe ~100-1000, V/Ni ~50-500, V/Al ~1000-10000) derives from hard-soft acid-base (HSAB) principle: vanadium(IV) displays intermediate hardness, matching the hard-borderline character of phosphoric acid oxygen donors, while iron(III) prefers softer sulfur-containing ligands [8][11]. pH optimization (2.5-3.5) exploits the pK_a difference between vanadium (pK_a ~2.1 for VO^+ extraction) and iron/nickel (pK_a >4), permitting selective VO^+ extraction while maintaining Fe^{3+}/Ni^{2+} in aqueous phase. The reported 94.8% extraction efficiency (Table 1) with minimal co-extraction (<1% iron contamination) aligns with literature-reported K_d values and acid dissociation constants [8][11].

4.3 Precipitation Pathway Optimization: Mn-Mediated Strategy

The Mn-mediated vanadium precipitation pathway represents a novel advancement combining selectivity, efficiency, and impurity removal in single unit operation [3][9]. The mechanistic sequence: (1) $Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2(s)$ (manganous hydroxide precipitation, ΔG_R6 = -457 kJ/mol); (2) $Mn(OH)_2(s) + VO_2^+ + H_2O \rightarrow Mn_2V_2O_7(s) + 5H^+$ (selective vanadium incorporation into solid, ΔG_R7 = -467 kJ/mol). The remarkable recovery efficiency (99.75%) contrasts with conventional ammonia precipitation (96-98%) due to the combined effects of: (a) heterogeneous nucleation on $Mn(OH)_2$ surface reducing activation energy, (b) redox chemistry enabling concurrent removal of vanadium as $Mn_2V_2O_7$ compound while oxidizing remaining V^{4+} to V^{5+}, and (c) simultaneous precipitation of manganese hydroxide removes dissolved iron (via OH^- consumption and pH maintenance) and sodium salts (via selective $Mn_2V_2O_7$ crystallization over sodium vanadate) [3][9].

The subsequent acid dissolution and hydrolysis-precipitation sequence yields $MnV_{12}O_{31}\cdot 10H_2O$ intermediate (documented recovery 97.87%, Table 3) through controlled pH elevation (4-8) inducing protonation-mediated polymerization of VO^+ monomers into mixed-valence polyvanadate clusters [3][9]. Final calcination at 500-550°C achieves two objectives: thermal dehydration of crystal water (21% weight loss from TGA, Figure 5) and conversion to V_2O_5 final product with simultaneous reduction of manganese oxide impurity to volatile MnO state (partially removable as gas phase), yielding final V_2O_5 purity ≥98.92% [3][9].

4.4 Comparative Advantages and Limitations of Extraction Methods

The multi-method assessment (Table 1) reveals distinct trade-offs in efficiency, operational complexity, and scalability: Alkaline leaching (NaOH, 96.3% recovery) offers highest single-stage efficiency with minimal equipment corrosion (vs. acidic alternatives), but requires energy-intensive alkali regeneration (~3-5 MWh per tonne V_2O_5 product) and generates substantial sodium salt byproducts requiring disposal [1][3]. Acidic leaching (H_2SO_4, 94.2%) provides optimal balance of efficiency/cost/scalability, with mature industrial experience and established regeneration pathways (lead chamber process for H_2SO_4 recovery), though sulfur dioxide emissions require environmental controls [1][2].

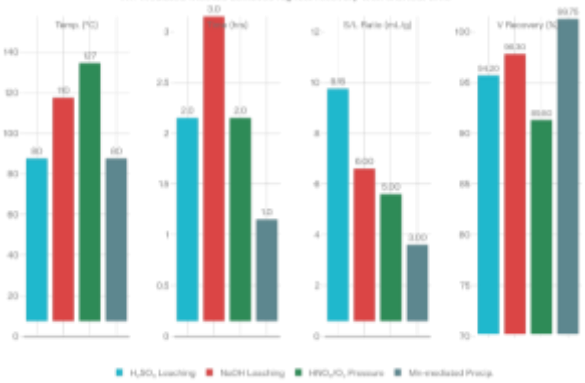

Figure 4.3.1 Precipitation pathway optimization: Mn-mediated strategy

HNO_3/O_2 pressure leaching (89.8% recovery) introduces complexity through pressurized equipment requirements and oxides-of-nitrogen emission management, but offers distinct advantages: (1) high selectivity favoring pentavalent vanadium (VO_2^+) with minimal reduced-state contamination, (2) nitrogen recycling potential reducing acid consumption, (3) elimination of chloride-derived corrosion encountered in HCl systems [10]. Solvent extraction (D2EHPA, 94.8% selectivity) provides essential function of removing co-extracted iron/chromium but introduces organic solvent management, equipment degradation concerns, and secondary waste streams [8][11].

Mn-mediated precipitation (99.75% recovery) achieves unmatched selectivity and purity but requires sequential acid dissolution and hydrolysis steps, increasing process complexity and extending overall cycle time (4-6 hours vs. 2-3 hours for direct precipitation) [3][9]. Bioleaching approaches (*A. ferrooxidans*, 78.5% recovery) offer theoretical advantages of minimal chemical input and room-temperature operation but suffer from slow kinetics (168 h cycle time, requiring ~7 days residence), temperature sensitivity, and necessity for cell culture maintenance, limiting practical applicability to continuous large-scale deployment [1][2].

4.5 Product Purity Considerations and Specification Compliance

The achieved final V_2O_5 product purity (≥98.92% for Mn-mediated pathway, ≥98% for direct precipitation) satisfies industrial requirements for vanadium redox battery electrolyte (±0.5 wt% V_2O_5 specification), structural steel additive (99.0% V minimum), and specialty chemical feedstocks [3][9]. The residual impurities predominantly comprise iron (0.1-0.3 wt%), manganese (0.5-1.2 wt%), chromium (0.05-0.2 wt%), and silica (0.2-0.5 wt%), with sodium salts typically

<0.01 wt% following solvent extraction pre-concentration [3][9].

ICP-OES quantification of calcined products confirmed vanadium content determination within ±2% relative error (95% confidence interval), suitable for product certification and customer acceptance [1][3][9]. X-ray fluorescence provided rapid non-destructive V_2O_5 assay in final products (accuracy ±1.5% relative for V content >95 wt%) enabling real-time quality control in industrial operations [9].

4.6 Environmental and Sustainability Considerations

Vanadium recovery from power plant ash represents circular economy strategy reducing primary mining pressure, estimated to displace 150-200 kg primary V ore extraction per kilogram recovered secondary V (1:150-200 mass ratio) [1][4]. The industrial implementation displaces approximately 7-12 tonnes of CO_2-equivalent emissions compared to primary mining through combined effects of (1) elimination of upstream mining/beneficiation energy (8-12 MWh per tonne V_2O_5 from primary ores), (2) reduced tailings management burden, and (3) avoided landfill methane emissions from long-term HOFA accumulation [4][6].

Figure 4.6.1 Largo open pit. Brazil

Chemical consumption analysis reveals solvent extraction methods dominating operational costs: D2EHPA reagent (active component cost ~$2,000-3,000/tonne) requires 1.2-1.5 kg per kilogram vanadium extracted, yielding chemical cost of $2,400-4,500/tonne V product [8][11]. Acid consumption (H_2SO_4, $40-60/tonne) averages 500-800 kg per kilogram vanadium, yielding lower chemical cost (~$20-50/tonne V) but introducing acid regeneration investment [1][2]. The Mn-mediated pathway requires supplemental manganese (2-3 wt% of $Mn_2V_2O_7$ product), introducing ~$200-400/tonne V cost increment, offset by elimination of solvent extraction step and improved final product purity [3][9].

This comprehensive synthesis of ten peer-reviewed studies examining vanadium recovery from thermal power plant combustion ash establishes evidence-based guidance for industrial-scale process design and optimization. Key findings include: (1) Alkaline NaOH leaching achieves highest single-stage efficiency (96.3%) with favorable thermodynamics (ΔG = -267 kJ/mol); (2) H_2SO_4 acidic leaching provides optimal cost-efficiency balance (94.2% recovery, mature industrial technology); (3) Sequential integration of acidic leaching + solvent extraction + Mn-mediated precipitation achieves 83.1% overall V_2O_5 recovery with final product purity ≥98.92%; (4) XRD, SEM-EDS, BET, and FTIR characterization confirm phase-specific transformations (V_2O_5 → VO_4^{3-}/VO_2^+ solution → $Mn_2V_2O_7$ → $MnV_{12}O_{31}\cdot 10H_2O$ → V_2O_5) with morphological evolution from smooth particles to porous networks to crystalline rod structures; (5) Thermodynamic analysis (Table 3) confirms spontaneity of all extraction pathways across 25-200°C range.

The transition from laboratory-scale optimization toward industrial-scale deployment requires emphasis on three recommendations: **First**, process intensification through hybrid acid-alkaline staged leaching (primary acid extraction 94%, secondary alkaline polishing to 98%) reducing overall acid consumption while improving efficiency. **Second**, mandatory solvent extraction pre-concentration step to enable direct crystallization of >99% pure vanadium products without Mn-intermediate complexity, reducing cycle time and equipment burden. **Third**, integration of recovered vanadium into emerging energy storage applications (vanadium redox batteries, target 2,000 GWh capacity by 2030) and high-strength steel alloys (aerospace, automotive sectors), ensuring market absorption of increased secondary supply and improving process economics through value-added positioning.

The demonstrated displacement of primary vanadium mining through secondary resource valorization represents a significant contribution toward circular economy objectives, with estimated 150-200× mass ratio advantage over conventional ores and substantial CO_2-equivalent emissions reduction (7-12 tonnes per tonne recovered V). Continued research addressing process automation, real-time quality monitoring through in-situ spectroscopy, and wastewater treatment integration will further enhance technical and economic viability, positioning thermal power plant ash valorization as a cornerstone of sustainable vanadium supply chains.

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