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Recovery of Vanadium from LD slag, A state of the art report, Part 1 - Facts and metallurgy of Vanadium

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Keywords:

LD-slag, extraction, recovery

SUMMARY

This report is a summary of the vanadium seminar held in Stjärnholm, 11-12 April, 2005. The topics included in the report are as follows:

- General on vanadium metallurgy, from the resources to the final vanadium products
- Current available processes for recovery of vanadium from V-bearing hot metals from ironmaking processes
- Most dominating V-extraction process from V-bearing ores
- R&D works on the field of vanadium extraction being performed so far
- R&D experiences on extraction of vanadium in Sweden

The production of vanadium is mainly based on secondary materials, such as steel-making slag. This report is therefore of great importance for the participating companies, like SSAB and LKAB, in this MISTRA project regarding vanadium extraction. Particular attention has been paid to analyse the possibility to recover vanadium from the steel plant using 100% LKAB pellets containing about 0.2 % V_2O_5 . The vanadium ends normally up in a LD-slag containing approximately 5 % V_2O_5 .

The report is mainly based on:

- Textbook "Extractive metallurgy of vanadium" by C K Gupta and N Krishnamurthy, 1992, 640 pages
- MEFOS's own experience in the recent years
- SSAB's experiences in the past since the 70's
- Literature review in this MISTRA-project
- Theoretic calculations performed within the MISTRA-project

The emphasised subjects have been:

- Recovery of vanadium from secondary materials, specially from LD-slag
- Production of FeV based on vanadium in LD-slag

This report consists of two major parts:

Part 1 Facts and metallurgy of vanadium

Part 2 Recovery of vanadium from iron and steelmaking, international and Swedish experience

Part 2 is, however, only open for the participating partners in the MISTRA V-group.

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1 VANADIUM, ITS SOURCES, PRODUCTS AND APPLICATIONS

1.1 Vanadium element and its sources

Vanadium is an element discovered in 1839 by Swedish physical chemist Nils Gabriel Sefström in iron produced from Taberg ore, Småland, Sweden. It is a typical transition metal with multivalent: +2 to +5. In fact, vanadium is more deposited on the earth than base metals like Ni, Zn, Cu and Pb.

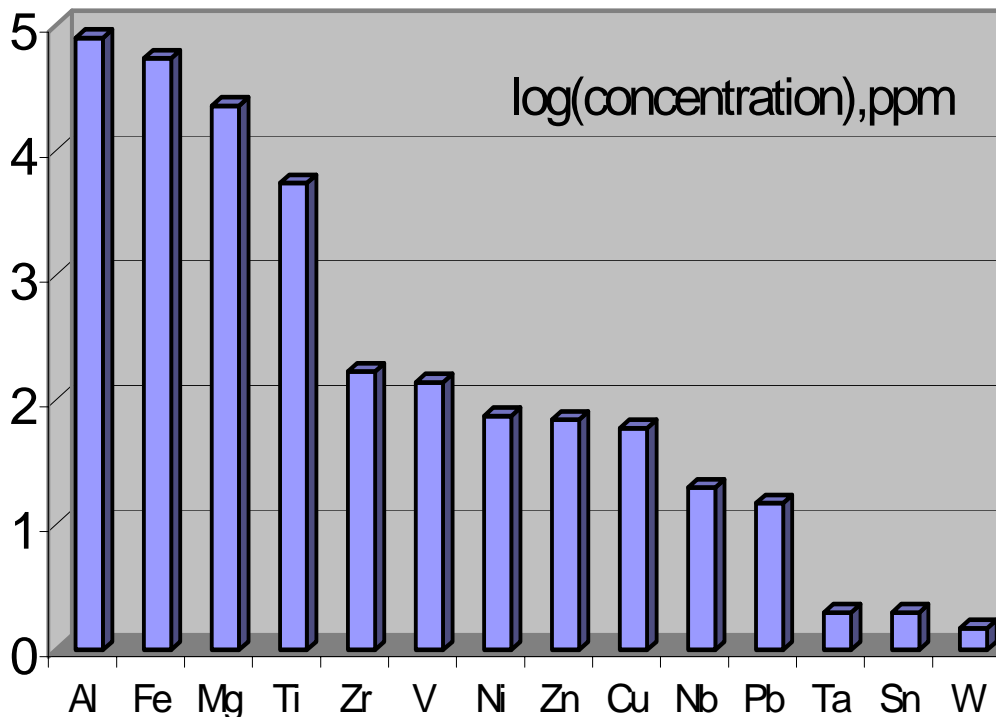
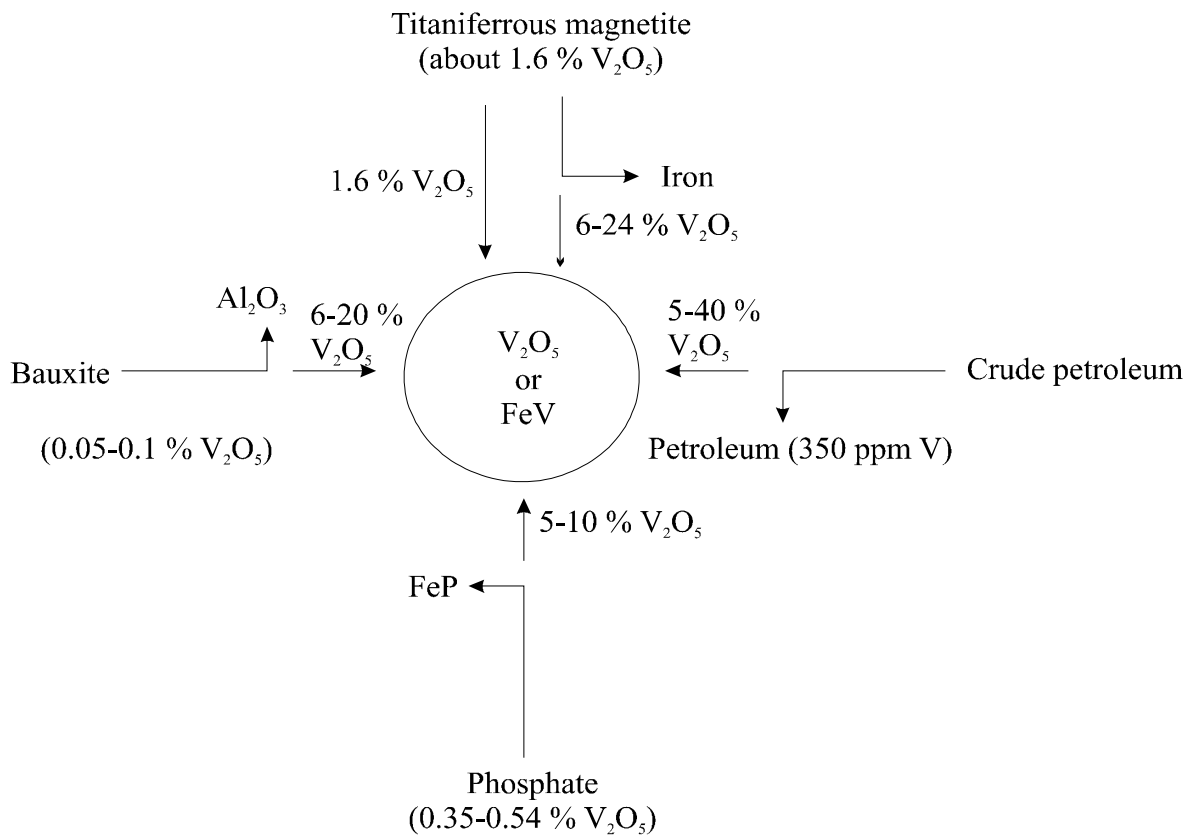


Figure 1 - The abundance of vanadium and other important metals on the earth

The estimated total world vanadium sources are accounted for 56 300 000 ton. The world vanadium production up to 1989 was about 917 000 ton, which is about 1.64 % of the deposited vanadium known so far.

The distribution of the major V-sources is shown in Figure 2. As shown, it exists mainly in the form of titaniferrous magnetite. Most of the current V-production is based on this mineral either by direct soda treatment or via iron- and steelmaking processes.

The content of vanadium in the SSAB LD-slag alone is about 4 000 ton per year. This can be compared with the world V-production of about 30 000 tons 1997.



Major V-sources	Distribution, %
Titaniferrous Magnetite	46
Crude Petroleum	9
Phosphate	39

Figure 2 - Major V-sources, by-products and co-products for V-extraction

1.2 Vanadium products and their applications

The major V-products and their main applications are shown in Figure 3. It can be summarised as follows:

- FeV-alloy, mainly for the steel industry
- V₂O₅, mainly as catalyst and for FeV-production
- V₂O₃ mainly for FeV-production
- VN for direct alloying of V and N
- V-metal for use in Al-V-Ti alloy

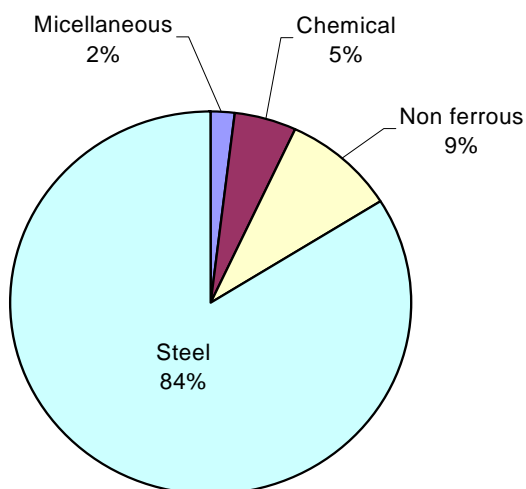


Figure 3 - Distribution of various applications of vanadium

The average V-consumption per ton steel worldwide is about 0.04 kg per ton steel mainly for the use in HSLA products. The average V-content in Swedish steel products is much higher due to much more sophisticated special steels produced in this country, 0.1-0.15 kg V per ton steel.

The total FeV-production in the world in 1997 is about 30 000 tons of vanadium. As indicated in Figure 3, the vanadium industry is very much dependent on the steel industry. It could be said that no steel industry, no vanadium industry.

1.3 Effect of Vanadium on steel

The effect of vanadium in steels could be summarised in the followings:

- VC-formation: improved hardness and wear resistance to tool steels at elevated temperatures.
- Precipitation of VC and VN: extra strength to structural and forging steels/limit the grain growth (strength and toughness).
- Delaying the formation of bainite and pearlite: it increases martensite hardenability.
- A ferrite stabilizer suppressing bainite formation.

The application of vanadium in steels is shown in the table below.

Steel sorts	V-content, %	Functions of vanadium
HSLA steels pearlite grade (Nb-Ti-V)	0.03-0.4	V: dispersion strengthening, grain refiner Ti/Nb: carbide precipitation
Tools steels (W-Mo-V)	1-5	- primary V_4C_3 -formed at 1 200-1 300 °C abrasion resistance increased - secondary (fine) V_4C_3 precipitated at 530-570 °C, secondary hardening and high tempering resistance
Forging steels (medium carbon)	0.03-0.2	precipitation of V-carbides in the interlamellar ferrite of eutectoid pearlite
Low-alloy ferrite steels (Cr-Mo-V)	0.2-0.7	- retarding tempering temperature - V_4C_3 more stable than Cr- and Mo- carbides: secondary hardening reactions - V_4C_3 more effective in retarding the softening process at higher temperatures

2 VANADIUM DEVELOPMENT DURING THE 20TH CENTURY

It is clearly shown in Figure 4 that there was a rapid increase of the V-production from the 60's to the 80's, and after that it has been kept at a rather stable level. The world vanadium production in 2004 was about 41 000 tons as compared to about 30 000 tons in 1998. The annual increase of the vanadium consumption is expected to be 5 % in the coming years.

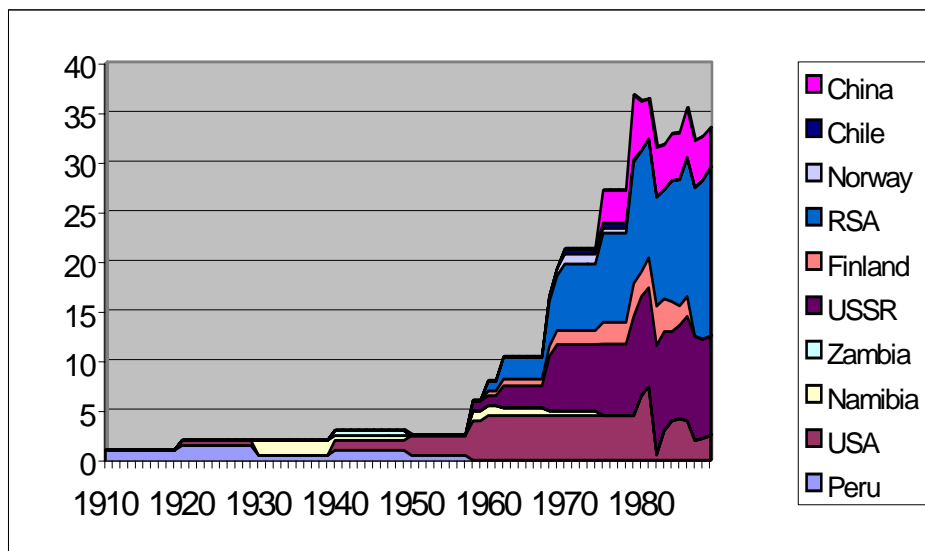


Figure 4 - Historic world vanadium production from 1910 to 1989, in 1 000 tons

Countries	V-bearing ore type
RSA/Russia/China/Norway/Finland	Titaniferous magnetites
USA	-V in clay (Wilson Springs), -U-V Ore(Colorado Plateau), -V in Phosphates(Western States)
Peru	Asphaltite
Chile	Magnetite
Namibia and Zambia	Pb/Cu/Zn vanadates

3 VANADIUM MARKET AND PRICES

3.1 The vanadium market

The total production of FeV in the world 1998 is about 30 000 tons. The production of FeV is mainly concentrated in the EU, USA, South Africa, China and Japan. It is estimated that the annual increase of the vanadium consumption will be 5 % in the coming years due to further development of the HSLA steels. The V-demands and supply and their dependence on world steel production is clearly shown in Figure 5. Please keep in mind that the steel production for 2005 is more than 1 billion tons.

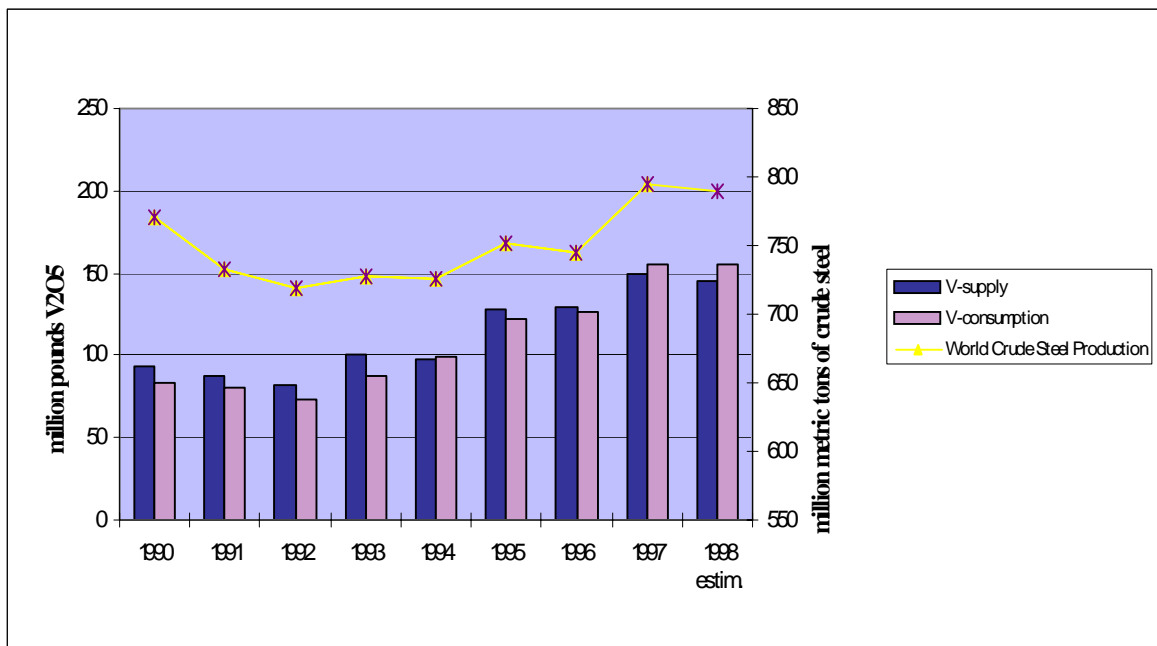


Figure 5 - V-demand and supply, and the world steel production

The production of FeV has historically been dominated by a few countries as shown in Figure 6.

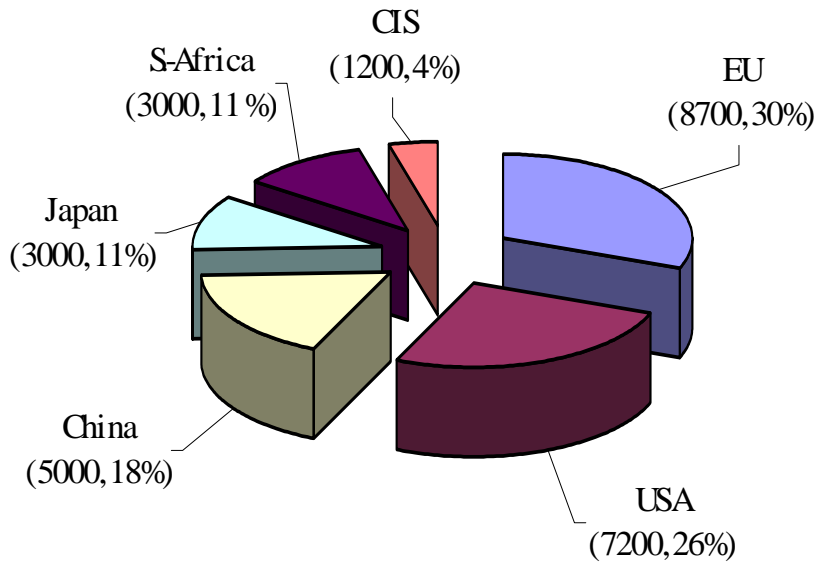


Figure 6 - The world FeV production in 1998, 1 000 tons

For 2004, the world vanadium production is estimated to 47 000 tons. This is an increase with 5 % compared to 2003. The major V-producing countries are summarised in the table below.

	2002, tons V	2003, tons V	2004, tons V
South Africa	20 500	20 100	17200
China	13 200	13 200	14 000
Russia	8 000	5 800	8 000
Australia	3 060	160	0
Kazakhstan	1 000	1 000	1 000

For these countries, the vanadium products are mainly prepared directly from roasting of titaniferrous ore concentrate and/or via a vanadium-rich slag (V-slag) from pre-treatment of V-bearing iron melt (0.3-1.2 % V).

A considerable amount of FeV produced in Japan, USA and EU is based on petroleum residue and spent catalyst. They also import a large amount of V-slags from South Africa, China and Russia for V₂O₅-and FeV-production.

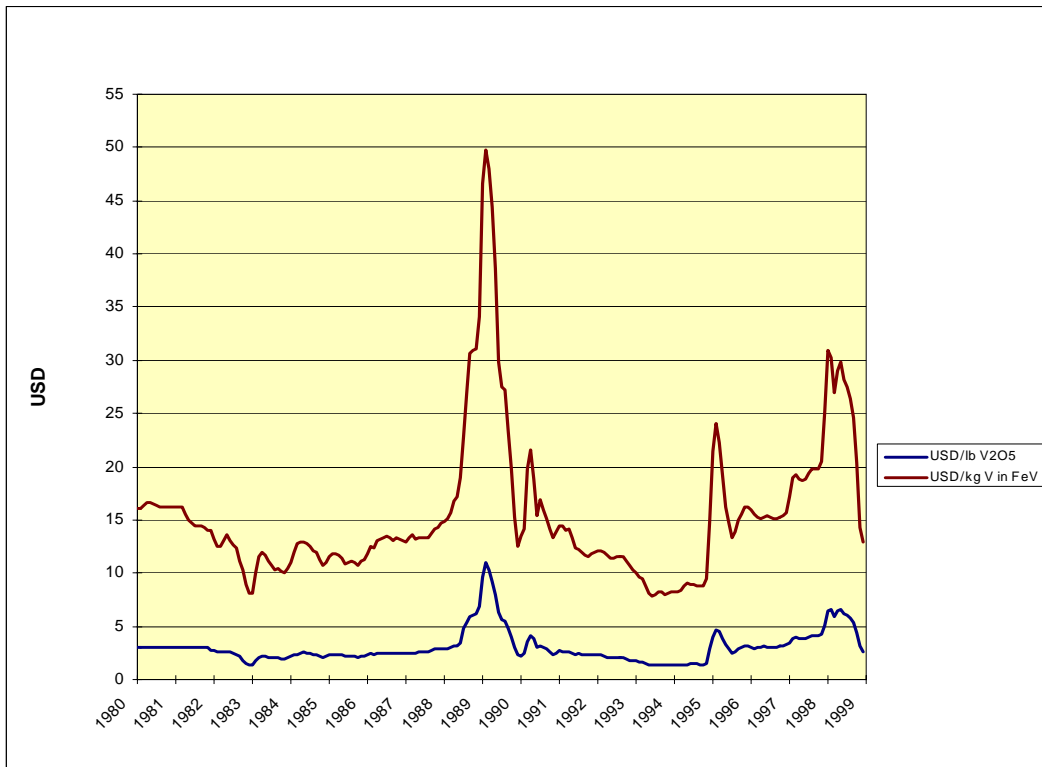
The demand on vanadium for 2004 is about 51 000 tons, which is an increase of 15 % compared with 2003.

The current capacity utilization for vanadium production is about 80 %.

3.2 The vanadium prices

The price of vanadium products is volatile as indicated by Figure 7. The price of V-slag is hard to set since the quality is rather different from one deliverer to another. Usually the price of V-slag is based on the contract between the individual V-slag deliverer and the V_2O_5/FeV -plants.

Averagely, the V-price has been about 15 US\$/kg V. In the last year, the price has been up to 130 US\$/kg V. At this moment, November 2005, it is about 45 US\$/kg V. The exceptional price increase in the last year is partly due to the strong demand from the steel industry and partly due to the permanent shut down of the Australian mine of Xstrata (up to 10 % of world vanadium capacity) .



FeV-price, 1980-2000, US\$/kg V

FeV-Prices 1997-2005

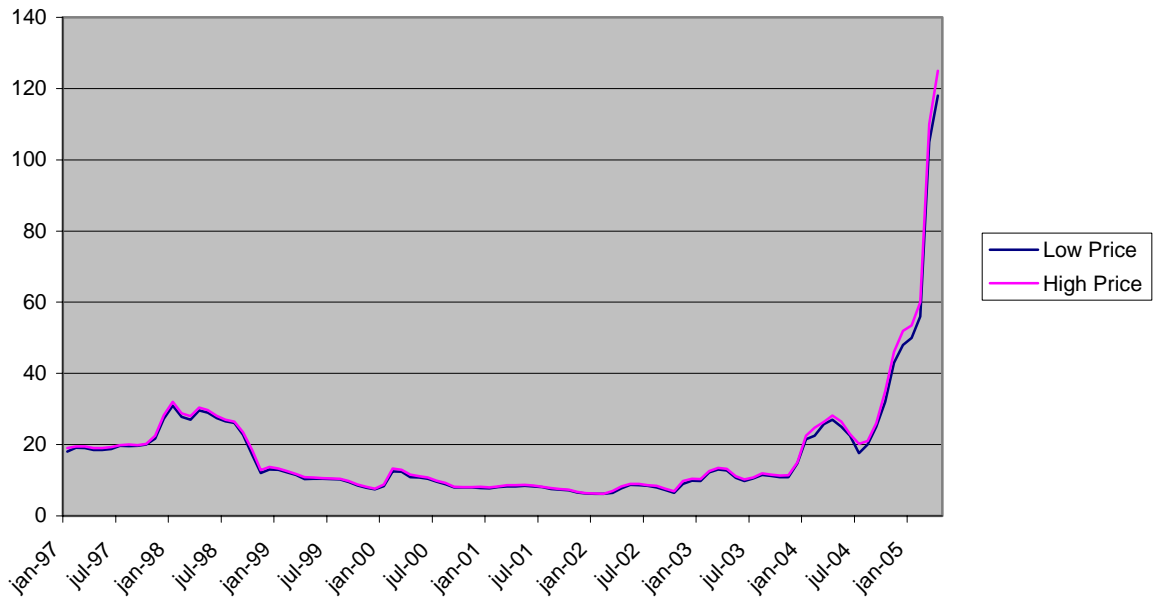


Figure 7 - The vanadium price, US\$/kg V, during 1980-2000 and 1997-2005

4 VANADIUM PRODUCTION ROUTES

The available vanadium production routes is summarised in Figure 8.

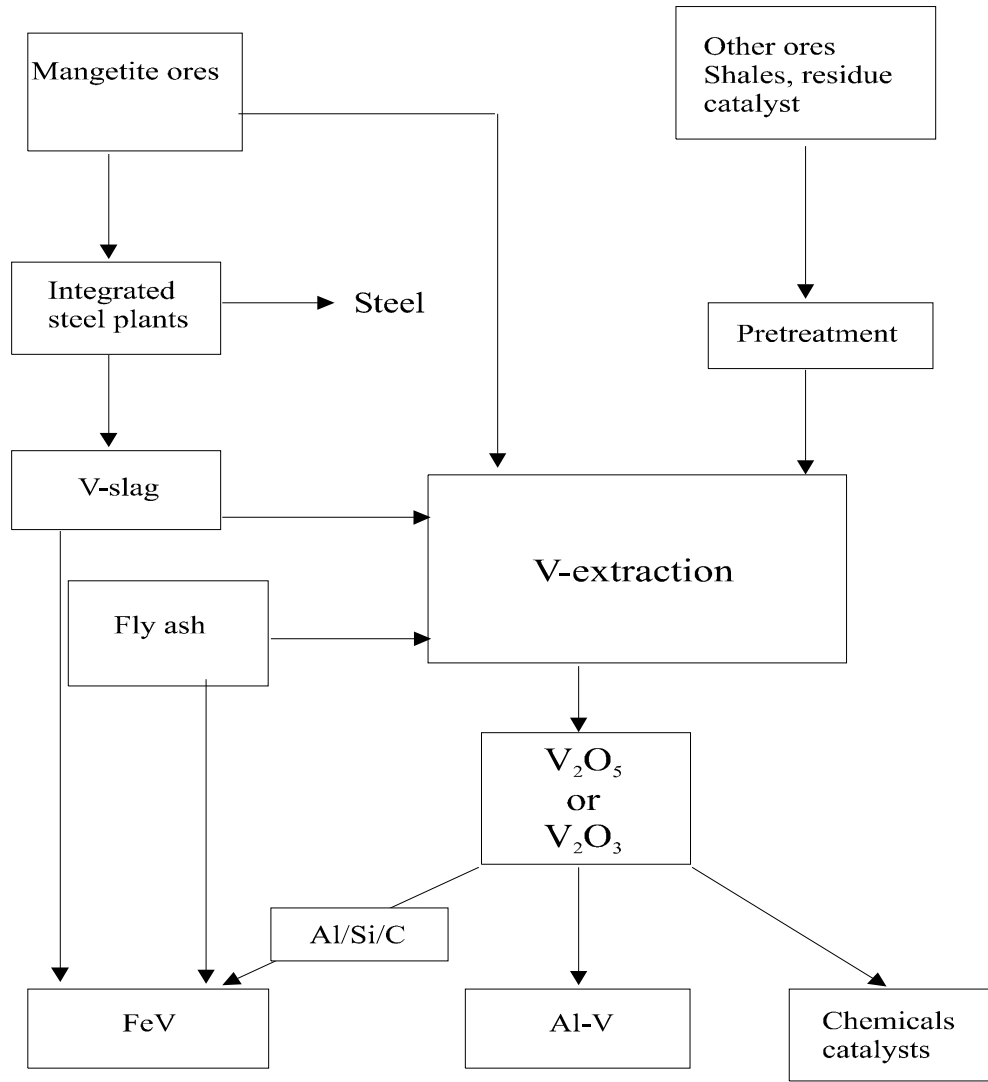


Figure 8 - Vanadium production routes

As shown the main raw materials are:

- titaniferrous magnetite
- spent catalyst
- petroleum residue
- fly ashes

The main final products are:

- FeV
- V₂O₅
- Al-V-alloy

The different approaches from raw materials to V-products are described more in details in the following chapters.

4.1 Vanadium extraction

Extraction of vanadium from the major V-bearing raw materials are shown Figure 9.

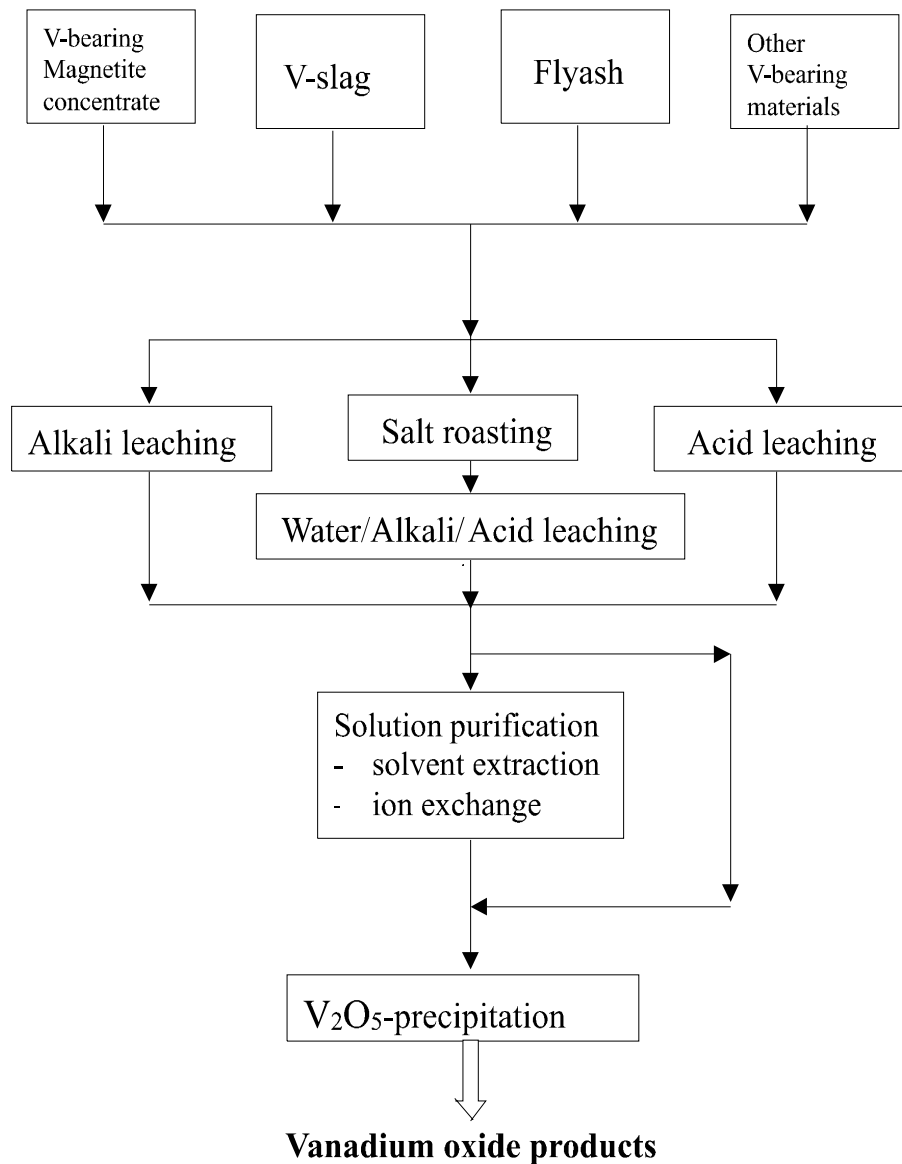


Figure 9 – Flow sheet of vanadium extraction

There are three steps in V-extraction:

- salt roasting
- leaching and purification
- precipitation and V₂O₅-fusion

4.2 Salt roasting

The purpose of salt roasting is to render vanadium in water soluble forms. The major chemical reactions concerned are described the tables below. The roasting process is normally carried out in a rotary kiln. The retention time is up to 10 hours.

4.2.1 Chemical reactions of roasting

Reagents in the table below could be used for the roasting purpose.

Reagents	Chemical reactions	Temperature
NaCl, vapor	$2\text{NaCl} + \text{H}_2\text{O}(\text{g}) + \text{V}_2\text{O}_5 = 2\text{NaVO}_3 + 2\text{HCl}(\text{g})$	800-900 °C
NaCl, without vapor	$2\text{NaCl} + \text{V}_2\text{O}_5 = 2\text{NaVO}_3 + \text{Cl}_2(\text{g})$	
Soda	$\text{Na}_2\text{CO}_3 + \text{V}_2\text{O}_5 = 2\text{NaVO}_3 + \text{CO}_2(\text{g})$	900-1 200 °C
Na ₂ SO ₄	$\text{Na}_2\text{SO}_4 + \text{V}_2\text{O}_5 = 2\text{NaVO}_3 + \text{SO}_3(\text{g})$	1 200-1 230 °C

4.2.2 Advantages and disadvantages of the roasting processes

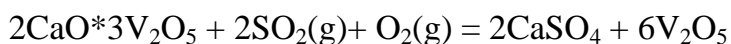
Salt roasting	cheapest, selective attack on V
Soda roasting	non-selective
Sulfate roasting	selective, higher temperature

Soda roasting is probably the most used method today due to the high environmental requirement.

4.2.3 Common problems

Common problems for these processes are side reactions.

Free lime: formation of insoluble vanadates, therefore should be stabilised by sulfation



Free silica: formation of a low melting $\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot 4\text{SiO}_2$

4.2.4 Process requirements

Process requirements are:

- free silica, <3%,
- free lime, <1%
- free oxygen, >4%, for roasting to guarantee the V-oxidation

4.3 Leaching

The purpose of leaching step is to dissolve vanadium in an aqueous solution.

4.3.1 Leaching of salt roasted materials

The salt-roasted materials are leached in water, acid or alkali solutions as described below.

Water	Most common used industrial methods, solution: 30-50g V ₂ O ₅ /l, pH=7-8
Acid/H ₂ SO ₄	Ensure the water insoluble V-compounds such as Ca-, Mg- and Fe-vanadates will be solved
Alkali/soda	U-V ore where both U and V will be extracted into the aqueous solution.70-80 % V and 75-85 % U recovery Na ₂ CO ₃ will release V ₂ O ₅ from CaO-vanadate: $2CaO \cdot 3V_2O_5 + 2Na_2CO_3(aq) = 2CaCO_3 + 3NaVO_3(aq)$

4.3.2 Direct leaching of V-ores

There are also methods for direct leaching of V-ores. These methods, which hardly exist today due to environmental reasons, will generate a huge amount of leaching residues.

Acid/H ₂ SO ₄	V-sources: U-V ore, catalyst, fly ash, boiler residue. Effective but not selective to vanadium i.e. impure V-bearing solution will be obtained
Alkali	V-sources: fly ash, boiler residue. Not as effective as acid but selective to vanadium Higher temperature and pressure

4.4 Vanadium precipitation and V₂O₅-fusion

Precipitation is determined by pH, concentration and temperature and can be done in many ways. Red cake precipitation is one of the many alternatives.

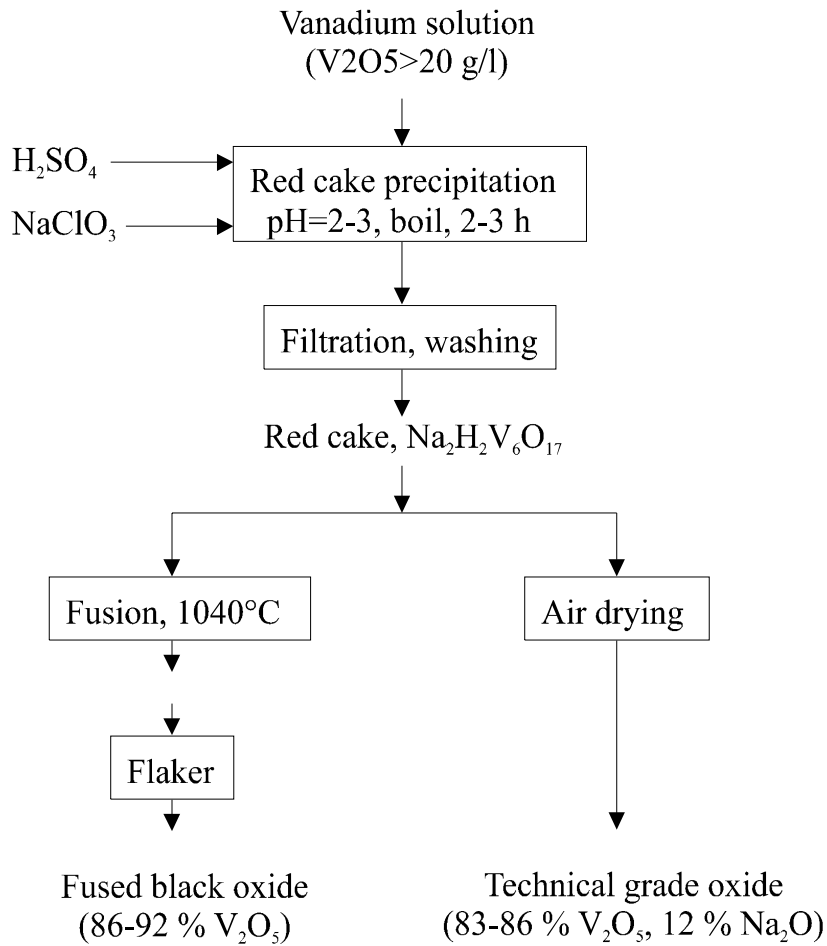


Figure 10 - Red cake precipitation

5 COMMERCIAL PROCESSES FOR V-EXTRACTION

Some typical commercial processes are shortly described in the followings.

5.1 Direct V-extraction from titaniferrous magnetite, the Vantra process

The Vantra process is a typical direct V-extraction process based on direct use of titaniferrous magnetite. The process flow sheet is shown in Figure 11.

The Vantra process uses a magnetite concentration with 1.65 % V_2O_5 . This means that the roasting step has to treat also the 98 % “no V_2O_5 ”-fraction and the process generates a large amount of tailings. There are also other variations of the process, but the principle remains the same.

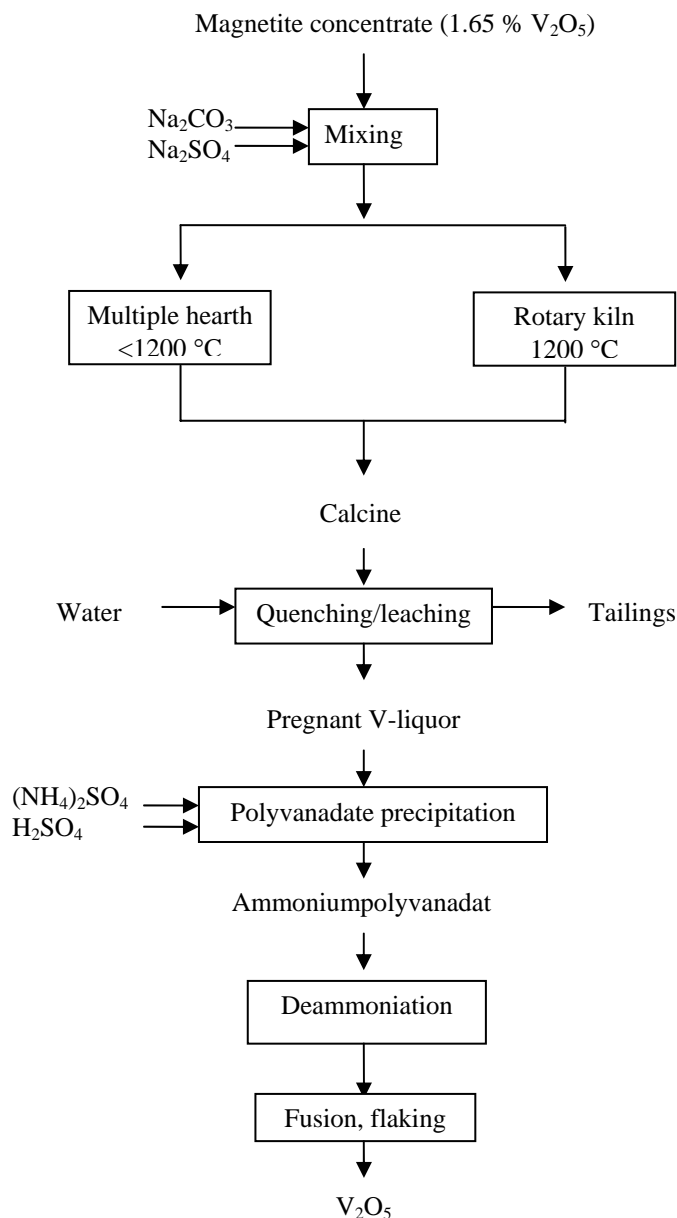


Figure 11 – Vanadium extraction by the VANTRA process

5.2 V-recovery from by pre-treatment of hot metal, the Highveld process

Highveld Steel and Vanadium Corporation in RSA are the biggest V-slag producer in the world. The Highveld process for vanadium recovery from hot metal is described in details in Figure 12. The produced V-slag with about 24 % V_2O_5 is further treated for V_2O_5 and FeV production. A large fraction of Highveld V-slag is exported to the EU, Japan and the USA for further processing. The Highveld process has been applied since the early 80's for V-oxidation from hot metal prior to the LD-process. The V-oxidation step is based on the well-known shaking ladle concept developed at MEFOS in the 70's. There are similar V-recovery processes in China, Russia and New Zealand. These will be described in part II of this report.

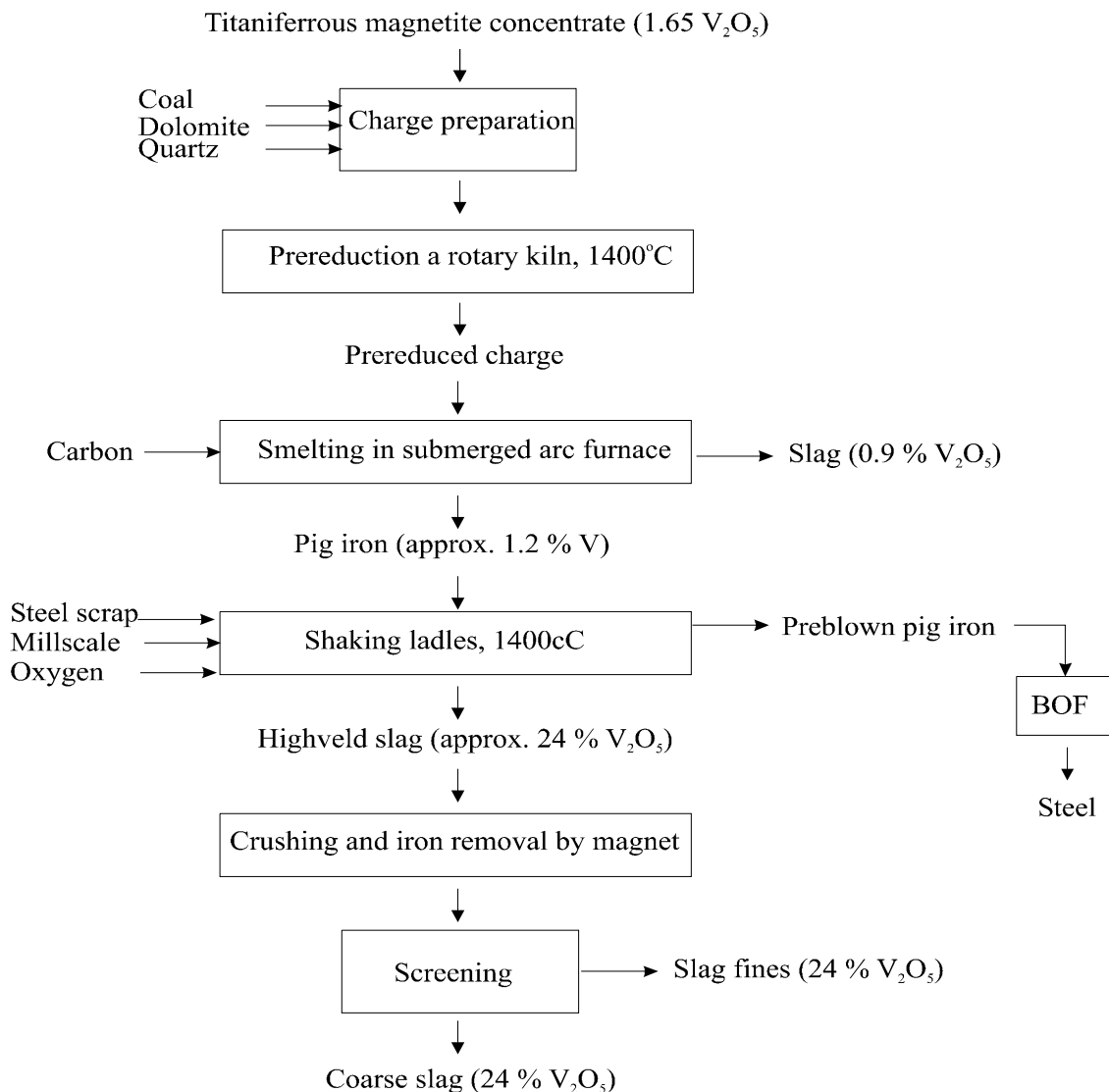


Figure 12 - Pyrometallurgical V-recovery process at Highveld Steel

5.3 Direct V-recovery from converter slag, Talcahuano, Chile

The process flowsheet of the direct V-recovery from converter slag is shown in Figure 13. This method is of interest for the MISTRA project since the used converter slag has almost the same chemical composition as the SSAB LD-slag, although this process is no longer in use. The chemical composition of the slag used is shown in the table below.

V ₂ O ₅	CaO	SiO ₂	P ₂ O ₅	Fe	MnO	MgO	Al ₂ O ₃
5.7	47	11	3.2	15	4	2.5	1.2

It has been claimed that V₂O₅ in the slag exists in various calcium vanadates. The purpose of the first process step, pyrite roasting aims at liberating V₂O₅ from the calcium vanadates. The high lime content was thus a major disadvantage since it will consume more pyrite in the roasting step and more sulphuric acid in the subsequent leaching step. Calcium will end in the stable compound, CaSO₄.

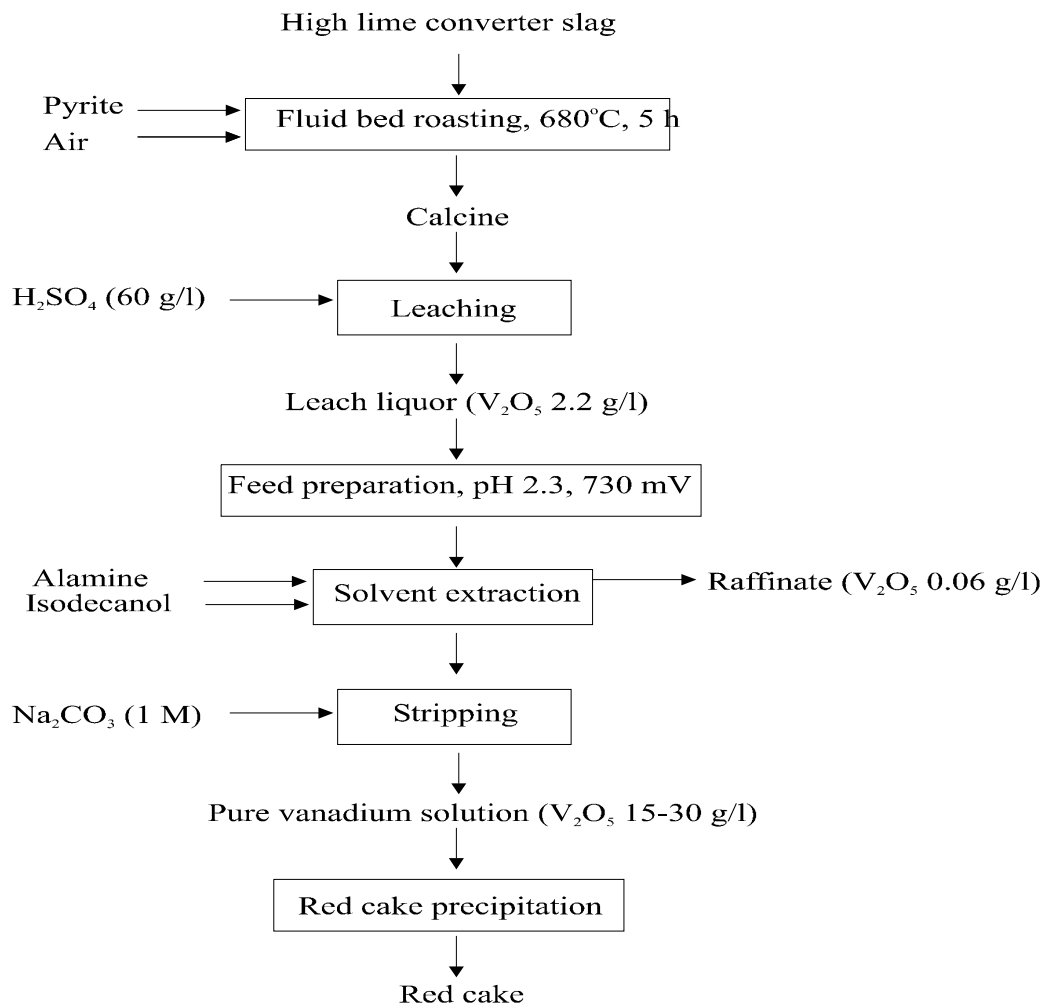


Figure 13 - Vanadium extraction from a high lime converter slag

The biggest problem for this process is that it will generate more solid waste than the treated LD-slag due to the formation of CaSO₄.

5.4 Processing of fly and boiler ash

A quite frequently used V-source is residue from use of the Venezuelan oil. The vanadium content in the crude oil, residual oil, petroleum coke and finally fuel ash are shown in the table below.

Venezuelan crude oil	150 ppm V
Residual oil	600 ppm V
Coke product(petroleum coke) after concentration	4 000 ppm V
Fuel-ash	15 % V ₂ O ₅

The major constituents in the fuel ashes are normally C, V, S, Fe, Ni, aluminosilicates. There are two types of fuel ashes:

- Fly ash: collected in electrostatic filter
- Boiler ash: deposit on the ash pit beneath the flame zone or outside the boiler tube, less amount but higher V-content

There are both hydro- and pyrometallurgical processes for V-recovery from the fuel ashes as shown in Figure 14 and 15.

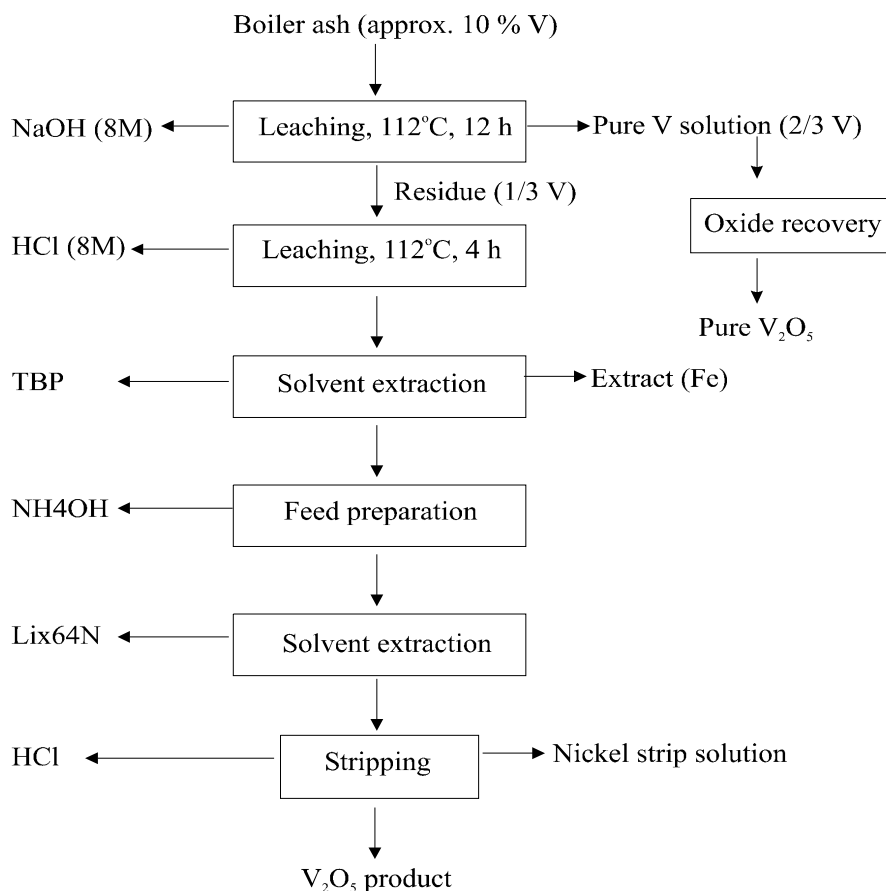


Figure 14 - Hydrometallurgical recovery of vanadium from boiler ash

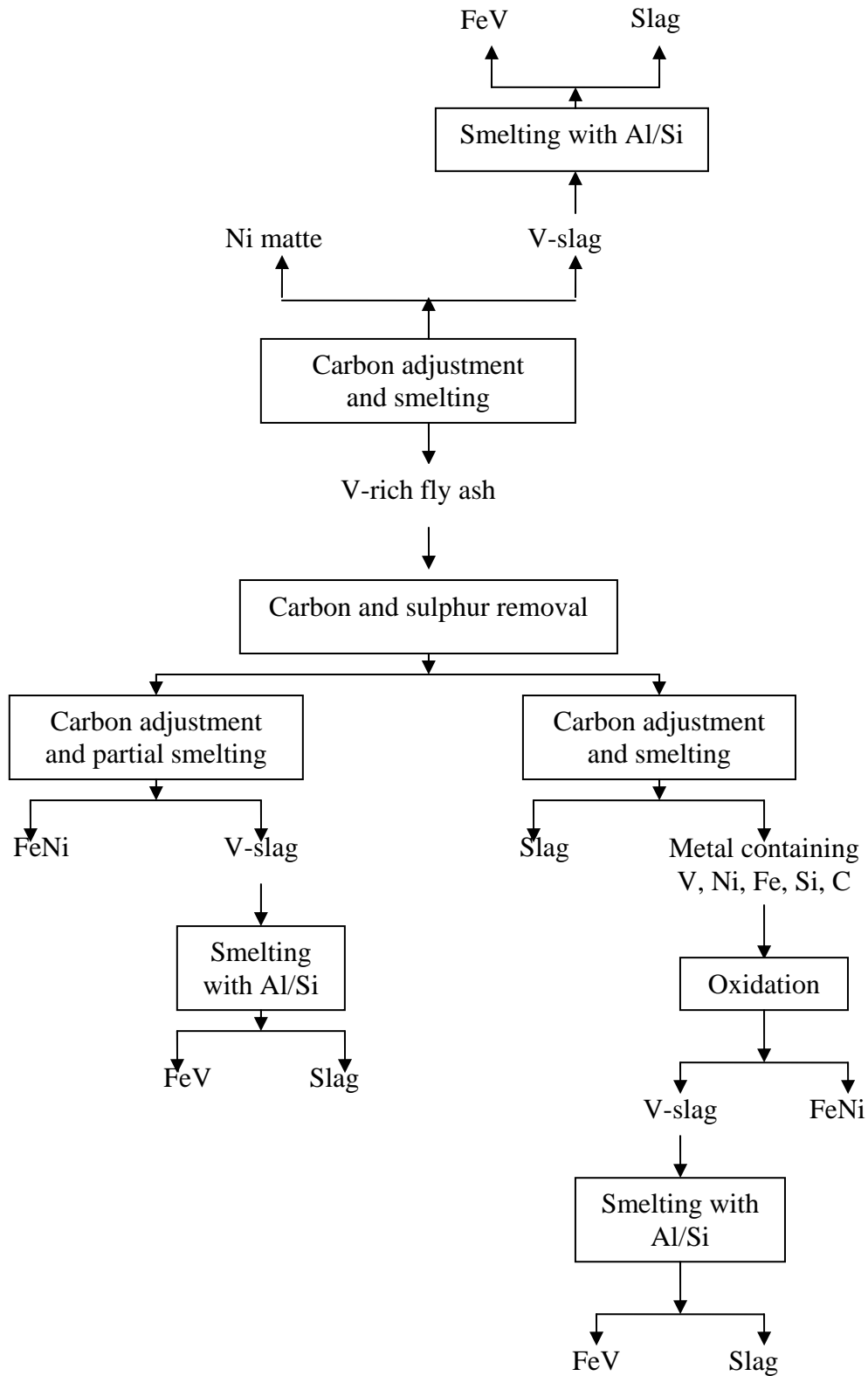


Figure 15 - Pyrometallurgical recovery of vanadium from fly ash

5.5 V-recovery from Spent Catalyst

Petroleum refining catalyst for desulphurization is normally MoO_3 promoted with CaO on Al_2O_3 as carrier. During desulphurization V is deposited on the catalyst as V_3S_4 which accumulates to a high V-concentration 5-30 % V. When spent, this catalyst is processed for vanadium recovery.

There are different methods for recovery of vanadium from the petroleum refining catalysts. Two of them are shown in Figure 16 and 17. In addition to these two processes, Gulf Chemical has a 10 MW DC-furnace for recovery of valuable metals from the catalysts.

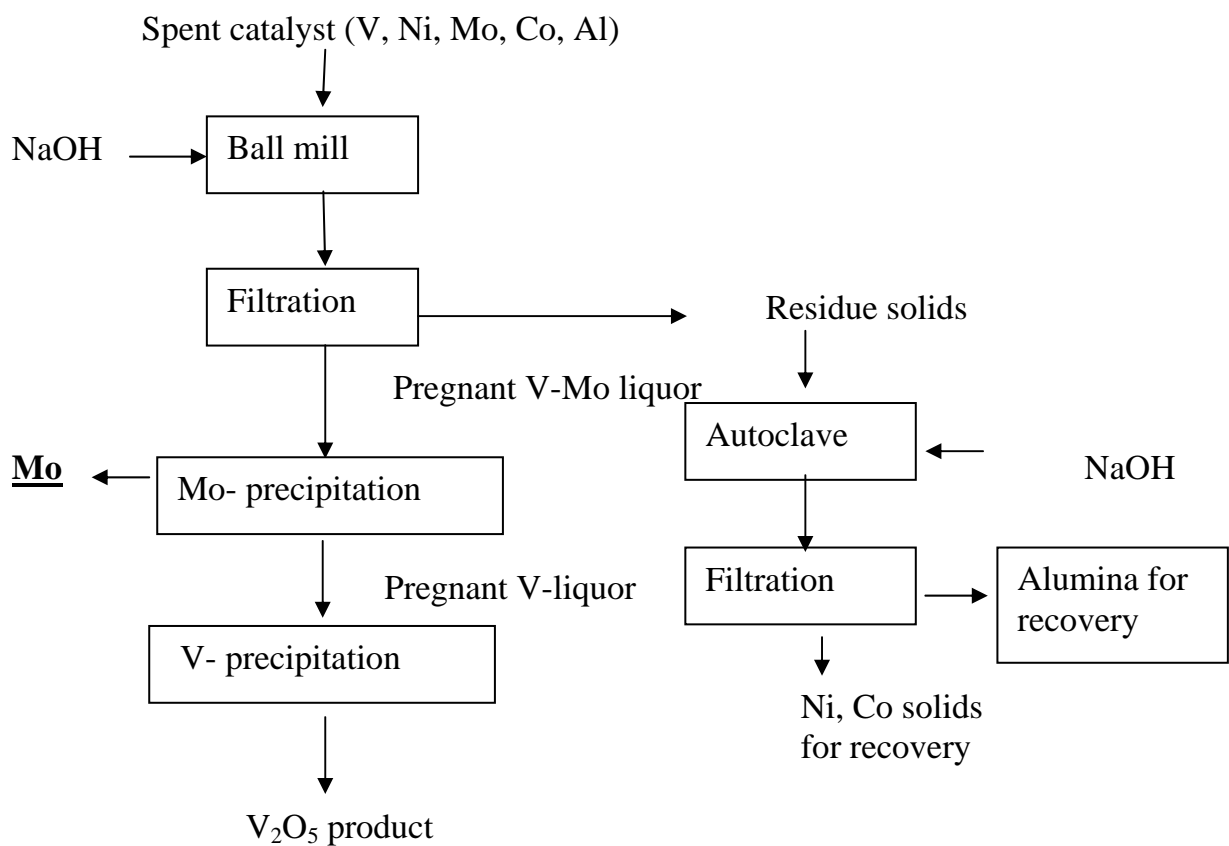


Figure 16 - Vanadium recovery from spent catalyst, CRI-MET process

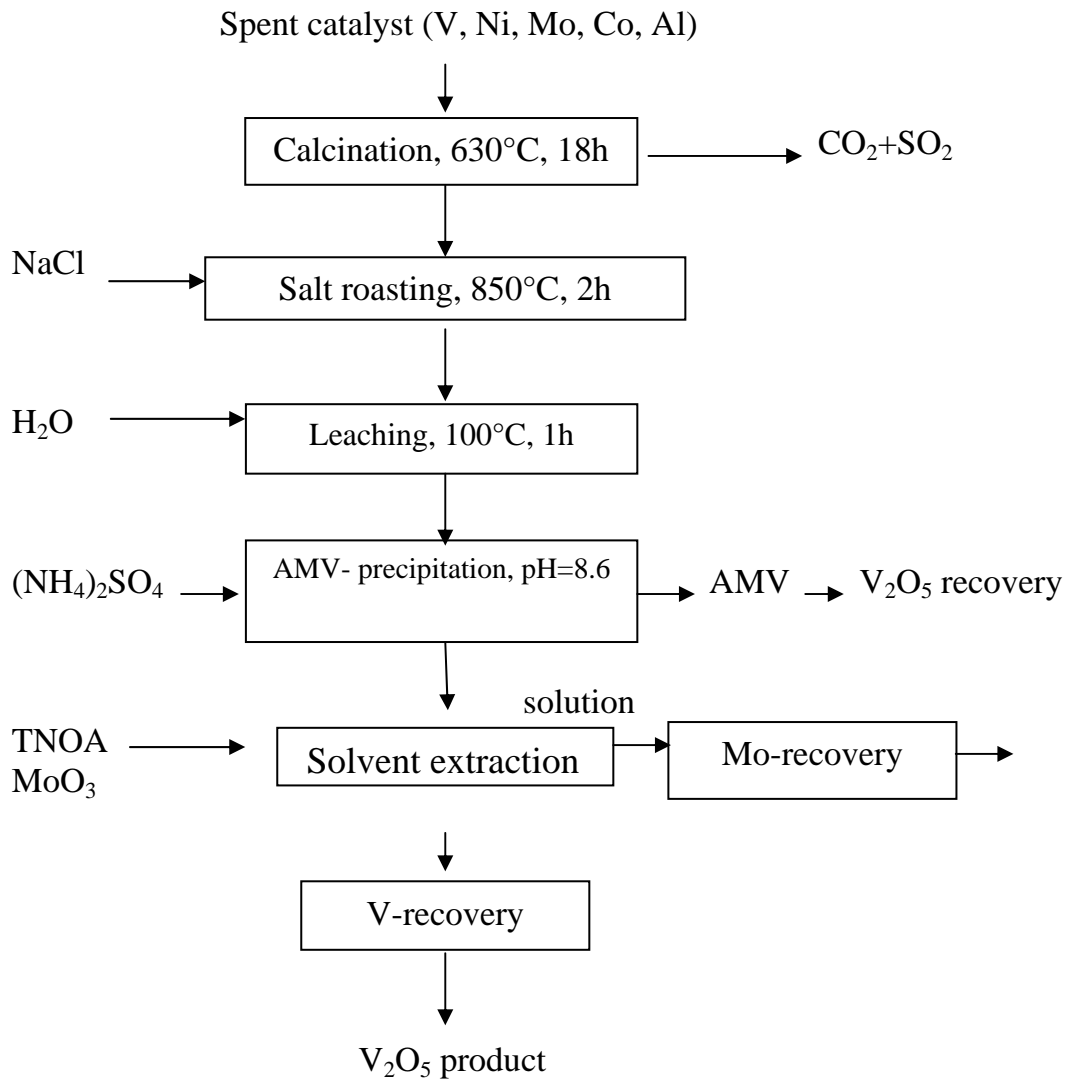


Figure 17 - Recovery of vanadium and molybdenum from spent catalyst

6 PRODUCTION OF FERROVADIUM

The V-content and the maximum allowed content of impurities in the most common FeV-products in the market are shown in the table below.

FeV-alloys	V	C, max	N, max	Al, max	Si, max	P, max	S, max	Mn, max
50-60 % V	50-60	0.2		2.0	1.0	0.05	0.05	
70-80 % V	70-80			1.0	2.5	0.05	0.1	
80 % V	77-83	0.5		0.5	1.25	0.05	0.05	0.5
Carvan	82-86	10-15		0.1	0.1	0.05	0.1	0.05
FeV-car-bide	70-73	10-12			0.5	0.05	0.05	0.05
Ferovan	42,min	0.85			7.0			4.5
Nitrovan	78-82	10-12	6	0.1	0.1	0.05	0.1	0.05
FeV45	42-48	1		0.3	7	0.4	0.4	4

The production of FeV is normally based on V_2O_3 or V_2O_5 using Al or FeSi as reductant. When Al is used the heat generated during the reduction will be sufficient for the process meaning that no external heating is needed. When FeSi is used as reductant, an electric furnace is normally applied for heat supply. For the modern FeV plants, Al is normally used as a reductant and an electric furnace is applied to ensure even better control of the processes. The slag is a high Al_2O_3 slag, which is sold for use as ladle slag formers for steel industry.

7 BIOGRAPHS

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8 ACKNOWLEDGEMENT

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THE SWEDISH STEEL PRODUCERS' ASSOCIATION

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