VANADIUM

PRODUCTION AND APPLICATION

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ABSTRACT

The main application of vanadium is alloying of steels, consuming about 85 % of the total vanadium production.

A survey is given on vanadium-bearing minerals, raw material availability and reserves, and vanadium production which amounted to about 20.000 metric tons in 1987 in the Western World.

A short survey of the market situation is followed by a thorough description of the process for recovery of vanadium oxides from titano-magnetite converter slags and the further processing to ferro-vanadium.

The report is concluded by an outlook on future market potentials of vanadium, making allowances for the presently known new vanadium projects.

INTRODUCTION

GfE, Gesellschaft für Elektrometallurgie is a major producer of ferro-alloys since many decades. The most important products in this field are ferro-chrome and ferro-vanadium.

GfE produces Materalloys such as VAl and MoAl for the highly important TiVAl-alloys which are particularly applied in the field of aeronautics and space technology and a wide range of V-Chemicals.

In the field of tantalum and columbium oxides, salts, metals and alloys are produced in different degrees of purity - with ores and synthetic concentrates being the basic materials.

A significant activity is the field of special alloys, in particular the production of magnet alloys (AlNiCo and Sm/Nd-based alloys), alloys for hydrogen storage, alloyed powder for powder metallurgy as well as granulates and targets for PVD coating technology.

The Gesellschaft für Elektrometallurgie has 3 production facilities in West Germany:

- The Nuremberg Works with its main activities vanadium, tantalum, columbium and special alloys. This plant is the birthplace of the company and of the Metallurg Group as well, and represents the largest processing facility for vanadium in the Western World.

  Fig. 1. GfE Nuremberg Works

- Elektrowerk Weisweiler with its main product ferro-chrome.

- Schmelzwerk Rhina GmbH, a 50 % joint venture with Bayer AG.

- The co-ordination of all activities is carried out at the head office at Düsseldorf.

GfE is a member of the Metallurg Inc. with its headquarters in New York, which has production facilities, mines and sales agencies worldwide. With the Cambridge Works of Shieldalloy Metallurgical Corporation, Metallurg has the largest American production facilities for ferro-vanadium in the United States.

1. APPLICATIONS OF VANADIUM

Vanadium is applied in a large number of industrial fields, important examples are:

- The production of oxidation catalysts;
- The production of pigments for paints and ceramic colours;
- Various applications in the field of high technology such as
  * fluorescent materials for colour television screens;
  * neutron flux monitors;
  * energy saving fluorescent tubes;
  * high performance batteries.
- And of course the main field of application: the steel industry.

As the following table shows, 84 % of the vanadium produced is applied in the steel industry.

Table I. Vanadium Consumption in the Western World 1987

Steel industry	84 % =	17,472 tons V
Non-ferrous industry	9 % =	1,872 tons V
Chemicals	5 % =	1,040 tons V
Others	2 % =	416 tons V
Total		20,800 tons V

Vanadium has a large affinity to the interstitial elements carbon and nitrogen at high temperatures. This property is the main reason for the use of vanadium in many classes of alloy steels. Table II shows the final consumptions of vanadium in the USA in recent years.

Table II. Fields of Application for Vanadium

Use	Consumption %
Carbon steel	19.24
Stainless and heat-resisting steels	0.73
Full-alloy steel	24.01
HSLA steel	33.85
Tool steels	10.39
Non-ferrous alloys	8.63
Cast iron	0.79
Superalloys	0.69
Welding and alloy hard-facing rods and materials	0.16
Catalytic uses	0.95
Miscellaneous and unspecified	0.56
Total	100.00

Vanadium forms very stable carbides, nitrides and carbonitrides. As precipitations in the steel, these compounds promote fine grain size, increase hardenability and improve wear resistance.
In carbon steel, already small amounts of vanadium improve the tensile strength and the resistance to heat. The vanadium-nitride-precipitation increases the rupture stress and the yield strength. Likewise, vanadium addition reduces the sensitivity to brittle fracture.

Alloyed structural steel contains between 0.05 % up to about 1.3 % of vanadium. The vanadium content in HSLA (high strength low alloy) steel is about 0.05 %, mainly in combination with molybdenum, columbium and/or chrome. The main application in this class of steel is in pipeline production.

The addition of vanadium in the range of 0.08 - 0.12 % improves the wear resistance of rail steels considerably. Wear resistance is brought by an increase in strength and hardness, both linked to the presence of vanadium carbide.

Highly creep-resistant steels with 10 - 17.5 % Cr, up to 27 % Ni and about 2 % Mo contain 0.1 - 0.7 % vanadium. The application of this class of steels is in power stations and gas turbines.
Likewise we found V-contents of about 0.3 - 2.8 % in Ni- and Co-based superalloys.

Also cast iron will be alloyed with vanadium between 0.25 - 0.5 % to stabilize the cemented phase. Strength machinability and wear resistance will be improved by forming a very fine perlit structure.

This spectrum of possible applications clearly shows the significance of vanadium for the steel industry, which is why a survey should be given on this element's sources, its production and its long-term supply.

2. SOURCES OF VANADIUM

Looking at the distribution of the elements in the 16 km thick earth's crust according to Table III.

Table III: Frequency of the Various Elements in the Earth's Crust

Place of frequency	ppm	Element:
1	466,000	oxygen
2	267,700	silicon
3	84,100	aluminium
4	70,700	iron
5	52,900	calcium
6	32,000	magnesium
7	23,000	sodium
8	9,100	potassium
9	5,400	titanium
10	1,400	hydrogen
11	1,400	manganese
12	1,050	phosphorus
13	625	fluorine
14	260	strontium
15	260	sulfur
16	250	barium
17	230	VANADIUM
18	200	carbon
19	185	chromium
20	130	chlorine
21	105	nickel
22	100	zirconium

it is evident,that fortunately vanadium is no rare element, for example it occurs more frequently than copper and zinc together. Nowadays vanadium minerals no longer play a major role - apart from carnotite - in vanadium production.

At present there are three mineral sources that are of major significance:

- The most important minerals by far are the V-bearing titano-magnetites. Usually they are not used for the direct production of vanadium, but in a slag concentrate which occurs as a joint-product during smelting of titano-magnetites in a special steel process. In these slags the vanadium content of the titano-magnetites is enriched by a factor of 10 - 15.

- The second source of vanadium, which is increasingly taking on significance, are vanadium bearing oil combustion residues, especially those of crude oils from Central America which have high vanadium contents.

- The U-V-bearing carnotites, processing of which, however, is linked with uranium requirement, are of minor importance for vanadium recovery.

The worldwide distribution of Vanadium is shown in Figure 2 (Mineral Deposits of Vanadium)

Fig. 2. Mineral Deposits of Vanadium.

3. PRODUCTION PROCESSES

3.1 Vanadium Oxides

Basically, there are two methods for the production of vanadium oxides. These are acid decomposition and the alkaline roasting process.

Acid decomposition is mainly applied for processing carnotite. First of all, the ore is processed to a concentrate, is then ground and dissolved in sulfuric acid. Uranium and vanadium are dissolved and are separated by means of a solvent extraction process. The re-extracts are used for the production of vanadium oxides which is carried out via the intermediate ammonium-vanadate.

The most important raw materials for the alkaline roasting process are the vanadium-bearing converter slags resulting from the smelting process of titano-magnetites. Titano-magnetite crude ore contains an average of 0.3 - 1 % V2O5, 1.5 % at the most. If the V2O5 contents in crude ore are higher than 1 % then the direct production method is considered, by which the ore is ground, concentrated, mixed with soda, roasted and the vanadium extracted from this roasting charge.

If the raw materials have lower vanadium contents, a vanadium bearing pig iron has to be produced. In a refining step the vanadium is then blown from the pig iron in a shaking ladle. This results in a slag containing approx. 20 % V2O3. This is the actual raw material required for the alkaline roasting process.

The slag has the following average composition (in weight percentage).

Table IV. Typical Composition of V-bearing Converter Slags

V_2O_3	19.8	TiO_2	4.8
Al_2O_3	5.0	MnO	4.0
CaO	2.9	SiO_2	16.0
MgO	2.7	$Fe_{met.}$	10.0
Cr_2O_3	5.5	C	0.3
FeO	29.0	P	0.02

The stages of processing the vanadium bearing slag to the roasting charge are shown in Figure 3.

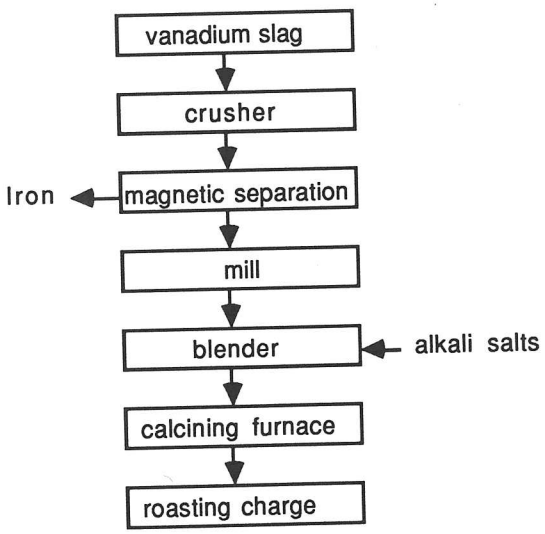

Fig. 3. Roasting of V-bearing Converter Slags

The slag is crushed, ground and most of the metallic iron is removed by means of a magnetic separator. Following this, the ground material (< 100 µm) is blended with alkali salts and oxygen-roasted in a roaster at 800°C. During the roasting process vanadium, which is contained in the slag as spinel FeO · V2O3 is converted to water-soluble sodium vanadate. In this step undesirable elements such as phosphorus, silicon, iron and chrome are decomposed, and these have to be separated in a special purification step.
Figure 4 shows the further processing stages of the roasting charge to ammonium-poly-vanadate (APV).

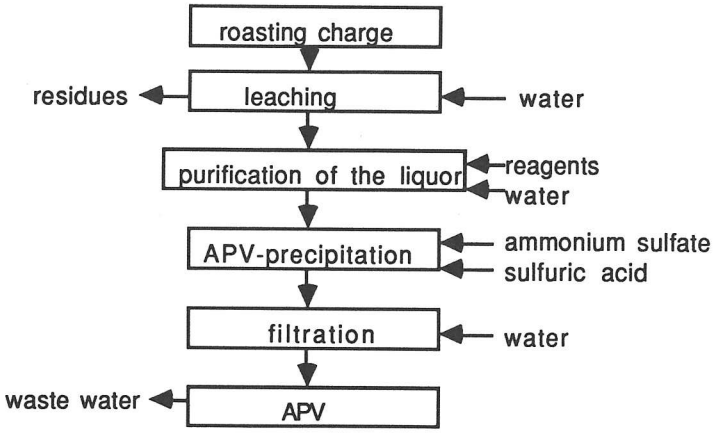

Fig. 4. Ammonium-Poly-Vanadate (APV) Preparation

The roasting charge is leached with water, during which all water-soluble components are dissolved. Subsequently the liquor is purified by which the elements P, Cr, Si and Fe are mostly removed. By adding ammonium sulfate and sulfuric acid ammonium-poly-vanadate is precipitated at pH 2-3 and approx. 90°C. The precipitated ammonium-poly-vanadate is separated from the mother liquor by filtration, is then washed with water and dried. Figure 5 shows the further processing of dried ammonium-poly-vanadate to V2O5 or V2O3, respectively.

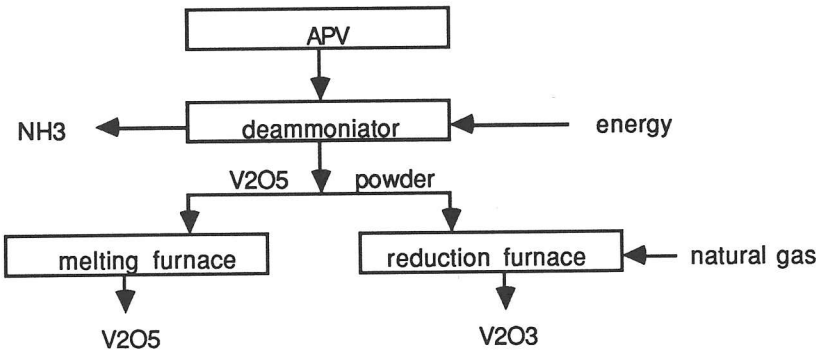

Fig. 5. Processing of APV to Vanadium Oxides

The dried ammonium-poly-vanadate is thermically decomposed to V2O5 powder in a rotary tube furnace, melted in a melting furnace and cast into flakes. Alternatively, V2O5 powder can also be treated with reducing gases such as hydrogen or natural gas in a reduction furnace and can be reduced to V2O3.

3.2 Production of Ferro-Vanadium from V-Oxides

For the production of ferro-vanadium the V-oxides V2O5, V2o4 and V2O3 are aluminothermically reduced by the Goldschmidt-Process. When estimating the thermodynamic values and when calculating the possible adiabatic temparatures you discover that when reducing V2O5 with aluminium there is an excess of energy which makes slag resulting from internal production necessary for damping the reaction.

Furthermore, thermodynamic calculations show that when using V2O4 heat is released to such an extent that there is just enough energy for the process to run off self-sustained. So when using this oxide there is no surplus energy which has to be drawn off.

If V2O3 is aluminothermically reduced there would not be enough liberated energy for a self-sustained process, i.e. the slag and metal would not melt down sufficiently. A possibility in this case would be to reduce V2O3 with aluminium in an arc furnace by which the shortage of energy is brought into the process by an electric arc.

In order to produce ferro-vanadium from V2O5 or V2O4, respectively, vanadium oxide is blended with aluminium shot and scrap iron and the aluminothermic compound is brought to a reaction by an ignition mixture consisting of sodium peroxide and aluminium shot. Aluminothermic reactions go off very rapidly so that within only a few minutes block weights of more than 2 tons of ferro-vanadium can be produced. As soon as the reaction has ended, the liquid metal separates itself from the liquid slag and after it has cooled down the metal block can be separated from the slag block.

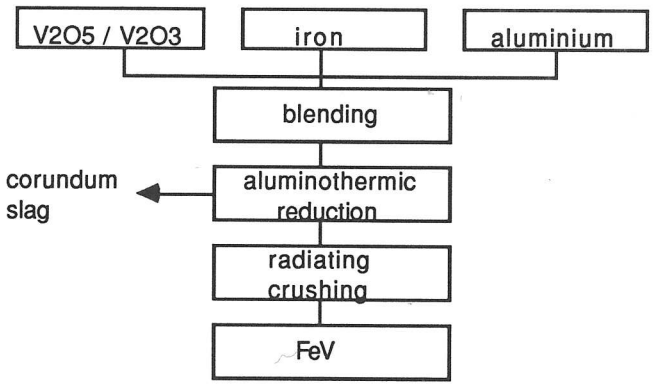

Fig. 6. Aluminothermic Production of Ferro-Vanadium

By applying this process FeV-80 is obtained which corresponds to the following standard analysis:

Table V. Standard Analysis for FeV 80 as per DIN 7563

V	78 - 82 %	P	max. 0.06 %
Al	max. 1.5 %	As	max. 0.06 %
Si	max. 1.5 %	Cu	max. 0.10 %
C	max. 0.15 %	S	max. 0.05 %

3.3 Direct Production of Ferrovanadium from V-bearing Slags

The second important process for the production of ferrovanadium is the direct processing of V-bearing slags in electric arc furnaces. This process is carried out at the Cambridge Works of Shieldalloy Metallurgical Corporation. This is a proprietary multiple step process for production of a 42-46 % V ferrovanadium having a trade name of Ferovan.

4. FUTURE PROSPECTS

Figure 7 shows that the state of vanadium supply and vanadium demand is relatively balanced which in the long run has kept the prices on an even level in the past.

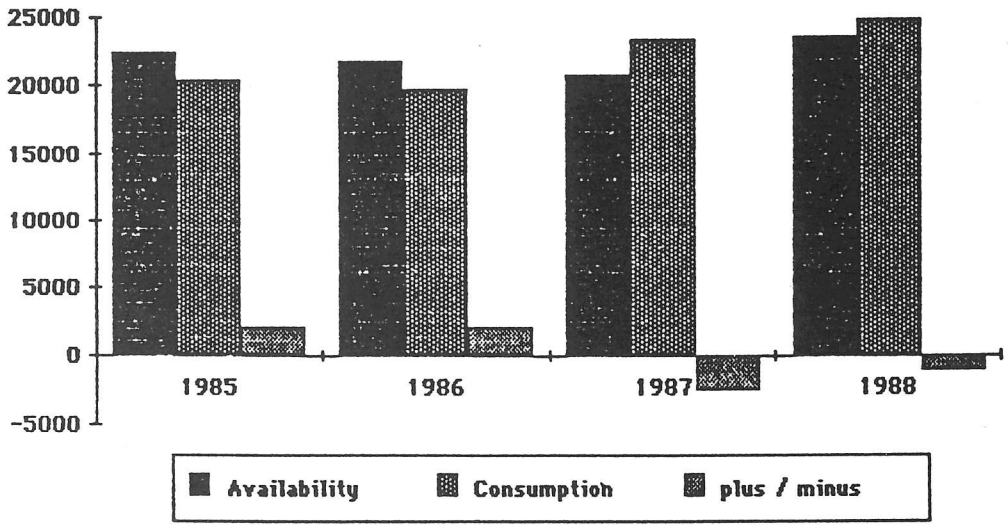

Fig. 7. Vanadium-Availability and Consumption/ Western World (in terms of Vanadium-Pentoxide)

The drop in production between 1986 and 1987 was particularly due to the shutdown of Rautaruukki/Finnland, production which could not be completely made up for by the increased Chinese production.
The consumption in the years 1986 to 1988 increased due to the good steel market mainly in the USA and in Japan and basically due to the positive development of alloyed steel production.

This is the reason for the high vanadium prices at present. It is expected, that due to planned and already completed commissionings of production facilities, such as for example VANSA ins South Africa, Swenskt Stal in Sweden, Agnew in Australia, Kerr McKee in USA and New Zealand Steels, on a medium-term basis the price of vanadium will reach a level again that can be accepted both by consumers as well as by suppliers of vanadium.

Therefore vanadium will remain an attractive alloying addition for steel now and also in the future.

5. REFERENCES

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(6) BGR Illustration: Vanadium Deposits

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