THE DEVELOPMENT OF VANADIUM INDUSTRY IN CHINA

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ABSTRACT

China has abundant resources of vanadium (V). The representative first works in China for V extraction by hydrometallurgy was erected in 1942. After the founding of the People's Republic, it had been reconstructed and improved under Russian experts' help and set in motion since 1958. Through a period for research and pracrice, the daily output reached 1 ton of ferrovanadium in 1962.

Since 1959, steel works produced a small amount of V slag, which had a high content of V. By using such a slag as raw material, Jinzhou works got better results in production. Then V slag bases were founded successively. With their help, Jinzhou works reached its second phase production capacity by the project in 1965.

Within the past 30 years, Jinzhou works had tested and consumed various kinds of V containing materials in production and a lot of experience were accumulated. Technology and quality of certain products had caught up with those of advanced countries. In order to meet the increasing demand on V and to disperse the location of V industry, several works were erected in the 60s for processing slag into V pentoxide and ferroalloy. The Panzhihua steel and V slag complex was founded in the early 70s.

The author has put forward measures for improvement in the field of production of V slag, extraction of V by hydrometallurgy, environmental protection and development of new products. After a comprehensive description on the research of new technology, the author has emphasized that every new technology has its advantages and disadvantages, only those had been proved better in fact by experiment can be applied in production.

China's V industry has reached a higher level both in technology and scale of production. While reviewing the past and summing up experience, let's compare ourselves with advanced countries' and see where we lag behind, coordinate activities of government and enterprises to promote V industry to a new epoch of prosperity.

In order to speed up the development of V industry, the author suggests: to rationalize the utilization of resources, to increase the recovery of V, must expand the application of V in steelmaking and pay more attention to the scientific research and production of HSLA steels. Surplus may be exported.

INTRODUCTION

Although V is a rare element, its content in earth's crust is comparatively high. China has abundant V resources. Its new V mineral deposits are discovering more and more. V containing minerals are mainly titano-magnetite, phosphoric iron ores, carboneferrous shales or stony coals and clay in the second place.

The use of V in industry is chiefly as alloying element in steel. It is extensively used in alloyed tool steels, structural steels, spring steels and some kinds of superalloys. Especially, highspeed steels can not be made without V. According to the amount of consumption, more V is used in the production of HSLA steels for natural gas pipelines and wide-span railway bridges. V is also an alloying element in titanium alloys, which are important for structural materials of modern aircrafts and spacecrafts. To the next, V is used in chemical engineering for catalysts in the production of sulfuric acid, fertilizer and organic syntheses.

The usage of V is so extensive and important, at the same time China is rich in V resources. Thus, full use of them to develop V industry either for domestic use or for export shall be beneficial to the nation.

REVIEW OF THE HISTORY

Period when the Works Founded under Japanese Aggression

The predecessor of the first works for hydrometallurgy of V in China--Jinzhou Ferroalloy Works was called "Manchu Special Ironmaking Co. Ltd". It was founded in 1942. the Japanese imported technology from Germany to produce V from the titanomagnetite of Chengde. The concentrate was transported to Jinzhou, roasted in rotary kilns with addition of sodium sulfate, and then leached with water, a V liquor was separated in thickeners. By adding ferrous sulfate solution to the liquor, iron vanadate was precipitated out. Using this low grade concentrate of V, a ferrovanadium of 30%V was made. The quality was low, and the amount was small. Archives were nothing left after the invaders' surrender. The recovery of V can only be estimated by analysis of the residue left in the site[1]. It is thus obvious that the technology wasn't successful.

Period for Restoration of Production

since 1954, preparatory works for restoration of V production was started. On the one hand, tests on roasting of the old concentrate from Chengde were done for determination of roasting temperature and the percentage of sodium sulfate in mixture. On the other hand, a whole process test for production of V via V slag was carried out under the direction of Russsian expert I. F. Krasnih[1]. 2400 t of concentrate was transported from Jinzhou to Benxi for briquetting and then carried to Daye for test of blast furnace smelting and bessemer blowing to obtain V slag. The slag was thereafter ground into fine powder and iron particles in it were magnet separated in Benxi. At last, experiments were made for roasting the slag in a rotary kiln of 10.6 m in length at the Institate of Applied Chemistry in Changchun. Leaching and precipitation of V pentoxide and then smelting of ferrovana-

dium were also done there. Scientific basis for the Jinzhou project was thus obtained. Jinzhou works was planned to produce 40% ferrovanadium by using concentrate in the first phase and slag in the second phase.

Early Days of the Concentrate Process

The first phase of construction of Jinzhou ferroalloy works was gone in motion in 1958. Problems had arousen as poor yield, formation of rings in the kiln, therefore the works suffered low output and high cost. Later investigations found that the low yield was due to the concentrate, which although was not low in V content (0.8% pentoxide), its coarse grain size was unfavorable to extraction of V. At the same time, coarse grain size and impurities in the sodium sulfate additive were found harmful too. Thereafter, principle was decided on improving the quality of raw materials, the concentrate was reground to pass 200 mesh. And the operators were trained more skillful gradually. To the end of 1962, the daily output of 3 kilns reached to 1 t of ferrovanadium, the recovery exceeded 70%, and the production was steady.

COURSE OF DEVELOPMENT AND THE PRESENT CONDITION

Changeover to Slag Process and the Development of Slag Production

Since 1959, a small amount of V slag was used for trial production. Even though the quality of the slag at that time was not high, the production efficiency by using it was much higher than that by using concentrate for it had a pentoxide content of 6-15%. Consequently, central and local governments made huge investments in the foundation of V slag bases. Jinzhou ferroalloy works increased its capacity to the norm of second phase of construction. While the steel works supporting Jinzhou with V slag, Jinzhou had done its best for the promotion of slag production.

Some of the early slags had poor quality, the reasons are:

-Low content of V and high content of phosphorus in the pig iron.

-Higher silicon content was maintained in the liquid iron, it lay often at the level of 0.8%, nevtheless, its optimum value mustn't exceed 0.4%.

-The bessemer furnace for slag blowing was lined with dolomite clinker, so calcium oxide went into the slag.

It was improved afterwards by adoption of effective measures.

Panzhihua has the most important V and titanium mineral resources. As a result of the metallurgical difficulties caused by the complicated mineral composition, thorough researches and tests were done for the construction of Panzhihua Iron and Steel Complex. The Ministry of Metallurgical Industry had organized and lead many institutions of higher learning, researching and designing institutes and enterprises in this task and achieved great success as "New technique for the blast furnace smelting of high titanium titanomagnetite", which is in the lead in the world. This may be praiseworthy as a good example of cooperation with devotion of every partner's efforts.

The disadvantage of Panzhihua V slag was difficult separation from iron inclusions, especially, the slag at the early time was often wrapped up in iron, that caused difficulties in breaking and separating of them. The problem was solved later by research and improvement of furnace profile and parameters of equipments, and the successful erection in 1978 of industrial equipment, which can annually produce V slag in several scores of thousand tons, was ensured. The quality of the slag obtained was also improved. It cotained V pentoxide over 18%. The rate of oxidation of V in molten iron reached 88.5%, recovery exceeded 73%. But these were somewhat lower than the advanced in the world.

Improvments in Technique of V Hydrometallurgy in Jinzhou Works As a Typical Works.

Within the past 30 year, Jinzhou ferroalloy works had used many types of raw material in tests and production. They were, titanomagnetite, V slag from basic and acidic bessemers and oxygen top blow bessemer, V slag from channel type furnace, initial slag of basic open hearth furnace and carboneferrous clay etc. By researches and tests on these raw materials, V extraction technique was mastered, technical and economical indexes were improved and experience in respect of V extraction was accumulated:

-Fine grinding of the slag: Grinding of the slag to pass 120 mesh even finer is favorable to increase the rate of oxidation, but at the same time, problems in dust-catching of flue gas and control of silt-formation must be solved. Through the practice in several years, behavior of the silt-formation and a technique to control it was worked out.

-Air separation of iron: Iron magnetically separated from V slag contains quite a few slag in mixture. At the beginning it was washed with water to separate, but the result wasn't satisfactory, and the slag recovered must undergo dewatering and drying. Soon afterwards, the iron was treated by air separation and dust-catching. The overall recovery can thus be increased by 0.5%.

-Selection of additives and their proportion to the slag: Through the practice in many years, principles on the selection of additives was clear, and optimum proportion to the slag was worked out. Then, the problems of low oxidation rate and ring-formation in the kilns were solved.

-Electro-static dust-catcher for the flue gas from kilns: For the first time to recover the slag dust in the flue gas, which contains chlorine. The total V recovery can be increased by 2.5%. At the same time, condition for the first and second items in this subheading was created.

-Persistence on the use of rotary kilns: European V works used to roast the slag in multihearth furnaces, but Jinzhou works persisted on the use of rotary kilns. By learning after experience of alumina plant, the rotation speed of kiln was increased. Although the retaining time was shortened, but the roasting result wasn't affected and the output was increased by 30%. This may be due to the more vigorous tumbling of the burden, that enhanced the heating and oxidation.

-Extraction of V by only once roasting: At the early days, to finish the extraction of V, the slag must be roasted 3 times and leached 2-3 times for the quality of slag was poor. Later, it was changed to twice roasting and twice leaching, and experiments on once roasting plus either acidic or alkaline leaching.

Nowadays, advanced know-how is mastersd and twice roasting basically disappeared. Application of this method can increase the output by 30% decrease the consumption of energy by 15-20%, and V content in the residue may be the lowest among V works throughout China.

-Precipitation of ammonium polyvanadate; At the past, V pentoxide was precipitated from the liquor by hydrolysis by adding sulfuric acid. The purity of the product was only 85-90%. Although the V pentoxide by metavanadate process had good quality but the consumption of ammonium salt was very high, so it was used only for the production of aluminum-V alloy. Later, the precipitation of ammonium polyvanadte by adding sulfuric acid and ammonium sulfate was succeeded on reference of foreign literature[2]. The purity of V pentoxide obtained can be increased to exceed 98%. It is favorable for both export and domestic use. This achievement had been passed appraisal and won prize for scientific and technological achievements of the Chinese Ministry of Metallurgical Industry.

-Smelting of 50% ferrovanadium in electric furnace; Originally, Russian national standard was used, the V content in ferrovanadium not lower than 35%. later on, the Chinese standard had changed this to not lower than 40%. After study and investigation step by step, a technology for smelting 50% ferrovanadium by silicothermic process in electric furnace was succeeded. The furnace output can thus be increased, and the power consumption was lowered. The product can meet the demand of foreign customers and need lower expenses for packaging and transportation.

-Smelting ferrovanadium directly from V slag; In cooperation with the Beijing Researching Institute of Iron and Steel and others, a 35% ferrovanadium was smelted from V slag after partial removal of iron in it. This alloy can be used for low-alloyed steels.

-Treatment of drainage; The waste water after precipitation of V contains sulfuric acid, sodium sulfate and ammonium sulfate, especially, it contains toxic hexavalent chromium, and must be treated to detoxify before drainage. Jinzhou works experienced a method of reduction with iron scrap and ferrous sulfate plus precipitation with lime and another method of reduction with sulfur dioxide plus neutralization. "Fast reactor" of Thyssen water technique Co. of West Germany was imported for this purpose. Its performance is good.

The Technical Level Reached and Gap Remained in Jinzhou Works

Through a series of mesures described above, V production in Jinzhou works today had reached a higher technical level, for some kinds of products, even approached international level in quality and techical and economical indexes.

-Quality of V pentoxide flakes see Table I.

Table I. Quality of V pentoxide

Grade	V_2O_5-98	V_2O_5-99
Content of V_2O_5	98% min.	99%min.

The recovery from slag can reach international level, when in favorable conditions.

-V pentoxide powder, 99% or more.

-Ferrovanadium, grades and method of smelting see Table II;

Table II. Ferrovanadium

Grade	FeV40I	FeV50I	FeV75I
V% min.	40	50	75
Method of smelting	Electro-silico-thermic	Electro-silico-thermic	Alumino-thermic

-V metal, produced by electrolytic refining, in the form of dendrites, grades see Table III;

Table III. V metal

Grade	V-022	V-021	V-03
Purity, V%	99.0	99.5	99.9

For special demand, contents of impurities may be decided on negotiation.

-Aluminum-V alloy, made by aluminothermic process, can be used for titanium based alloys or aluminum based alloys, see Table IV;

Table IV. Al-V alloy

Grade	AlV40	AlV50	AlV70	AlV80
V%	40	50	70	80

Gap in V production lies in these respects as bad working circumstance and inadequate labor protection; environmental pollution hasn't been thoroughly prevented; treatment of flue gas from kilns and furnaces is insufficient; degree of automation is low due to lack of advanced instruments.

Erection of Numerous V Works

Due to the increasing demand for V and to the consideration of rationalizing location of V works, several new V works were erected successively in the midst of 60s. They had mastered the technology of V extraction through a period for practice, some of them had developed to a fair size.

Among the works utilizing the widely occurred V containing carboneferrous shales, stony coals and clays to produce V, there are works in Hubei and Hunan, whose industrial experiment was done in Jinzhou in 1963. In Guangxi, a large resource of this type was found newly. Some of them burn the stony coal in power plant boilers, and the ash may be used for V extraction. Others roast the stony coal with common salt as additive. Their profit is good. It isn't owing to any advanced technology, but to the cheap raw materials and high price of products. Just the reverse, such small plants have two main disadvantages, namely; high consumption and serious environmental pollution. For example, some of them had damaged a lot of crops by their flue gas. These are problems awaiting solution.

DIRECTION FOR THE DEVELOPMENT IN FUTURE

Suggestions on Measures to Improve the Present Process

-In the respect of slag production; To increase extraction rate of V from molten iron, it consists of; proportion subjected to blowing, rate of oxidation and the recovery of slag produced. Must improve the separation between iron and slag in order to get more slag. Don't put molten iron to steelmaking without extraction of V slag or lose the slag already produced, for these shall waste the precious V resources.

-In the respect of V hydrometallurgy: Careful researches should be done to increase the recovery and labor productivity, to improve the working circumstance and labor protection. Improvements on the technique of decomposition and fusion of ammonium polyyanadate are also necessary.

-In the respect of environmental protection: To research the utilization of substances remaining in the waste water after detoxification of chromium, such as the recovery of soda and ammonium salt.

-In the respect of new products:
Complex alloys: ferrosilicovanadium, silicomanganese-V, silicocalcium-V. New types of V additives for steel : V carbide, V nitrocarbide, nitroferrovanadium, V oxy-carbide.
Improvement in the smelting of high grade ferrovanadium. Tests on the application of electroaluminothermic process.

Researches on New Processes

For the second phase construction of Panzhihua steel and V base, according to the policy of "let a hundred flowers blossom and a hundred schools of thought contend" , miscellaneous processes other than the present blast furnace liquid iron--V slag process had been recommended, mainly:

-Pelletizing with sodium salt additive: To pelletize the V containing concentrate and sodium salt, roast and leach with water to extract the V content. Same as the process used in Finland, roasting pellets in shaft furnace. Only the problem of smelting the leached pellets in blast furnace should be solved.

-To reduce the concentrate in solid state, in rotary kiln, shaft furnace or a fluidized bed furnace, and then to melt it and set to separation of metal and slag. To extract V from the slag, and the liquid metal set to steelmaking.

-Liquid iron--soda slag process: This process is similar to the desulfurization technique for liquid iron outside furnace. Adding soda ash or baked natural soda and blowing oxygen to liquid iron in a ladle. Let sulfur, phosphorus, silicon and V oxidize totally to form sodium salts and go into slag, which can be treated chemically to recover V and soda. The remaining metal, so-called "semi-steel" has low content of impurities can easily be smelted into steel with a little amount of slag or without slag. But this soda slag has a great deal of impurities, its later processing shall be difficult. A technique of roasting in mixture can solve this problem.

--Other processes of liquid iron-V slag or soda slag: To reduce pellets from concentrate in rotary kiln, to melt in electric furnace and separate liquid iron and waste slag . The former is subjected to V extraction by V slag or soda slag process. For example, the Highveld Co. in S. A. produces V slag in shaking ladle by this process.

-Steelmaking slag process: Smelting the V containing liquid iron into steel directly, and the slag from steelmaking can be used for recovery of V by hydrometallurgy or smelting of low-grade ferrovanadium after concentration by means of pyrometallurgy. Round about 1977, a series of experiments on this process had been done in Chinese works.

-Process of returning single slag: To return the V containing slag from steelmaking into blast furnace to concentrate the V content into liquid iron, and then to obtain V slags with higher or very high V content. These slags are then treated by either hydrometallurgy or pyrometallurgy to obtain V products. Tests were carried out in Panzhihua and other works, one of them applied this process partially in production. The process was practised by German works in old days.

All these new processes have their advantages, disadvantages and difficulties in practice. Only when the diffisulties solved, the disadvantages overcome and the advantages elaborated through researches and experiments, a process can just be used commercially. Here is no need to discuss in more detail.

CONCLUSION AND SUGGESTIONS

China is rich in V resources. Her V industry had prosperously developed mainly through her own efforts. The present process of liquid iron-V slag has reached a considerable technical level and scale in production. Reviewing the history of development of V industry, experiences on achievements should be concluded and at the same time, gap between the advanced countries should be found. Then, coordinate efforts of various quarters and absorb experiences of advanced enterprises in the world. Strengthen researching and testing works and lead the V industry to a new epoch of development. Thus more profit can be gained, and the modernization of the nation can be promoted. For this purpose, a few suggestions are given as follows:

To give full play of the V resources, that means fully utilize them and mustn't waste or lose any V at will. Must try the best to increase the utilization rate of V, to increase recovery during every stage in the technological process, so that to recover V to the maximum extent. The recovery of V from concentrate to V slag in Chinese works is less than half at the present time, they have great potentialities to improve indeed.

To extend the application of V in steelmaking: To extend the application of V in alloyed steels partially as substitute for molybdenum. At the same time develop the production of V containing HSLA steels. For a less amount of HSLA steels can replace more amount of ordinary steel products, for example, one ton of the former may equal to 1.3 ton of the latter. This means economy both on steel and energy in many cases. Dr. Korchensky from Union Carbide Co. U.S.A., after his visit to Wuhan and Anshan steel complexes in China, had given vivid lectures for recomandation to use more V in our domestic steelmaking . In China, steels of manganese-V, manganese-molybdenum-V, manganese-V-boron and manganese-V-nitrogen alloy systems had been researched and fabricated for pressurized vessels, reinbar and beams of railway bridges. For example, the Jiujiang bridge over Yangzi River is designed to use manganese -V-nitrogen steel. Recently, Anshan steel complex had done research and tests on the use of silicocalcium-V alloy for the deoxidation of rail steel.

For extention of the use of V, a disadvantageous factor must be overcome. That is the embrittlement of steel due to precipitation hardening. For this purpose, a technology called controlled rolling can be used to prevent the embrittlement with increasing strength.

Moreover, high price of V hinders its application. At the present time, both V slag and V products are comparatively high in price, this is harmful to spread

its use and exportation. In order to cut down the price, it is needed to improve technology and to revise the cost accounting of V slag production.

When the V produced is in excess of domestic use, the remainder may be exported to earn foreign exchange. For this purpose, must be active to find market of V products abroad and improve their quality to meet customers' demand. Of course, this is also decided to the market price and rate of taxation in both export and customers' import duties.

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