

# Environmental geochemistry and ecological risk of vanadium pollution in Panzhihua mining and smelting area, Sichuan, China\*

TENG Yanguo (滕彦国)<sup>1\*\*</sup>, NI Shijun (倪师军)<sup>2</sup>, ZHANG Chengjiang (张成江)<sup>2</sup>,  
WANG Jinsheng (王金生)<sup>1</sup>, LIN Xueyu (林学钰)<sup>1</sup>, and HUANG Yi (黄艺)<sup>2</sup>

<sup>1</sup> College of Water Sciences, Ministry of Education Key Laboratory of Water and Sediment, Beijing Normal University, Beijing 100875, China

<sup>2</sup> Department of Geochemistry, Chengdu University of Technology, Chengdu 610059, China

**Abstract** Vanadium is a trace element widely distributed in the Earth's crust. Naturally high levels of vanadium are recognized mainly in basic rocks and minerals, particularly in titaniferous magnetite. And the anthropogenic sources of vanadium include fossil fuel combustion and wastes including steel-industry slags. In the last few years, the authors have made investigations and assessments on the environmental geochemistry and ecological risk of vanadium in the Panzhihua mining and smelting area. In the study area, anthropogenic vanadium resulted from mining, extracting and smelting of V-Ti magnetite; vanadium pollution of topsoil and sediments occurs mainly in the mining and extracting area, smelting area, slag dumping area, tailing dam and coal mining area. In the soil, the chemical speciation of vanadium shows: insoluble residue > organically bound > Fe (amorphous) oxide-bound > Mn oxide-bound > soluble component. Vanadium pollution can cause potential harmful effects on ecological systems, and lead to animal poisoning and human disease. So vanadium pollution should be monitored on a regular basis in the Panzhihua area.

**Key words** vanadium; environmental geochemistry; ecological risk; Panzhihua area

## 1 Introduction

Vanadium (V) is a relatively abundant element which is widely distributed in nature; however, workable V deposits are very rare (World Health Organization, 2001). Vanadium is a trace element, which may be beneficial and possibly essential for human beings, but certainly essential for some living organisms (Crans et al., 2004). However, vanadium has aroused ever increasing interest in the past few decades because of its toxicological effects on human beings and animals (World Health Organization, 1990; Nriagu and Pacyna, 1998; Almedeida et al., 2001; Mukherjee et al., 2004), and of diverse sources of pollution and its dramatic role in constituting a major risk to the global environment in facing silent epide-

mic of metal poisoning (Nriagu and Pacyna, 1988).

Vanadium occurs in the minerals vanadinite, partronite, and carnotite. It accounts for about 0.01% of the total in the crust (Budavari et al., 1996) and was derived mainly from titaniferous magnetite containing 1.5%–2.5% vanadium pentoxide, which is mined in South Africa, Russia, and China (Health and Safety Executive, 2002). Smelting of iron ores produces a lot of vanadium slag that contains 12%–24% vanadium pentoxide, which is used for the production of vanadium metal (World Health Organization, 2001). Vanadium pentoxide is also produced by solvent extraction from uranium ores and by a salt roast process from boiler residues or residues from elemental phosphate plants. Ferrovandium can be obtained from vanadium pentoxides or vanadium slags in the alumino-thermic process (World Health Organization, 2001). All crude oils contain metallic impurities, including vanadium, which is present as an organometallic complex. The concentrations of vanadium in crude oils range from 3 to 260 mg/kg and in residual fuel oil, from 0.2 to 160 mg/kg (National Academy of Sciences, 1974). During the burning of fuel oils in boilers and furnaces, vanadium is left behind as vanadium pentoxide in solid residues, soot,

ISSN 1000-9426

\* This study was granted by the China Ministry of Science and Technology under the program of "Ecological and Environmental Monitoring, Forecasting and Management System in the Mining Area" (No. 2004DIB3J110) and "Development and Experiment of Ecological and Environmental Monitoring and Forecasting Technology for the Mining Area" (No. 2005BA901A03).

\*\* Corresponding author, E-mail: teng1974@163.com

boiler scale, and fly ash. Vanadium is also present in coal, typically with the concentrations varying between 14 and 56 mg/kg (World Health Organization, 2001). The hard metal industry uses small amounts of vanadium carbide in the production of tungsten carbide tool bits. Vanadium pentoxide is used as the catalyst for a variety of gas-phase oxidation processes, particularly the conversion of sulfur dioxide to sulfur trioxide during the manufacture of sulfuric acid. The most frequently used vanadium pentoxide catalyst contains 4%–6% vanadium in the form of vanadium pentoxide on a silica base (World Health Organization, 2001). Vanadium pentoxide is also used in some pigments and inks used in the ceramics industry to impart a colour ranging from brown to green. Vanadium pentoxide can be used as a colouring agent to provide ultraviolet filtering properties in some glasses (World Health Organization, 2001).

Natural high levels of V are recognized primarily in basic rocks and minerals, particularly in titaniferous magnetite. However, the concentrations of anthropogenic V in the environment have increased significantly in recent years as the demand for V tends to increase in high-temperature industrial activities including steel-iron refining, electronics and dyeing, etc., though the major sources of V in the surface environment are the combustion of fossil fuels and resultant wastes (Lepp et al., 1995; Nriagu and Pirrone, 1998; Kabata-Pendias and Pendias, 2001). Since V is always present in these materials, its concentrations can be used as a tracer to monitor the degree of environmental pollution (Soldi et al., 1996).

Vanadium is a major trace metal in fossil fuels and the combustion of these materials provides a significant source of vanadium to the environment (Duce and Hoffman, 1976). These are the major environmental vanadium fluxes resulting from human activities; other sources are the products of coal combustion, leachates, and effluents from mining and milling of uranium and titanium ores (Nriagu and Pacyna, 1988; Hope, 1997).

Although high V concentrations in the surface environment would not pose an immediate threat to the global ecosystem, a high level of anthropogenic V can cause a local environmental hazard (Hope, 1994, 1997). During the last few decades, the facade of vanadium as a “slightly” toxic and carcinogenic element has been eventually ratified to an essential trace element with anti-diabetic and anti-carcinogenic properties (Mukherjee et al., 2004).

There are several publications on vanadium geochemistry in geological processes and its toxicity, but there are only a few studies that focus on the environmental geochemistry of V in surface environment and ecological risks. In this paper, we carried out environmental geochemical surveys; the

objectives are: (1) to investigate vanadium pollution and (2) to assess ecological risk of vanadium in the study area.

## 2 Study area

The giant Panzhihua V-Ti magnetite [ $\text{Fe}(\text{V},\text{Ti})_3\text{O}_4$ ] deposit, located in the southern part of the NS-trending Panxi rift valley, along the Jinsha River (upstream of the Yangtze River) in Southwest China, provides 20% Fe, 64% V and 53% Ti supplies for China, and it is celebrated as the most famous base of V-Ti magnetite production in the world. Vanadium-titanium magnetite ores contain Fe, Ti, V, Si, Al, Ca, Mg, Na, K, O, S, Cu, Co, Ni, Ga and so on.

The mining camp includes 6 large-scale (Panzhihua, Baima, Taihe, Hongge, Xinjie and Badong) iron deposits hosted in basic-ultrabasic intrusions, numerous medium-sized coal, clay, dolomite, limestone deposits, and minor graphite, manganese and barite deposits. Production facilities include a large steel manufacturing mill and a steel rolling mill. The extensive mining and processing activities have exerted major environmental impacts (Ni Shijun et al., 2001; Teng Yanguo et al., 2000, 2001, 2002, 2003).

Mining activities have left huge uncovered slopes, large areas of dumping waste rocks and extensive tailings dams. 11.50 million tons of Fe ore are mined per year, and more than 680 million tons of excavated ore and gangue, and 220 million  $\text{m}^3$  of tailings have been deposited near the Jinsha River, thus creating severe threat of trace metal pollution both in the mining area and further down stream towards the Yangtze River (Ni Shijun et al., 2001; Teng Yanguo et al., 2000, 2001, 2002).

## 3 Methodology

We have carried out some environmental and geological investigations since 1997. Systematic sampling was conducted to collect topsoil samples in July 2000. Topsoil sampling was carried out under similar geochemical background, so it is convenient to analyze environmental impact on soil due to mining activities. The soil samples were dried and sieved to obtain the less than 0.063 mm fraction. The contents of vanadium in soil samples were measured by using of the ICP-MS method at the Institute of Geochemistry, Chinese Academy of Sciences. The analysis results are listed in Table 1. According to the method described by Berrow et al. (1978) and Micera and Sanna (1998), the chemical species of vanadium in the soil were analyzed, and the analysis results are listed in Table 2.

**Table 1. Concentrations of vanadium in different materials in the Panzihua area (mg/kg unless specially noted)**

Medium	Vanadium		Analysis method or data source
	No. of samples	Mean (mg/kg)	
Topsoil	19	105.57	ICP-MS
Subsoil	19	111.36	ICP-MS
Stream sediment	87	199.11	XRF
Xigeda Formation siltstone	10	116.29	ICP-MS
Basic-ultrabasic intrusion	18	141.47	ICP-MS
Tailing		143.5	Li Honglu, 1999
Slag		6.25 (V <sub>2</sub> O <sub>5</sub> ,%)	Qiu Kehui et al., 2002
Mine water		2.32–30 (mg/L)	Yang Jingzhong and Liu Fuzhong, 1995
Tailing dam water		3–61 (µg/L)	Yang Jingzhong and Liu Fuzhong, 1995
	Stream	3 (µg/L)	Hamada, 1998
Average natural contents	Cultivated soil	20–93	Connor and Shackette, 1975;
	Uncultivated soil	15–110	Shackette and Boermgen, 1984; Brownlow, 1996
	Vegetation ash	2.6–23	
China soil background value		82.4	China Environmental Monitoring Station, 1990
Unfiltered water from the Yangtze River		0.24–64.5 (µg/L)	Zhang Licheng and Zhou Kezhun, 1992
Filtered water from the Yangtze River		0.02–0.46 (µg/L)	

Sediment samples were collected in May 2002. The samples were dried at 35°C and sieved to obtain the less than 0.125 mm fraction. The contents of V in the sediment were measured by using the XRF method in Chengdu University of Technology, and the analysis results are listed in Table 1. In addition, we also collected and analyzed some environmental samples such as V-Ti-magnetite ore, duns, gangue and slag, and the analysis results are also listed in Table 1.

## 4 Results and discussion

### 4.1 Distribution of vanadium

In the study area, vanadium was enriched in soil, air, water, sediment and plant (Teng Yanguo et al., 2002, 2003; Liao Ziji, 1995).

#### 4.1.1 Distribution of vanadium in the sediment

The data of vanadium in the sediment are

presented in Table 1. The distribution pattern of vanadium in the sediment is plotted in Fig. 1. The average concentrations of vanadium in the sediment (199.11 mg/kg) in the study area are much higher than those in the global shales (140 mg/kg) (McLennan & Murray, 1999). Vanadium pollution in the sediment is recognized mainly in the mining and extracting area, smelting area, slag dumping area, tailing dam and coal mining area (Fig. 1).

#### 4.1.2 Distribution of vanadium in the soil

The data of vanadium in the topsoil are presented in Table 1. The distribution pattern of vanadium in the topsoil is shown in Fig. 1. The average concentrations of vanadium in the topsoil (105.57 mg/kg) in the study area are much higher than the soil background value of vanadium (82.4 mg/kg) in China (China Environmental Monitoring Station, 1990). Vanadium pollution in the topsoil is seen mainly in the mining and extracting area, smelting area, slag dumping area, tailing dam and coal mining area (Fig. 1).

**Table 2. Chemical speciation of vanadium in the soil (mg/kg)**

Sample No.	Soluble component	Organically bound	Mn oxide-bound	Fe (Amorphous) oxide-bound	Insoluble residue	Total vanadium
3A	0.40	3.42	1.13	2.49	111.49	118.93
3C	0.52	3.85	1.22	2.60	131.13	139.32
4A	0.65	4.66	1.86	3.10	183.36	193.63
4C	0.72	4.60	1.05	2.78	135.11	144.26
7A	0.60	4.14	1.56	3.49	192.16	201.95
7C	0.75	4.81	1.54	3.12	107.34	217.56
21A	0.45	3.75	1.23	2.99	149.26	157.68
21C	0.50	3.58	1.49	2.36	173.09	181.02
25A	0.70	4.70	1.69	3.59	173.63	184.31
25C	0.62	4.48	1.80	4.16	207.26	218.32

A. Topsoil; C. subsoil; site Nos. 3 and 4 from the upstream and downstream of the tailings dam; site No. 21 from the mining area; site No. 25 from the coal mining area.

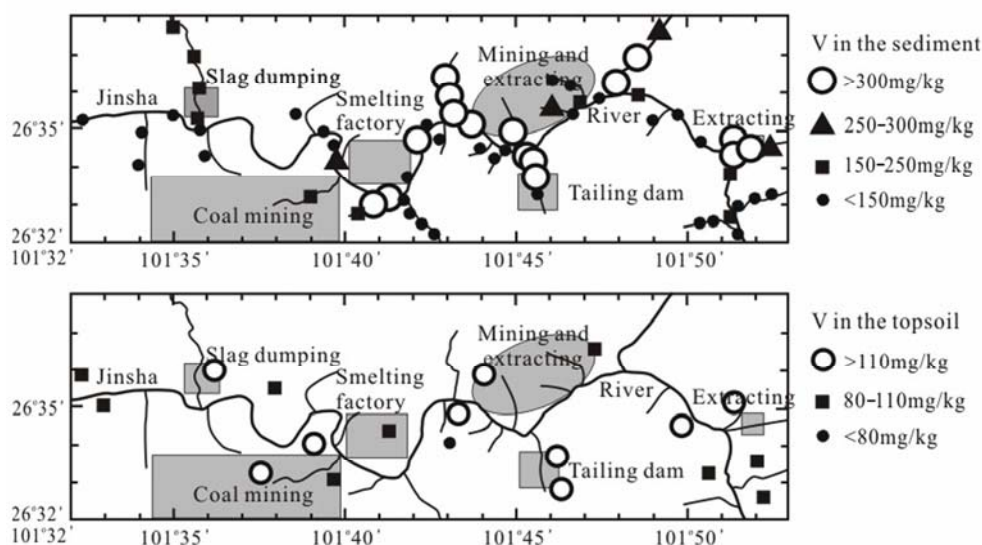


Fig. 1. Concentration distribution of vanadium in the sediment and topsoil.

In soil vanadium is associated with iron oxides, argillaceous minerals and organic fraction (Poledniok and Buhl, 2003). Soluble components are exchangeable and contain vanadium adsorbed on the solid surface. Organically bound vanadium is related to bioaccumulation and consists of vanadium adsorbed on the surface of organic matter or bound with the matter. The residues contain metals occurring in the crystal lattices of primary and secondary minerals in the soil and they are firmly fixed and under natural conditions they are not available for plants (Poledniok and Buhl, 2003).

Chemical speciation of vanadium in the soil is listed in Table 1 and shown in Fig. 2. In the soil the chemical speciation of vanadium shows: insoluble residue>organically bound>Fe (amorphous) oxide-bound>Mn oxide-bound>soluble component. Similar

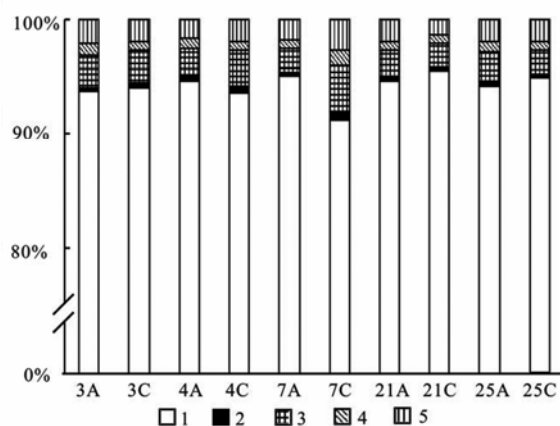


Fig. 2. Distribution of chemical species of vanadium in the soil. 1. Insoluble residue; 2. soluble component; 3. organically bound; 4. Mn oxide-bound; 5. Fe (amorphous) oxide-bound. A. Topsoil; C. subsoil; site Nos. 3 and 4 from the upstream and downstream of the tailing dam; site No. 21 from the mining area; site No. 25 from the coal mining area.

chemical forms of vanadium are found in the topsoil and subsoil. In the mining area (site number 21), the soluble vanadium is lowest. In the soil, because of the low solubility of vanadium, the metal is difficult to uptake by plants directly. Therefore, only a little vanadium could directly find its way into the food-chain.

#### 4.1.3 Distribution of vanadium in the rocks

In the study area, the sedimentary rocks (Xigeda Formation Siltstone) contain as much vanadium as 116.29 mg/kg, higher than that in global sandstones (20 mg/kg) (Turekian and Wedepohl, 1961). In the basic-ultrabasic intrusions, the concentrations of vanadium range from 1.76 to 1072.93 mg/kg (averaging 141.47 mg/kg). Vanadium resultant from weathering of basic-ultrabasic and other types of rocks may find its way into the environment.

#### 4.1.4 Distribution of vanadium in the water

In the study area, water pollution was observed in the mining and smelting area (Teng Yanguo et al., 2003). In mine water, the concentrations of vanadium are up to 2.32–30 mg/L (Yang Jingzhong and Liu Fuzhong, 1995), significantly higher than those in unfiltered and filtered water from the Yangtze River (0.24–64.5 $\mu$ g/L and 0.02–0.46 $\mu$ g/L, respectively) (Zhang Licheng and Zhou Kezhun, 1992). In addition, the concentrations of vanadium are very high in tailing dam water (3–61 $\mu$ g/L) (Yang Jingzhong and Liu Fuzhong, 1995).

## 4.2 Anthropogenic sources of vanadium

Evidence that the environmental levels of

vanadium are increasing has aroused great concern over the injection of vanadium into the environment from anthropogenic sources (Hope, 1997). Current vanadium emissions owing to artificial industrial activities at present have been estimated to account for about 30% of the total atmospheric loading (Hope, 1994, 1997). In the Panzhihua area, anthropogenic vanadium is thought to have comes from mining, extracting and smelting of V-Ti magnetite (Teng Yanguo et al., 2001, 2002). From 1973 to 1978, a total of 2150 t/a  $V_2O_5$  was dumped into the Jinsha River, a total of 2160 t/a  $V_2O_5$  was released into air and a total of 10760 t/a vanadium slag was dumped (Liao Ziji, 1995).

In the process of extracting V-Ti magnetite, about 6000000 t/a tailings were discharged as effluents. The average concentration of vanadium was 143.5 mg/kg, so about 816 t/a vanadium was discharged as effluents.

From 1970 to 1992, about 32000000 tons of steel slag had been dumped. The average concentration of  $V_2O_5$  was about 6.25% (Qiu Kehui et al., 2002) in the steel slags, so from 1970 to 1992, a total of 2000000  $V_2O_5$  was dumped.

#### 4. 3 Ecological risk of vanadium pollution

In the soil, the concentrations of vanadium causing toxic effects in plants may vary between 10 mg/kg and 1300 mg/kg, depending on plant species, the form of vanadium, and soil type (Hopkins et al., 1977). In the case of its concentrations lower than 2 mg/kg, vanadium will positively influence among others chlorophyll synthesis, potassium consumption or nitrogen assimilation (Poledniok and Buhl, 2003). Vanadium of higher concentrations is toxic for the plants as it causes chlorosis and limits plant growth (Kabata-Pendias & Pendias, 1993). Kaplan et al. (1990) found that vanadium, in case its concentrations are over 80 mg/kg, would cause significant reduction in *Brassica* biomass in sandy soil; however, in the concentrations up to 100 mg/kg, there would be no effect in loamy sand (World Health Organization, 2001). The differential response was attributed to greater accumulation of vanadium by plants growing in sand soil (World Health Organization, 2001). In the Panzhihua area, the concentrations of vanadium in plants in the mining area are different from those in non-industrial areas (Table 3). In the industrial area, vanadium was uptaken by plants. For example, in silk cotton, which is also named Panzhihua flower, vanadium was enriched so significantly as to be 3.5 times that in the non-industrial area than in the industrial area.

Since 1965, huge solid wastes including steel slags, tailings and duns from mining activities were

discharged in the study area. A total of 0.68 billion tons of solid waste were discharged from some mining districts. There were present many potentially toxic materials in these solid wastes. These solid wastes were leached by surface water and precipitation; some potentially toxic elements could be released into the environment (Teng Yanguo et al., 2002, 2003). Human healthy and ecological risks were imposed by steel-industry slags in the environment (Proctor et al., 2002).

**Table 3. Vanadium in the plants in the study area**

Plant	Non-industrial area	Industrial area
<i>Plantain</i>	2.17	9.26
<i>Silk cotton</i>	0.84	2.95
<i>Mandarin orange</i>	1.00	14.56
<i>Yunnan pine</i>	2.26	4.96
<i>Yunnan ketelearia</i>	0.88	9.80

Data source: Liao Ziji, 1995.

The pervasive occurrence of vanadium in nature and its wide use in various industrial processes have enhanced its inputs into the environment. This has prompted us to elucidate the impact of vanadium on the aquatic environment, the primary body for industrial effect discharge (Chakraborty et al., 1998). It is evidenced that vanadium pollution can cause toxicity to aquatic organisms (World Health Organization, 2001). Ringelband and Karble (1996) found that population growth in the brackish water hydroid *Cordylophora caspia* was significantly impaired at 2 mg/L vanadium over a 10-day exposure period (World Health Organization, 2001).

In animals, pentavalent vanadium has been shown to be accumulated in the lung, following repeated exposure. There is information suggesting that inorganic vanadium compounds be absorbed, following inhalation, and subsequently excreted via the urine with an initial rapid phase of elimination, followed by a slower phase, which would presumably reflect a gradual release of vanadium from body tissues (World Health Organization, 2001).

In recent years the number of V-affected patients is ever increasing (Schwartz and Dockery, 1992). Since the 1940s, epidemiologists have reported the acute effect of vanadium on the workers who complain of allergic reactions such as asthma, conjunctivitis and rhinitis (Sjöberg, 1950; Browne, 1955; Musk and Tees, 1982; Kitani et al., 1998). Vanadium may be responsible for lung disease (Snyder, 1999). In the Panzhihua area, the lung disease was common among the workers engaged in vanadium production (Li Chaolun, 1994). Risks to human health and the environment will vary considerably, depending upon the type and extent of exposure to vanadium. Responsible authorities are

strongly encouraged to characterize risks on the basis of locally measured or predicted exposure scenarios (World Health Organization, 2001).

## 5 Conclusions

The Panzhihua area is the most famous base of V-Ti magnetite production in the world. Extensive mining and processing activities have caused severe environmental impacts. In the study area, vanadium is enriched in soil, air, water, sediment and plant. The anthropogenic vanadium is considered to have come from mining, extracting and smelting of V-Ti magnetite. Vanadium pollution in the topsoil and sediment is produced mainly in the mining and extracting area, smelting area, slag dumping area, and tailing dam and coal mining area. In the soil, the chemical speciation of vanadium shows: insoluble residue > organically bound > Fe (amorphous) oxide-bound > Mn oxide-bound > soluble component. Vanadium was intaken by plants in the industrial area (especially in the area where V-Ti-magnetite is mined and smelted) in the Panzhihua area. Vanadium pollution can cause potential harmful effects on ecological systems, and lead to animal poisoning and human disease. So vanadium contamination in the Panzhihua area needs to be monitored on a regular basis.

**Acknowledgements** The authors would like to thank the members of this consortium from Beijing Normal University and Chengdu University of Technology. Special thanks are also due to Prof. John Malpas, Dr. N.S. Duzgoren-Aydin of the University of Hong Kong and Dr. Qi Liang of the Institute of Geochemistry, Chinese Academy of Sciences.

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