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ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 1271−1278
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Soil vanadium pollution and microbial response characteristics from stone coal smelting district

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Received 23 April 2014; accepted 13 July 2014

Abstract: A field investigation was performed to study the content, speciation and mobility of vanadium, as well as microbial response in soil from a stone coal smelting district in Hunan province of China. The results showed that the contents of soil V ranged from 168 to 1538 mg/kg, which exceeded the maximum permissible value of Canadian soil quality for V. The mean soil V content from wasteland area reached 1421 mg/kg, and those from the areas related with slag heap, ore pile and smelting center were 380, 260 and 225 mg/kg, respectively. Based on the results of the modified BCR sequential extraction procedure, V contents in the mobile fractions varied from 19.2 to 637 mg/kg accounting for 7.4%−42.3% of total V, and those of V(+5) species were between 21.9 and 534.0 mg/kg. Soil enzyme activity and microbial basal respiration were adversely affected by high level of soil V. More attention should be paid to soil V pollution and potential hazardous surrounding the stone coal smelting district.

Key words: vanadium; soil pollution; mobility; microbial response; stone coal smelting district

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1 Introduction

Vanadium (V) is a ubiquitous trace element and the average content of V in soil of the world has been established at 90 mg/kg [1]. However, high content of V can be accumulated in soil due to anthropogenic sources, such as fossil fuel combustion, tailing leakage and metal plants [2]. Mining and smelting activities, especially for vanadiferous magnetite, cause V pollution widespread in many countries [3,4]. For instance, the total contents of V in soil from the vicinity of V mine in South Africa varied from 1570 to 3600 mg/kg [5], and the ranges of V contents in soil are 208−938 mg/kg from smelting area and 112−591 mg/kg from mining area in Panzhihua region of China [4].

Environmental increasing levels of soil V have raised many concerns [3]. Although the total content of V is still useful in many areas, the knowledge of speciation is of primary importance because the toxicity, mobility, bioavailability, and bioaccumulation depend on the chemical species [4]. The biological and physiological characteristics of V also depend on its oxidation states which primarily are +4 and +5 valent cations in minerals [6]. Generally, V(+5) is more mobile and more toxic to both plants and animals than V(+4) compounds [5], and it is essential to quantify V(+5) species in soil [7]. Furthermore, soil enzymatic activities are highly sensitive to trace metals and can reflect the structure and functions of microbial communities [8]. The high levels of V have an adverse effect on the soil microbial biomass and enzyme activities [9].

Vanadium compounds exist in over 50 different mineral ores and in association with fossil fuels, particularly coal and crude oil, which is mainly mined in South Africa, Russia and China [10]. Stone coal is an important source of V [11], and its resource has accounted for most of the domestic reserve of V resource in China, especially in western region of Hunan province [12], where there are intensive industrial activities of V extraction from stone coal. Soil V contamination from the vicinity of vanadiferous magnetite smelting areas in China was serious [4]. However, there is little information about soil V pollution, mobility as well as microorganism biochemical characteristics affected by industrial activities of V extraction from stone coal. In this study, the main aims were: 1) to study soil V pollution characteristics in different areas surrounding a

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Foundation item: Project (41201492) supported by the National Natural Science Foundation of China
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DOI: 10.1016/S1003-6326(15)63727-X

stone coal smelting district; 2) to elucidate V speciation, mobility and V(+5) species in soils; and 3) to determine the effect of V pollution on soil enzyme activities and basal respiration.

2 Materials and methods

2.1 Study area and soil samples collection

The study was conducted in the district surrounding a plant for V extraction from stone coal, which locates in southern Chenxi county, western Hunan province, China (Latitude of 28°10′12.40″−28°10′23.42″, Longitude of 110°13′18.81″−110°13′36.34″). The V smelting plant was set up and manufactured V_2O_5 product in 2005.

A total of 17 soil samples in the depth of 0−20 cm were collected from five areas around the V smelting plant in March, 2012, including ore pile area, smelting centre area, slag heap area, farmland area and wasteland area (Fig. 1). Area description and number of soil sample are summarized in Table 1. As a control, two soil samples from agricultural field, which is 1 km far away from the smelting district, were collected. Each soil sample consisted of five homogenized subsamples weighing about 1.5 kg, was placed in polyethylene bags and transported to the laboratory. After large pieces of plant material and stones were removed, soils were sieved through 2 mm mesh. Part of samples were kept moist in the dark at 4 °C for soil microbial activities analysis. The remaining soil samples were air-dried, crushed and sieved through 0.2 mm mesh for analysis.

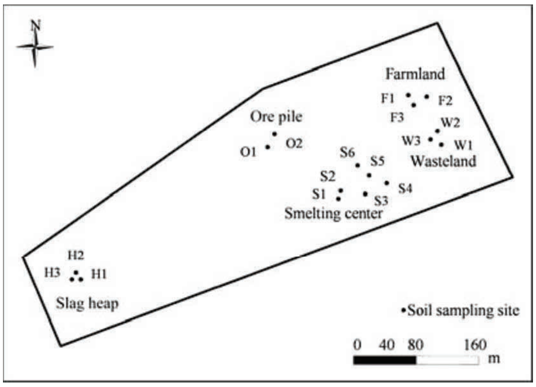

Fig. 1 Sampling sites surrounding V smelting district

Table 1 Description of soil samples collected from different areas surrounding V smelting district

Sampling area	Number of soil sample	Area description
Ore pile	O1−O2	Depository for ore, vegetables growing nearby
Smelting centre	S1−S6	Centre of the smelting plant including vicinity of chimney
Slag heap	H1−H3	Red soil covered by much slag
Wasteland	W1−W2	Soils appeared black with dusty smell
Farmland	F1−F3	Vegetables and vegetation grown in the soils
Control (CK)	C1−C2	Agricultural soil

2.2 Sample analysis

2.2.1 Soil physico-chemical properties

The physico-chemical properties of soil samples were analyzed according to the general methods described by LU [13]. The pH was determined using pH meter with a ratio of soil to deionized water of 1:2.5 (w/v). The content of organic matter (OM) was determined by a volumetric method of $K_2Cr_2O_7$-heating, and cation exchange capacity (CEC) was determined by extracting with a 1.0 mol/L NH_4OAc solution (pH 7.0). Free Fe_2O_3 and free Al_2O_3 in soil were extracted with a dithionite citrate system buffered with sodium bicarbonate, and amorphous Fe_2O_3 and amorphous Al_2O_3 were extracted with ammonium and oxalate under dark place, respectively. Then, they were determinated by spectrophotometric method.

2.2.2 Soil V species

Soil samples were digested with the mixture of HNO_3−H_2O_2 to determine the total V content [14]. The modified three-step Community Bureau of Reference (BCR) sequential extraction was described by RAURET et al [15] and applied to assessing V fractions in the samples. It basically consists of three extraction steps, i.e., extraction with 0.11 mol/L acetic acid (acid-extractable fractions), extraction with 0.5 mol/L hydroxylamine hydrochloride at pH 1.5 (reducible fraction), and reaction with 8.8 mol/L H_2O_2 followed by extraction with 1.0 mol/L ammonium acetate at pH 2 (oxidizable fraction). Additionally, residual fraction, which consisted of dissolving the final residue, was digested using the same digestion procedure described for total V determination [14].

Vanadium leachability from soil was determined using standard toxicity characteristic leaching procedure (TCLP) [16]. V(+5) species in soils were extracted with 0.1 mol/L Na_2CO_3 described by MANDIWANA and PANICHEV [17].

Concentrations of V in extractable and digested solutions were determined with an inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XSP, USA). The accuracy of the digestion procedure and analytical method was checked with standard reference material for soil (GBW−08303) obtained from China National Center, yielding analytical error <10%.