



Short communication

The leaching of vanadium(V) in soil due to the presence of atmospheric carbon dioxide and ammonia

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ABSTRACT

The natural leaching of vanadium(V) with CO_2 from soil-water in the presence of ammonia, a known precursor to atmospheric aerosols, has been tested by bubbling carbon dioxide through soil suspension with varying amount of ammonia. It was found that the leaching of V(V) is enhanced in the presence of ammonia. From the results of the investigation, it could be concluded that atmospheric CO_2 in the presence of ammonia (the only atmospheric gas that increases the pH of soil-water) could naturally leach V(V) from soil. Furthermore, it was also shown that the presence of $(\text{NH}_4)_2\text{CO}_3$ in soil could enhance the leaching of toxic V(V) species thereby making it bioavailable for both plants and animals.

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1. Introduction

The properties of an element depend on its oxidation state and hence the identification and accurate quantification of different species are essential in evaluating the comprehension of its biological and physiological functions, as well as potential toxicity. Vanadium is a metal which exists in oxidation states ranging from 0 to +5, although the forms naturally found in the environment are +3, +4 and +5 [1]. It is generally recognized that its biological action depends on its oxidation state and its toxicity increases as the valence increases, that is why pentavalent compounds are the most toxic [2,3].

Vanadium at trace amounts represents an essential element that is generally known to have insulin-mimetic activity demonstrated both in animal models and in clinical studies on a limited number of diabetic subjects [4]. However, numerous reports have warned of the carcinogenicity and toxicity of vanadium at higher concentrations [5,6]. Vanadium poisoning symptoms reported include nervous depression, kidney failure, heart attack, anaemia and lung cancer [7]. On the other hand, vanadium's presence in soil at concentration lower than 2 ppm is positive as it enhances chlorophyll synthesis, potassium consumption or nitrogen assimilation but at higher concentrations it causes chlorosis and limit growth [8].

Ammonia, a component of the atmosphere, plays a major role in the neutralization of cloudwater and aerosols [9]. Deposition of ammonia and ammonium compounds contributes to water and soil acidification and may cause forest damage [10]. Though ammonia gas has a relatively short lifetime in the atmosphere of a few hours to a few days, the ammonium ion, in contrast, as an aerosol, has a lifetime on the order of 1–15 days [11]. The ammonium ion in soil-water system could typically react with insoluble vanadates to form soluble ammonium vanadate thereby transferring toxic V(V) into solution, making it mobile and available to living things. The accumulation of V(V) in both plants and animals including humans could ultimately result in symptoms of vanadium poisoning.

There are several sources of ammonia gas into the environment, viz., fertilizer application, mobile sources, industry, waste water treatment plants, human breath and perspiration, forest burning and slash burning, livestock waste, etc. Atmospheric ammonia is eventually deposited to land and water where it can leach V(V) from soil-water system in the presence of atmospheric CO_2 [12–15].

Studies have also shown that nitrogen in the urine of livestock is in the form of urea, $\text{CO}(\text{NH}_2)_2$, that hydrolyze to form ammonium carbonate [16]. As shown in the following reactions, the decomposition of ammonium carbonate in soil frees up ammonium ions during hydrolysis which is facilitated by the enzyme urease, that is abundant in soils and plant roots as well as in animal feces [17,18]:



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The ammonium ions can then interact with insoluble vanadate compounds thereby transforming them to soluble compounds and make them available to both plants and animals.

In the present study, the natural leaching of V(V) from soil with CO_2 in the presence of ammonia was investigated. Soils collected around Vametco, South Africa, one of the world's leading producers of vanadium minerals were the subject of this study and vanadium content was quantified by electrothermal atomic absorption spectrometry (ET-AAS).

2. Experimental

2.1. Instrumentation

A PerkinElmer Atomic Absorption Spectrophotometer model AAnalyst 600 with Zeeman background correction system was used for all measurements. The Analyst 600 spectrophotometer was equipped with AS-800 autosampler and the whole system has been controlled by means of AAWinlab control software running under Microsoft Windows program. All determinations were carried out at analytical line of V 318.4 nm, with a 0.7 nm band pass using hollow cathode lamp of vanadium, operating at 25 mA. The tubes of transversely heated graphite atomizer with integrated L'vov's platforms were used for atomization of vanadium.

2.2. Reagents and standard solutions

Standard stock solution containing 1000 mg l^{-1} V(V) as NH_4VO_3 (Merck) was used for the preparation, by appropriate dilution, of working standards. Ultra-pure water (resistivity $18.2 \text{ M}\Omega$) was obtained with Milli-Q water purification system (Millipore Corp., USA) and had been used for all dilutions and samples preparation. Ammonia, 25% (v/v), $(\text{NH}_4)_2\text{CO}_3$ (Rochelle, South Africa) and $(\text{NH}_4)_2\text{HPO}_4$ (Rochelle, South Africa) were used to leach V(V) from soil. CO_2 (Afrox, South Africa) was used to leach V(V) from soil samples. A mixture of HNO_3 (Merck) and HCl (Merck) was used to dissolve the residue after ashing the sample. Argon (Afrox, South Africa) was used as a protective gas throughout.

3. Analytical procedure

3.1. Samples

Soil samples were collected around Vametco vanadium mine in the field with history of cattle poisoning [5]. The soil samples representing the upper soil layer were dried and homogenized by grinding in an IKA A11 milling system to a grain size less than $200 \mu\text{m}$.

3.1.1. Leaching of V(V) in soil with CO_2 in the presence of ammonia

Approximately 1.0 g soil in 250.0 mL deionized water was left undisturbed for 24 h in a plastic bottle. One milliliter of sample was filtered through hydrophilic PVDF $0.45 \mu\text{m}$ filter and analyzed for V(V) by ET-AAS. Carbon dioxide was bubbled continuously through the suspension of soil at a flow rate of 50 mL min^{-1} and the sample was filtered and analyzed every 10 min for periods of time ranging from 0 to 2 h to determine the concentration of V(V).

On another experiment, approximately 1.0 g soil was transferred into a plastic bottle, 250 mL of deionized water was added and ammonia solution (5.00 mL) was added periodically into the soil suspension while bubbling CO_2 at 50 mL min^{-1} . The sample solution (1 mL) was then filtered through hydrophilic PVDF $0.45 \mu\text{m}$ filter and analyzed every 10 min by ET-AAS to determine the con-

centration of V(V) leached in time intervals in the presence of ammonia.

3.1.2. Leaching of V(V) with $(\text{NH}_4)_2\text{CO}_3$

Twenty-five milliliters of 10^{-3} to 2 M $(\text{NH}_4)_2\text{CO}_3$ were added to approximately 0.25 g of soil, accurately weighed in separate 100 mL glass beakers. The contents in each beaker was boiled for 5 min, allowed to cool to room temperature and diluted to 25.00 mL in a 50 mL plastic tube. One milliliter of the sample solution was filtered through hydrophilic PVDF $0.45 \mu\text{m}$ filter prior analysis by ET-AAS. Similarly, approximately 0.25 g of soil was left overnight in 25.00 mL in 1 M $(\text{NH}_4)_2\text{CO}_3$ to evaluate the leaching ability of this reagent solution at room temperature.

4. Results and discussions

4.1. The leaching of V(V) from soil in the presence of ammonia

The analytical signals representing the amount of V(V) leached by water, saturated solution of carbon dioxide and saturated solution of carbon dioxide in the presence of ammonia, are shown in Fig. 1. The results show that the presence of ammonia in a soil suspension saturated with CO_2 enhances the leaching of V(V) from soil. The results of the investigation showed that the leaching of V(V) compounds from soil increases as the pH increases due to addition of ammonia (Fig. 2). From this observation it could be concluded

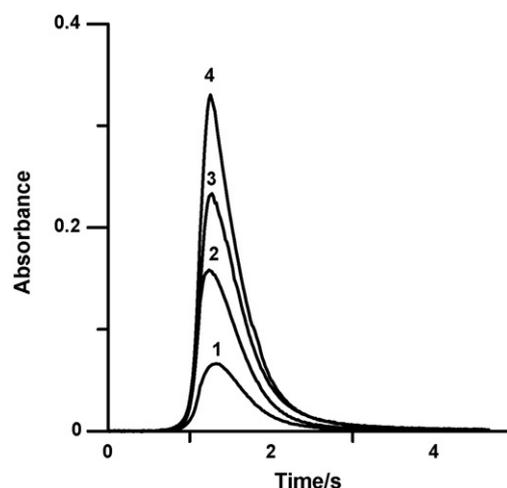


Fig. 1. Absorbance signal representing the amount of V(V) extracted by (1) water; (2) water saturated with CO_2 ; (3) water during the bubbling of CO_2 in the presence of ammonia after 30 min; (4) water during the bubbling of CO_2 in the presence of additional ammonia after 60 min.

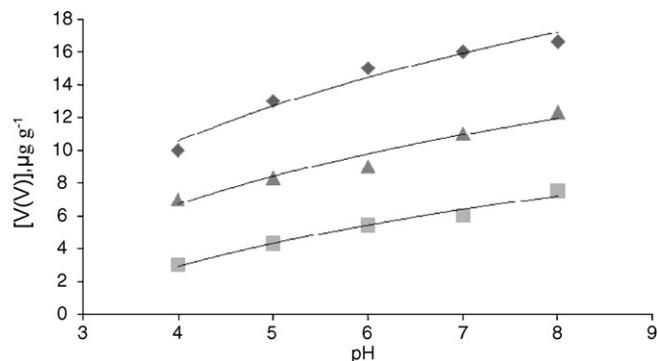


Fig. 2. Concentration of V(V) leached with CO_2 as a function of the pH as ammonia is added: (■) soil 115; (▲) soil 225; (◆) soil 335.

Table 1
Results of the determination of vanadium(V) in soil samples.

Sample	Water-soluble [V(V)] ($\mu\text{g g}^{-1}$)	[V(V)] ^a ($\mu\text{g g}^{-1}$)	[V(V)] ^b ($\mu\text{g g}^{-1}$)	[V(V)] ^c ($\mu\text{g g}^{-1}$)	Total [V] ^d ($\mu\text{g g}^{-1}$)
Soil 110	1.4 ± 0.1	14.7 ± 0.5	30.2 ± 1.2	41.8 ± 0.8	7155 ± 210
Soil 220	2.2 ± 0.3	6.0 ± 0.4	11.6 ± 0.8	16.5 ± 1.0	685 ± 25
Soil 230	0.6 ± 0.1	4.4	9.2 ± 0.3	12.0 ± 1.2	490 ± 40
Soil 440	298 ± 15	285 ± 22	625 ± 35	1520 ± 105	2790 ± 200

^a Soluble V(V) in un-boiled 1 M (NH₃)₂CO₃.

^b V(V) leached with one portion of 1 M (NH₃)₂CO₃.

^c V(V) leached with 1 M (NH₄)₂HPO₄.

^d Total vanadium concentration obtained after complete acid digestion.

that the leaching of V(V) with CO₂ in soil in the presence of ammonia is enhanced due to an increase in CO₃²⁻ ions (as pH increases) that ultimately react with vanadate ions. The highest concentration of V(V) was leached at pH 8 as further increase of pH was not possible due to the formation of buffer between the weak acid (H₂CO₃) and weak base (NH₃).

4.2. The leaching of V(V) from soil with (NH₄)₂CO₃

In order to obtain the maximum level of V(V) that can be extracted with (NH₄)₂CO₃ from soil, various concentrations of (NH₄)₂CO₃ ranging from 1 × 10⁻³ to 2 M were utilized and the results of such extraction are shown in Fig. 3. The results show that the amount of V(V) leached is proportional to the concentration of (NH₄)₂CO₃ and 1 M extracted high levels of V(V). The amount of V(V) extracted by 1 M (NH₄)₂CO₃ was equivalent to approximately 75% of total vanadium(V) as determined after leaching with 1 M (NH₄)₂HPO₄ (Table 1). Therefore, V(V) was leached completely with 1 M (NH₄)₂CO₃, only after the second leaching of the same sample with fresh portion of the leaching reagent solution. Furthermore, it was found that approximately 50% of the total concentration of V(V) is leached with 1 M (NH₄)₂CO₃ at room temperature in 24 h.

4.3. Mechanism behind the leaching of V(V) from soil

The equilibria in a saturated solution of carbon dioxide (25 °C) are expressed by

$$\text{CO}_2(\text{g}) = \text{CO}_2(\text{aq}) \quad K = \frac{[\text{CO}_2]}{P_{\text{CO}_2}} = 0.0337$$

$$\text{CO}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{HCO}_3^- \quad K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = 4.4 \times 10^{-7}$$

$$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-} \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11}$$

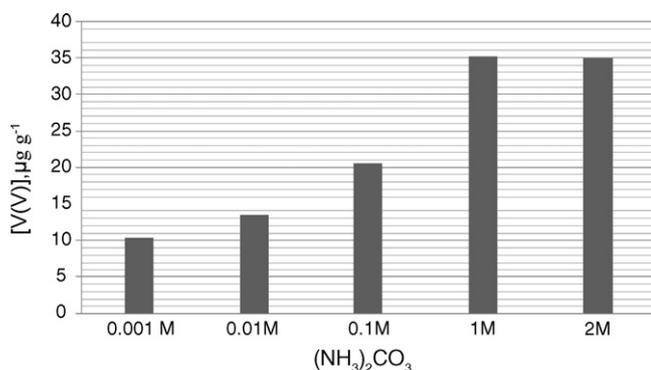
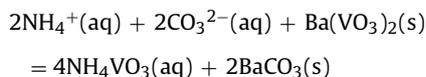
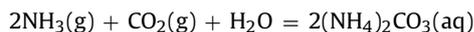


Fig. 3. Leaching of V(V) in soil with different concentrations of (NH₄)₂CO₃.

The ion product (ip) of carbon dioxide is obtained by multiplying these constants together with the pressure of carbon dioxide, i.e. $KK_1K_2P_{\text{CO}_2} = K_{\text{ip}} = [\text{H}^+]^2[\text{CO}_3^{2-}]$. At 25 °C and a pressure of 1 atm, the value of this constant is 7.0×10^{-19} . The saturated solution of CO₂ has a pH of 4.58 which represent 1×10^{-9} M carbonate ion concentration [19]. The addition of ammonia increases the pH to approximately 7.3 thereby increasing the concentration of CO₃²⁻ in solution by many orders of magnitude with the formation of (NH₄)₂CO₃(aq). The carbonate ions transfer insoluble vanadate complex into solution with the formation of soluble ammonium vanadate as shown by the following reaction equations:



Therefore, it can be concluded that the leaching of V(V) in soil-water with CO₂ is enhanced in the presence of ammonia and that NH₃ is the only gas in the atmosphere that naturally increases the pH of soil.

5. Conclusions

The results of the investigation showed that V(V) is leached from soil by bubbling CO₂ through soil suspension containing ammonium ions. The rate of leaching would depend on the pH of the soil solution. This implies that in the environment, the presence of atmospheric CO₂ and ammonia enhances the leaching of V(V) from soil thereby making it bioavailable to both plants and animals.

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