

Removal of Ammonium from Wastewater with the Mineral Vermiculite – Using PIGE for Nitrogen Monitoring

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Abstract. Solid samples were irradiated with a 4.2 MeV proton beam in a specially built chamber. The ion beam was extracted out of the cyclotron vacuum system through a 4 µm thick nickel foil. A helium gas flow of 10 cm³/min was used to avoid interference from atmospheric nitrogen and oxygen. The emitted gamma radiation was measured with an HPGe coaxial detector located behind the chamber. The reaction ¹⁴N(p,p'γ)¹⁴N was employed for the determination of nitrogen. The peak at 1454 keV from the nickel foil was used for the normalisation. A pressed pellet of KNO₃ was used for nitrogen calibration. The method was evaluated using six different biological certified reference materials. A synthetic tobelite mineral was also used in the evaluation. The limit of detection for nitrogen in the mineral samples was about 1 mg/g. The set-up was applied for the determination of the total amount of nitrogen in vermiculite. The mineral vermiculite was treated in different ways to optimize for the ammonium uptake. The experiments were performed by doping samples in ammonium solutions and by analysing the samples with PIGE. The aim of the study was to find a product that could be used for the removal of ammonium from wastewater.

Keywords: Nitrogen, ammonium, PIGE, vermiculite.

INTRODUCTION

Vermiculite is a naturally occurring, phyllosilicate mineral consisting of two tetrahedral layers with an octahedral layer in between. Vermiculite clays are weathered micas in which the K⁺ ion between the molecular sheets, the interlayer, are replaced by hydrated Mg²⁺. The weak bonding afforded by these hydrated cations allows vermiculite to expand by heating. The hydrated cation in the interlayer is exchangeable to other cations. Exfoliated vermiculite has been commercially used as insulators and soil conditioner.

The discharge of large amounts of nitrogen into natural waters constitutes a serious environmental problem causing growth of nuisance algae. Therefore it is of interest to develop methods for nitrogen removal from wastewater. In this study the cation exchange properties of the clay mineral vermiculite were used to reduce the nitrogen content in the water.

Hydrated cations, mainly Mg²⁺, in the interlayer are then exchanged with ammonium (NH₄⁺).

The present study required a method for the determination of the total nitrogen concentration in the vermiculite product after doping with ammonium from an aquatic solution. The main requirements for the analytical method were that it should enable analysis of a large number of samples from different doping experiments and that the sensitivity should be in the per mill range. Encouraged by good results from direct particle-induced gamma-ray emission (PIGE) analyses of other light elements [1, 2] and partly also because of an increasing request for nitrogen analyses in general, an attempt was made to use PIGE for the direct analysis of pressed sample pellets of the doped vermiculite.

The principles of the PIGE method are well described in review articles [3, 4] and in the comprehensive work of Bird and Williams [5]. Measured gamma-ray yields for a number of energies

and particles have also been published [4, 6, 7]. These yields are useful in the interpretation of the gamma-ray spectra. The applicability of PIGE for the determination of nitrogen has been investigated earlier by Hänninen and Räsänen [8]. The kinetic energy of the incident protons and the thickness and composition of the exit foil were factors affecting the sensitivity of the method [8].

Several nuclear analytical techniques have been used for direct measurements of the nitrogen content. Both particles and gamma rays produced by nuclear reactions can be measured in nuclear reaction analyses (NRA). The nuclear reactions (d,p_0) and (d,α_0) have been used to detect nitrogen with a deuterium beam energy above 1.6 MeV. A deuterium microprobe has been applied to study ammonium-bearing minerals [9].

EXPERIMENTAL

Sample Preparation

The vermiculite samples used in this study were obtained from Kovdor (Russia), Grace VCX (Virginia, USA) and from Sanrec (Uganda). The crude vermiculite samples were ground and heated to 440°C. The samples were treated at room temperature in ammonium solutions. After the treatment they were flushed with deionised water to remove all excess ammonia solution from the surface, and dried at 50°C for 24 hours.

Elemental Analysis

The vermiculite samples were irradiated with an 8.8 MeV H_2^+ -ion beam from the Åbo Akademi MGC-20 cyclotron. The ion beam was collimated to a diameter of 2.5 mm and extracted out of the cyclotron vacuum system through a 4 μ m thick nickel foil (Goodfellow Cambridge Limited, NI000220). A specially built chamber was used for the irradiation (Fig. 1). The construction was based on a DN 50 flange and had a volume of 20 cm³. A helium gas flow of 10 cm³/min was used during the irradiation to avoid interference from atmospheric nitrogen and oxygen. Analyses of a nitrogen-free sample performed without the helium gas flow yielded a peak from atmospheric nitrogen corresponding to a concentration of 3 % in the sample. At impact with the exit foil the H_2^+ ions split into two 4.4 MeV protons. The energy loss of the protons was about 200 keV in the foil and in the helium gas resulting in an incident energy of 4.2 MeV. According to Hänninen and Räsänen [8] the optimum energy region for the $^{14}N(p, \gamma)^{14}N$ reaction is 4-4.5 MeV.

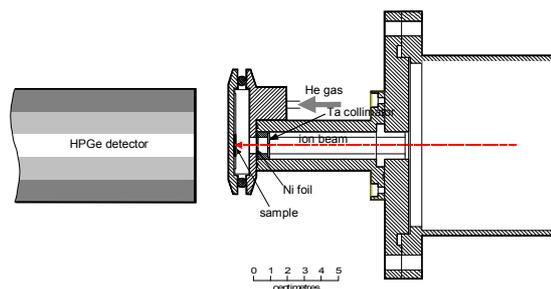


FIGURE 1. Schematic diagram (upper view) of the experimental set-up for determination of total nitrogen concentrations.

The emitted radiation was measured with an EG&G ORTEC high-purity germanium (HPGe) coaxial detector located 22 mm behind the flange of the chamber (Fig. 1). The relative detector efficiency at 1.33 MeV was 20.7 % and the resolution was 1.74 keV according to the quality assurance data sheet. The samples were irradiated for about 10 min and the obtained spectra were analysed for peak areas off line using SAMPO90 [10]. The peak area at 1454 keV from nickel (nickel extraction foil; $^{58}Ni(p,p'\gamma)$) was used for the normalisation of the other peak areas. The peak area from the nickel foil is proportional to the integrated charge on the sample. A pressed pellet of KNO_3 was used for calibration. The spectroscopic background was determined using a pellet of pure graphite. There were no peaks from nitrogen in the background. The method was evaluated using different certified reference materials (CRMs). Mainly biological CRMs were used due to lack of suitable geological reference materials.

RESULTS AND DISCUSSION

Analytical Considerations

Most of the gamma rays from ^{14}N (2313 keV) are due to a strong resonance at the proton energy 3903 keV of the $^{14}N(p,p'\gamma)^{14}N$ reaction. This proton energy corresponds to a depth of about 17 μ m in the sample. The resonance is very narrow ($\Gamma=106$ keV) and the mass analysed will therefore be very small (0.1 mg). On the other hand the method is not sensitive to traces of N_2 in the chamber nor to surface contamination of the sample. It is, however, important to choose a homogeneous sample for calibration. Repeated analyses of different spots on the pressed sample of KNO_3 show very small variations in the normalised yields (1 %, n=4). The linearity of the nitrogen concentrations versus the peak areas was tested with Energy Forest NJV 94-3, Energy Grass, NJV 94-4, Pine Needles NIST 1575, Energy Peat NJV94-1, Beech Leaves BCR 100 and Tomato Leaves NIST

1573 (Fig. 2). There are very small discrepancies from the calibration line obtained for the pressed pellet of KNO_3 .

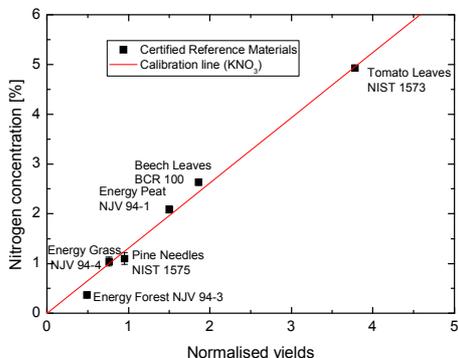


FIGURE 2. Certified nitrogen concentrations versus normalized peak areas for biological certified reference materials. The straight line shows the calibration obtained by KNO_3 .

The gamma energy 2313 keV corresponds to a transition from the 0^+ level to the ground level 1^+ in the ^{14}N nuclei [11]. The lifetime of the 0^+ level is 68 fs. The peak shape is Doppler shifted against higher energies due to the short lifetime and the measuring geometry (Fig. 1). The non-Gaussian peak shape renders some difficulties to the spectral analysis, but the detection limit is still low enough (1 mg/g) for the doping experiments.

In the analyses of geological materials, the use of the nickel peaks for normalisation is biasing if the sample itself contains nickel. To estimate the possible error a copper-nickel coin containing 25 % of nickel was irradiated and the peak areas were normalised with the peaks from the tantalum beam collimator at 136 keV. The obtained nickel peak at 1454 keV was about 100 % higher compared to the nickel peak in a spectrum of graphite. As the nickel concentration of the vermiculite samples was about 400 $\mu\text{g/g}$ when measured with particle X-ray emission analyses (PIXE) the contribution to the nickel peak area was thus less than 0.2 %.

As a further test the concentration of nitrogen in a pressed sample of synthetic tobelite [12] was determined. The obtained concentration was 3.55 ± 0.25 %. The concentration calculated from the formula $(\text{NH}_4)\text{Al}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$ is 3.71 %. The heat problem in nitrogen analysis of tobelite known from the use of electron microprobes [12] is apparently not a problem using a proton millibeam and currents less than 1 nA.

Effect of Grain Size on Ammonium Uptake

The grain size is of importance for the uptake of ammonium. Smaller grain sizes imply that larger areas

are in contact with the solution. But at a certain limit the mineral structure changes and the ability to exchange ammonium is lost. In the doping experiments 1 g of ground sample was mixed with 100 ml of the aqueous phase.

Two series of vermiculite samples were analysed with PIGE (Fig. 3). The A series of samples was treated at room temperature with 1800 mg/dm^3 ammonium solution for 24 h and the B series with a ten times more concentrated solution for 24 h as well. Three grain sizes 0.125–0.25 mm, 0.25–0.50 mm and 0.5–1.0 mm were used. In the figure the measured nitrogen contents are plotted against the median grain size in the interval. In the rest of the experiments the samples were ground to 75–125 micron grain size and doped in 10 000 mg/dm^3 ammonium solutions.

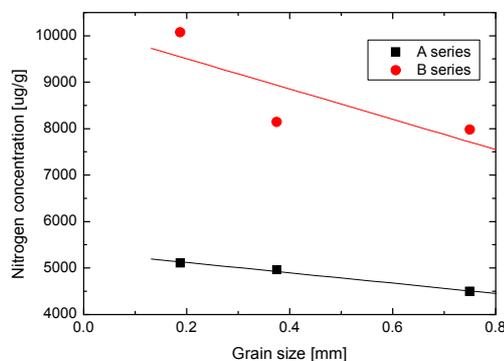


FIGURE 3. Nitrogen concentrations in doped vermiculite samples of three different grain sizes.

Ion Beam Characterisation of the Product

The crude vermiculite materials normally contain several other minerals as well, especially unaltered micas or other alteration products from the micas. These have a poor ability for cation exchange. It is therefore important to investigate different products to find a product with a high vermiculite content in order to maximize the uptake of ammonium.

Prior to the doping the concentrations of the main elements Si, Al and Mg in the crude vermiculite samples were determined. The nitrogen concentrations in these undoped samples were below the detection limit. In addition several other elements were determined in a separate run using the particle-induced X-ray emission technique (PIXE) and 3 MeV protons. The PIXE set-up at the Åbo Akademi University has been described in detail elsewhere [13, 14]. After the doping process the samples were re-analysed with PIGE to obtain the nitrogen concentration. The results of the ion beam analyses of vermiculite samples from different sources are listed in Table 1.

The vermiculite sample from the museum in Kovdor has the lowest concentration of potassium and calcium and the highest uptake of nitrogen (Table 1). The sample from Virginia contains a lot of potassium and calcium and the nitrogen uptake is low. An explanation is that the high potassium concentration hints for a high content of primary minerals such as phlogopite. Phlogopite has a lot of K^+ strongly bonded in the interlayer that is not exchangeable with ammonium.

TABLE 1. Crude vermiculite samples analysed with PIXE and PIGE. The N, Mg, Al and Si concentrations have been determined with PIGE and the other elements with PIXE. Nitrogen is determined in doped samples.

Element		Kovdor Vermipu	Kovdor Museum	Uganda Samrec	Virginia VCX
N	µg/g	4300	8400	6500	1500
Mg	%	15.6	14.5	10.6	12.4
Al	%	7.0	6.9	9.0	8.3
Si	%	17.2	14.1	17.8	18.8
K	µg/g	230	160	6700	50000
Ca	µg/g	4950	670	4260	18930
Fe	%	5.3	6.2	10.5	7.8

The hydrated cations Na^+ , Mg^{2+} , Ca^{2+} and Ba^{2+} in the interlayer of vermiculite can be exchanged with NH_4^+ . The hydrated Mg^{2+} ion is exchanged with four ammonium ions [15]. According to the cation exchange capacity value (CEC) of 120-150 meq/100 g [16] for vermiculite the maximum uptake of ammonium nitrogen would be about 3.4-4.2 % and the corresponding loss of magnesium about 1.4-1.8 %. However, most of the magnesium is located in the octahedral sites and will not be exchanged. It is therefore difficult to measure the loss although the interlayer magnesium plays an important role in the cation exchange.

The analytical results obtained by PIGE have been used for improving the uptake of ammonium in vermiculite [17] and the obtained vermiculite product has been used in larger scale for removal of nitrogen in wastewater from fox farms in Ostrobothnia, Finland [18].

CONCLUSIONS

An ion-beam set-up for the direct determination of the total nitrogen content in solid geological samples was developed. The helium flow prevented interference from atmospheric nitrogen. Normalisation based on the peak areas from the nickel foil should be used with precaution when analysing materials containing more than 1 % of nickel. The calibration of the method was evaluated by analysing synthetic tobelite and biological standard reference materials. KNO_3 was found suitable for calibration. The method was applied in a study of the ability for vermiculite to fix ammonium. The ground vermiculite product was

doped in ammonium solutions and analysed with particle-induced gamma-ray emission (PIGE) and particle-induced X-ray emission (PIXE). The results were applied for improving the vermiculites uptake of ammonium ions and its use for removing ammonium from wastewater.

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