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DTA OF Pt EXCHANGED VERMICULITE MINERAL

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DTA curves of Pt and Pd exchanged vermiculite mineral samples are presented. The minor structural changes brought by introduction of these cations in Mg and Ni vermiculites are explained. Results of chemical analysis and XRD are also discussed.

Transition metal ions exchanged clay minerals have been found recently to be of high applied interest [1–3]. Pt and Pd exchanged minerals are likely to be of further catalytic interest as these metals are already known to be of having catalytic affect with zeolite etc. [4–6]. Although a number of transition metal ion exchanged (Cu, Ni, Mn) smectites are reported, Pt and Pd exchanged clay minerals have rarely been synthesized [7] and therefore these products are of fundamental interest also.

Cations are exchanged into the interlayer space of the clay mineral normally from the chloride or nitrate salts of the cations. In case of Pt in particular such simple salts can not be employed. One could wonder whether the complexes made out of these cations of big dimensions can be introduced which does not pose problem for exchanging Cu, Ni, Ca, Al etc.

Experimental method

The vermiculite is from Prayssac, South of France which has been thoroughly characterized by the author [8]. Sample of fraction in 50 μ has been taken for study here.

The mineral is repeatedly washed with water and then sieved in wet condition. The exchange of Mg of the natural vermiculite to Ni^{2+} is done in very weak acidic medium to avoid precipitation of $Ni(OH)_2$. The p_H of suspension was 7.5 to which few drops of N/100 HCl was added to bring the p_H to 3.5.

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The contact period was half an hour after which the suspension was centrifuged. The vermiculite was then reacted with 2N $NiCl_2$ for (16 h) four times; each time the washing was done with distilled water. The last three exchanges were made with 1N $NiCl_2$. After each washing it was verified that no chloride ions remain in the suspension before next exchange process. The need to pass through minor acid condition has been explained previously [7]. This allows to have maximum base exchange possible with one cation only. In this case, Ni could be exchanged with almost total elimination of other interlayer cations. Unless the first exchange is made with H^+ present in acid, the exchange of Mg and other ions to Ni becomes partial only. It was examined in XRD that the contact with acid did not change the structure of the mineral.

The bi–ionic vermiculite (Ni–Pt) and (Ni–Pd) minerals were prepared from the above Ni–vermiculite. For exchange of Pt, $Pt(NH_3)_4Cl_2$ and for Pd, $Pd(NH_3)_4Cl_2$ solutions were taken. The tetrammine complexes of Pt and Pd were taken instead of the chloride salts because of insolubility in water of the latter. The tetrammine complexes of Pt and Pd were prepared by adding the Pt and Pd chloride salts separately to a boiling solution of NH_4OH. The NH_4OH added was in excess of the stoichiometric composition.

The DTA equipment used was "Setaram". The analysis was carried out in air with a heating rate of 600 deg/h. About 8 mg of the mineral was taken for each analysis.

Results and discussion

Chemical analysis of the samples are reported previously [2]. The structural formula are as follows:

a) Natural vermiculite before exchange:

$$(Si_{2.82}Al_{1.17})\ (Mg_{2.36}Al_{0.205}Fe^{3+}_{0.475}Fe^{2+}_{0.004})\ Mg_{0.245}\ K_{0.051}\ Na_{0.001}\ O_{10}\ (OH)_2$$

b) Ni–vermiculite

$$(Si_{2.82}Al_{1.17})\ (Mg_{2.36}Al_{0.205}Fe^{3+}_{0.475}Fe^{2+}_{0.004})\ Ni_{0.27}\ O_{10}\ (OH)_2$$

c) Mg–Pt vermiculite

$$(Si_{2.82}Al_{1.17})\ (Mg_{2.36}Al_{0.205}Fe^{3+}_{0.475}Fe^{2+}_{0.004})\ Mg_{0.267}\ Pt_{0.003}\ O_{10}\ (OH)_2$$

d) Ni–Pt vermiculite

$$(Si_{2.82}Al_{1.17})\ (Mg_{2.36}Al_{0.205}Fe^{3+}_{0.475}Fe^{2+}_{0.004})\ Ni_{0.267}\ Pt_{0.003}\ O_{10}\ (OH)_2$$

e) Ni–Pd vermiculite

$$(Si_{2.82}Al_{1.17})\ (Mg_{2.36}Al_{0.205}Fe^{3+}_{0.475}Fe^{2+}_{0.004})\ Ni_{0.175}\ Pd_{0.095}\ O_{10}\ (OH)_2$$

It can be seen thet the exchange process has not changed the composition of the tetrahedral and octahedral layers.

The DTA curves of Mg and Mg–Pt vermiculite are shown in Fig. 1 and for Ni–Pt and Ni–Pd in Fig. 2. The first endothermic peak representing the removal of first layer of interlayer water molecules (vermiculite is known to have two layers of water molecules in the interlayer space complexing of course the cations), is seen in all the four mineral samples around 120°. However, in case of Ni–Pd vermiculite sample, this peak was found to occur at 119° but without any sharp thermal change unlike in other samples. This peak occurs at 124° in the naturally occurring vermiculite (Fig. 1). The exchanged minerals show the interlayer water molecules to be slightly less strongly held (equivalent to 3-4°) than the initial mineral.

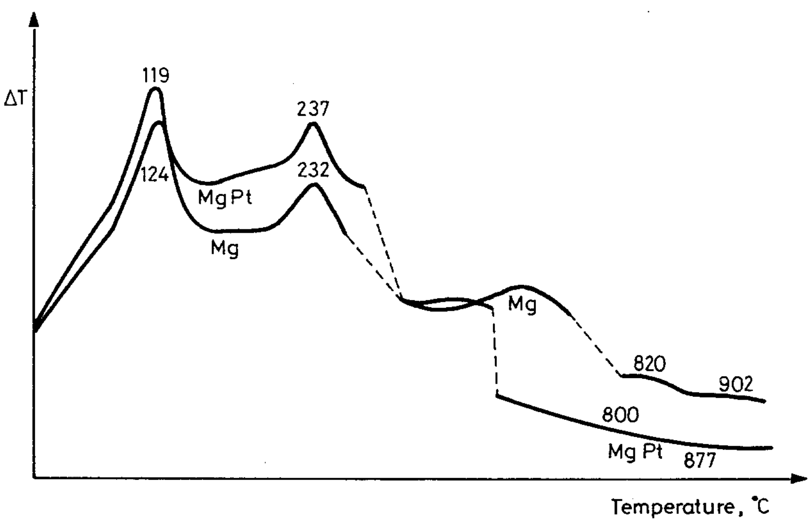

Fig. 1 DTA curves of Mg and Mg–Pt vermiculites

The endothermic peak at about 235° is quite distinctive in the four mineral samples specially in Ni–Pd vermiculite where it was found to have disappeared. The temperature for occurring this peak in natural mineral is

232° which is retarded by 5° in Mg–Pt and by 13° in case of Ni–Pt vermiculite. Pt ion thus retains the water molecules with higher binding energy than in naturally occuring mineral; Pt forms a strong complex with water molecules in the interlayer space. Lack of appearance of this second peak in case of Ni–Pd vermiculite shows that only a single layer of water molecules is formed here; of course it is not totally absent.

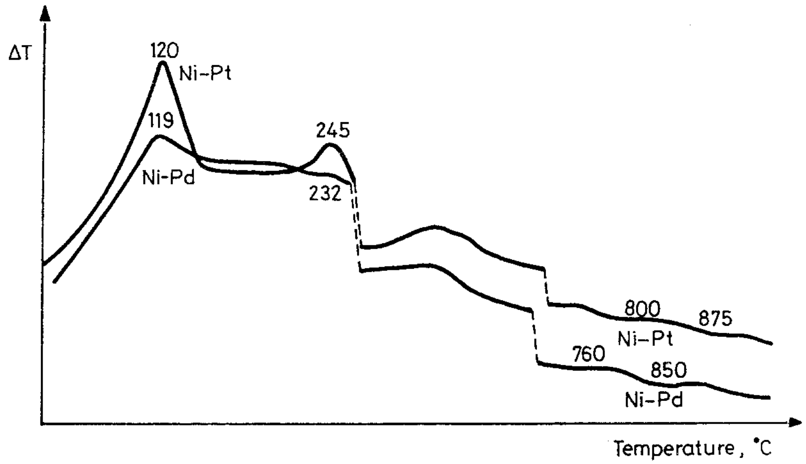

Fig. 2 DTA curves of Ni–Pt and Ni–Pd vermiculites

The transformation of the phyllosilicate structure to the oxide phases takes place earlier in case of the exchanged vermiculite than in the natural vermiculite. It is represented by a peak which is slightly more distinct in Ni–Pd than in the other three mineral samples.

Conclusions

Introduction of Pt in the interlayer space having either Mg or Ni ions does not bring in any thermal change while Pd-containing Ni-vermiculite is thermally different than the other mineral. However, it may be concluded that Pt and Pd can be incorporated in the interlayer space without major structural change.

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Zusammenfassung — DTA-Kurven von Pt- und Pd-versetzten Vermikulitmineralproben werden beschrieben. Es wird eine Erklärung für kleinere Strukturveränderungen gegeben, die durch den Einbau dieser Kationen in Mg- und Ni-Vermikulit auftraten. Ergebniße aus chemischer und röntgenografischer Analyse werden ebenfalls diskutiert.