The Science Reports of the Kanazawa University, Vol. III, No. 1, pp.187—192, March, 1955.

On the Hydrated Halloysite from Wajima, Ishikawa Prefecture, Japan

By

Seizi SUGIURA

(Received December 1, 1954)

Abstruct

The milky white clay mineral found in the "fire-clay" from Wajima city, Ishikawa Prefecture, has been determined to be hydrated halloysite with the composition, $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$. The mineralogical data are as follows : hardness 2.5, specific gravity 2.33, index of refraction $n = 1.527 \sim 1.532$. The chemical analysis by K. Kasama, SiO_2 39.78, Al_2O_3 34.69, Fe_2O_3 0.55, CaO 0.36, MgO 0.28, K_2O 0.57, Na_2O 0.16, H_2O 22.78, total 99.17%. The X-ray powder diagram and D. T. A. curve of the mineral are similar to those of the hydrated halloysite from Joshin mine, described by T. Sudo.[*4)]

Introduction

In July 1953 the writer investigated the fire-clay deposit of Noto Province which had been known as "Hotozuna" clay used in making fire brick. The Hotozuna clay had high refractoriness and a milky white clay mineral was found in the clay deposit. The investigation of the mineral was made, using optical, chemical, X-ray, thermal and other methods.

Occurrence

The "fire-clay" is found in several deposits in Wajima District. The mineral in question is occurred in two of them. The one is known as the "Hotozuna" clay deposit at Ichinosaka, and the other is a clay deposit near Sue. These localities consist of Anamizu formation of Miocene, Tertiary.

The detailed stratigraphy is as follows;

Anamizu Formation (Miocene, Tertiary)
- Sadahiro beds (grayish tuff)
- Komata beds (alternation of tuff and tuffaceous sand)
- Konogi beds (volcanic conglomerate)
- Agglomerate beds

The "Hotozuna" clay deposit is in Komata beds which consist of alternation of andesitic tuff and tuffaceous sand. The rocks are partly changed to clay by hydrothermal alteration and rich in quartz grains. The mineral fragments in question of $2 \sim 3$ cm diameter are containd in the lower part of the altered zone. The Sue clay deposit is in Sadahiro beds. Sadahiro beds consist mainly of middle or fine grained grayish tuff,

and partly of breccia or agglomerate. These rocks have few quartz grains, and the mineral in question is fine-grained with maximum 5 mm diameter.

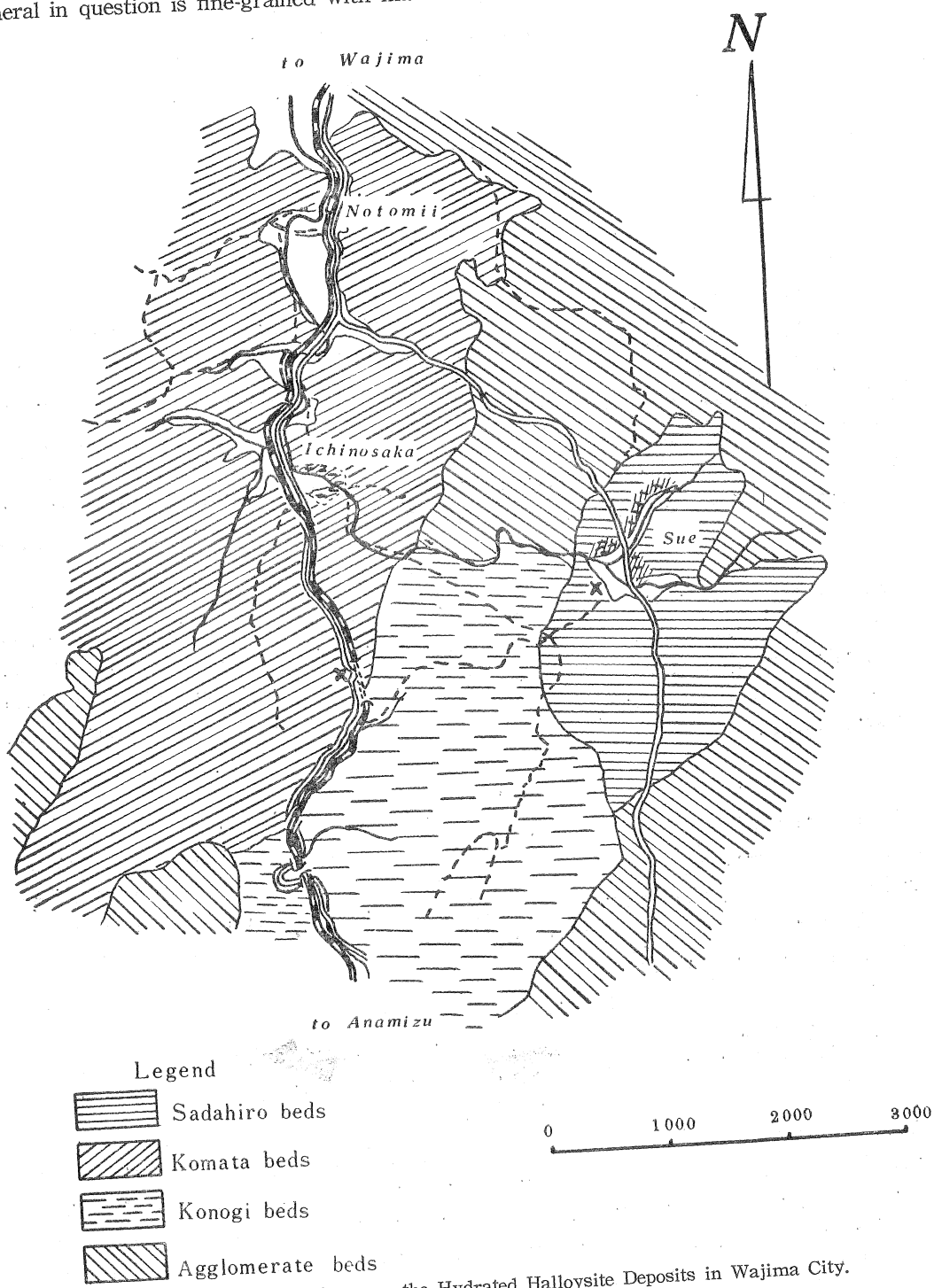

Fig. 1 Geological Map near the Hydrated Halloysite Deposits in Wajima City.

Physical Properties

The mineral from Ichinosaka is milky-white in color and has a greasy feel. Hardness is 2.5. The specific gravity measured with a pycnometer is 2.33.

The indices of refraction determined by the immersion liquid mixed with cederwood oil and cinnamic aldehyd, are 1.527~1.532. The thin section shows weak double refraction with banded arrangement under crossed nicol as shown in Fig. 2.

Chemical Composition

The specimens for the chemical analysis were occurred from Ichinosaka and purified by the magnifying-glass and binocular microscope in order to eliminate guartz grains, limonite stains and other minerals. For ignition loss by H_2O, the measurement with a balance were made four times within heating from room temperature to 1000 °C. The results are given in Table I. The data of hydrated halloysite from Joshin, Gumma, described by T. Sudo[*4] were compared with them. The chemical composition is represented by the formula $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$.

TABLE I.

Chemical composition of hydrated halloysite

	Wajima city*	Joshin Mine
SiO_2	39.78	38.97
Al_2O_3	34.69	34.43
Fe_2O_3	0.55	2.06
CuO	0.36	
MgO	0.28	
K_2O	0.57	
Na_2O	0.16	
H_2O	22.78	24.66
Roomtemperature—80°	9.13	
80—500	0.84	
500—600	12.19	
600—1000	0.62	
Total	99.17	100.12

(*Anal. by K. Kasama)

X-ray Examination

The specimens for the X-ray examination are the same as for the chemical analysis. The X-ray powder patterns obtained by the X-ray powder photograph and the Geiger Counter X-ray spectrometer were identical with those of hydrated halloysite from Joshin Mine.[*4] The observed intensities and measured spacings are listed in Table II and Figure 3 (A), (b). The patterns show no existence of allophane or dehydrated halloysite.

Thermal Study

The differential thermal analysis was carried out on the pulverized specimens of the

TABLE II.

X-ray Powder Pattern of hydrated halloysite

Wajima city		Joshin Mine	
I	d	I	d
20	10.1	17	10.1
10	4.49	10	4.44
	4.36	3	4.13
8	3.40	5	3.35
	3.35		
5	2.584	3	2.565
5	1.683	1.5	1.690
10	1.490	2.5	1.480
	1.479		
3	1.290		
3	1.240		

The radius of the camera used for powder reflection was 28.65 mm, and the wave length was Cu_{k_α} 1.5405 A. Powder reflection recorded on the chart of Philip's Geiger Counter X-ray Spectrometer.

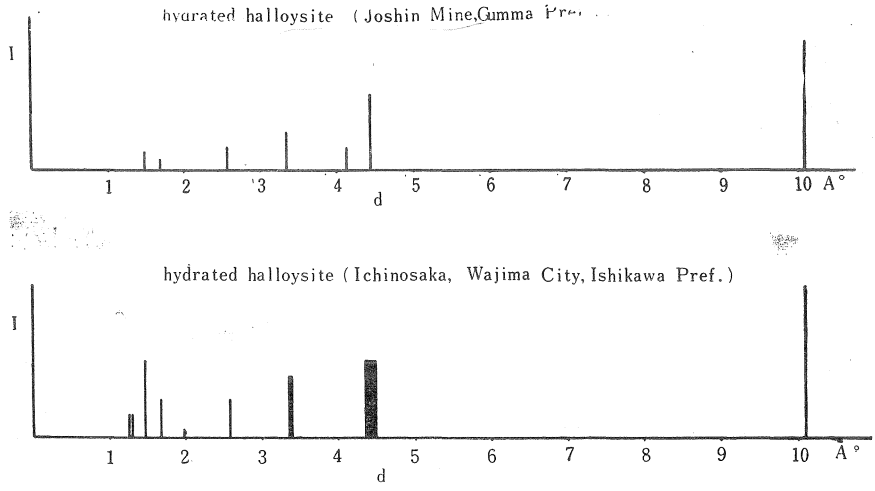

Fig. 3 (A) X-ray Powder Diagram

mineral from Ichinosaka. The curve of the sample examined by Fukuo of Nagoya University of Engineerig shows the endothermic peaks at 113 ℃ and 551 ℃ and the exothermic peak at 957 ℃ (Fig. 4). The curve of another sample examined by T. Sudo is slightly different from that of the former. It is to be supposed that such impurities as limonite ingredients were mingled.

Electron Micrograph

The electron micrograph taken by H. Takahashi shows two types. (Fig. 5 (A), (B), (C)). One of them shows fibers which look like long hollow pipes while in the other, short prismatic grains are found. Short prismatic grains have also hollow pipe structure, and they look like aggregates of fragments of long hollow pipes. The irregular form presented by T. Sudo*7) are not existent. Therefore, the two types are the same; the one is long and the other short.

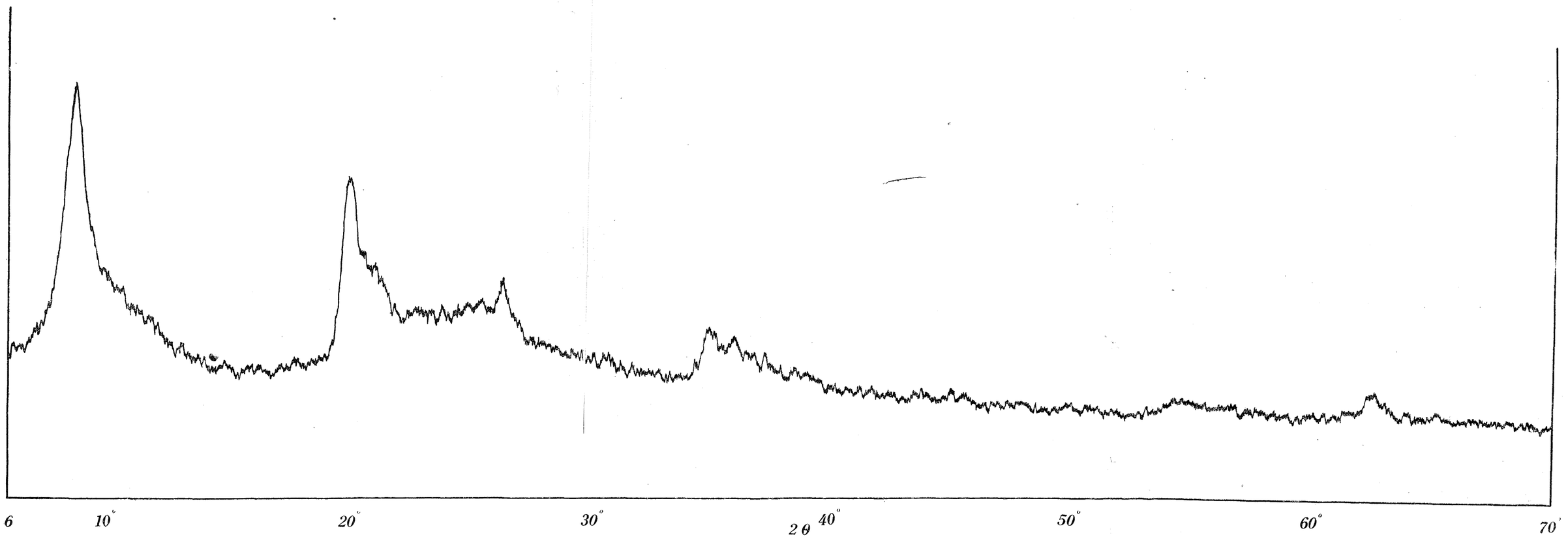

Fig. 3 (B) X-ray diffraction spectrogram of hydrated halloysité
Powder reflection recorded on the chart of Philip's Geiger Counter X-ray Spectrometer, filtered Copper radiation, 30—35KV, 10—15Ma, Scan speed 1° per minute, time constant 4 second angular aparture 1°.

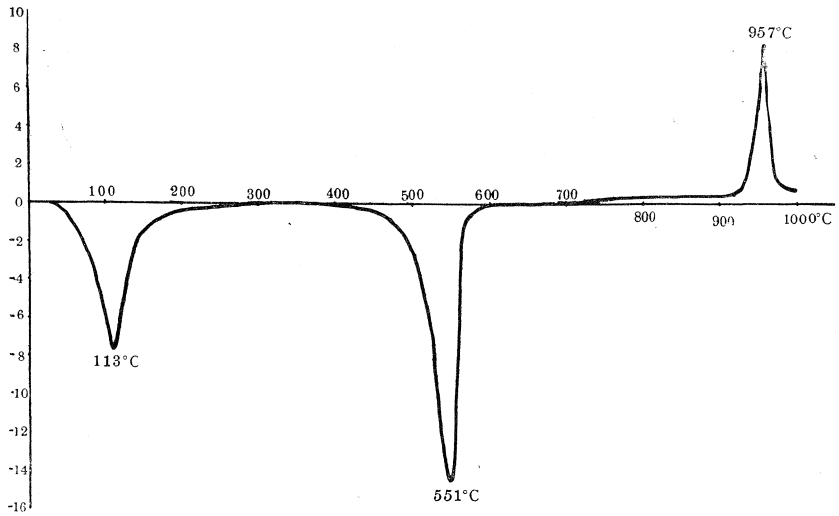

Fig. (4) D. T. A. Curve of hydrated halloysite from Wajima city
The D. T. A. curve was recorded under the mean heating rate of 10° per minute.

Staining Test by Organic Substances

Several drops of alcohol solution of p-amino phenol were applied to the pulverized mineral, having grain size between 100 and 200 mesh. In a white porcelain spot analysis plate the mineral shows yellowish brown color. This test is characteristic in kaolinite, dehydrated halloysite, and hydrated halloysite.

Summary

The results of those experiments show that the mineral in question is identical with hydrated halloysite, and not with any other minerals. The high refractoriness of the fire-clay in this district is mainly due to the presence of the hydrated halloysite.

Acknowledgment

The writer wishes to offer his sincere thanks to Prof. Sudo, the Institute of Geology and Mineralogy of the Tokyo University of Education. The writer is also indepted to Mr. K. Kasama, the Industrial Art Institute of Ishikawa Prefecture for the chemical analysis, to Mr. Fukuo, the Nagoya University of Engineering, for the differential thermal analysis, to Mr. H. Takahashi, the Institute of Chemistry of the University of Tokyo, for the electron micrograph and to Mr. K. Yamada, the Geological Institute of the University of Kanazawa, for his cooperation in the geological survey.

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Fig. 2 Photomicrograph of hydrated halloysite from Wajima City
crossed nicol ×60

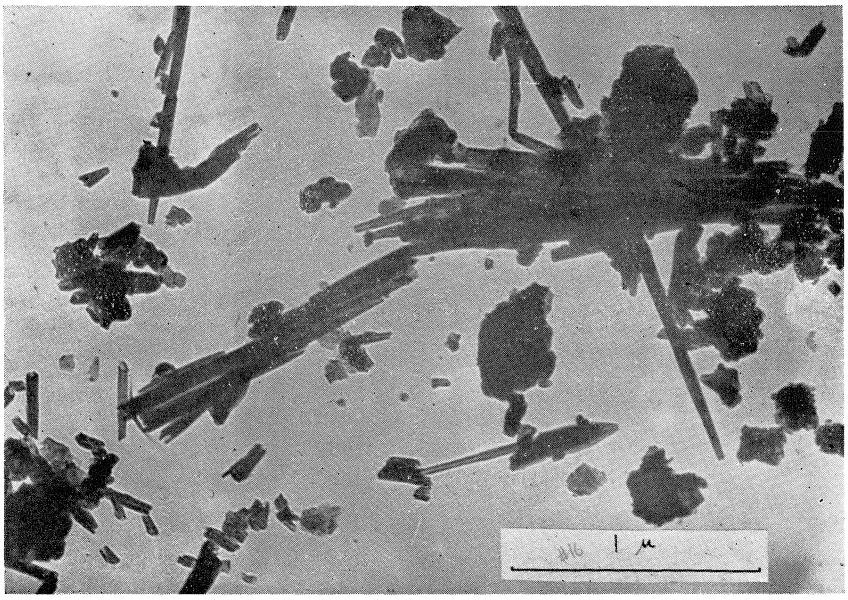

Fig. 5 (A) Electron Micrograph of hydrated halloysite from
Wajima City.

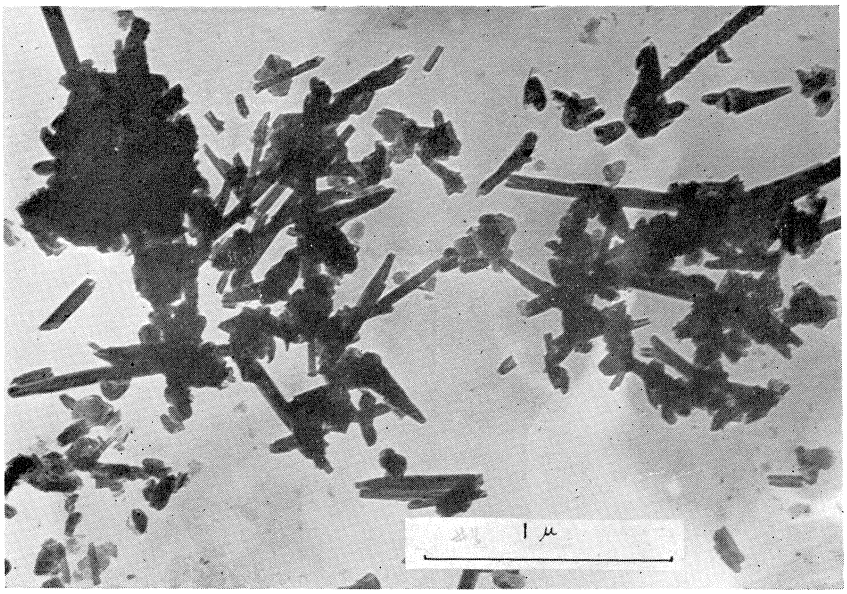

Fig. 5 (B) Electron Micrograph of hydrated halloysite from Wajima City.

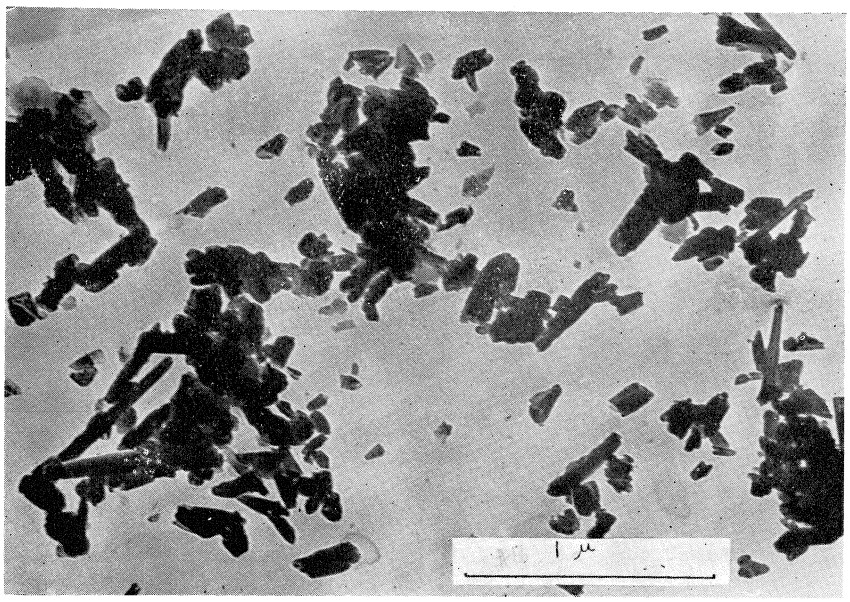

Fig. 5 (C) Electron Micrograph of hydrated halloysite from Wajima City.