THE SELECTIVE DISSOLUTION AND INFRA RED SPECTROSCOPY METHODS FOR IDENTIFICATION OF CLAY MINERALOGY IN ANDISOLS

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ABSTRAK

Mineral liat alofan, imogolit dan ferihidrit merupakan mineral liat amorf yang sulit diidentifikasi dengan sinar X (X-ray) karena menghasilkan kurva tanpa bentuk. Untuk itu diperlukan analisis lain yang dapat mengidentifikasi mineral tersebut. Percobaan ini dilakukan untuk mengetahui analisis yang dapat dilakukan untuk mengidentifikasinya. Metoda yang dilakukan adalah'selective dissolution' dan spektroskopi infra merah. Percobaan ini dilakukan di lapangan untuk mengambil sampel dari profil tanah Andisol, dan di laboratorium untuk analisis keberadaan mineral liatnya. Hasil percobaan menunjukkan bahwa metoda 'selective dissolution' dapat mengidentifikasi mineral tersebut secara kualitatif dan kuantitatif. Metoda spektroskopi infra merah dapat mengidentifikasi mineral itu secara kualitatif. Kedua metode ini dapat digunakan untuk mengidentifikasi alofan, imogolit dan ferihidrit pada Andisol.

Key words: minerai liat amorfik, Andisols, spectroskopi infra merah.

INTRODUCTION

Indonesia is one of the most active volcanic area in the world, with 129 volcanoes spread over in its various islands (Sudradjat, 1992). The activity of volcanoes yields the pyroclastic materials as the source of parent material of the volcanic ash soils, classified as Andisol in Soil Taxonomy (Soil Survey Staff, 1990). Andisols in Indonesia spread over 6.5 million ha or around 3.4 % of the total area. Andisols is one of the most important agricultural region especially for the plantation and horticulture (Lembaga Penelitian Tanah, 1992).

Andisol is a productive soil, but it has not been used optimally yet. This soil has the typical and unique characteristics as a low bulk density, a high permeability, a stable structure, a high content of active Al/Fe, a high phosphate fixation, and a variable charge (Shoji et al, 1993). The nature and chemical characteristic, morphology and physic of Andisol are interconnected with the non crystalline minerals like allophane and ferrihydrite, and the para-crystalline mineral like imogolite, founded in the soil (Wada, 1989).

Allophane is considered as the most active components in volcanic ash soil, because it has high specific surface area and many active functional bunches (Farmer et al, 1991). The presence of allophane gives the unique characteristic of Andisol, because of its variable charge, open and random structure, and phosphate fixation (Wada, 1989; Tan 1992, Van of Ranst, 1995). The high phosphate fixation by allophane made the phosphate availability decrease.

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Egawa (1977) explained that in Andisol only 10 % of applied P fertilizer could be used by crop. The high percentage of losing P fertilizer is a serious problem in Andisol.

Allophane with a molar ratio of Al/Si equal to 2.0 have identified in the clay fraction in Andisol in New Zealand and Japan (Parfitt and Hemni, 1982). The identification of clay mineral becomes a basic process for having data in determining management of Andisol over there. Therefore the identification of clay minerals of Andisol in Indonesia is required to conduct the optimal management to increase the productivity of such soil. Though many agricultural areas in Indonesia is influenced by the activity of volcanoes, the complete analyses data of Andisol cover morphology, physic, chemical, biology, and especially the clay mineralogy are still rare.

The clay minerals normally could be identified by using of the XRD (X-Ray Diffractometer). However, identifying the non crystalline and para-crystalline minerals like allophane, ferrihydrite and imogolite with XRD do not give the expected result, due to they don't display the specific curves as the crystalline minerals like kaolinite, montmorilonite, etc. Therefore, the other methods are required for determining the clay minerals in volcanic ash soils.

The methods used for identification of clay minerals in the volcanic ash soils are the selective dissolution method (ammonium oxalate, Dithionite Citrate Bicarbonate/DCB) and infra red method.

The analysis of clay minerals in volcanic ash soil using the selective dissolution and infrared spectroscopy methods have done in New Zealand and Japan. The similar analysis have not yet done in Indonesia, though this is a basic analysis required before conducting the application research in Andisol. The accurate and correct data regarding the clay mineral is highly assisted to improve the productivity of Andisol.

Soils developed from volcanic ash have typical minerals called short range order minerals like allophane, imogolite, and ferrihydrite. Analysis of those minerals with X-Ray Difractogram (XRD) will yield the curve without form, therefore they often referred as the amorphous or non crystalline minerals. The method for analysis those minerals are selective dissolution and infrared spectroscopy.

Analysis with infrared spectroscopy gave qualitative data, while analysis with selective dissolution gave quantitative and qualitative data. Analysis with both methods will yield more precise data in identifying the short-range order minerals in the volcanic ash soils. These data will be useful for focusing the management of such soils

MATERIALS AND METHOD

This research used two profiles of Andisol obtained from Mt. Tangkuban Parahu. Samples were taken from every identifiable horizon in the profile. Stipulating the location of the profile is pursuant by the map of geology, soil, and topography. Research was done in the field and in the laboratory. The field research was done for determining the location of observation and for taking samples. Laboratory analysis was done in the Laboratory of Balai Besar Keramik in Bandung for infrared analysis and the in the Laboratory of Soil Science in the Bogor Institute of Agriculture for specific analysis. Specific analysis is the analysis using the selective dissolution consist of ammonium oxalate, dithionite citrate bicarbonate (DCB) and pyrophosphate acid; and the analysis of surface reactivity and reactivity of fluoride through the measurement of pH NaF.

Extraction with ammonium oxalate (Blakemore *et al*, 1987) was done by shaking 1 g soil with 100 ml of 0.2 M ammonium oxalate pH 3 in dark condition during 4 hours. The measurement of Al, Fe, and Si extracted were done by AAS. The measurement of P was done by spectrophotometer. Extraction with pyro-phosphate acid (Blakemore et al, 1987) was done by shaking 1 g soil with 100 ml Na-Pyrophosphate 0.1 M during one night. The rest of the solution was used for analyzing the C-organic by using Walkley and Black method.

Analyzing of surface reactivity was done by measured the H_2O pH (1: 2.5) added with NaF solution and the pH was measured again after 2; 60; 120; 180 minutes and 24 hours. The result of this measurement was an evolution of NaF pH which been converted to determine how many OH bunches discharged into solution. The solution was then titrated with 0.01 M HCl up to the pH was equal again to the pH of H_2O. The amount of HCl used can be calculated for the index of fluoride reactivity.

Analysis with infrared spectroscopy used solid soil example, where 1 mg clay fraction was mixed and milled carefully by 100 mg KBr then removed into mould and depressed by using vacuum or hydraulic pump or with pressure of 10 000 - 15 000 pound $inch^{-2}$. The result was a thin transparent plate with 13 mm diameter and 0.3 mm thick. This plate is then put down into infra-red cell completed by crystalline KBr window.

The data got from analysis will be tested their relationship with one another, especially the analysis result of Alo and Sio (Al and Si which extracted with ammonium oxalate) and the evolution of NaF pH, Alp and Fep (Al and of Fe extracted with pyrophosphate acid) and C-Organic. The allophane content be calculated by using the formula : % Allophane = % Sio x 7,1.

RESULTS AND DISCUSSION

Analysis of Selective Dissolution

Ammonium oxalate solution

The percentages of Al (Alo), Fe (Feo) and Si (Sio) dissolved by ammonium oxalate presented in Table 1. The percentages of Sio tend to increase with the increasing of soil deepness showing that the Si leached to the substratum. The Sio values express the existence of the non-crystalline mineral in this soil, because it initially coming from the non crystalline minerals like allophane and imogolite.

The non-crystalline inorganic material formed by Al can be anticipated by using the difference between Alo and Alp. The concentration of (Alo – Alp) ranged about 0.16 – 3.58 %. That value is higher at the subsurface horizon, showing the degradation proportion of Al-organic complex and the improvement of Al-inorganic linkage at deeper substratum. The ratio of Alp/Alo showed the colloidal fraction composition. This ratio decrease with the increasing deepness. If the value is more than 5, it means the domination of organic acid in the weathering process. If the value is less than 5, it means the domination of carbonic acid in the weathering process. The composition of molar ratio of Al/Si in allophane accounted from (Alo-Alp)/Si ranged about 1,0-2,5. The allophane content ranged about 5 - 33 %. This value increased with increasing the deepness. A number of allophane and Al-humus complexes were found at the surface. The formation of allophane at the upper horizon was influenced by the input of organic materials

Table 1.   The estimation content of allophane and ferrihydrite in clay faction analysed with ammonium oxalate.

Profile	Horizon	% Si_o	% Al_o	% Fe_o	% Allophane*	% Ferrihydrite**
I	A	1,35	3,53	1,83	10	3
	AB	2,00	4,82	2,31	14	4
	Bw1	2,66	5,90	3,30	19	6
	Bw2	3,42	7,65	2,80	24	5
II	A	1,33	3,20	2,04	9	3
	AB	1,51	3,53	2,12	11	4
	Bw1	1,54	3,55	1,46	11	2
	Bw2	1,15	2,58	1,16	8	2
	BC	1,26	2,75	2,22	9	4

Keterangan: * = % allophane = % Si_0 x 7,1; ** = % ferrihydrite = % Fe_0 x 1,7

and the acidity of soil. The pH value above 5 will support the formation of allophane on the surface horizon.

The pH value of 5 is the critical value for the formation of allophane, and the pH less than 5 is required for the formation of Al-humus complex. When the pH is more than 5, there are enough number of Al to form the allophane. The allophane was formed at the pH between 5.0–7.0 at an udic temperature regime, where the cation of hidroxy aluminum reacted to form allophane. The increased value of Feo with the increasing deepness do not show a certain tendency. The ferrihydrite identification is more difficult because of the lowness crystallinity.

The allophane content at the clay faction ranged about 5 - 33 %. This content is usually higher at the subsurface horizon compared to the

Table 2.   The amount of Al, Fe and of C the dissolved in pyrophosphate in the fine fraction

Profile	Horizon	% Al_p	% Fe_p	% C_p	Fe_o- Fe_p	Al_p/Al_o	(Al_p+Fe_p)/ C_p
I	A	0,61	0,54	5,00	0,69	0,33	0,23
	AB	0,84	0,66	4,32	1,20	0,42	0,35
	Bw1	0,57	0,49	4,20	1,59	0,24	0,25
	Bw2	0,48	0,22	3,52	1,71	0,16	0,20
	BC	0,39	0,29	3,20	1,73	0,13	0,21
II	A	0,87	0,29	4,76	1,54	0,40	0,24
	AB	0,76	0,19	3,72	1,54	0,28	0,25
	Bw1	0,55	0,14	3,52	1,92	0,22	0,20
	Bw2	0,96	0,10	3,32	1,32	0,33	0,32
	BC	1,18	0,22	2,64	1,85	0,53	0,53

surface horizon. The formation of allophane at surface horizon was controlled either by the volcanic ash input, organic materials and soil acidity.

The analysis result of using selective dissolution to estimate the percentages of allophane and ferrihydrite can be seen at Table 1. While the amount of Al, Fe and C the dissolved in pyrophosphate presented Table 2.

The organic complex of Al and Fe extracted with pyrophosphate (Alp and Fep) was low and decrease with the increasing deepness. The ratio of Alp/Fep also decrease with the increasing deepness. This expressed that the formation of Al-humus complex is more dominant surface horizon. The formation of allophane happened especially in the subsoil.

The ratio of (Alp+Fep)/Cp ranged between 0.20-0.53 do not expressed certain tendency. Allophane was dominant with ratio 0.1 – 0.3. The value of Sio decreased with the increasing of ratio (Alp and Fep)/Cp. The ratio more than 0.1 is the critical point. Most of Andisol have (Alp and Fep)/Cp value between 0.2 – 0.3. A number of Si, Al and Fe in the clay faction were dissolved by ammonium oxalate. Oxalate extraction does not eliminate all amorphous materials. About 9 – 55 % of Sio, Alo and of Feo were extracted during the extraction. The clay with higher allophane content usually compared to sand and silt fraction. This indicated that the non-crystalline aluminum silicate is more concentrate in the finer fraction.

Dithionite Citrate Bicarbonate (DCB) Solution

Sid and Ald values were smaller than Sio and Alo. This indicated that allophane was not dissolved by DCB. Meanwhile the DCB dissolved all the fixation of Fe. Soils with high Fed showed the high precipitation. The high precipitation supported the weathering of the ferromagnesian minerals containing many Fe. The Fed and Ald usually tend to be accumulated in the substratum, and usually reflected in the red coloured soil, expressed the iron oxide or hematite mineral. Table 3 shows the DCB solution in the clay faction.

Analysis with infra red spectroscopy (IR)

Analysis with infra red showed that allophone and imogolite have band at 3475, 1440, 975 and 600 cm^{-1}. Band at 4700, 800, 900, 1030, 3700 cm^{-1} show

Tabel 3. DCB solution in the fine fraction

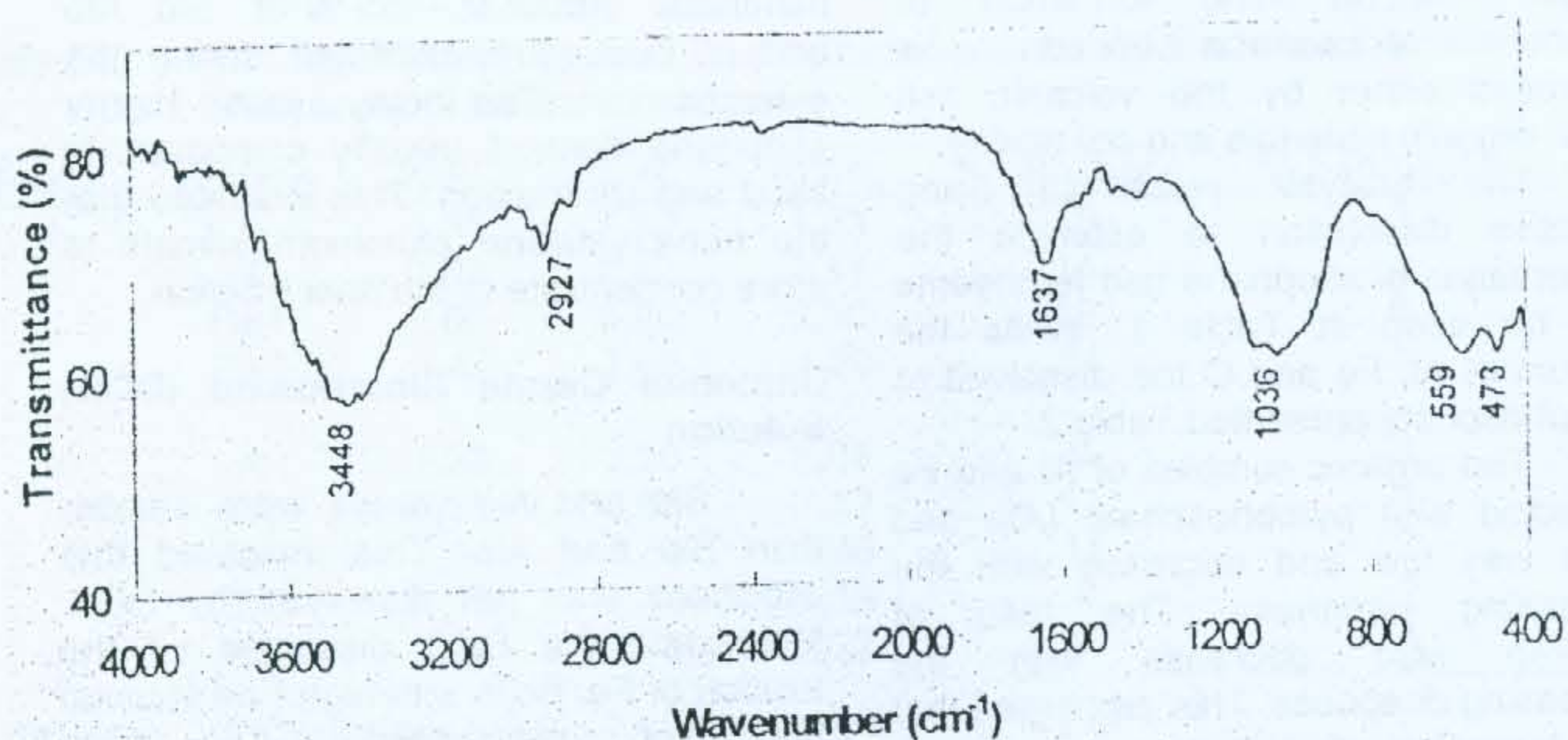| Profile	Horizon	% Si_d	% Al_d	% Fe_d	$Fe_d - Fe_o$	Fel_o/Fe_d
I	A	0,03	0,68	0,84	-0,31	1,37
	AB	0,02	0,49	0,72	-1,15	2,60
	Bw1	0,01	0,53	0,84	-1,24	2,48
	Bw2	0	0,50	0,78	-1,15	2,47
	BC	0	0,47	0,71	-1,31	2,84
II	A	0,02	0,38	1,25	-0,19	1,15
	AB	0,07	0,50	1,72	0	1,00
	Bw1	0,17	0,34	1,52	-0,54	1,36
	Bw2	0,08	0,47	1,46	0,04	0,98
	BC	0,04	0,60	2,36	0,29	0,88

Figure 1. The infra red spectrum of the clay faction at Profile 1

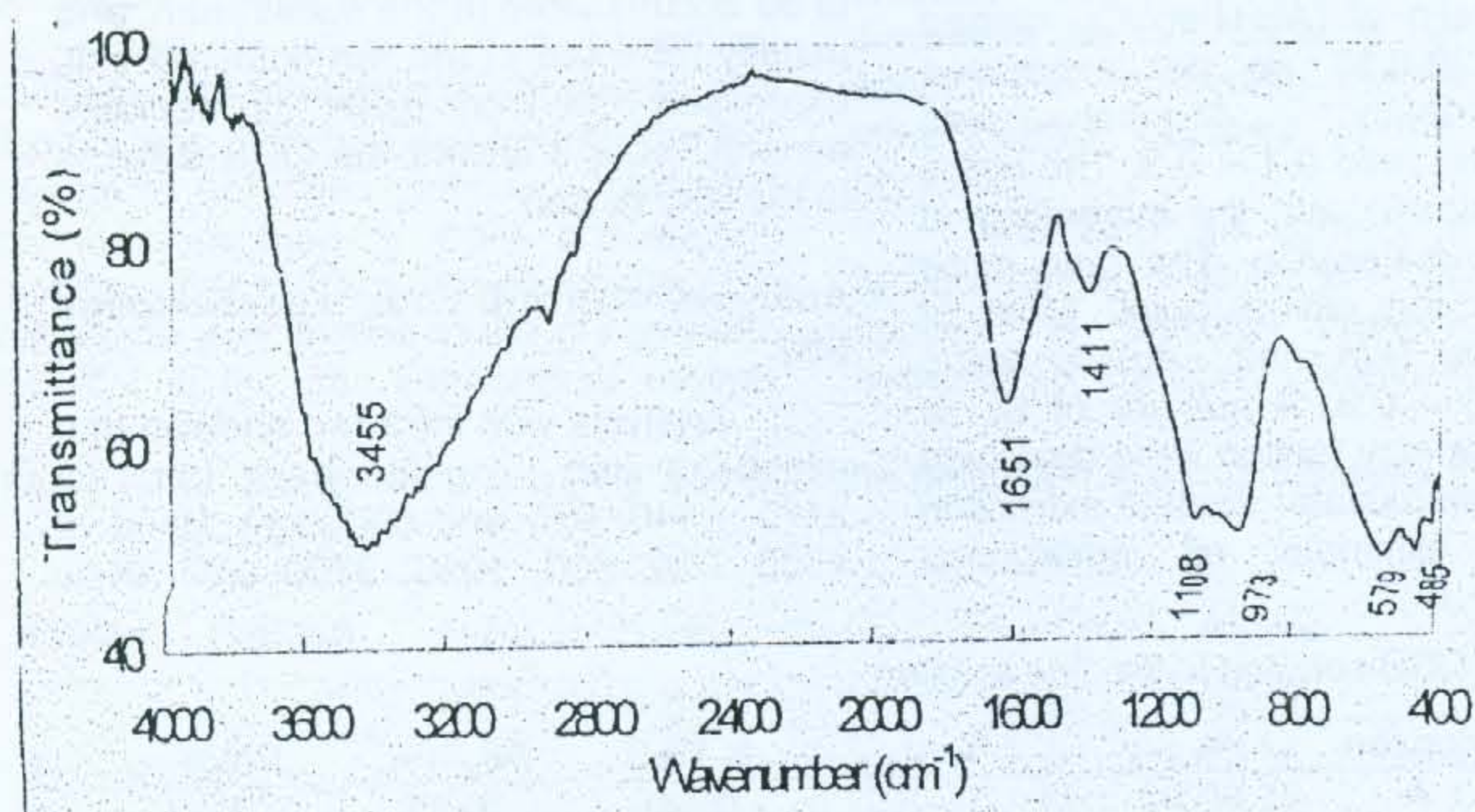Figure 2. The infra red spectrum of the clay faction at Profile 2

the existence of halloysite, while band at 1250 - 1100 cm^{-1} show the existence of volcanic glass.

Allophane has four primary absorption region of infra red. First region reside at 3475-3500 cm^{-1}, because of the vibration of OH^- at octahedral AlOH and tetrahedral SiOH when absorp water. Therefore that is referred as the region of functional grup. The second region emerged at 1400 and 1440 cm^{-1} because of the vibration of deformation HOH in permeating water. The third region at

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$800-1400 \text{ cm}^{-1}$ is so-called the fingerprint, because expressing the vibration of Al-OH and Si-OH. The fourth region reside in at $400-800 \text{ cm}^{-1}$ caused by the fixation of Si-O.

Allophane showed a single absorption band, while imogolite showed two maximal absorptions at $940 - 100 \text{ cm}^{-1}$. The infra red band of allophane is wider than the band of imogolite, because of its smaller mineral order. The band spectrum at 975 cm^{-1} showed the existence of allophane in the richness Al environment. The higher allophane content due to the higher Al content tend to be formed in acid soil with well drain and udic temperature regim. In general allophane was formed of volcanic glass at pH 5 - 7 in acid condition.

CONCLUSION AND SUGGESTION

Conclusion

1. The selective dissolution method can be used to identify the minerals in the volcanic ash soil qualitative and quantitatively
2. Infra red spectroscopy method can be used to identify such minerals qualitatively
3. Both methods can be used to identify the minerals in the volcanic ash soils

Suggestion

1. Identification of clay mineral in volcanic ash soils should always be done for having the correct data about the mineral content so the soil management can be more accurate.
2. Identification with selective dissolution method is more suggested, because the method can identify the clay mineral qualitative and quantitatively.

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pencapaian kesejahteraan masyarakat. Namun demikian, pemanfaatan sumberdaya alam khususnya di wilayah yang sedang berkembang terbentur pada kualitas sumberdaya lainnya, seperti manusia dan kelembagaan, yang masih rendah sehingga pemaanfaatan sumberdaya alam belum optimal. Akibatnya kelestarian sumberdaya alam sebagai penyangga, penyokong, dan penyedia kebutuhan pembangunan menjadi kurang terjaga. Untuk mencegah degradasi sumber daya alam, perlu ada upaya pengelolaan sumberdaya alam yang dapat menunjang pembangunan wilayah secara berkelanjutan, khususnya dalam aspek sosial dan ekonomi.

Pengelolaan sumberdaya alam merupakan upaya secara sadar, terencana dan terpadu dalam pemanfaatan, penataan, pemeliharaan, pengawasan, pengendalian, pemulihan dan pengembangan sumberdaya secara bijaksana untuk meningkatkan mutu lingkungan hidup sebagai modal dasar pembangunan. Secara formal, pengelolaan sumberdaya alam ini telah dituangkan dalam Undang-undang No.4 Tahun 1982 tentang ketentuan pokok pengelolaan lingkungan hidup dan kemudian direvisi dalam Undang-undang No. 23 Tahun 1997 (UUPLH).

Berdasarkan undang-undang tersebut, pengelolaan lingkungan hidup di Indonesia berasaskan pelestarian lingkungan hidup yang serasi dan seimbang guna menunjang pembangunan yang berkesinambungan bagi peningkatan kesejahteraan manusia. Dalam konteks wilayah, peran penting pengelolaan sumberdaya alam dirumuskan dalam Undang-undang No.24 Tahun 1992 yang menyatakan bahwa untuk menunjang pengembangan wilayah secara berkelanjutan perlu diketahui arahan dan batasan wilayah sesuai fungsi utama kawasan.

Secara umum tujuan pengelolaan lingkungan hidup di Indonesia adalah:
1. tercapainya keselarasan hubungan antara manusia dengan lingkungan hidup sebagai tujuan membangun manusia Indonesia seutuhnya
2. terkendalinya pemanfaatan sumberdaya secara bijaksana
3. terwujudnya manusia Indonesia sebagai pembina lingkungan hidup
4. terlaksananya pembangunan berwawasan lingkungan untuk kepentingan generasi sekarang dan mendatang
5. terlindunginya negara terhadap dampak kegiatan yang menyebabkan kerusakan dan pencemaran lingkungan.

Dengan demikian, pembangunan yang diharapkan adalah pembangunan yang berkelanjutan dengan memperhatikan fungsi dan peran sumberdaya alam. Untuk menunjang hal tersebut, pemerintah telah mengeluarkan beberapa peraturan perundang-undangan yaitu Peraturan Pemerintah No. 51 Tahun 1993 tentang Analisis Mengenai Dampak Lingkungan, Kepmen No. 02/MENKLH/1/1988 tentang penetapan Baku Mutu Lingkungan, KEPRES NO. 23 Tahun 1990 jo. KEPRES No. 77 Tahun 1994 tentang pembentukan Badan Pengendali Dampak Lingkungan, UU No. 24 Tahun 1992 tentang Penataan Ruang, serta peraturan perundang-undangan lainnya. Melalui perangkat peraturan tersebut diharapkan pengelolaan sumberdaya alam dapat diupayakan seoptimal mungkin dalam menunjang pembangunan yang berkelanjutan, khususnya dalam menjaga kelestarian dan keberlanjutan fungsi sumberdaya alam.