

Development of HASClay[®] as a high-performance adsorption material

— Developing adsorbents for energy conservation systems from a kind of clay nanoparticle —

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Given the need to reduce greenhouse gases, we have developed an inorganic porous material, HASClay, which possesses excellent water vapor adsorptive efficiency, and the ability to dehydrate using a low grade heat source. In this paper, we explain how the synthetic process of HASClay was developed from a study of naturally existing clay and nanomaterials, and the requirements for widespread use as an adsorption material for energy conservation.

Keywords : HASClay, energy conservation, desiccant air conditioning, moisture conditioning material, synthesis method

1 Objective of the research

In the 21st Conference of the Parties (COP21) of the United Nations Framework Convention on Climate Change (UNFCCC) that was held in Paris in December 2015, the Paris Agreement was adopted as the new framework following the Kyoto Protocol. Further energy savings will be necessary for Japan to reduce greenhouse gases to prevent global warming. The energy-saving technology in Japan has seen innovative development since the 1990s when the reduction of greenhouse gases became a serious social issue. The use of waste heat has also advanced, and currently, waste heat of 100 °C or higher is utilized efficiently, but the technology to use low-temperature waste heat of less than 100 °C is being researched.

There are two types of energy-saving systems using low-temperature waste heat: the adsorption heat pump (adsorption refrigerator) that uses heat generation and absorption that occur when water vapor or ammonia is adsorbed/desorbed by the adsorbent, and the desiccant air conditioning system by which energy saving efficiency can be increased through effective water vapor removal. Desiccant air conditioning uses desiccant rotors including adsorbents to dehumidify and then lowers the temperature to the target temperature. Figure 1 shows the outline diagram of the desiccant air conditioning system. The dehumidification part is separated into the dehumidification zone and reuse zone. In the dehumidification zone, the air taken in from the outside is dehumidified and then supplied to the room, while in the reuse zone, the room air is warmed with a heater to recover the air by releasing the water vapor adsorbed in the dehumidification zone. The adsorption heat pump and the desiccant air conditioning

system have been in existence since the 1990s, but zeolite and silica gel were used as adsorbents. There was a demand for adsorbents that were capable of adsorption/desorption at low temperature of 100 °C or less.

Against such a background, in Japan, the development of adsorbents that can be reused at low temperatures of 40–80 °C was conducted from the late 1990s to early 2000s. The development of adsorbents such as AFI- or CHA-type low-temperature reusable zeolite (AQSOA[®]), mesoporous silica (TMPS), or polymer adsorbents (TAFTIC[®]) was conducted. Allophane and imogolite were candidates of clay nanomaterials at the time, and their water vapor adsorption isothermal curves are shown in Fig. 2.^{[1]–[4]} As can be seen,

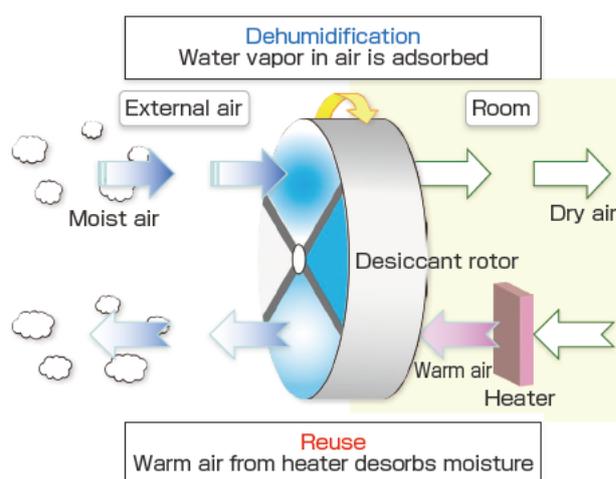


Fig. 1 Outline of the desiccant air conditioner that uses water vapor adsorbent

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the adsorption isothermal curves can be roughly divided into two. One is the S-shaped curve that shows rapid start-up in a certain relative humidity range as in the low-temperature reused zeolite and mesoporous silica, and the linear type in which the relative humidity and water vapor adsorption volume show a linear relationship without rapid start, as in the polymer adsorbents and allophane. With adsorption heat pump, the operating environment temperature, waste heat temperature, and cold water temperature in the system are controlled, and because the operating humidity range is determined by these three temperatures, an adsorbent with an S-shape with rapid start-up in the operating humidity range is suitable. On the other hand, because the desiccant air conditioning takes in air with varying humidity, an adsorbent with a linear property where adsorption is possible at a wide humidity range is more suitable.

In this context, (1) no merit was seen in developing adsorption heat pump because the device size would be twice as large as the absorption heat pump that was already widely used, and (2) the adsorption isothermal curves of allophane and imogolite that we had been studying showed a linear characteristic in the medium humidity range. Therefore, we decided to target desiccant air conditioning, and develop a linear inorganic water vapor adsorbent that has performance equivalent to polymer adsorbents.

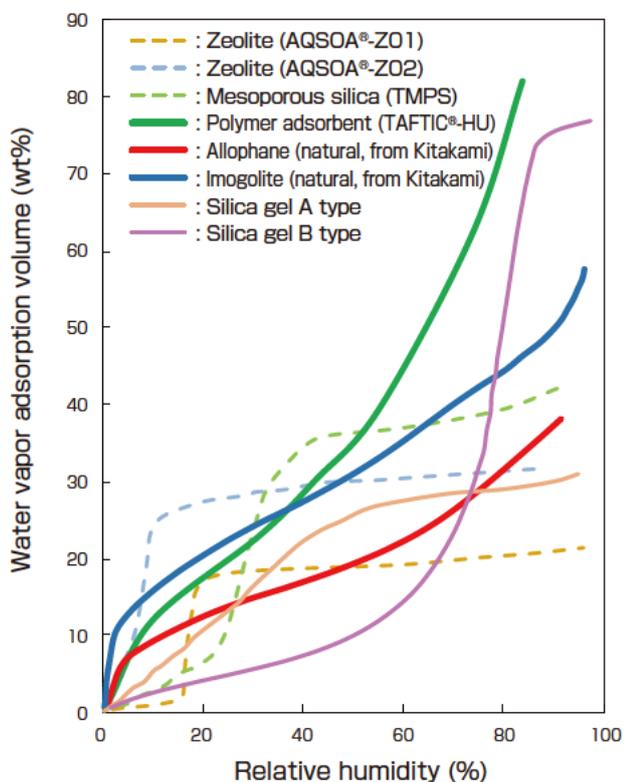


Fig. 2 Water vapor adsorption isothermal curve of the adsorbents that can be reused by low-temperature treatment (AQSOA®-Z01^[2], AQSOA®-Z02^[2], TMPS^[3], TAFTIC®-HU^[4])

2 History of the development (1990s–2005)

2.1 Nanoparticles that exist in the soil

The National Industrial Research Institute of Nagoya (NIRIN), Agency of Industrial Science and Technology to which the authors belonged had been researching ceramics and metals in the Chubu region since its inception in 1952. The work of the Imperial Ceramic Experimental Institute, which was one of the institutes integrated when NIRIN was established, was carried over to Unit 6 (later, Department of Ceramic Technology), and the ceramics research was continued there. The authors were at the Raw Materials Technology Laboratory, Department of Ceramic Technology, and engaged in the research on clay, the raw material of ceramics, as well as utilization of pore that was a major clay characteristics. Allophane and imogolite were clays that had interesting forms.

When one hears of nano-capsules and nanotubes, one immediately thinks of C₆₀ fullerene or carbon nanotubes, but nano-capsules and nanotubes exist in the weathered soil derived from volcanic ash. These are substances known as allophane and imogolite. Allophane has the shape of nano-capsules with a diameter of 3.5–5.0 nm, while imogolite is in the shape of nanotubes with an exterior diameter of 1.8–2.2 nm and length of several ten nm–several μm. The schematic diagrams of allophane and imogolite structures are shown in Fig. 3,^{[5][6]} and the transmission electron microscope (TEM) photographs are shown in Fig. 4.^[7] The basic structure of allophane and imogolite is the SiO₄ tetrahedron in which the pinnacle is the hydroxyl group bond, and the bottom three oxygen atoms are shared with aluminum, inside the gibbsite sheet composed of aluminum hydroxide. This structure does not include the Si-O-Si bond, and the distance between oxygen atoms of the gibbsite sheet that is bonded to the silicone is quite short. The gibbsite sheet is curved due to this misfit, and this gives the characteristic structure to allophane and imogolite.

Since allophane and imogolite can be seen occasionally in the soil derived from volcanic products such as pumice or volcanic ash, they were mainly studied in the field of soil science until about 1990, but later, they were investigated for their functions as catalysts or gas storage materials. They not only have special nano-size shapes and high specific surface areas, but also have excellent hydrophilicity and adsorption capacity. Therefore, they are studied for application to adsorbents of hazardous pollutants, humidity controlling agents that autonomously control the humidity in the living area, polymer nano-composites, and for application in medical fields.^[8]

2.2 Development of humidity controlling building materials using allophane

Japanese buildings were traditionally constructed with wood and mud, and therefore, had good humidity control,

condensation prevention properties, and fungicidal properties, but problems of condensation began to develop as highly airtight buildings were constructed. Corresponding air conditioning facilities became necessary, but from the perspective of energy savings and facility management, humidity controlling building materials were developed to give humidity control functions to the materials themselves.

Allophane was used as such a humidity controlling building material. Allophane dehumidifies when the humidity increases, and humidifies when the humidity decreases, and is capable of maintaining the humidity range in which people can live comfortably. The successful development of humidity controlling tiles using allophane was conducted jointly with a company.^[9] These humidity controlling tiles with allophane are used in the building of AIST Chubu.

2.3 Development of imogolite

Imogolite is composed of naturally existing nanotubes. Since the amount existing in nature is extremely small, it was necessary to synthesize it. The synthesis was already done by Farmer *et al.* in 1977, but it was conducted in dilute concentration. We succeeded in synthesizing at higher concentration of about 10 times the conventional method, by adding a desalination procedure to the processes.^[10] Even using this method, only a few grams could be recovered by dehydrating 1 L of the solution, and it was one digit less compared to general clay synthetic products in terms of

production efficiency. On the other hand, when imogolite was evaluated as a heat exchange adsorbent for adsorption heat pump using hydration heat measurement, it was found that it had excellent capacity even by reuse at 40 °C,^[11] but we were unable to conduct a practical evaluation.

3 History of the development of new adsorbents (2005–present)

3.1 Breakaway from imogolite

After completing the synthesis and evaluation of imogolite as a heat storage agent by 2003, we looked at various applications for use as nanotubes, and started activities for realizing practical use and pioneering new usages.

The first foothold was a research commission from the Shingijutsu Kyokai (New Technology Association) that was subcontracted by the Japan Science and Technology Agency (JST) in 2004. The “Imogolite Synthesis and Application Technology Workshop” was set up, and investigations were done in the fields of environmental technologies, energy savings, and living environment. We also set up the “Imogolite Workshop” at AIST Chubu in 2006, and obtained opportunities to participate in exhibitions and others at the International Nanotechnology Exhibition and Conference (Nano Tech), and were able to hear voices from companies.

We found that the fields of application of imogolite included

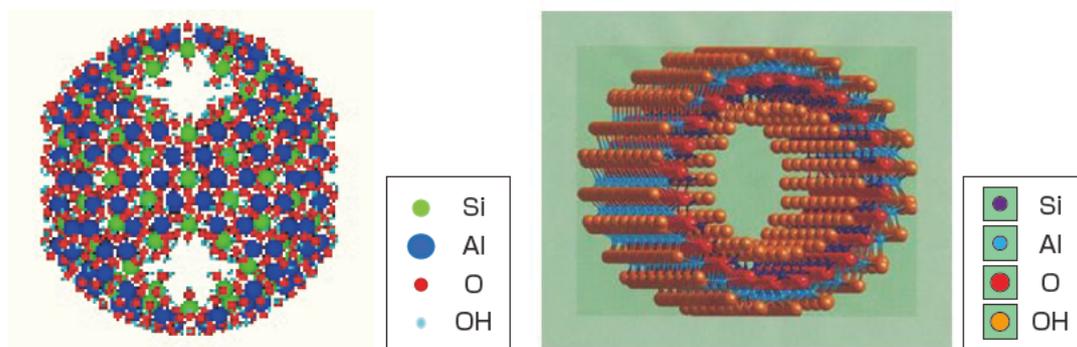


Fig. 3 Structural models of allophane and imogolite (Left: allophane^[5], right: imogolite^[6])

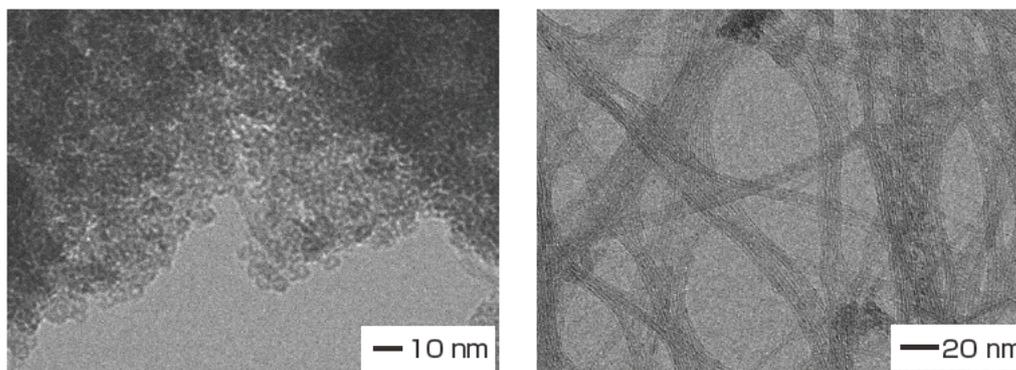


Fig. 4 TEM photographs of allophane and imogolite (Left: allophane^[7], right: imogolite^[7])

not only the desiccant air conditioning and humidity controlling building materials that we had been studying, but also many domains that the authors never imagined, including compositing with fibers, compositing with rubber, cell immobilizers, release control of aroma, and others (Fig. 5). Since imogolite is composed of nanotubes, we conducted joint research with Hokkaido University to evaluate safety in organisms.

As a result of talking to and conducting joint research with various companies, the following points can be raised as important.

- No matter how good the performance, if its synthesis remains at a laboratory level and there is no prospect for being handled by some company in the future, it is difficult for the company which will be using this material to evaluate in terms of sales and marketing.
- No matter how well it can be synthesized at a laboratory level, unless the method can be used for synthesis at an industrial level, the manufacturers cannot engage in production in tons.
- No matter how well the performance, the range of use will be narrowed if it is expensive, wide diffusion to society cannot be expected, and initial performance may not be attainable since it will be mixed with other substances to cut costs (the only field where it can be used despite high costs is the medical field).
- As can be seen with the case of asbestos, there is concern for the safety of nanotubes, even if we explain the

imogolite properties or its form after dehydration.

Considering the above points, we reached the conclusion that it was meaningless if we were stuck at the research level at AIST, even though the materials had interesting performance and were worthy of obtaining national development grants. It was necessary to conduct materials development that led to future practical use and was cost effective. Therefore, we decided to terminate the research of imogolite except for the medical field.

3.2 Development of a new adsorbent by setting target conditions

Learning from the research on imogolite described above, we conducted investigation on the possibility of forming composites of a HO-Si(-OAl)₃ structure, which is the basic structure of allophane and imogolite, and a single layer of layered clay. The schematic diagram of the structure of this new adsorbent is shown in Fig. 6. As the background of this idea, the HO-Si(-OAl)₃ structure, which is the basic structure of allophane and imogolite, is formed when the silicate aqueous solution in which the Si/Al molar ratio is prepared to 0.5 is mixed with an aluminum aqueous solution.^[12] We thought it was possible to form a 1:1 layer of layered clay where the molar ratio is 1.0 by increasing the Si/Al molar ratio, and to create a composite that contained the structures of the two substances.

On the other hand, we set the target values for the yield that enabled reasonable cost and mass production. For sales price, we targeted the price somewhere between that of silica gel (about 100 yen/kg) and zeolite (1,000 yen/kg) that were being used widely as adsorbents. We set the minimum necessary conditions needed for the synthesis at the beginning, and then started the development. The conditions are shown below (Fig. 7).

- (1) From the perspective of synthesis cost, it should be synthesized using raw materials of liquid glass, aluminum sulfate, and sodium hydroxide, to enable synthesis using substances with low raw material cost.
- (2) To enable industrial synthesis in tons, it should be synthesized using the method for zeolite which is widely

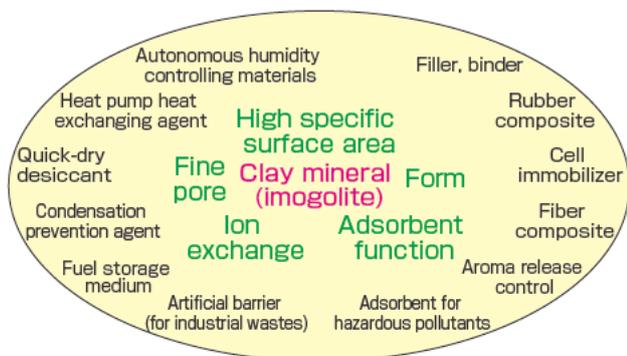


Fig. 5 Fields in which imogolite is used

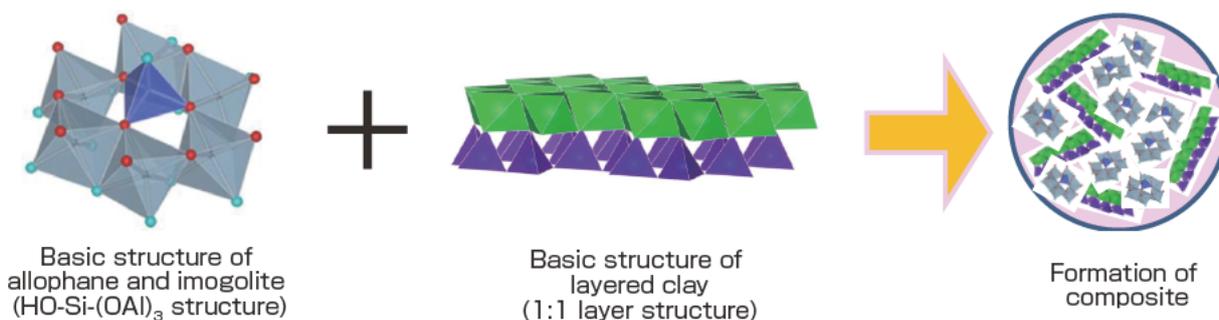


Fig. 6 Schematic diagram of the formation of new adsorbent structure

used where the heating temperature is less than 100 °C.

- (3) The method shall be one where synthesis can be accomplished at one cycle per day.
- (4) The synthesis efficiency (yield) shall be adjusted so the concentration at heating will produce 100 g or more of solid weight after dehydration of 1L of the solution.

The number of parameters to be investigated decreased by setting the binding condition as in (1)–(4), and we set the most important parameter as Si/Al molar ratio.

After setting such conditions, we attempted the synthesis of materials that showed adsorption volume of more than 30 wt% at relative humidity of 60 %, and had a linear adsorption isothermal curve. As a result, we succeeded in synthesizing an excellent water vapor adsorbent called HASClay[®].^[13]

The name HASClay[®] is derived from the fact that in its x-ray diffraction pattern, although there was no peak or layer structure of amorphous hydroxyl aluminum silicate (HAS), there was a peak for clay sheet. Also, the product was not a mixture of two substances but was one substance, and this was deemed the composite of HAS and clay, hence the name HASClay. The performance of HASClay was about 45 wt%, which greatly surpassed the initial target value of 30 wt% at relative humidity of 60 %. Considering the prospect of this future adsorbent we trademarked the product.

3.3 Study of the structure of HASClay and categorization by performance

Along period of two years was required for us to reach HASClay[®]. First, we were able to synthesize the material that was the primary substance of HASClay[®] (HASClay grade III or HASClay GIII). However, in ordinary analysis such as powder X-ray diffraction, we were unable to determine the difference between allophane and a Si/Al amorphous substance, and the difference could be seen only by solid NMR.

To clarify the structure of this substance, we temporarily suspended the conditions we set in Subchapter 3.2, and shifted to the identification of the substances. In the synthesis

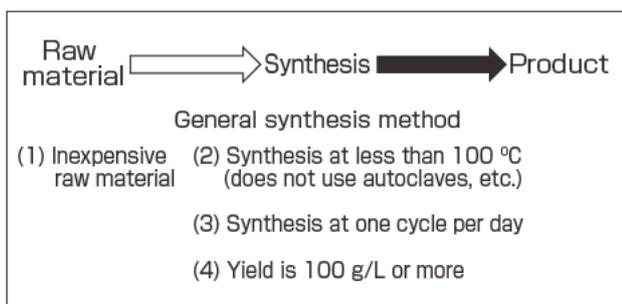


Fig. 7 Conditions necessary for the synthesis of new adsorbents

procedure, we conducted the removal of salts such as sodium chloride and sodium sulfate by centrifugation that was mandatory in high-concentration synthesis of imogolite, and the synthesis temperature of 98 °C or less was raised to 110 °C or more. As a result, by desalination, the water vapor adsorption capacity increased (HASClay grade II or HASClay GII). By further removing the salts and heating for 4 h at 200 °C, we discovered a substance that could be clearly identified by X-ray powder diffraction, and this was called the highest performing HASClay[®] (HASClay grade I or HASClay GI) that was the composite of amorphous aluminum silicate and low-crystalline clay. The HASClay GII and GIII became HASClay GI when it was heated for 40 days at 98 °C, and they were called HASClay precursors.

The X-ray powder diffraction patterns for HASClay GI and HASClay GIII are shown in Fig. 8,^[13] the ²⁹Si-NMR spectra in Fig. 9,^{[14][15]} and their TEM photographs are shown in Fig. 10.^{[14][16]}

In X-ray powder diffraction, HASClay GI had two types of peaks: one was a broad peak corresponding to the reflection of layered clay minerals (*hk0*) at around $2\theta = 21^\circ$ and 35° , and the other was a broad peak characteristic to amorphous aluminum silicate at around $2\theta = 26^\circ$ and 40° . In contrast, HASClay GIII had only one broad peak that was characteristic to amorphous aluminum silicate at around $2\theta = 26^\circ$ and 40° .

In the ²⁹Si-NMR spectrum, HASClay GI had a sharp peak at -78 ppm and a broad peak at -86 ppm and -110 ppm. The sharp peak of -78 ppm was caused by the structure similar to allophane and imogolite, and the remaining -86 ppm peak corresponded to the structure of layered aluminum silicate such as vermiculite, while the -110 ppm peak appeared in the area of peaks caused by a structure where all sides of Si tetrahedron had the Si-O-Si bonds. HASClay GIII showed a sharp peak at -78 ppm that arose from the structure similar to allophane and imogolite in the ²⁹Si-NMR spectrum, and

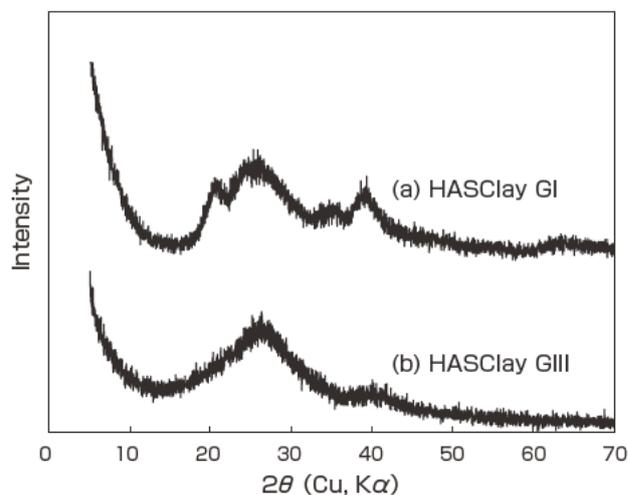


Fig. 8 Powder x-ray diffraction pattern of HASClay

Table 1. Category and comparison of HASClay

Name	Synthesis temperature	Desalination before heating	Manufacturing cost	Specific surface area
HASClay®-GI	150 ~ 200 °C	Yes	High	750 ~ 850 m ² /g
HASClay®-GII	80 ~ 100 °C	Yes	Somewhat low	550 ~ 650 m ² /g
HASClay®-GIII	80 ~ 100 °C	No	Low	450 ~ 550 m ² /g

another -86 ppm peak that corresponded to the structure of layered aluminum silicate such as vermiculite.

In TEM observation, HASClay GI was composed of particles of a size about 10 nm,^[14] while HASClay GIII was composed of particles of 2–10 nm sizes and hollow spherical particles of 2–3 nm sizes like allophane.^[16]

The x-ray powder diffraction pattern of HASClay GIII showed the diffraction pattern of amorphous aluminum silicate, and it could not be differentiated from other amorphous aluminum silicates in the TEM observation. The differentiation of the amorphous aluminum silicate was made possible by the solid ²⁹Si-NMR spectrum that showed two peaks of one derived from the allophane and imogolite

structure and the other derived from the clay structure.

The category and comparison of the three types of synthesized HASClay are shown in Table 1, and their water vapor adsorption isothermal curves are shown in Fig. 11. In HASClay performance, it is estimated that the reason the performance increases by desalination before heating is related to the formation of imogolite. In the synthesis of imogolite, it is known that the growth of nanotubes is inhibited in the presence of anions of chloride ions.^[10] Therefore, it is necessary to remove the anions for the development of structures like imogolite to a certain degree.

By the way, heating at 200 °C was a taboo for those who had been studying imogolite. This was because we knew that

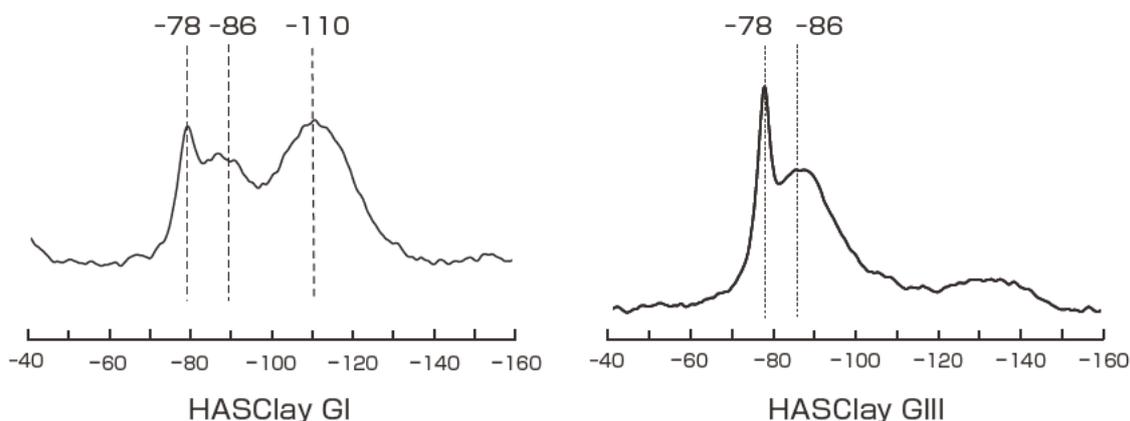


Fig. 9 ²⁹Si-NMR spectra of HASClay

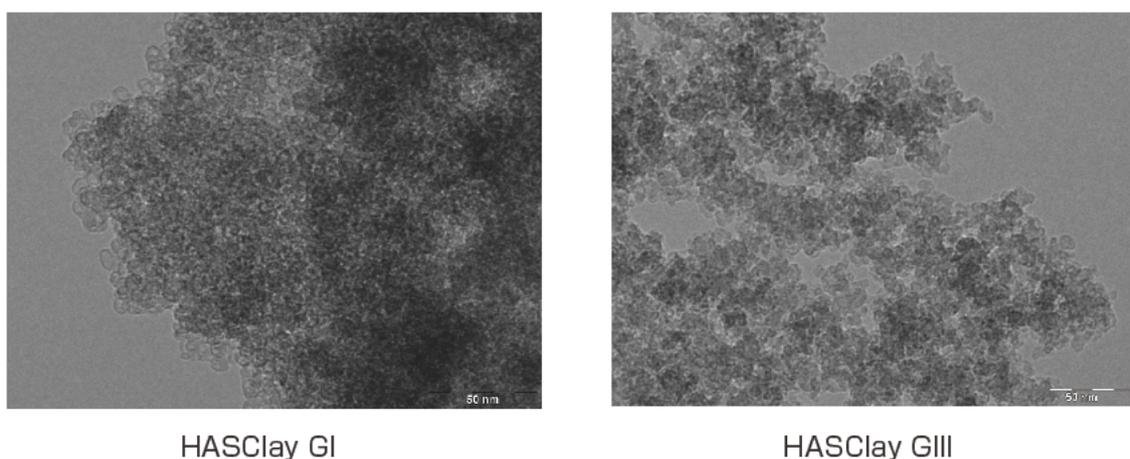


Fig. 10 TEM photographs of HASClay (Left: HASClay GI^[16], right: HASClay GIII^[14])

phase separation occurred when heating was done at 120 °C or higher, and imogolite would not be produced.^[17] This taboo was broken by one question from an assistant staff who said, “What happens when HASClay GIII is heated at high temperature?” At that time, the project was almost over and we had time on our hands, so we went ahead to actually see the phase separation phenomenon, but this led to the discovery of a new substance. We thought it was important not to blindly accept what we had experienced thus far, and to listen to and not reject the ideas of novices. However, over one year passed after the discovery of HASClay GIII before we discovered HASClay GI.

4 Scenario after the development of adsorbents

4.1 Role of AIST in the initial product realization

Although it became possible to develop excellent adsorbents, for industrial mass synthesis, we decided to go ahead with the commercialization of HASClay GIII product since its synthesis method was simple.

The investigation of desiccant rotors that was our primary objective was done using the new material HASClay GIII through joint research with a company that wished to fabricate a desiccant rotor using imogolite. About 1 kg of powder was synthesized without any problem, and good results were obtained in the papermaking test. In the next stage, we shifted to the fabrication of the rotor by actual

full papermaking, and the amount necessary was 40 kg of powder. In addition to the fact that we were not sure that the synthesizing company would accept this request, we expected that about half a year was necessary, and therefore, the synthesis was conducted at AIST. Although it was already confirmed that the synthesis of 1 kg per batch was possible, the time needed for washing after heating synthesis was a hurdle. This was solved by the *suihi* method (washing method where the HASClay and a large amount of water are mixed and then left to stand, and the water is separated from HASClay that settles at the bottom of the container by gravity). Our great gain was that we learned the necessary tricks for HASClay synthesis by repeating the procedure for large-volume synthesis. Ultimately, we synthesized 40 kg of materials three times in about eight months. As a result, it seemed that good performance of a desiccant rotor could be obtained, and when we asked the company that had handled imogolite synthesis before, it willingly agreed to synthesize HASClay. This was before the press release, but it was important that the company which would conduct the synthesis and the company which would use the product were starting to take action.

The fact that a company was at a preparatory stage of synthesizing and supplying HASClay was an extremely important factor in doing the press release later.

The development of the desiccant rotor was conducted in the following framework: AIST developed the synthesis method of the material with excellent adsorbent/desorbent capacities; the synthesis company developed the mass synthesis method that enabled synthesis in tons and adjusted particle grinding to create suitable particle distribution for fabricating the desiccant rotor; and the desiccant rotor manufacturing company fabricated the high-performance rotor using the HASClay precursor that was supplied by the synthesis company.

4.2 Development for the expansion of usage

Initially, the development of HASClay was conducted as development of adsorbents for desiccant air conditioning, but other uses were considered since it showed excellent adsorption of water vapor.

In the evaluation for humidity controlling building material, it was demonstrated that when the interior finishing material containing HASClay and gypsum was used, the power consumption of air conditioning was reduced.^[18] The demonstration test at the Experimental Building for Environment-Friendly Building Materials of AIST Chubu is shown in Fig. 12. In the evaluation of this humidity controlling building material, there were very few cases where the evaluation of the humidity controlling performance was done for the entire room instead of a test piece at a research lab level. It is important that the evaluation be done in the form close to actual use, and we had great advantage

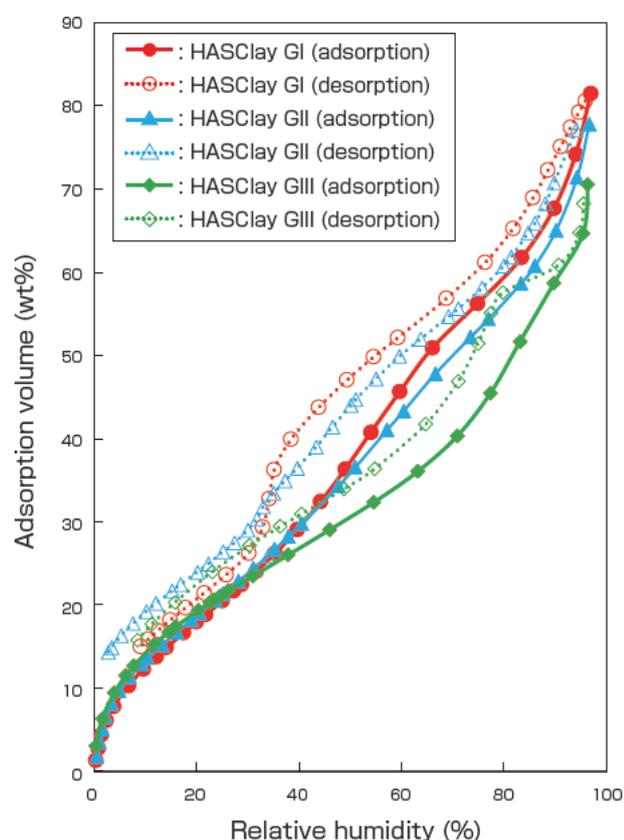


Fig. 11 Water vapor adsorption isothermal curves of HASClay

since we had experience in studying the humidity controlling material using allophane as shown in Subchapter 2.2.

The research of the humidity controlling building materials was conducted in a framework where the synthesis company supplied the synthesized HASClay precursor, this HASClay precursor was used at the Experimental Building for Environment-Friendly Building Materials of AIST Chubu, and AIST conducted the performance evaluation.

For the adsorption evaluation of carbon dioxide, it was shown that the adsorption volume was higher at atmospheric pressure or higher, compared to the generally used zeolite.^[19] For the adsorption of carbon dioxide, we had the experience of conducting subcontracted development of a substance using imogolite that could store carbon dioxide under a high-pressure condition.

4.3 Development for expanding the market

As explained above, we were able to show the adsorption capacity of water vapor and carbon dioxide, and since we had prospect for companies to produce HASClay and to fabricate desiccant rotors, we did a press release to widen the market. For water vapor, we conducted a press release in October 2008 using the data for HASClay GI, and for carbon dioxide, we did one using the data for HASClay GIII in December 2008.

The reaction after the press releases was great. There was much interest in vapor adsorption, and we received numerous inquiries. On the other hand, for carbon dioxide, although we had inquiries from companies that had high carbon dioxide emission like iron making and cement, the majority of inquiries were from educational science magazines.

Concerning the demands from outside AIST, there were many that were quite unimaginable for us within the institute, and we filed patents jointly following joint research. Although it is possible to imagine one application for one material, we felt the importance of collaborating with outside



Fig. 12 Application of interior finishing material that contains HASClay
(At AIST Chubu)

organizations for variation. Figure 13 shows the development of HASClay usage one year after the press release. The fields in which imogolite is used as shown in Fig. 5 and the fields for HASClay shown in Fig. 13 are basically the same. When imogolite and HASClay are compared carefully, in the adsorption of water vapor, imogolite has high adsorption/desorption in the low-humidity range and high-humidity range, while HASClay has high adsorption/desorption in the medium-humidity range, and therefore it is more suitable as a desiccant air conditioning material. On the other hand, the form of imogolite is tubular, while the form of HASClay is granular, and the use as a filler that was considered for imogolite cannot be covered by HASClay.

The promotion of photosynthesis in greenhouse cultivation using carbon dioxide was a rather shocking research. In general, the recovery and use of carbon dioxide are mostly conducted for the reduction of carbon dioxide emission to prevent global warming, while the use of carbon dioxide in the agricultural field is not for preventing global warming, but is purely for improving productivity and quality. Fortunately, we were able to work with the people from the Nara Prefecture Agricultural Research and Development Center who were experts in strawberry species development and cultivation, and we obtained public funds to develop a carbon dioxide recovery and delivery system unseen before.^[20] At the time of application to the public funds, we stated that carbon dioxide could be stored using HASClay, but the project was ultimately successful because we made the decision to switch to zeolite in the middle of the R&D due to efficiency consideration.

The research for the recovery and use of carbon dioxide involved the following framework: AIST worked on the selection of suitable materials for the recovery of carbon dioxide; the Nara Prefecture Agricultural Research and Development Center and Tohoku Agricultural Research Center, National Agriculture and Food Research Organization investigated the effect of carbon dioxide on strawberries, roses, and Eustomas; and the companies fabricated the whole heat exchange system that decreased the temperature of exhaust

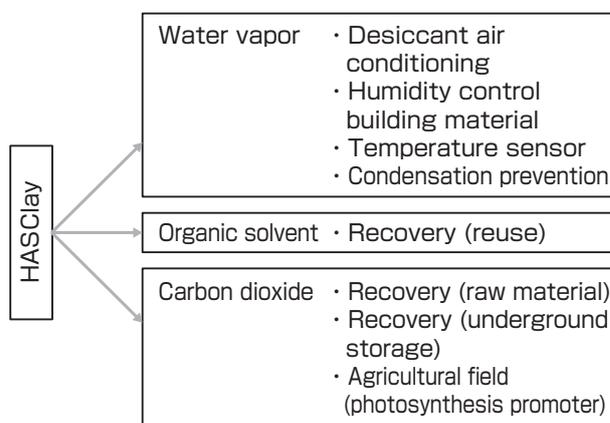


Fig. 13 Fields in which HASClay is used

gas and the CO₂ storage layer as well as the construction of the NO_x and SO_x removal device and dehumidifying systems.

5 Future issues

We discussed the development of HASClay and its application to the present, and the whole flow is shown in Fig. 14. Looking back, we feel that if we started from the sudden discovery of HASClay, it would have been difficult to set up a solid framework that we have now. We were able to achieve what we have now through the experiences with research of clay minerals, research of humidity controlling materials and nanomaterials in natural soil, and synthesis and use development of imogolite.

However, HASClay has not yet made major social contribution. For HASClay to be used more widely, the issue at this point is to change it from powder to a readily usable form. The manufacture of granules is essential, and it is also necessary for the desiccant rotor to be able to meet various requirements.

There are two major points that can be given for future development. As a material, it is necessary to find an adsorbent that has the same performance as HASClay GI, which was the target of the initial new material development, and that can be mass synthesized using inexpensive material at low temperature of 100 °C or less. To increase the production volume of HASClay, it is necessary to develop a new system and build a new industry. A professor of a university said to me, “The person who developed the material knows most about that material. That’s why the person who developed the material is the most likely person to develop a good system.”

We shall continue to develop materials to achieve the initial objective, and we shall also work on the design

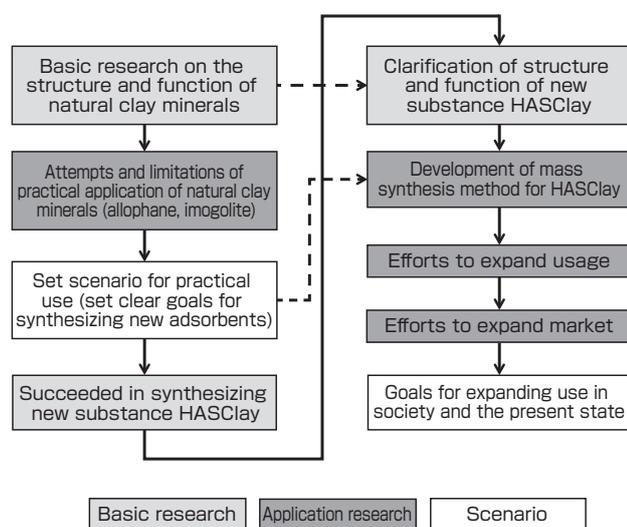


Fig. 14 Development of HASClay and flow up to present

and construction of a new system to spread the use of this material.

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Discussions with Reviewers

1 Overall

Comment (Shigeo Togashi, AIST)

With the results of basic research on the structure and function of natural clay as its base, you present the course of synthesizing clay mineral HASClay and achieving its practical use through joint research with companies, through a scenario where clear goals have been set, to realize new use of clay minerals in society.

After you became aware of the limitations of the use of natural clay materials, you shifted to synthesis, and then went back to basic research to clarify the structure and function of the newly synthesized substance HASClay. This led to the improvement of the synthesis method for HASClay and the expansion of its use.

The scenario is developed as you go back and forth between the basic and application research after setting up a scenario with clear goals, and the range of use is expanded through joint research with the private sector. This paper can be evaluated highly as a *Synthesiology* paper.

Comment (Toshimi Shimizu, AIST)

This paper describes the details for the development of the inorganic porous material HASClay[®] that is a composite of amorphous aluminum silicate and low-crystalline clay, and its application as adsorbents in desiccant air conditioning. After becoming aware of the limitations of natural adsorbents such as allophane and imogolite, you leave them to develop a new adsorbent. You present a scenario in which various requirements are overcome in chronological order. The R&D scenario described is interesting because the issues are solved to obtain the required functions for energy-saving dehumidifier/humidifier by considering inexpensive raw materials, synthesis costs, mass production, and adsorption performance. I think this paper is suitable for publication in *Synthesiology*.

2 Development of the scenario

Comment (Shigeo Togashi)

For development of the overall scenario described herein, please add a flow diagram. Please include the topics of this paper in that diagram, and refer to other *Synthesiology* papers on how to create the diagram.

Answer (Masaya Suzuki)

Based on your comment on the development of the overall scenario, I categorized the items into three categories—basic research, application research, and scenario—and added Fig. 14 in “5. Future issues.”

3 Composition of the elemental technologies**Comment (Toshimi Shimizu)**

The structure of the first draft is merely a chronological presentation of a usual R&D story, and I feel there is a lack of synthesesiological analysis expected for a *Synthesiology* paper. When you set the final target of the adsorbent as use in desiccant air conditioning, the issues to be solved seem to be the drastic improvement of synthesis yield, mass production in tons, reduction of raw material and adsorbent costs, safety of the nanotube substance, and the improvement of adsorption performance as indicated by the linear adsorption isothermal curve. You describe as the elemental technologies the concentration, reaction temperature, desalination, heating, and other conditions during synthesis. However, the correlations between the issues and elemental technologies are not clear. From the perspective of what kind of R&D scenario the authors wrote and how the issues were overcome, I think you need to add a slightly more technological description (especially Subchapters 3.2 and 3.3 of the first draft). To do so, it is important to first draw the correlation diagram of elemental technologies. Although there is no example that's exactly the same, there are *Synthesiology* papers on adsorbents and others that may serve as reference for creating the diagrams that show the elemental technologies and development framework. For elemental technologies, you may be able to refer to “Development of massive synthesis method of organic nanotube toward practical use—Integration of molecular design, molecular synthesis and safety assessment for materials having market competitiveness” [*Synthesiology—English edition*, 1, 169–176 (2008)] and “Novel functional gels and their commercial distribution as chemical reagents—New development of functional soft-materials” [*Synthesiology—English edition*, 5, 181–189 (2012)]. For the development framework and relationship with companies, please refer to “A novel technology for production of drinking water in emergencies—Specific material for selective nitrate adsorption” [*Synthesiology—English edition*, 4, 156–161 (2012)].

Answer (Masaya Suzuki)

Thank you for your advice on the necessity for drawing the diagram of elemental technologies in conducting synthesesiological analysis. I felt it was difficult to present a composition diagram of elemental technologies for inorganic substances, unlike the organic nanotubes and polymer gels, but I added the findings so far to Subchapter 3.2. For technological details, I made additions to Subchapter 3.3. For development organization, I added a text to Chapter 4.

4 Definition, birth, and naming of HASClay**Comment (Toshimi Shimizu)**

In the first draft, it is unclear what exactly HASClay is. In the paper, it says that you looked at the Si/Al molar ratio as a strategy to solve the issues on raw material costs, synthesis costs, production volume, synthesis yield, and others. Obtaining a hint from the fact that natural imogolite has constant composition ratio, while natural allophane is amorphous with unstable molar ratio between 0.5–1.0, you investigated the adsorption property of the individual products for water vapor, which were obtained by changing the molar ratio. However, the criteria that determine the final grade of HASClay are not the Si/Al molar ratio or the adsorption property, but they seem to be synthesis conditions,

particularly temperature conditions and the manufacturing methods involving desalination treatment.

Is HASClay a product with well-defined structures that can only be manufactured under rational synthesis conditions, or is it a product obtained in the course of a reaction process? The readers who specialize in chemistry will be greatly interested in the essence and nature of HASClay. Please describe the structural, morphological, and analytical properties and definitions of HASClay as much as you know or are allowed to disclose. I think you also need to discuss how you differentiate from similar adsorbents whose main ingredients are aluminum silicate, from the viewpoint of intellectual property strategy.

In relation to this, please describe further the need to grade HASClay, and the definitive factor in the birth of HASClay that required two years for its development. Also, HASClay seems to be a trademark, but can you give additional discussion on how you came up with the name and why you decided to trademark this product?

Answer (Masaya Suzuki)

Since I did not provide explanation on the substances and attributes of HASClay, I made additions to Subchapter 3.3. The origin of the name is due to the fact that in x-ray diffraction, although there was no peak or layer structure of amorphous hydroxyl aluminum silicate (HAS), the peak for clay sheet could be seen. Also the product is not a mixture of two substances but consists of one substance that is deemed the composite of HAS and clay, hence the name HASClay. Along with the trademarking, I described this in Subchapter 3.2.

5 Structure of nano-adsorbent**Comment (Toshimi Shimizu)**

Allophane and imogolite have well-defined sizes and dimensions as independent structures of nanometer scale. On the other hand, HASClay seems to be a composite of low-crystalline clay and amorphous aluminum silicate that contains imogolite of low-purity. To deepen the understanding of general readers for HASClay, I recommend you provide the structural figures of allophane and imogolite that are already known, as well as a photograph that depicts the powder form of HASClay.

Answer (Masaya Suzuki)

As you indicated, the structural diagrams of allophane and imogolite and the TEM photograph of HASClay are essential in showing the composition of elemental technologies of HASClay and the HASClay structure. The structural diagrams of allophane and imogolite were placed in Subchapter 2.1, while the TEM photograph of HASClay was added to Subchapter 3.3.

6 Development organization and role division**Comment (Toshimi Shimizu)**

In conducting joint research with companies specializing in the adsorbents for desiccant air conditioning, materials for room humidity control, carbon dioxide recovery/use systems, and others, please provide additional discussion on the respective elemental technologies to solve the problems for public research institutions and companies, and the division of roles.

Answer (Masaya Suzuki)

Problem solving by public institutions and companies in desiccant air conditioning, room humidity control materials, and carbon dioxide recovery/use systems, and division of roles were explained in Chapter 4.

7 Fields in which HASClay is used**Question (Shigeko Togashi)**

For the fields in which imogolite is used as shown in the diagram in the first draft, what are the differences with the fields

in which HASClay is used, other than the possibility of practical realization?

Answer (Masaya Suzuki)

The fields in which imogolite is used and ones in which HASClay is used as shown in Fig. 5 of the final draft are basically the same. For the adsorption of water vapor, imogolite has high adsorption/desorption volume in the low humidity and high humidity ranges, while HASClay has high adsorption/desorption

volume in the medium humidity range. Therefore, HASClay is a more suitable material for desiccant air conditioning than imogolite. On the other hand, imogolite has a tubular form while HASClay has a granular form, and therefore, HASClay cannot be used as a filler that was the usage expected for imogolite. These points were added to “4.3 Development for expanding the market.”