A novel technology for production of drinking water in emergencies

— Specific material for selective nitrate adsorption —

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Underground water has been used as a suitable drinking water source for a long time. In recent years, however, not a small number of wells have become out of use as a drinking water source owing to pollution with nitrate or nitrite. A mobile water purification system has been developed with advantages in portability and cost to utilize the polluted wells in emergencies. The system has been achieved by the combination of nitrate ion selective adsorbent developed in our group and contactless supporting and shaping technology developed by a company which enables formation of a material into easy-to-handle shapes without decreasing the performance of the functional material. This paper mainly describes the development of the nitrate ion selective adsorbent material, which is the important elemental technology in the mobile water purification system.

***Keywords* :** Nitrate ion, ion specific adsorbent, distributed without any contact, drinking water, water purification

1 Background of research: Current situation of the underground water pollution[1]

The quality of underground water is published in the "Result of the Underground Water Quality Measurement" by the Ministry of the Environment. According to the Outline Survey for FY 2009[Note 1)], the percentage of wells that exceeded the environmental standard was about 6 %. By items, the environmental standard exceedance (3.8 %) of "nitrate-nitrogen and nitrite-nitrogen" was the highest. This was followed by arsenic (1.0 %), fluoride (0.5 %), lead (0.3 %), and boron (0.2 %). The top three items have not changed in ranking since the environmental standard items were added in 1999 (Fig. 1). Since 2003, there is a decrease tendency of "nitrate-nitrogen and nitrite-nitrogen" as seen in Fig. 1. It is assumed that the wells that were found to have underground water pollution would be excluded from the Outline Survey, and therefore, in turn the number of wells for continuous monitoring in Fig. 2 is increasing.

The wells that were found to be polluted in the Outline Survey becomes the subject of the Continuous Monitoring Survey[Note 2)]. Since the wells will be removed from the monitoring list if the pollution improves, the overall trend of pollution can be seen from the Continuous Monitoring Survey results. After the FY 2004, the number of wells with standard exceedance of "nitrate-nitrogen and nitrite-nitrogen" has been high and continues to increase (Fig. 2).

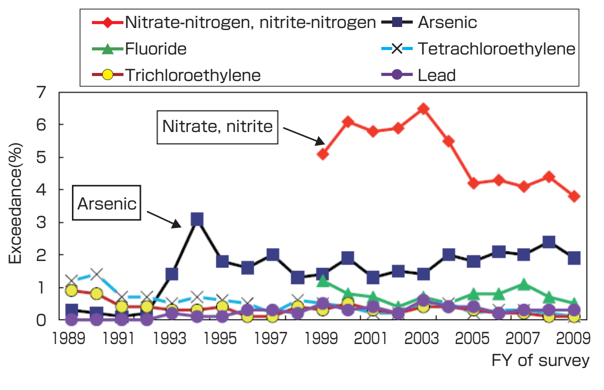

Fig. 1 Transition of the exceedance of environmental standard in the Groundwater Outline Survey (major items)

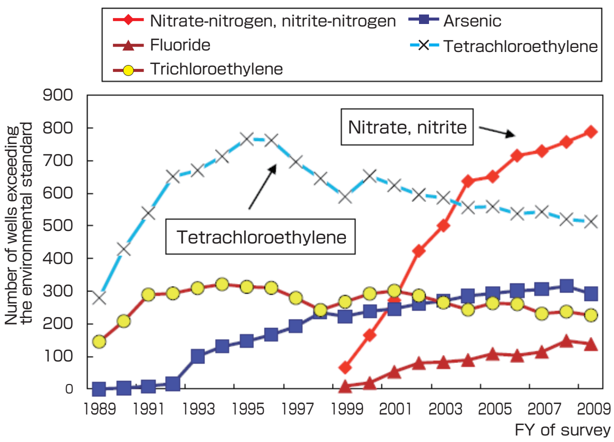

Fig. 2 Transition of the number of wells exceeding the environmental standard in Groundwater Continuous Monitoring Survey (major items)

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In the past five years, there were 530 cities, towns, and villages with wells that exceeded the environmental standard, and that dominates 31 % of all cities, towns, and villages. The cause of “nitrate-nitrogen and nitrite-nitrogen” pollution is mainly due to the nitrogen from fertilizer application, farm animal excrements, and sewage. In many cases there are multiple causes of pollution, and the range of pollution covers a large area.

When the water containing “nitrate-nitrogen and nitrite-nitrogen” over a certain concentration is consumed, it is known to cause methemoglobinemia, a disease where the oxygen deficiency occurs due to the loss of oxygen carrying capacity of the blood, mainly in infants. The environmental standard value for contamination of underground water for “nitrate-nitrogen and nitrite-nitrogen” is 10 mg/L or less, which is the sum of the concentrations of the “nitrate ion” and “nitrite ion” converted into “nitrogen”.

In a case where the pollution that exceeds the environmental standard is found in the groundwater, according to the Water Quality Pollution Control Act, the prefectures and ordinance-designated cities must take the following measures: 1) take measures such as installing drinking regulations, such as designating as undrinkable, from the perspective of protecting health, 2) conduct surveys to determine the range of pollution and to identify the source of pollution, and 3) promote measures such as purification considering the usage of the groundwater.

Attempts to remove the nitrate ion using the anion exchanger have been done, but the effect was limited in the presence of coexisting anions. Therefore we developed a novel adsorbent reagent[Note 3] that was selective for nitrate ion (Figs. 3, 4, and 5).The adsorbent reagent selective to nitrate ion is a layered double hydroxide (LDH) of aluminum and magnesium. It is an inorganic ion exchanger ($Mg_{0.80}Al_{0.20}(OH)_2Cl_{0.20}$) with anions with different Mg/Al ratios and ion exchangeability from the mineral called the hydrotalcite ($Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.125}$). The studies to increase the ion exchanging volume were done by increasing the aluminum content in the LDH, but it was found that the selectivity against nitrate ion appeared by decreasing the aluminum content. Also, since it was a chloride ion type, the nitrate ion could be adsorbed in water such as seawater that contains vast amounts of chloride ions.

The awareness of disaster prevention increased since the Great Hanshin Awaji Earthquake, and many local governments prepared the water purification system for emergency. However, the reverse osmosis (RO) system that can produce pure water from seawater requires power and cannot be operated readily by an untrained person, and therefore, a simple water purification system was in demand. In this R&D, we aimed at a product different from the RO system, and at a market of “simple device that can be operated manually without exterior power source”, and created a prototype. The water qualities were measured for raw water from rivers, wells, and pools. The river water did not contain harmful ion, and sufficient drinkability could be obtained with the combination of simple filtering and sterilization. Some well water exceeded the tap water standard value for nitrate ion in some regions, and selective adsorbent material for nitrate ion would be effective. For pool water, the bromate ion, an impurity of the chloride disinfectant, was detected in some cases, and it was necessary to use a removing reagent for bromate ion.

2 Objective of the R&D

In the Consortium R&D Project for Regional Revitalization of FY 2006, a joint research unit was organized centered around AIST and Teijin Engineering Ltd., with universities, public research institutions, and local small/medium companies such as Kyowa Chemical Industry Co., Ltd. The unit worked on the topic “Development of mobile water purification system by the contactless compositing of nano-particles with separating functions”.

AIST developed a nitrate ion removal system using a selective adsorbent reagent to make groundwater, which

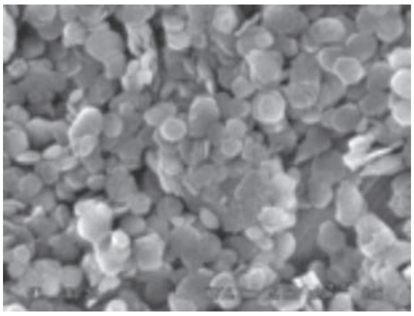

Fig. 3 SEM photograph of powder adsorbent reagent
Size of plate-like particle: width about 500 nm and thickness about 20 nm

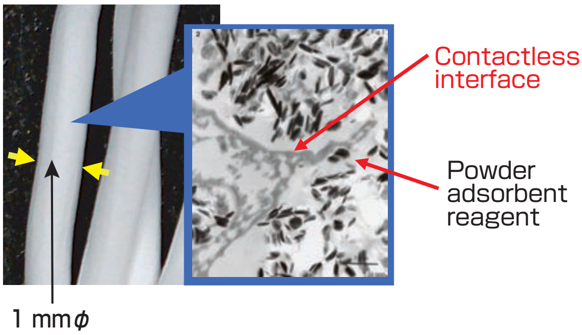

Fig. 4 SEM and TEM photographs of the fibrous adsorbent material
Diameter of the fiber is about 1 mm. The interior structure consists of powder adsorbent reagent sealed inside the porous polymer without contact.

is polluted by nitrate ions and is normally undrinkable, drinkable at times of emergency[2].

For the product to be realized, the following goals were set to fulfill the social demand (Fig. 6):

1) Price: 2 million yen per system; lower than existing product
2) Production capacity: 20 ton drinkable water per system per day; at 3 L per person, for about 6,000 people
3) Water quality: comparable level to tap water; clear the 50 items of tap water standard

To achieve these goals, the following targets were set, to be achieved by the end of the project:

1) Prototype: production capacity at 1/10 of the production model; 2 ton/day/system
2) High-speed processing of over 83 L/hour/system: 20 times or more of the column volume (about 4 L) per hour
3) Mobility
   - Downsizing to suitcase size: can be transported by one person
   - Combination of 1 μm particulate removal filter to counter cryptosporidium, organic material removal column for odor causing substance, etc., and nitrate ion removal column
   - Energy saving: manually powered, requires no power source such as electricity or engine, low noise
   - Operability: easy maintenance by simple principle and unitization
4) Nitrate ion removal: technological development to achieve drinking water standard (<10 mg/L)

The R&D scenario was as follows: AIST would reproduce the adsorption volume and selectivity functions of the “nitrate ion selective adsorbent reagent”, for which the AIST owns the patent, as the elemental technology (Fig. 3); Kyowa Chemical Industry Co., Ltd. would establish the mass production technology; and Teijin Engineering Ltd. would deploy the contactless supporting and shaping technology (Figs. 4 and 5) to manufacture the adsorbent material that will remove the nitrate ion while maintaining the function.

Teijin Engineering Ltd. was also looking at the greater market of functional material for water treatment, as in the powder activated carbon, by using the contactless supporting and shaping technology.

The emergency water purification system with the two functions, organic substance and nitrate ion removal, and the suitcase size prototype with no power source, manual pump, and unitization became the clear goals under the leadership of Teijin Engineering Ltd. (Fig. 7).

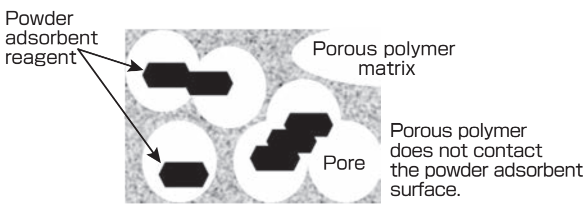

Fig. 5 Schematic diagram of contactless supporting and shaping

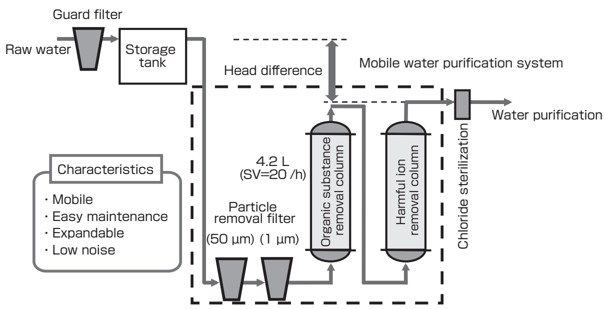

Fig. 7 Characteristic of the mobile water purification system and flow diagram

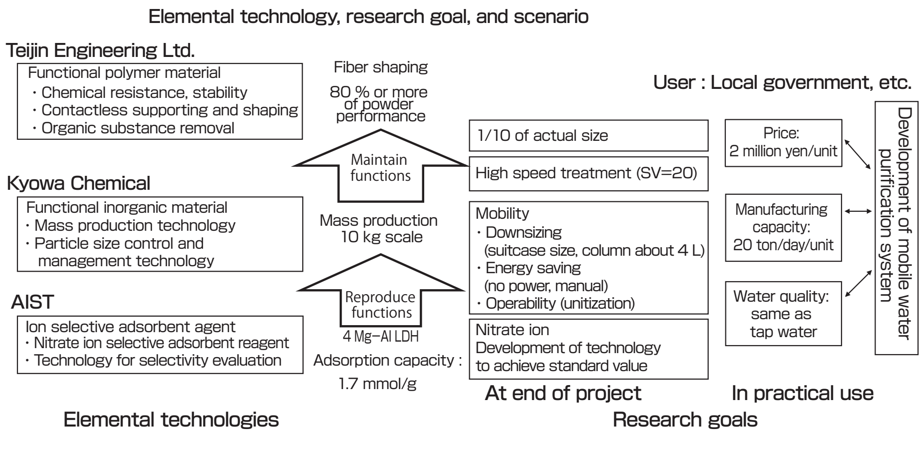

Fig. 6 Overview of the elemental technologies and research goals

3 Nitrate ion selective adsorbent "material" (topic for elemental technology needed for outcome realization)

3.1 Mass production technology (reproducibility of function)

Utilizing the experience of mass-producing similar compounds, Kyowa Chemical succeeded in the mass production of nitrate ion selective adsorbent by incorporating the AIST synthesis method into the industrial method. Although, by experience, Kyowa Chemical was aware of the positive correlation of the nitrate ion selectivity and crystalline property that were determined from the peak strength and half-value width of XRD, it was able to find the optimal synthesis condition when AIST evaluated the nitrate ion selectivity that Kyowa Chemical was unable to evaluate. To avoid clogging the nozzle when shaping, Kyowa's know-how was used for the pulverization and sifting of the adsorbent reagent, and the specification of particle diameter 45 µm or less, which was required by Teijin Engineering Ltd., was achieved.

The stance of conducting the R&D without leaking the corporate know-how to others by clearly setting the product specification, or adsorbent volume of nitrate ion > 1.7 mmol/g – powder adsorbent reagent, distribution coefficient ≒ 3000, is important in working with companies that have the technological capability.

3.2 Shaping technology (maintaining the function)

When shaping the powder adsorbent reagent, the binder ingredient covers the surface of the adsorbent and its performance decreases dramatically in the ordinary method where the adsorbent reagent and the binder are simply mixed. We conducted the shaping by using the liquid curing method for collecting lithium ion from seawater, but only about 60 % of the adsorbent performance could be obtained[3]. Treatment of large amount was difficult by the contactless supporting method[4] developed by Teijin Engineering Ltd., even when the researcher was resident at AIST Shikoku to conduct joint research over several years, and this was one of the issues.

The adsorbent material that could be produced at laboratory scale would not remove the nitrate ions when used in the large equipment at the plant. When this was carefully investigated at AIST, we reached the conclusion that the water, which in this plant was well water used directly, was suspect. We saw improvement by using the pure water line. Because the nitrate ion adsorbent material had high carbonate ion selectivity, the ion exchanging sites on the adsorbent material were all substituted when the adsorbent was washed with well water containing the carbonate ion, and the adsorbent became inactive against the nitrate ion.

We considered reviving the adsorbent material that failed to remove the nitrate ion with high concentration of saltwater, and found that it could be revived. That the spent nitrate ion adsorbent material could be used repeatedly was one of the unexpected results. However, it was also found that more pure water was required to produce the drinking water that could be manufactured by the water purification system. Therefore, the use of this system would be limited in times of normalcy. It was also projected that the nitrate ion removal performance would decrease if the carbonate ion was present in the polluted water.

4 Merit of the consortium and the remaining issues for commercialization (synthesis method for outcome realization)

Product realization was difficult with joint research with companies only. Therefore, we developed the nitrate ion adsorbent "material" by establishing a consortium and jointly setting the R&D objective. As a merit, the participating industry, government, and academia obtained the research funds as the joiners of the collaboration, and were able to focus on the product realization. By conducting the research using public funds, the private companies were given time limits and obligations, and this allowed them to achieve numerical objectives that they wrote in the proposals and were able to create a basic prototype (Fig. 8).

The follow-up research was continued for three years toward product realization. What remained were the developments of the system that instantly determines whether this water purification system can be used effectively, and the system for real time monitoring of the purification capacity. Teijin Engineering, the main body of the commercialization effort, terminated the development of this product in FY 2010.

5 Conclusion (evaluation of the results and future development)

Concerning the self-evaluation of achievements, we reached the fourth stage out of ten. It should be reemphasized that the issues that must be solved before commercialization are

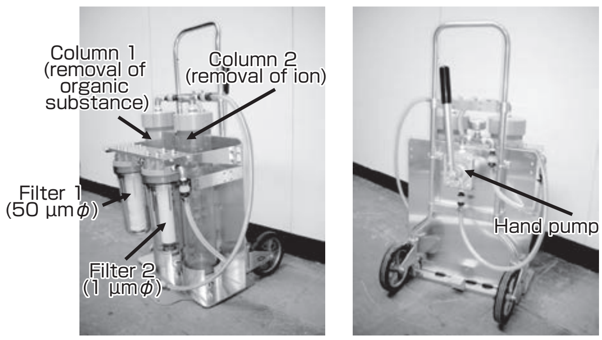

Fig. 8 Prototype of the mobile water purification system (exhibited at Hannover Messe 2008)

the function to instantly determine whether this purification system can be used effectively and the function to monitor the purification capacity in real time. We shall continue the R&D to solve these issues.

What I felt most strongly in this research is that the technology resides in people, and the continuation of technology is the responsibility of the organization. Among the people who cooperated in the joint research, there were the so-called baby boomers who were no longer in the forefront but had top-notch skills. Many things could be accomplished only because of their expert craftsman skills, and I fear that the technology may disappear if the organization is unable to pass on this technology.

The situation is similar at AIST, as the contract employees who accumulate the know-how by getting their hands directly on the project become distant from the work when a project finishes. When a foreign student learns the skills and returns to his/her home country, he/she can work as an expert of that research. However, an organization that fails to pass on the technology to the next generation because of some reorganization will cease to exist when the people with skills leave.

As the next development, we shall spend effort on the development of the sensor that can detect the nitrate ion in real time. The realization research of the ion selective adsorbent reagent will be done by applying the technology for selective adsorbents that was accumulated so far. This will be applied to resource, energy, environment, and health fields, and we hope this will produce some sort of product.

Acknowledgements

This technology was developed under the leadership of Takahiro Hirotsu, who was the Deputy Director of the Health Research Institute, AIST and the representative of "Development of mobile water purification system by the contactless compositing of nano-particles with separating functions", Consortium R&D Project for Regional Revitalization (FY 2006~2007). I express my thanks to: the engineers and researchers who participated in the project, including the people of AIST Shikoku, Teijin Engineering Ltd., and Kyowa Chemical Industry Co., Ltd.; the people of Awa Paper Mfg. Co., Ltd., Kagawa Prefectural Industrial Technology Center, Tokushima Prefectural Industrial Technology Center, Faculty of Engineering of the Kagawa University, and Naruto University of Education; and late Kyoya Tamura and Ryoichi Nishimura of the Shikoku Industry and Technology Promotion Center (STEP) who provided support as the managing entity.

Notes

Note 1) Survey conducted to understand the overall situation of the regional groundwater quality.

Note 2) Survey conducted for the continuous monitoring of the region in which pollution was detected.

Note 3) Here, the terms adsorbent "reagent" (Fig. 3) and adsorbent "material" (Figs. 4 and 5) are distinguished as follows.
Adsorbent reagent: a compound substance that can be expressed as one chemical equation. In the case of the inorganic ion exchanger, it is powder. In many cases, phase separation may be difficult if it is used directly for water treatment.
Adsorbent material: a material made by shaping the powder adsorbent reagent with binders, to make the phase separation easy when it is used in water treatment. Since it contains substances other than the active ingredient, performance per volume decreases compared to the powder adsorbent reagent.

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Completed the doctorate course at the Department of Molecular Science and Technology, Graduate School of Engineering Sciences, Kyushu University in 1993. Joined the Shikoku National Industrial Research Institute, Agency of Industrial Science and Technology in 1993. Worked as the planning officer of the Tsukuba Planning Headquarter, AIST. Also worked at the Research Institute for Environmental Management Technology and Health Technology Research Center. Currently, leader of the Health Hazard Reduction Technology Research Group, Health Research Institute. Participated in research on boron isotopes. Currently does research in the development of adsorbent reagent that is selective to harmful anions and the technology to reduce health hazard substances.

Discussions with Reviewers

1 Setting of the product specs

Question (Norimitsu Murayama, Advanced Manufacturing Research Institute, AIST)

Your indication of the product specs is very instructive: "The stance of conducting the R&D without leaking the corporate know-how to others by clearly setting the product specification is important in working with companies that have the technological capability". In this R&D, please tell us which organization took the leadership in setting the product specifications. Also, can you talk about your efforts on the breakdown from product spec setting to goal setting of the elemental technologies?

Answer (Akinari Sonoda)

As written in the Acknowledgement, the product specs were set under the leadership of Principal Researcher Hirotsu (currently Deputy Director) who was the research representative. As written in "2. Objective of the R&D", in setting the product specs, we set the goal that would allow us to win the competition against the current product, and the breakdown into elemental technologies started from there. Particularly, the aim at SV=20 was set for the flow rate, and we jumped into the experiment without certainties. As a result, although the treatment volume per column volume decreased, we were able to produce drinking water that fulfilled the tap water standards.

2 Reason the product was not realized

Question (Akira Kageyama, Innovation Promotion Headquarter, AIST)

This paper presents the development of the nitrate ion selective adsorbent "material" to supply drinking water in times of emergency, conducted jointly with private companies, and it achieves the technological objective through integrated R&D. On the other hand, the company made the final decision of halting the product realization of the water purification system. The reasons include the cost compared to the competing technology and the market size estimation (or projection) as well as the technological objective. Does that mean that the goal setting was too loose?

Answer (Akinari Sonoda)

One of the reasons was, as mentioned in "4. Merit of the consortium and the remaining issues for commercialization", we did not do the simultaneous development of real time monitoring technology, and the user could not determine the pros and cons of using this system.

In the initial goal setting, we conducted the R&D and prototype fabrication by setting our objective as creating a product that was distinctly different from the current RO system. However, looking back at the end of R&D, not only were the objective values insufficient, but also 1) market size projection, 2) cost setting, and 3) consideration of the market development were not sufficient in terms of differentiation against the existing technology. That means the goal setting was, as a result, not sufficient.

While the above comment includes my inferences, in the R&D with the objective of product realization, it is important to review these points and plan ahead with the cooperation of the partner company.

3 Continuation of the technology

Question (Norimitsu Murayama)

I think your comment "the technology resides in people, and the continuation of technology is the responsibility of the organization" is an extremely important issue. Can you tell us your specific ideas or comments on the continuity of technology?

Answer (Akinari Sonoda)

I think the continuity of the technology is difficult in AIST, because the institutes undergo reorganizations and terminations where the name of the institute is obliterated each time. Of course, it is not possible to pass on all the technologies, and perhaps certain technologies must be selected. For example, the technology that will be replaced by new technology and will never be used in the future may disappear, but the major technology that will be the main stream should be passed on by forming a group that includes all generations (age groups). The former Agency of Industrial Science Technology wasn't too bad in terms of continuation of technology, because it employed people to supplement the personnel quota. For the continuation of technology, the ideal is to have groups of five to seven people share common technologies at all times. One idea may be to have a larger category of the groups.