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Sanshi-suimei-ron—Fundamentals in environmental chemistry

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Abstract - Environmental Chemistry is defined as geological chemistry in which the effect of human activities is seriously taken into consideration. Often it has been erroneously taken as a technique to prevent ecosystem from chemical pollution. In this paper, the author proposes the Quadri-Principia of Empedokles, i.e., Fire (sunlight), Water, Soil and Air as the fundamental elements in Environmental Chemistry and discusses reactions and changes occurring in the atmospheric, hydrospheric and lithospheric environments from the standpoint of chemistry, physics, biology, geology, ecology and other social sciences. He describes fundamental conditions of the ideal environment and suggests the environmental engineering desirable in future.

INTRODUCTION

Long ago on the Earth, Nature was unaffected by human activities. However, those days with the rapid increase of human activities both in quality and in quantity Nature can no longer be understood without taking these activities into consideration. "Environmental Chemistry" can be defined as geological chemistry in which the effect of human activities is seriously taken into consideration. There are many so-called naturalists who insist that we should keep nature as it is and stop big development in order not to destroy nature. They also insist that we can do that if we avoid unnecessary consumption, because modern civilization is supported by it. However, it is clear that we cannot do this without sacrificing liberty and/or progress in civilization.

In this paper, the author wishes to set conditions by which the human population will continue to increase as it does now and people will continue to develop their civilization. Under such conditions, the way in which global environment changes must be anticipated, and what we should do to keep the environment healthy should be carefully planned.

FIRE, WATER, SOIL AND AIR: FOUR FUNDAMENTAL ELEMENTS IN ENVIRONMENTAL CHEMISTRY

The fundamental philosophy of natural sciences started from the quantumization of matter: that is, all substances or phenomena be composed of material quantum and energy quantum. The concept was first proposed by the Putagolas school which set the atomon as the fundamental unit particle. The concept appeared after a classical infinitely dividable concept believed by the Eleatic school.

The author proposes to introduce the Quadri-Principia of Empedokles as the basis of environmental chemistry. In this concept Fire, Water, Soil and Air are the fundamental elements which compose the Universe. This four elements theory was supported by many famous chemists until the 17th century. In modern chemistry, it is believed that about one hundred chemical elements beginning from hydrogen and going on to trans-uraniums are the atomic species; thus the four elements theory is now nothing more than a fairy tale. Even though the chemical elements themselves are found not "atomon" but can be divided into elementary particles, which are again not elementary but have a further fine structures in them. In spite of the fact that the atom is not the atomon but no chemist or physicist has ever apologized this misforecast, yet, they are still continuing to discover new "elementary" particles. Investigations in this area belong to the field of physics. Today, the domain of chemistry has become almost the same as that of physics, however chemists are concerned mainly with atoms and molecules, while very few bother with the elementary particles. In biology, the cell is the fundamental element but they are now paying much more attention to the area of molecular biology, and less to atomic levels. Thus, each scientific discipline in natural science has its own upper grade elements although all matter is made of the atomon: i.e. the molecule in chemistry and the biological cell in biology.

A similar way of thinking has to be applied to environmental chemistry. We have had to treat many environmental incidents, such as photo-chemical smog, oxygenless air and red tides, in any case by case after they happened. This way of doing things does not enable us to foresee accidents and thus avoid them. Pollution is caused by various human activities, but nature's self-cleaning ability enables it to recover sooner or later. What is this fundamental self-restoring ability? In the answer, Empedokles' four elements i.e. fire (sunlight), water,

*SANSHI-SUIMEI-RON (山紫水明論): Theory to preserve violet mountain and clear water (in Japanese and Chinese) soil and air are basic. When the environment is disturbed and one or more of these four elements is disrupted, it becomes weak and is apt to become ill, an illness which is hard to recover from and after becomes more serious. In the next section, I will discuss how Empedokles' elements function in the healthy and in the ill environment, taking the hydrosphere as an example.

CHEMICAL PROCESS IN THE HYDROSPHERE ENVIRONMENT

What kind of chemical processes are operating in the hydrosphere; i.e. in rivers, lakes and the sea? First let us consider the environment of the clean healthy hydrosphere like the main basin of Lake Biwa*. The northern part or the main basin is still a relatively clean oligotrophic lake, but the southern part of Lake Biwa, a so-called sub-basin belongs to a category of eutrophic lakes; i.e. the sub-basin contains a total amount of phosphorus of more than 0.02 ppm and nitrogen of more than 0.2 ppm. Here, the author proposes to define a "red-tide eutrophic" lake as that contains a total amount of silicon of more than 2 ppm besides phosphorus and nitrogen of the eutrophic amount.

Lake Biwa is believed to have existed for more than four million years, which means it is one of the oldest lakes in the world. From the beginning of human history, the chemical composition of the lake water seems to have changed very little, that is up to about twenty years ago (in 1965), when the amount of phosphorus gradually began to increase. In 1970, the content exceeded over 0.02 in the sub-basin; nitrogen concentration was over 0.2 ppm in both basins. This rapid increase in phosphorus is believed to have occurred for two reasons; the main reason is that the inhabitants in the heavily populated area around the sub-basin began to use cleansers containing much tri-polyphosphate in 1965. The lesser reason is that the farmers around Lake Biwa also began to use chemical fertilizers containing much calcium perphosphate at about the same time. The ecological environment is so delicate that the plankton suddenly began to increase when the concentrations of nitrogen and phosphorus exceeded the boundary values. Therefore, since 1970 the city water of Kyoto has tended to smell moldy, and the phenomenon has occurred repeatedly every summer since then. As is well known, nutrient elements for the water plants are nitrogen, phosphorus and silicon, in contrast to nitrogen, phosphorus and potassium for the land plants. Therefore, it is easily understandable that silicon would play an important role especially in the growth of diatoms and flagellums which have a hard cell-wall. In Lake Biwa, red tide can often be observed in the summer after a heavy rain at the mouth of inflowing rivers or in inland lakes where the silicon contents are relatively high.

Next, let us consider the chemical equilibria taking place in oligotrophic lakes such as the main basin of Lake Biwa. In the lakes of this category, (1) water is clean enough for sunlight to penetrate sufficiently deep, (2) water contains sufficient oxygen (and nitrogen etc.) even at the greatest depths, and (3) enough clay components produced by the rain weathering of igneous rock such as granite are supplied by rivers or gush out from the bottom. Under such conditions the chemical processes are taking place in the hydrosphere as shown in Figure 1. By these processes, the environment is self-cleaned to keep itself within the oligotrophic range. In the Figure, the arrow (upper) on the left shows the input of clay components and the lower arrow shows the polluting components. Igneous rock represented as $KAlSiO_4$ is hydrolyzed by rain weathering resulting in potassium, aluminum and silicate ions. The potassium ion represents alkali-metal and alkaline-earth elements and is present in water as soluble hydrated species. The ion $K(OH_2)_4^+$ is mostly conveyed to the ocean by being transferred among various ecosystems. Part of it remains in the bottom deposit by adsorption or coprecipitation. The aluminum ion $Al(OH_2)_6^{3+}$ represents earth elements and multivalent transition elements and forms almost insoluble hydrated hydroxide. The ion is neutralized in charge and followed by condensation (dehydration) polymerization, i.e., sedimentary rock formation in geological terms.

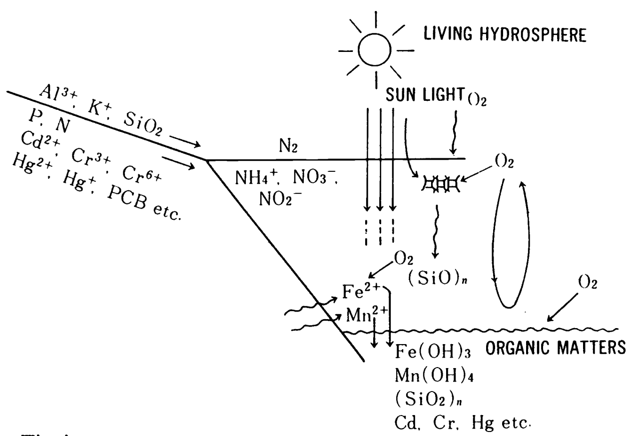

Fig. I
SELF-CLEANING PROCESSES IN OLIGOTROPHIC LAKE

$$Al(OH_2)_6^{3+} \rightleftharpoons Al(OH_2)_5(OH)^{2+} \rightleftharpoons Al(OH_2)_4(OH)_2^+$$

$$\rightleftharpoons Al(OH_2)_3(OH)_3 \downarrow \rightleftharpoons Al(OH_2)_2(OH)_4^- \cdots\cdots$$

$$n[Al(OH_2)_3(OH)_3] = [Al(OH)_3]_n + 3n\ H_2O$$

*The largest lake in Japan

Transition elements, for example iron, which gush out as ferrous ion is oxidized to ferric ion in the presence of sufficient dissolved oxygen and is precipitated similar to the aluminum ion.

$$Fe^{2+} + 1/4\, O_2 + 1/2\, H_2O = Fe^{3+} + OH^-$$

The generation of KOSEITETSU, so-called "lake-born iron" or the manganese nodule found in deep Pacific Ocean can be explained by this mechanism. The hydrosphere must be oligotrophic enough to contain oxygen in high concentration to keep the hydroxides insoluble. The silicon ion $Si(OH_2)_4{}^{4+}$ also forms hydrated hydroxide which forms precipitate of silica after condensation polymerization. However, the soluble hydroxide or the silicate ion is stable and hardly precipitates under ordinary conditions. Therefore, the concentration of silicate is relatively high in the inflowing rivers; the average concentration of silicate in Lake Biwa is of the order of 1 ppm and even lower when diatoms grow rapidly, but ten times more silicate generally exists in the inflowing rivers or inland lakes. In order to elucidate the difference, we performed broad laboratory investigations on the silicate precipitation. It was found that soluble silicate of low molecular weight can precipitate onto aluminum, ferric and manganese hydroxide if they are present. Once formed silicate precipitate can catch dissolved silicate on the surface; the skeleton of diatoms can also be the nucleus in coprecipitation. All of this sedimentation proceeds as a kind of dehydration polymerization. The precipitate thus formed may further be dehydrated for the long period of time and possibly under high pressure to form sedimentary rock. Some of them may be conveyed through the river that flows to the ocean. The removal of pollutants by the adsorption or coprecipitation onto clay components has been going on the Earth in a large scale for eons. This is the main part of the spontaneous self-cleaning process in the hydrospheric environment.

As is described before, silicate can exist not only in a mono-molecular state, but also as dimer, trimer and further polymers, which are charged to form colloidal particles. They can further adsorb inorganic ions in the course of their growth. Therefore, river water always contains mud irrespective of floods.

Sunlight can reach to the depth of the so-called "productive layer", which is twice as deep as the transparency. In that layer, carbonate assimilation by plant plankton exceeds to its decomposition. Therefore, in the summer when stagnation or water-layer formation is taking place, the lake water at the surface contains super-saturation oxygen and indicates an alkaline reaction. As a result, even at the deepest places the water dissolves enough oxygen, which oxidizes transition metals to a higher valency state. By that process, they form a less soluble precipitate or are coprecipitated onto other hydroxides. Under such conditions, not only inorganic but also organic pollutants such as the decomposed products of the excrement of living organisms or dead bodies, and industrial or domestic wastes such as PCB can be made non-poisonous by the photo-decomposition of sunlight and by oxidation decomposition by oxygen. After decomposition, they are transformed to carbon dioxide, water, simple nitrogen compounds and halogenide ions. However, phosphorus cannot be decomposed to form vaporizable compounds but remains in water for long period and contributes much to the eutrophication of the hydrosphere like in the case of the sub-basin in Lake Biwa.

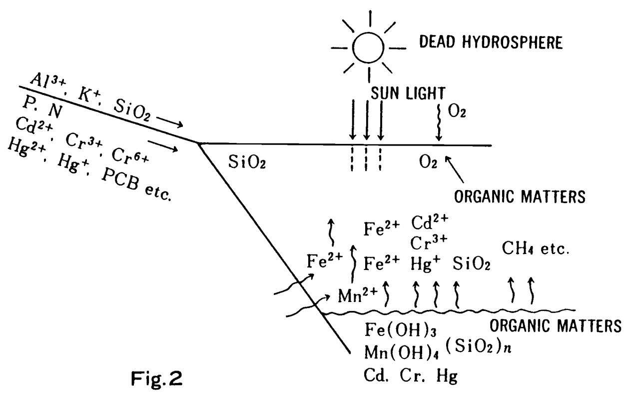

Fig.2
POLLUTING PROCESSES IN EUTROPHIC LAKE

In conclusion, if either of these four main elements, i.e., sunlight, water, soil and air, is eliminated or interrupted, the environment rapidly becomes ill. Once the supply of clay components (soil) to the hydrosphere decreases, precipitate formation also decreases and floating matters such as red tide cannot be carried down and heavy metals cannot be coprecipitated. Moreover, their re-dissolution from the precipitates takes place. In the process ions such as lead or cadmium dissolve first remaining the calcium silicate precipitate behind, in accordance to the Paneth-Fajans-Hahn's Adsorption Rule. As transparency decreases, carbonate assimilation decreases resulting in the increase in organic matter, which consumes dissolved oxygen. The decrease in oxygen again causes an increase in heavy metals because of the reduced state. The dissolution of metals can be accelerated with the presence of organic matters because some of them may act as a ligand and form soluble complexes with the metals. These organometallic compounds are often more poisonous than simple inorganic metals as in the case of organic mercury formed in the natural hydrospheric environment from inorganic wastes. Thus, the lack of more than two elements cooperates to turn the hydrosphere in a worse direction as can be seen in Figure 2, which shows the chemical processes taking place in a eutrophic lake or in the further deteriorated hydrosphere.

RECOVERY OF THE HYDROSPHERE ENVIRONMENT

In the old days the rivers often flooded so that the construction of dams seemed to bring many benefits; not only preventing floods but also being used for electric power and for various kinds of water supplies as well as recreation. However, in the old river before dam construction, water was running as a shallow stream absorbing sunlight, dissolving enough air, and mixing clay components everywhere; all of these stopped completely after the construction of dam. This means that most of the self-cleaning ability was lost. Similar circumstances occur in the case of landfills along the shores of lakes and sea coasts. Waves coming to the white sand beach form a thin layer at the end, mix with sands, sunlight and air keeping both the beach and water clean, that is up to the construction of the landfill outer sea wall, which prevents all of these three main elements from contact with the water. The result is uncleaned water moving up and down along the wall.

In the future in Japan, people may have to live on landfills located mostly on the continental shelf. To do that, I suggest that it be mandatory for those who build landfills to also build "public sea shore" as shown in Figure 3 (right side): the wall must be 50 meters or more outside the desired border. The wall hidden below sea level will keep the white sand beach or the rocky beach inside the wall. The public sea shore thus constructed can be used not only to keep the environment in a healthy state but also to furnish people recreation areas and to protect against further pollution from inside.

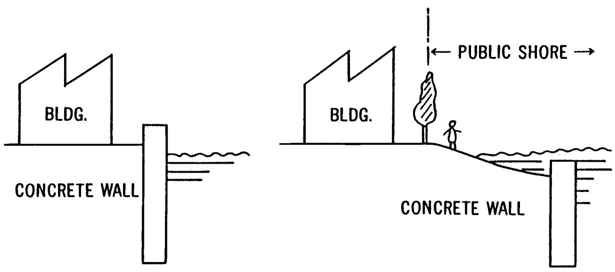

Fig.3
LEFT:CONVENTIONAL RECLAIMED LAND,
RIGHT:RECLAIMED LAND WITH PUBLIC SHORE

Similar ways have to be considered in the construction of dams in rivers and lakes. The artificial water-fall, rapid streams, the circulation of bottom water to the surface and addition of clay in proper way are the main points to realize. At present in Japan, in most cases in the construction of large civil engineering works, compensation is paid to the sufferer such as the fishermen's association, but little attention is paid to protect to restore a healthy environment. In the future, research should aim at determining how much of each of the four elements would be lost by the construction and how to protect and restore these missing elements.

ENVIRONMENTS IN THE LITHOSPHERE AND ATMOSPHERE

The lithosphere (land) environment in the area of highly populated towns or of heavy industries tends to be seriously damaged. The situation is sometimes so deteriorated as to become more desolate than a desert especially underground which is of course hidden from public eyes. Due to broad areas of pavement, the ground in large towns cannot absorb rain water which is mostly collected in the drainage channels and conveyed directly to rivers and to the sea. Also, the air cannot diffuse into the ground because of this impermeable surface. In large modern towns they need much more water than in former times not only because of the lack of drinking water but also for use as a heat exchanger in air conditioning facilities. Many modern industries use much more groundwater than before mainly for washing out the waste and for the dilution of water so as to meet pollution standards. Therefore, the land itself is much drier, and as a result fewer micro organism are able to live there than before. The level of groundwater goes down and the space is replaced by air. There is a large amount of biological waste as well as industrial and domestic wastes there, and these gradually begin to oxidize in the absence of water. As a result, under the ground in the town temperature is often much higher than that on the surface, and the oxygen content is too small for a man to function underground as in subway or underground shopping arcades etc. The atmospheric environment is also seriously disturbed in highly populated zones, where the air is separated from water, soil and sunlight. It is said that so-called "forest bathing" is good for the health, but the wood alone does not affect to the air. In a forest, the air comes into contact with water and its components are exchanged directly with soil going to and from the ground, that is where gaseous obstacles do not exist to prevent the sunlight from reaching the surface. These conditions which furnish all of Empedokles' four elements keep the atmospheric environment clean and free from pollution on a continuous basis.

This is a desirable condition both from the viewpoint of man and nature, of which man is an integral part. It is in man's best interest as well as being his responsibility to nature to maintain a high quality of the environment, including its lithosphere atmosphere and hydrosphere as well as the urban living-sphere. We environmental chemists must work with other natural scientists and with social scientists too to fulfill this responsibility. Thanks to the Empedokles' Principia, protecting and restoring nature's self-purification capacity will help us do this.