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Wet-Oxidation Waste Management System for CELSS

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ABSTRACT

A wet oxidation system will be useful in CELSS as a facility to treat organic wastes and to redistribute inorganic compounds and elements. However at rather higher temperatures needed in this reaction, for instance, at 260 °C, only 80% of organic carbon in a raw material can be oxidized, and 20% of it will remain in the liquid mainly as acetic acid, which is virtually non-combustible. Furthermore, nitrogen is transformed to ammonium ions which normally cannot be absorbed by plants. To resolve these problems, it becomes necessary to use catalysts. Noble metals such as Ru, Rh and so on have proved to be partially effective as these catalysts. That is, oxidation does not occur completely, and the unexpected denitrification, instead of the expected nitrification, occurs. So, it is essential to develop the catalysts which are able to realize the complete oxidation and the nitrification.

MANY RESEARCH EFFORTS have been funded to make wet oxidation systems commercially available for the purpose of treating organic wastes, particularly sewage sludge, and since 1957, the Zimmermann Process (Zimpro) has been successfully used in the USA, Japan and other countries. This system seems useful in a Closed Ecological Life Support System (CELSS) to treat and reduce organic components of wastewater from plants, human beings and so on, into inorganic

compounds (and elements).

But it seems that the discussions on the applicability of wet oxidation to CELSS does not fully reflect the experiences and results obtained in this field. This paper will discuss the usefulness and the unsolved problems of wet oxidation in CELSS on the basis of authors' ten-year research on wet oxidation of sewage sludge.

EXPERIMENTAL METHODS

Wet oxidation is a reaction in which organic or reductive compounds are oxidized in the presence of liquid water. This reaction occurs between 100°C and 374°C which is the critical temperature of water, so the reaction should be carried out in a pressure vessel (autoclave) to prevent evaporation of water.

All data shown later are the results of autoclave tests. The pressure in the autoclave at a given reaction temperature is determined as a sum of the pressures of water and gases which are introduced into the reactor at a room temperature before the beginning of the experiment. Therefore, it is impossible to keep the reaction pressure below a saturated vapor pressure of water at the given reaction temperature.

Before an experiment, it is necessary to introduce enough oxygen gas into the reactor so as to accomplish the intended oxidation. The rate of oxygen gas in the reactor to the chemical oxygen demand

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(COD) of a raw material is called "added oxygen index(R)". In the case of R=1, it means that the exact quantity of oxygen has been added to oxidize the raw materials completely.

Pure oxygen gas or a mixture of oxygen and nitrogen gases has been used. Even after the determination of "R", it is possible to exchange the gas ratio of oxygen to nitrogen at will. You have only to increase or decrease the volume of the raw material. Sewage sludge is used as a raw material.

EFFECTS OF THE REACTION TEMPERATURE

CARBON - Fig.1 shows the relation between the reaction temperature and total organic carbon(TOC). The temperature is increased from 110°C to 310°C at an interval of 50°C. Pressures are all set at 75kgf/cm² except in the case of 310°C, where the pressure is controlled at 115kgf/cm². The reason why high pressures are applied at lower temperatures of 110°C or 160°C will be discussed later. The reaction time, after the temperature of the reactor reached the designed temperature, is 30 minutes. Added oxygen index(R) is unity and pure oxygen is used as an oxygen source.

Total organic carbon[TOC(mix)],

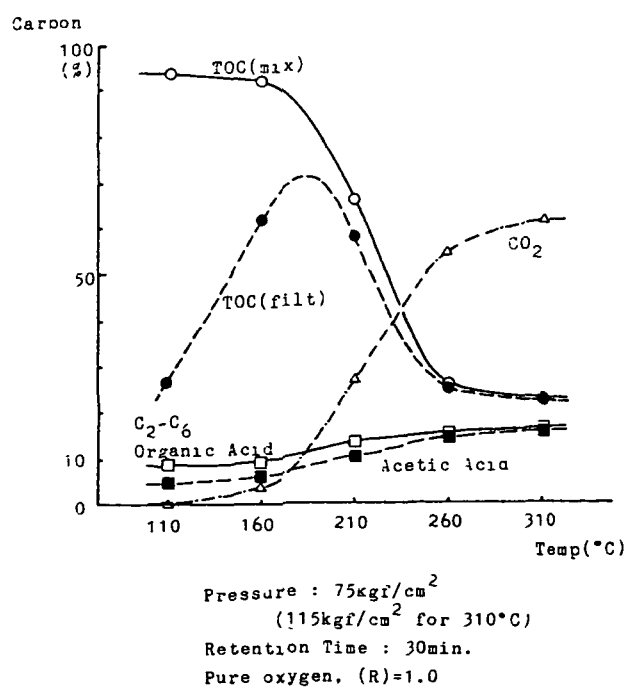


Fig.1 Reaction Temperature and TOC

filtrable organic carbon[TOC(filt)] and converted carbon quantities of acetic acid, C₂-C₆ organic acids (the sum of acetic, propionic, i-butyric, n-butyric, i-valeric, n-valeric, i-capric, n-capric acids) in oxidized liquors are shown in fig.1 as the percentage of carbon quantities of the raw material versus the respective temperature.

The behaviour of TOC(mix) curves in the figure shows that the oxidation occurs when the temperature is higher than 160°C, and this process becomes more active at the higher temperature. However when the temperature exceeds 260°C, the reaction will not proceed any more. The value of TOC(filt) increases with the increase of temperature and passes through the highest value in the range of 160°C to 210°C, then it decreases and approaches to the curve of TOC(mix) after 210°C.

In the case where the raw material is sewage sludge, solubilization of suspended organic compounds occurs first at a temperature less than 160°C, then both solubilization and oxidation proceed in between 160°C and 210°C, and after 210°C oxidation only occurs.

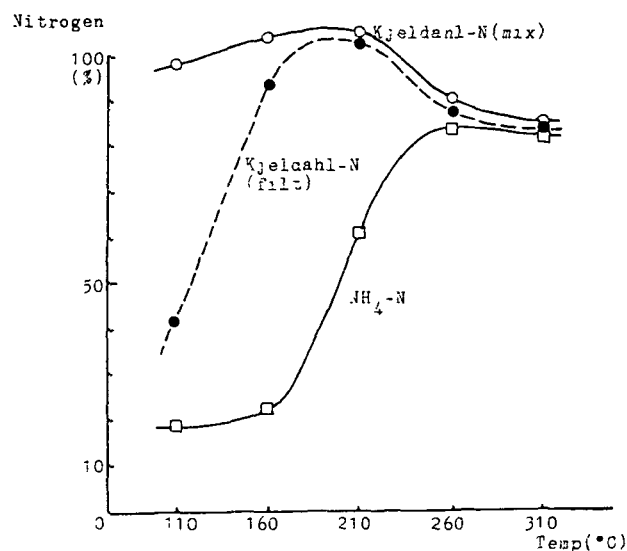
With the increase of reaction temperature, amount of C₂-C₆ organic acids increases and their quantity reaches two-thirds of TOC(mix) at temperatures higher than 260°C. On the other hand, the ratio of acetic acid in C₂-C₆ organic acids increases with the increase of the reaction temperature. When it reaches 260°C, acetic acid occupies nearly the total amount of C₂-C₆ organic acids, and maintains this amount independently to the increase of temperature thereafter.

This does not mean that the reaction had reached equilibrium. Acetic acid, whose concentration ranges from zero to 16g/l as converted carbon quantities, is not oxidized at all, even if excessive oxygen is added to the reactor. Therefore the main products in wet oxidation is "acetic acid" in addition to carbon dioxide and water.

NITROGEN - Fig.2 shows the relation between temperature and nitrogen output. As the temperature becomes higher, the solubilization of suspended nitrogen compounds occurs, and it is almost

completed at 160 °C. But this solubilization does not result in the formation of ammonia. Between 160°C and 210°C, at which both the solubilization and the oxidation of organic compounds occur, production of ammonia increases rapidly. Even if the solubilization has been completed, soluble nitrogen compounds do not become ammonia totally at 210 °C, but at 260 °C.

In wet oxidation without catalysts, the nitrogen compounds may not be oxidized to nitrite and nitrate. On the other hand, forms of nitrogen usable by plants are nitrite and/or nitrate with the exception of some plants such as rice. So in CELSS, it is impossible to apply oxidized liquor directly to plant culture in hydroponic solutions. It is

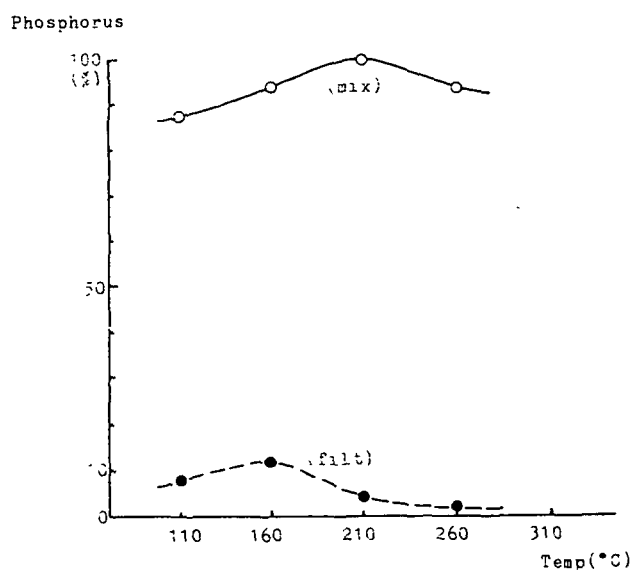


Pressure : 75kgf/cm²
(115kgf/cm² for 310°C)
Retention Time : 30min.
Pure oxygen, (R)=1.0

Fig.2 Reaction Temperature and Nitrogen

necessary to convert ammonia to the forms nitrite and/or nitrate by catalysts or by any other means. The decrease of Kjeldahl-nitrogen above 260°C is due to either the denitrification or NO_x formation.

PHOSPHORUS - Fig.3 shows the relation between the temperature and phosphorus output. The percentage of total and soluble(filterable) phosphorus in the oxidized liquor to the quantity of raw material versus the respective



Pressure .75kgf/cm²
(115kgf/cm² for 310°C)
Retention Time : 30min.
Pure Oxygen. (R)=1.0

Fig.3 Reaction Temperature and Phosphorus

temperature is shown. The ratio of phosphorus in the liquid to the total phosphorus quantity is remarkably small comparing with the one of nitrogen in the liquid to the total nitrogen quantity, which gives only approximately 10 per cent at best. This may be caused by the fact that sewage sludge contains various cations such as calcium ions which produce insoluble salts with phosphorus. In CELSS, the wet oxidation should function to re-supply nutrient sources for plant culture in hydroponic solutions. It is rather desirable for nutritious elements such as phosphorus, nitrogen etc. to be dissolved in water. Therefore, this phenomenon is not favourable in making use of wet oxidation in CELSS. The behavior of phosphorus in wet oxidation has not been elucidated except in the case of sewage sludge. In this respect, the study of phosphorus is greatly needed.

EFFECTS OF THE REACTION TIME

CARBON - Fig.4 shows the status of TOC along with time. The reaction temperatures are 210°C and 260 °C. In either cases, the percentage of TOC(mix)

and TOC(filt) to the quantity of a raw material is shown in relation with time. Pressure is kept 35kgf/cm^2 in the case of 210°C , and 75kgf/cm^2 in the case of 260°C . The added oxygen index(R) is unity, and pure oxygen is used as a oxygen source. As this is a batch process, time is needed to reach the designated temperature. In order to know the changes of TOC in the heating process, the quantity of TOC is checked at the temperature of 160°C . The results are shown in the same figure.

The oxidation at 260°C occurs markedly in the initial 15 minutes. But after that, the reaction curve declines gradually. Fig.4 indicates that, only 80 per cent of TOC(mix) is oxidized at 260°C , even if the reaction time exceeds 45 minutes. The solubilization has finished before the temperature of the reactor reaches the designated temperature. As a result, TOC(filt) quantity will be the same as TOC(mix).

At 210°C , only 15 per cent of TOC(mix) is oxidized at zero minute on the horizontal axis of reaction time in fig.4. The decrease of TOC(mix) is remarkable during the first 15 minutes, even if it does not show so rapid a decrease as seen at 260°C . After that, the oxidation curve declines gradually. The solubilization of TOC reaches a plateau status after the 15-minute

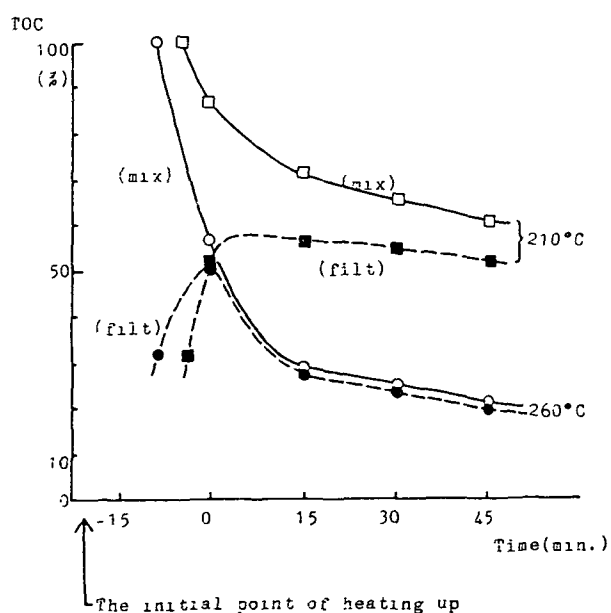


Fig.4 Reaction Time and TOC (1)

process. But suspended TOC, i.e. TOC(mix) minus TOC(filt), does not disappear even after 45 minutes.

TOC(mix), TOC(filt) and the converted carbon quantities of acetic acid and $\text{C}_2\text{-C}_6$ organic acids are shown in fig.5 in relation to their percentage to raw materials versus a time. The reaction temperature in this case is 260°C . The other experimental conditions are the same as in fig.4. As it was explained previously, the solubilization of TOC has finished before the reaction temperature reaches the designated temperature. $\text{C}_2\text{-C}_6$ organic acids reach their maximum within

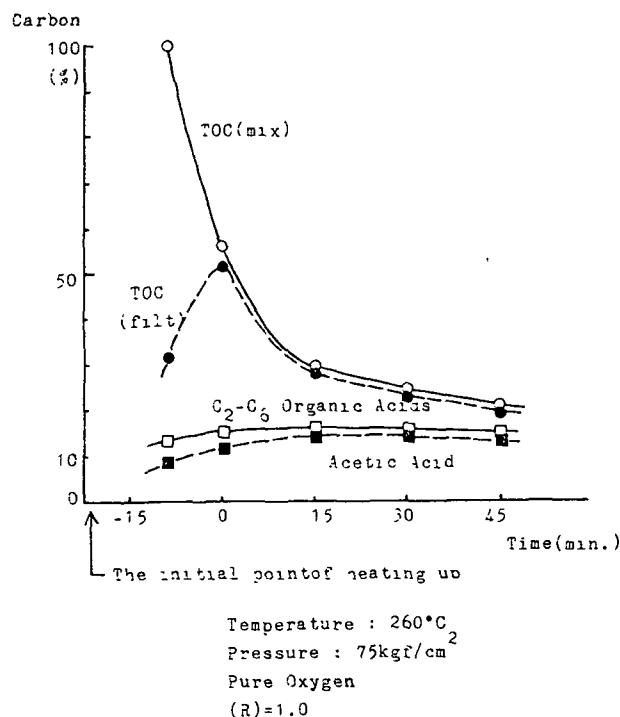


Fig.5 Reaction Time and TOC (2)

15 minutes and do not decrease any more despite that TOC(mix) decreases. The ratio of acetic acid to $\text{C}_2\text{-C}_6$ organic acids increases with time until 30 minutes but does not decrease even after 45 minutes.

Fig.4 and 5 show that the reaction temperature determines the upper limit of the oxidation. Considering the results of fig.1 together with fig.4 and 5, it is understood that only 80 per cent of organic compounds in raw materials is oxidized even at the reaction temperature of 310°C , and the remaining 20 per cent is non-combustible and consists mainly of

acetic acid.

Probably, acetic acid will not be oxidized at more than 310°C. In CELSS, it is desirable that organic compounds in a raw material are wet-oxidized

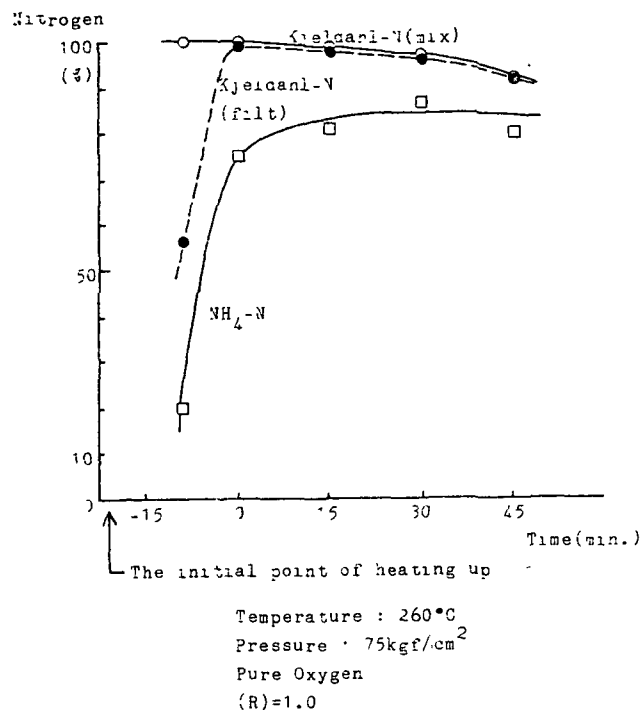


Fig.6 Reaction Time and Nitrogen

completely, and then it is necessary to develop the catalysts which have capability to oxidize acetic acid completely or to change the course of the reaction of wet-oxidation without producing acetic acid.

Nitrogen - Fig.6 shows the status of the nitrogen over time. The conditions in fig.6 are the same as the ones of in fig.5 experimentally and materially. The solubilization of the suspended nitrogen compounds has finished before the reactor has reached the designated temperature. The dissolved nitrogen compounds has led to ammonia in the same time. After the designated temperature has been realized, the Kjeldahl-nitrogen curve declines gradually with time. The percentage of ammonia to the Kjeldahl-nitrogen forms the plateau status after 15 minutes.

TIME-COURSE OF VARIOUS KINDS OF MATERIALS

Fig.7 shows the time-course of

various kinds of materials in wet oxidation. Each material is wet-oxidized under the conditions of 260 °C and 75kgf/cm². Pure oxygen is used as an oxygen source. As discussed previously, acetic acid is virtually non-combustible, so only a few percent of acetic acid are oxidized. About 50 per cent of stearic acid is oxidized in an hour. Casein, sewage sludge and cellulose show similar characteristics to one another in the time-course curves. It can be easily recognized by their positions in the figure that formic acid and starch are easily oxidized.

It is also known that cyanates in raw materials are oxidized to ammonia at 100 per cent, and 0.01 per cent of it remains in gas. Sulfur, sulfide or sulfite, is oxidized to sulfate and remains in liquid. Sodium, potassium and chlorine ions are intact under the wet oxidation, and remain in liquid.

There are various kinds of materials, some are easy to oxidized, and some are not. The research of wet oxidation in the CELSS project should start based on the elaborate choice of suitable raw materials.

In CELSS, raw materials will be

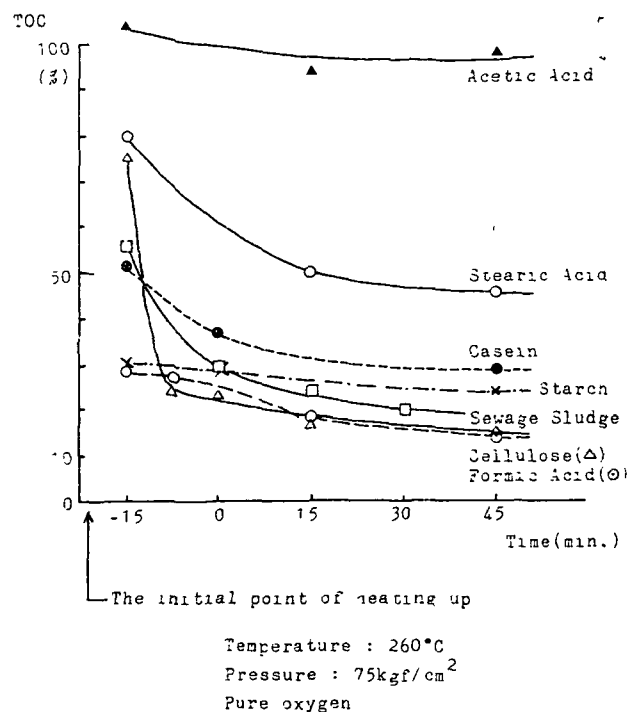


Fig.7 Time-course of Various Kinds of Materials

kitchen and laundry wastewater, feces, non-edible parts of plants, used hydroponic solution, trash and so on. They are entirely different from sewage sludge in character. Although the results of wet oxidation studies of sewage sludge cannot be applied directly to CELSS, because the fundamental phenomena are the same, the results of wet oxidation studies of sewage sludge can be of reference to the studies of CELSS.

BEHAVIORS OF METALS

The author has not yet studied the behaviour of metals in wet oxidation experimentally, but has done so in the field. The studies of a wet oxidation facility of sewage sludge in the Yokohama north-side-sewage-treatment plant, whose operating conditions are 240 °C in temperature, 72 kgf/cm² in pressure and 1 hour in retention time, show that most of Cd, Zn, Cu, Pb, Cr, Mn or Fe contents in a raw material are transferred to solid after the wet oxidation.

One man, even in a normal life, usually uptakes daily 0.05, 10.9, 5.85, 2.77, 0.177, 0.354, 0.022mg of Cd, Zn, Mn, Cu, Pb, As, Hg respectively. These are excreted and uninated daily at 1000 to 1200mls. It is unknown how much part of the respective element will be in liquid or solid after the wet oxidation. Therefore, trial oxidation in the CELSS project should be carried out after the studies of the metal behaviors have been established.

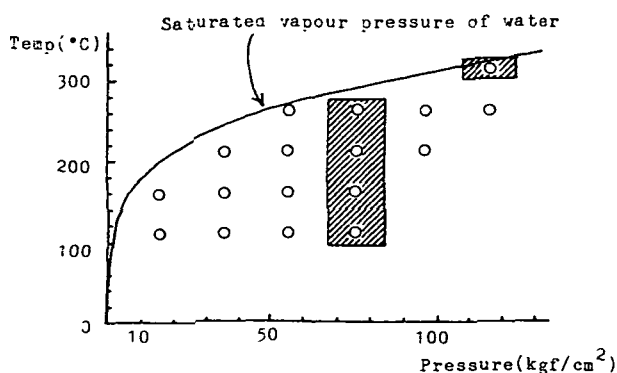


Fig.8 Saturated Vapour Pressure of Water

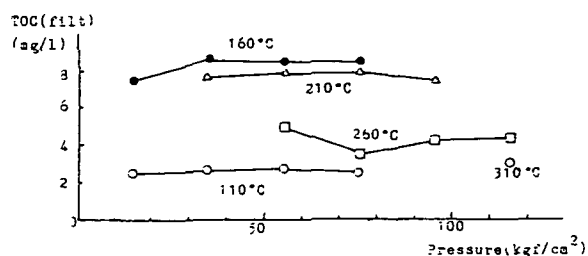
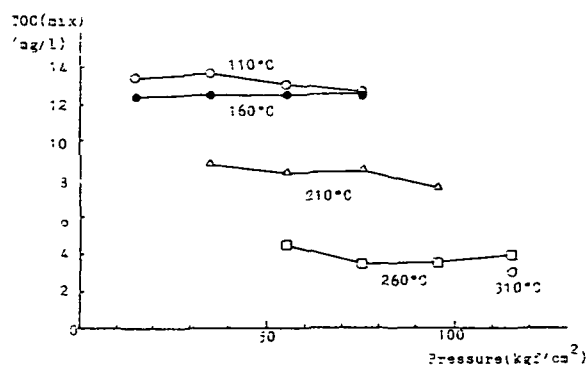


Fig.9 Pressure and Oxidized Ratio

PRESSURE AND OXIDIZED RATIO

Reaction pressure of the wet oxidation is determined as the sum of saturated vapor pressure of water at a certain reaction temperature and the pressure of gases which were introduced into the reactor at room temperature before the beginning of the experiment.

Fig.8 shows a curve of a saturated vapor pressure of water. A reaction cannot take place in the conditions of any temperature-pressure combination above the curve. Experiments to study pressure effects are carried out under the conditions of temperature-pressure combinations below the curve shown in the figure(*). The reaction time is 30 minutes and the added oxygen index(R) is unity. The results of tests executed under these combinations of condition are shown in fig.9.

Fig.9 shows that the oxidized ratio depends on the reaction temperature only. This fact is true also in the case in which a mixed gas of oxygen and nitrogen is used as an oxygen source. It means that a pure oxygen gas is not a necessary material as an oxygen source in the wet

(*)The experimental conditions adopted in fig.1-3 are the ones enclosed by the hatched area in this figure.

oxidation. In other words, the essential fact is to supply a necessary quantity of oxygen in either pure or mixed status. This fact may be favorable to CELSS.

EFFECTS OF CATALYSTS

As discussed earlier, organic compounds in raw materials can not be oxidized completely and nitrogen compounds remain in liquid in the form of ammonia in the wet oxidation. If and when a wet oxidation facility is used in CELSS, it is desirable that carbon in organic materials shall be involved in a gas recycling system in a form of carbon dioxides and that nitrogen in them is transformed to plant-available nitrates, by completing the oxidation process. In order to realize the above process in a short time without by-products, it is supposed that there would be no alternative way besides utilizing certain catalysts for the time being.

From a sewage-sludge-treatment point of view, the authors have been engaged in research to develop the catalysts so that the wet-oxidation system can exhibit a similar function to a usual combustion furnace system, and remove nitrogen from liquid.

As the result of surveys, it has become clear that noble metals such as Pt, Pd, Rh and Ru among the transition elements are hopeful as catalysts. These metals are needed to be supported on carriers made of alumina and titania etc.

To prevent suspended particles in liquid from poisoning a catalyst, filtrated-wet-oxidized-sewage-sludge output is used in the wet oxidation tests on the catalysts. One catalyst has been used 20 times in wet oxidation of fresh filtrates. The results are as follows.

When a Pt or Pd catalyst is used, nitrogen in the liquid is denitrified at 100 per cent. When a Ru or Rh catalyst is used, a half of nitrogen in the liquid is denitrified. The rest remains in the liquid as a nitrate when Ru is used and as ammonia when Rh is.

On the other hand, organic compounds are not catalytically oxidized at all, when Pt is used. The wet-oxidized output of TOC decreases to a half of a control, when Rh is used. The oxidation catalysis

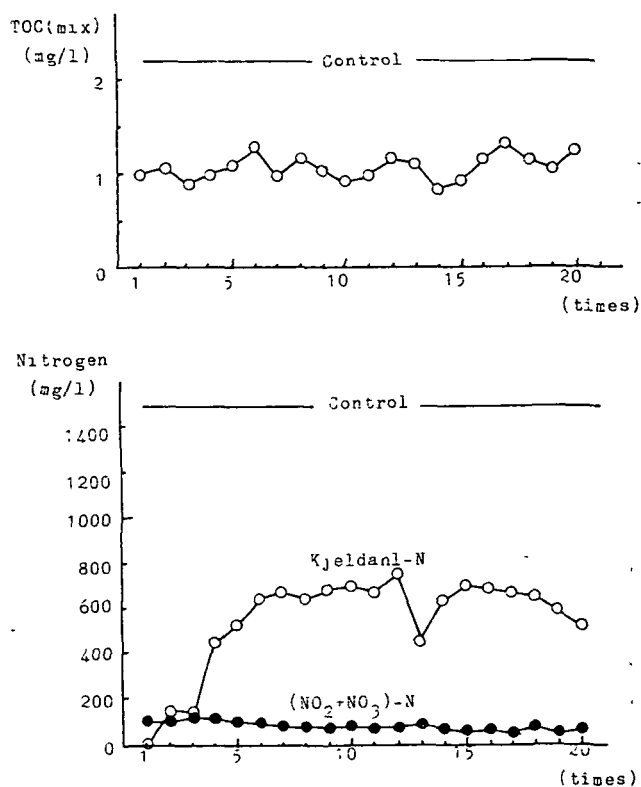


Fig.10 Effects of Rh Catalyst

of Ru or Pd is better than that of Pt and worse than that of Rh. The result of Rh is shown in fig.10.

Good catalysts for both oxidation and nitrification have not yet been found up to now. Therefore, research should be initiated to develop the catalysts which shall be involved in a recycling system of CELSS, will not be poisonous to working staff as well as living things in a space station, and shall have a effective catalysis for oxidation and nitrification.

CONCLUSIONS

The behaviors of various kinds of materials in wet oxidation were shown and the applicability of wet oxidation to CELSS was discussed. In Japan, a wet-oxidation facility for CELSS has been designed already. In this regard, the following projects are to start promptly:

- (1) To manufacture a trial wet-oxidation facility,
- (2) To execute tests of wet-oxidation for selected materials which are expected to be used in practice, and
- (3) To observe the behavior of the

materials.

The complete solubilization of raw materials will be a desirable way from the element-redistribution point of view. On the other hand, in the case of insoluble phosphorous compounds, there would be no problem if they should be sprinkled to a plant culture in a hydroponic solution, and, at the same time, if the plant culture would be able to utilize them as nourishment.

In this respect, studies and

discussions to confirm if each element, in a wet-oxidation output, is desirable in a liquid, solid or a gas phase. Thus, further studies on chemical-form controllable catalysts of each element can commence effectively.

Acknowledgement

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