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CHARACTERIZATION OF THE DEGREE OF STABILITY OF WASTE WATER SLUDGES

Progress Report No. 1

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TABLE OF CONTENT

INTRODUCTION

The experimental part of the project "Characterization of the Degree of Stability of Waste Water Sludges, COST 68/2" started January 15,1974. Prior to this date no experimental work had been done. This first test series was finished at the end of April 74 although the analytical work is not yet completed. This progress report therefore gives only part of the information from this test series that the research group hopes to obtain, and no detailed discussion of the result can be given at this time.

A more comprehensive progress report will be completed July 1974.

RESEARCH OBJECTIVE

The overall objective of the "Characterization of the Degree of Stability of Waste Water Sludges" are twofold:

1. To find one or several parameters that can be used as a measure of the degree of stability of wastewater sludges and to define in terms of the measured parameters what is meant by a fully stabilized sludge.

2. To develop one or several methods that are useful for determining the degree of stability of sludges in the daily operation of wastewater treatment plants. An effort will be made to find methods that are easy to perform with a minimum of expensive laboratory equipment.

During the period January 15 to April 18, 1974 batch aerobic stabilization of primary sludge, mixed primary-chemical (Al) sludge and septic tank sludge were done in three pilot digesters, each with a volume of 60 liters. The temperature was held constantly at 18 ^{o}C. The objective of this test series was to investigate the change in several parameters during the process.

PARAMETERS USED

The parameters used in the first part of this study is shown in table 1 below. (See Appendix A for Analytical Test Procedures.)

Table 1. Parameters used.

Parameter		Sludge	Supernatant
Temperature	^{o}C	x	
pH		x	
Oxygen	mg O_2/l	x	
Oxygen-uptake rate	mg O_2/g VSS.hr.	x	
TSS	mg/l	x	
VSS	mg/l	x	
BOD	mg/l	x	x
COD	mg/l	x	
ATP	mg ATP/mg VSS	x	
Protein	mg/l	x	
Carbohydrate	mg/l	x	
NH_4	mg/l-N		x
NO_2 + NO_3	mg/l-N		x
Odor intensity index		x	
Lead acetate test		x	
CST	s	x	

PRELIMINARY RESULTS AND DISCUSSION

Odor intensity of sludges during the stabilization process and during storage of sludges

Evolution of odorous gases is one of the major problems with sludge handling. Odorous gases are produced through biological breakdown of organic material. The most common cause of odors is H_2S and the conditions that lead to H_2S production also favour the production of odorous organic compounds. These compounds include mercaptans, indoles, skatoles and other nitrogen and sulphur bearing compounds.

Strong offensive gases from raw sludges will disappear during the first stage of the aerobic stabilization process. Figure 1 shows that septic tank sludge with a strong offensive odor prior to stabilization had a rapid decrease in Odor Intensity Index (OII) during the first six days of aeration. During the following aeration period only slight changes in odor intensity would take place.

Since storage of sludges quite often is necessary at small treatment plants before the sludge is trucked to a centrally located dewatering station or directly to a sanitary landfill, odors created during the storage period are of prime importance.

Figure 2 shows the change in Odor Intensity Index (OII) during 14 days of storage of primary sludge.

Figure 3 shows the maximum Odor Intensity Index (OII) measured through the 14 days storage period as a function of the detention time in the aerobic digester. Generally the odors from the sludges during storage were less offensive with increasing detention time in aerobic digester. This was true for all three types of sludges investigated. However, this was not true for a detention time less than 10 days. Short aeration periods (less than 10 days) would not make the sludges more suitable for storage since they would give a higher rise in odor intensity during storage than the raw sludge.
A possible explanation for this might be that organic material is solubilized during the early stages of the aeration process and thus more easily decomposed during anaerobic storage.

No detailed classification of the odours was made during our tests. However, during the stabilization process there was a change in type of odors although this change did not result in a reduction in Odor Intensity Index (see figure 1). The change was from a rotten, very offensive odor to a more "soil" type odor. During storage there could be a transition from the earth type odour back to the offensive odor. This was especially true for septic tank sludge.

Odor Intensity Index (OII) is not a very practical parameter to use as a measure of sludge stability. First of all it requires four persons or more to perform the test. In the authors opinion this alone makes the test applicable in research type work only. It is important, however, to tie parameters that can be used in practical operation of treatment plants to the odor problem created by sludges.

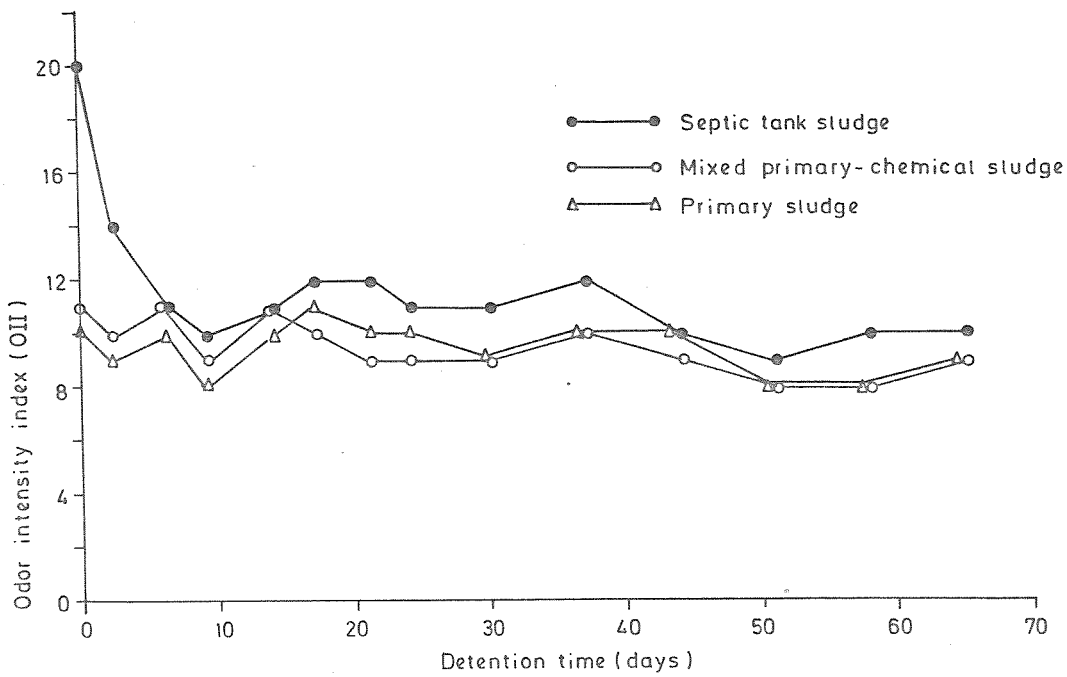

Figure 1. Odor Intensity Index vs. Detention Time in Aerobic Stabilization Unit.

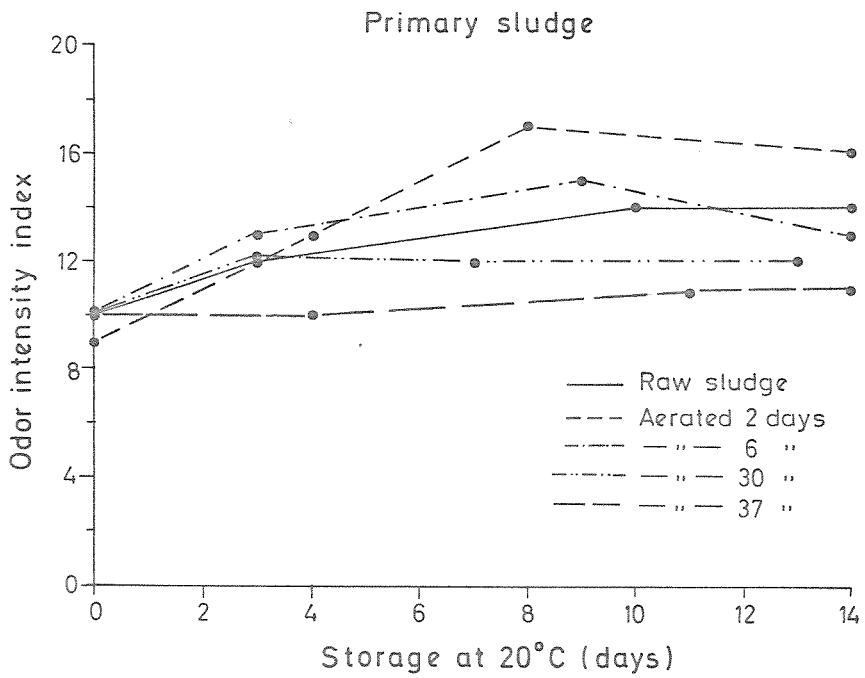

Figure 2. Odor Intensity Index vs. Storage at 20 °C.

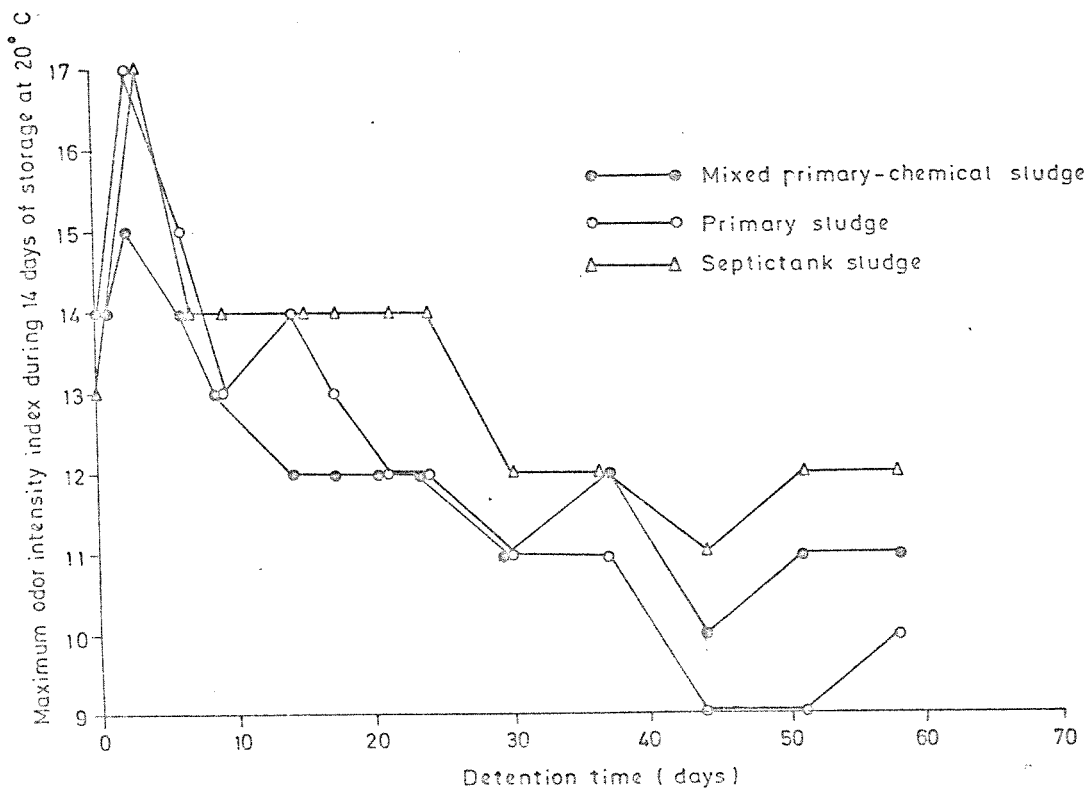

Figure 3. Maximum Odor Intensity Index during Storage vs. Detention Time in Aerobic Stabilization Unit.

Change in oxygen uptake rate during sludge stabilization

Oxygen uptake rate has been proposed by several researchers as a parameter for measuring sludge stability. Data obtained in this study is shown in figure 4. During batch operation an increase will occur during the first few days of aeration and then a gradual decrease will take place. It seems to be possible to establish a limit on oxygen uptake rate for a given sludge, and values below this limit would then indicate a fully stabilized sludge.

However, several factors influence the oxygen uptake rate during aerobic stabilization. The most important factors are listed below:

1. Type of sludge
2. Temperature
3. Operation of aerobic digester (batch vs. continuous)
4. Microbial composition of the sludge.

The influence of the type of sludge on the oxygen uptake rate during stabilization has been investigated. This will be discussed in detail when all the data have been analyzed.

The effect of temperature on the oxygen uptake rate for mixed primary-chemical sludge is shown in figure 5. This data is based on continuous digester operation.

The influence of type of sludge, temperature, batch vs. continuous operation etc. must be considered if oxygen uptake rate shall be used as a measure of sludge stability. A more fully discussion of this will be made during this project.

ATP during aerobic stabilization

The potential of ATP measurements for providing valid approximations of sludge stability is studied during this project. Figure 6 shows a typical change in ATP during aerobic stabilization for primary sludge and septic tank sludge. Since ATP is neither found in dead cells nor associated with any non-living material, figure 6 indicates that the number of living organisms decreases with an increase on detention time in the digester. Also the ratio ATP/VSS shows that the viable portion of the volatile suspended solids decreases during aerobic stabilization.

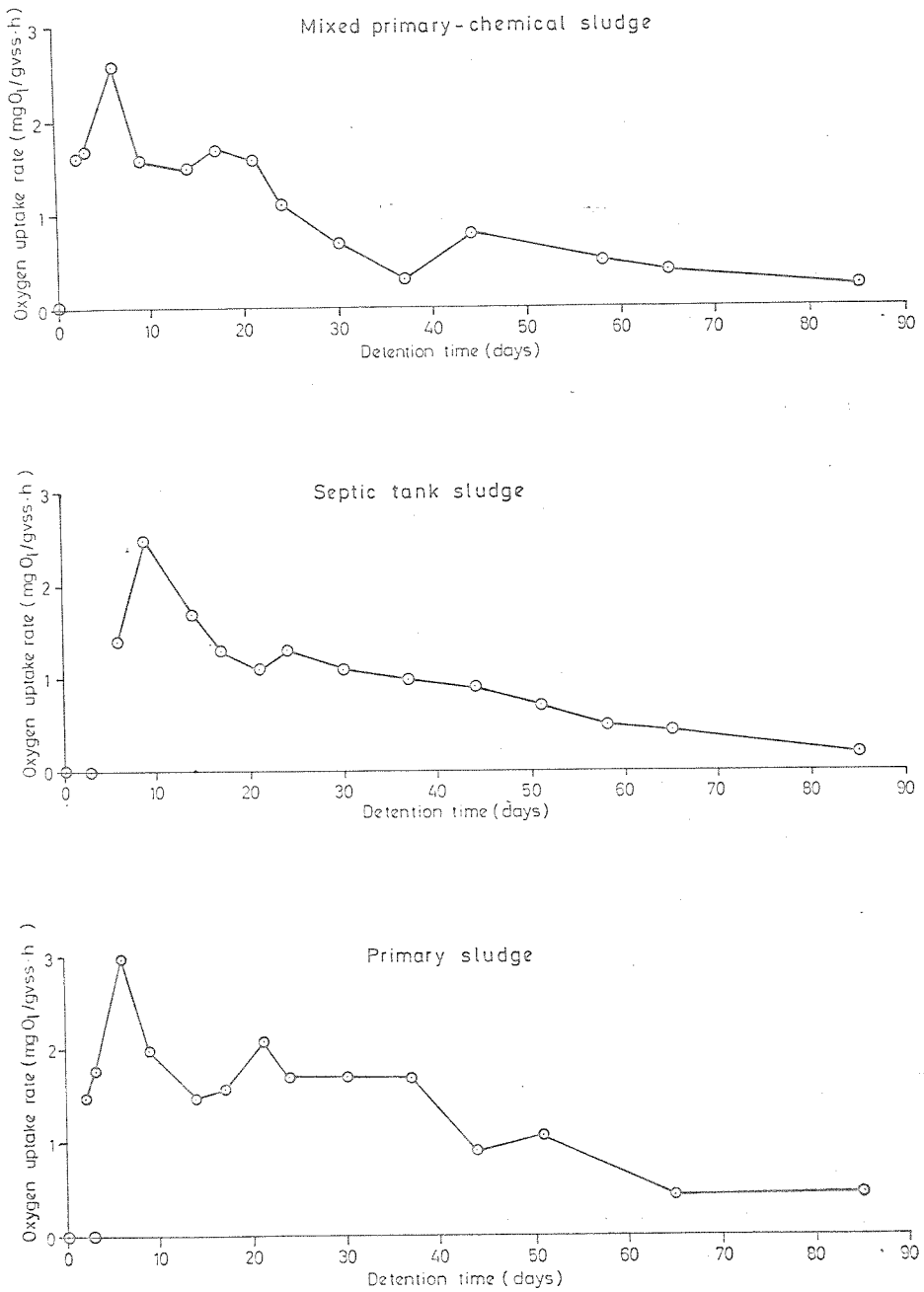

Figure 4. Oxygen Uptake Rate vs. Detention Time in Aerobic Stabilization Unit.

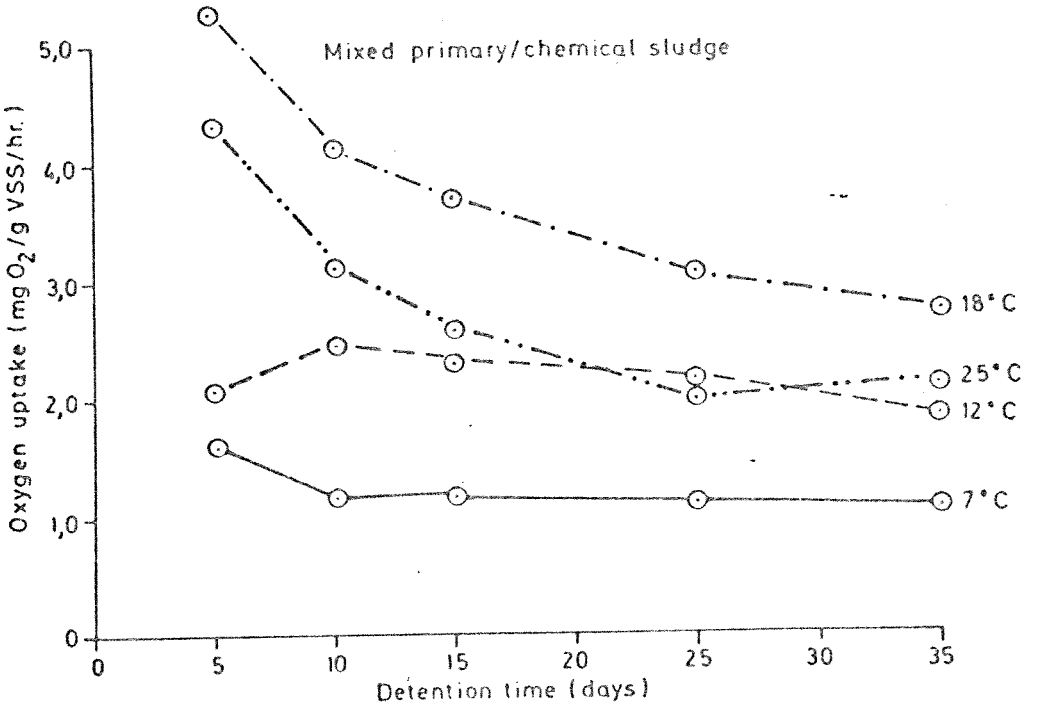

Figure 5. Oxygen Uptake Rate vs. Detention Time in Aerobic Stabilization Unit at 7, 12, 18 and 25 °C ("continuous" flow, batch fed units).

ATP might be a possible way of measuring sludge stability. The test series January 15 - April 18, 1974, however, indicates that ATP measurements for alum sludges (and probably iron sludges) are influenced by precipitation of ATP during the extraction process. A study of this analytical problem is under way at NIVA.

TSS and VSS as a method for measuring sludge stability

The content of volatile suspended solids as a percentage of total suspended solids has been proposed as a measure of sludge stability. In this author's opinion it is not a good parameter since the overall change is very small. Analytical inaccuracy would easily influence the result.

The overall reduction of VSS during the stabilizing process might be a usable method for measuring stability. Changing character of the raw sludge fed into an aerobic digester and the operation of the units might make this method less applicable in practical operation. A more detailed discussion of this will be carried out at a later date. (See figure 7.)

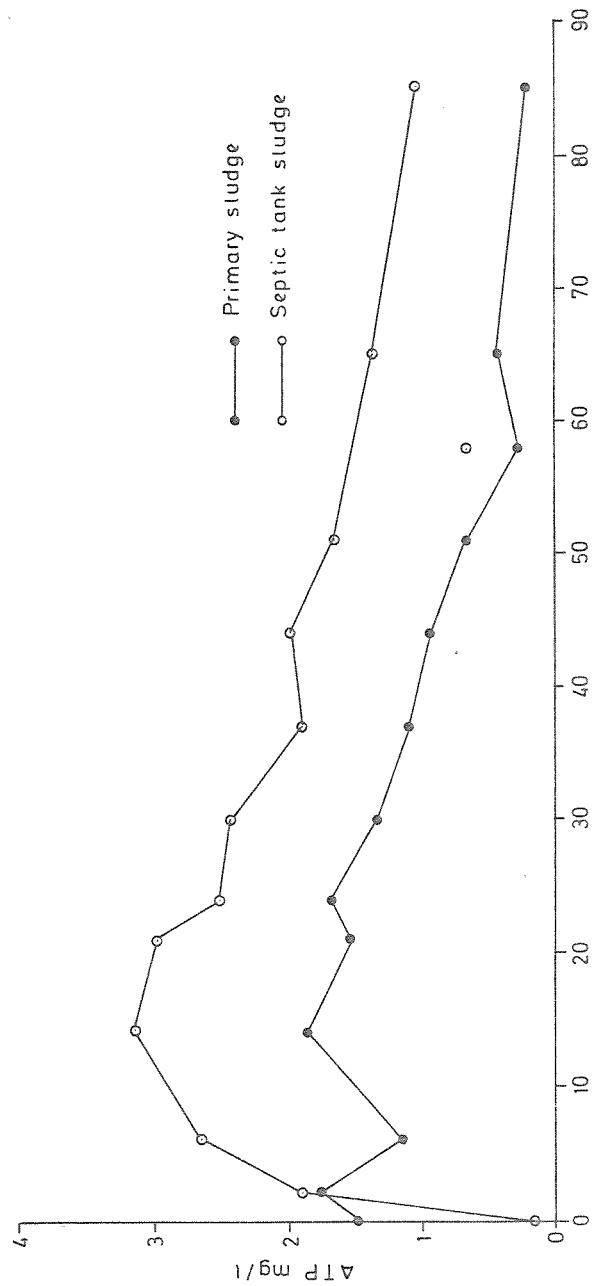

Figure 6. ATP vs. Detention Time in Aerobic Stabilization Unit.

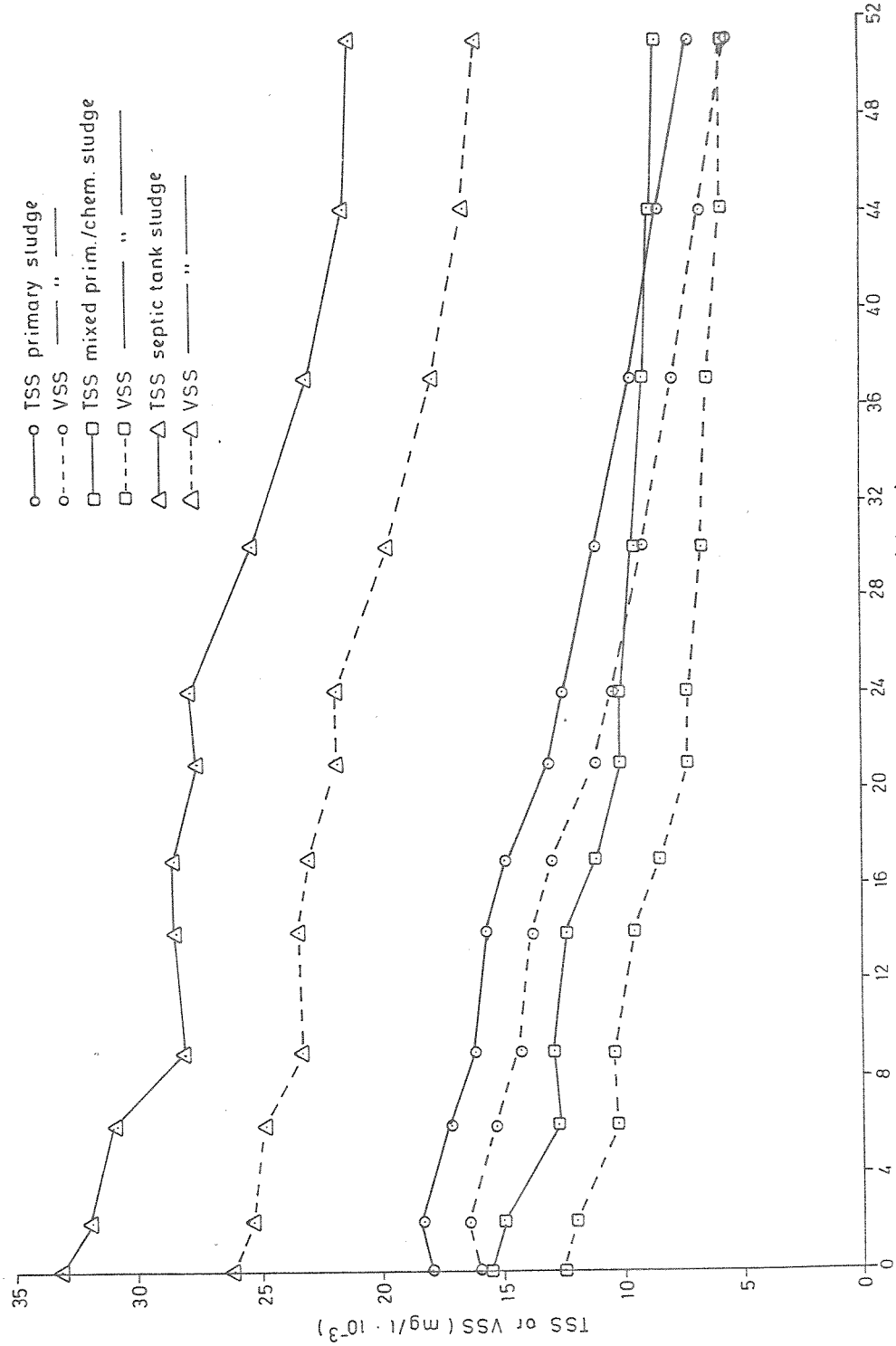

Figure 7. TSS and VSS vs. Detention Time in Aerobic Stabilization Unit.

Protein and carbohydrates content of sludges as a parameter of sludge stability

The protein and carbohydrate content of sludges changes during stabilization. A typical curve is shown in figure 8. The protein content (measured as mg/l) does not change very much with an increase in detention time in the aerobic digester. This is not so with the carbohydrate content. Based on the result shown in figure 7 it seems as if the ratio of protein to carbohydrates could be used as a measure of sludge stability. However, not all the sludges tested show the same typical change in protein and carbohydrate content. More work has to be carried out before any statements are made as to these parameters' applicability as a method for measuring stability.

Dewatering characteristics as a measure of sludge stability

Previous work done at NIVA indicates that aerobic stabilization (continuous process) generally improves filtration properties of sludges except at low temeratures. During the test series January 15 - April 18, 1974 this was not true for primary sludge regardless of the degree of stabilization. Septic tank sludge and mixed primary-chemical (alum) sludge showed an initial increase in CST/%SS values followed by a gradual decrease (see figure 9).

Based on our work at the present time it does not seem very likely that filtration properties can be used to indicate degree of sludge stability..

Rüffer's lead acetate test

Only a limited amount of the test material has been analyzed at the present time. At NIVA this test has been used in several projects to gain a wide experience with the method under different conditions. When this material has been analyzed, an evaluation of the method as a measure of sludge stability will be given.

Flotation-test

This method utilizes the gas evolution of sludges during storage as an indirect indicator of sludge stability. Nitrification during the aerobic stabilization process followed by denitrification during storage (evolution of N_2-gas) tends to influence the test result. Work is done at the present time to inhibit the denitrification step during the test.

No information on this method's applicability can be given at the present time.

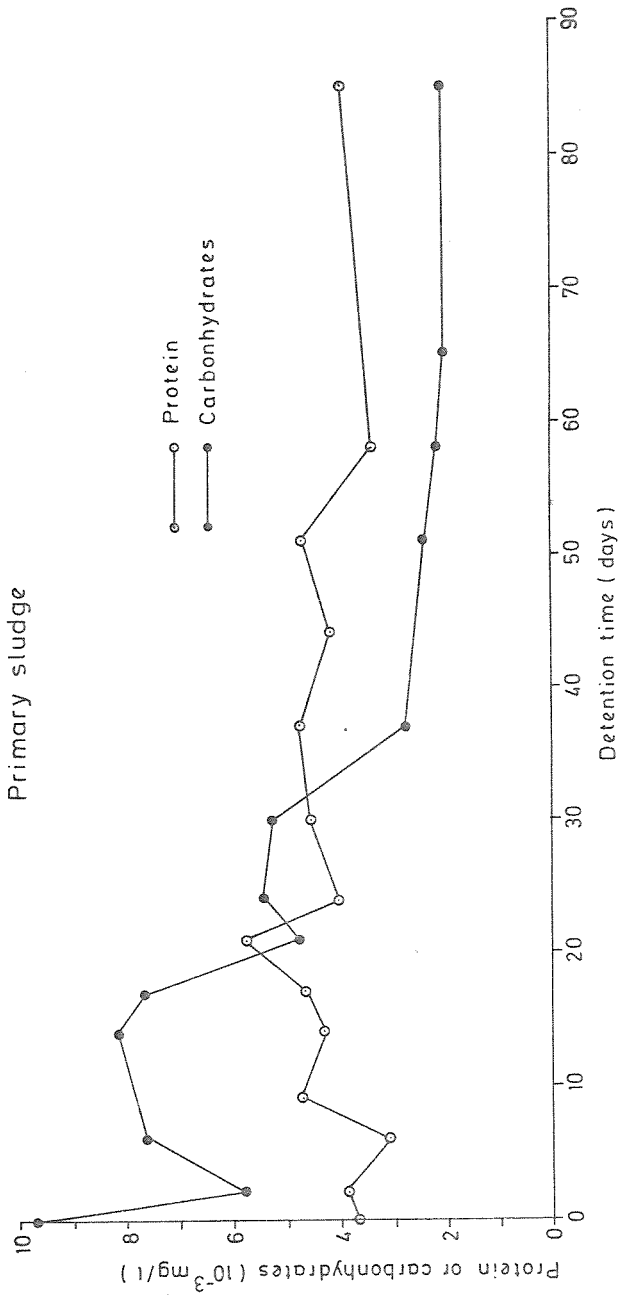

Figure 8. Protein and Carbohydrates vs. Detention Time in Aerobic Stabilization Unit.

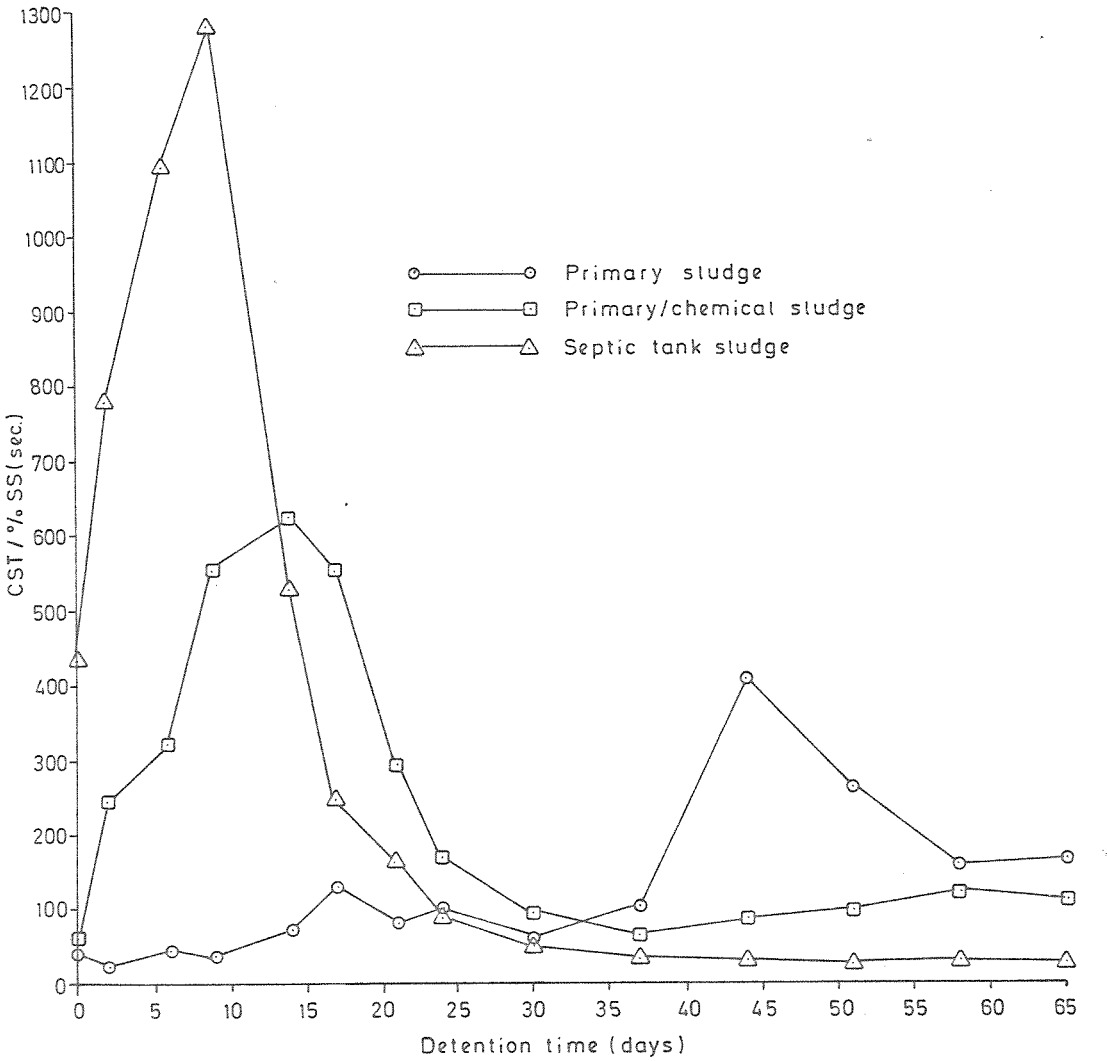

Figure 9. CST/%SS vs. Detention Time in Aerobic Stabilization Unit.

CONTINUATION OF THE WORK

At present an evaluation of the material obtained during the first test series is done at NIVA. A more complete discussion of this data is necessary, before a detailed plan for the continuation of the project is made. The author hopes to complete this in July 1974.

However, three separate "sub-projects" are worked on at the present time. Those projects have more defined objectives. The following gives a short description of these projects:

1. An evaluation of the flotation test and Rüffer's lead acetate test during aerobic stabilization. (Period April 18 - June28, 74)

A more detailed study of these two test methods were initiated since it became apparent during our experimental work started January 15, 74, that this series would not give enough information. This was especially true regarding the influence of nitrification - denitrification on the flotation test.

2. Analysis of ATP on chemical sludges (Al and Fe).
(Period June 1 - July 1, 74)

Since ATP is used in this project, an effort is made to find out what influence the Al (or Fe) content of sludges has on ATP measurements.

3. Sludge stability of lime-treated sludges. (Period June 4 - July 4, 74)

The lime added to the sludges during lime stabilization will inhibit the biological processes normally taking place. Lime stabilized sludges are not permanently stabilized in the same manner as sludges stabilized under aerobic or anaerobic processes since no reduction of organic material will take place. The objective of this study is to evaluate possible parameters for measuring sludge stability of lime treated sludges.

A P P E N D I X A

ANALYTICAL PROCEDURES

(Research Proposal, COST 68/2 Sept. 1973)

In the following discussion only those methods that differ from the procedures set fourth in Standard Methods for the Examination of Water and Waste Water will be discussed.

Hydrogen Ion Concentration

A Radiometer, Type PHM with a combined electrode type GK 2311C, GK 2303C, will be used to determine pH. The pH-meter will be calibrated against Radiometer buffer solutions pH 6.50 and pH 4.65.

Dissolved Oxygen

Dissolved oxygen (D.O.) will be determined with YSI-Oxygen meter, model 54.

Oxygen Uptake Rate

The oxygen uptake rate will be measured with YSI-Oxygen meter, model 54, equipped with YSI Oxygen probe. A recorder, Leeds and Northrup, Speedomax H, will be used for plotting change of D.O. in a 200 ml test bottle vs. times. The oxygen uptake rate would then be the slope of the line (mg/l/min).

Total Suspended Solids

Total suspended solids will be determined gravimetrically: a 70 ml volume is centrifuged in a Sorvall Superspeed Centrifuge, type SS-1, KSB-1 for approximately 10 minutes; the clear centrate is withdrawn from the centrifuge tupe and the solids put in a aluminium foil dish and dried at 103 ^{o}C overnight; in the morning, they are placed in a dessicator and weighed. All tests are run in triplicate.

Volatile Suspended Solids

Samples from the total suspended solids test are placed in the muffle furnace at 560 °C for one hour. Then they are placed in a dessicator and weighed.

Capillary Suction Time (CST)

A CST apparatus, Model 92, manufactured by Triton Electronics Ltd., is used for this test. The principle of the method is that filtration is achieved by the suction applied to the sludge by the capillary action of an absorbent filter paper of standard grade. A standard-sized circular area in the center of the filter paper is exposed to the sludge, while the rest of the paper area is used to absorb the filtrate drawn out by the capillary suction of the paper. The instrument records the time the filtrate takes to travel between two concentric circles, 3.2 cm and 4.5 cm in diameters. The 1 cm diameter funnel will be used for all tests. All tests will be run at room temperature (20-22 °C). Each sample will be run three times and the final CST value recorded is the numerical average of the three tests.

Odor Intensity Index

The method recommended in "Standard Methods" will be used (identical to ASTM D1292). A panel of at least 4 persons will be used.

Rüffer's Lead Acetate Test

Rüffer's Lead Acetate test is used as a measure of degree of stabilization. 100 ml bottles with glass stoppers are filled with 50 ml of sludge. A strip of lead acetate paper is fastened between the bottle and the stopper. The time required for the lead acetate paper to change from white to brown due to evolution of H_2S is recorded.

ATP-Measurement

The quantitative determination of ATP by bioluminescence is dependent on: (a) firefly luciferace enzyme being absolutely specific for ATP, (b) the rate of the reacting being directly proportional to the concentration of ATP, assuming that other reactants are in excess, and (c) the emission of one photon of light for each molecule of ATP which is hydrolyzed. The overall reaction is as follows:

$$\text{Luciferin (reduced)} + \text{ATP} + O_2 \xrightarrow[\text{Luciferace}]{Mg^{++}} \text{Luciferin (oxidized)} + PP_i + \text{AMP} + H_2O + h\nu$$

When a sample containing ATP is injected into the enzyme preparation, there is an immediate burst of light in the range of 560-580 mμ. The intensity of light declines in a semi-exponential fashion. The area under this curve is proportional to the amount of ATP in the sample.

The ATP measurements is made using a JRB-ATP Photometer form JRB Incorporated, San Diego, California, U.S.A. According to the JRB-ATP Photometer Instruction Manual (1971), the instrument works in the following manner:

> When a sample is placed in the sample chamber after injection of ATP and the dark slide is pulled out, light strikes the photocathode of the phototube, liberating electrons which casade through the photo-multiplier to produce a current proportional to the light intensity of the sample. This current is converted and amplified to produce a proportional voltage. This voltage is fed into a voltage-frequency converter where a pulse train is produced whose frequency is proportional to the input voltage.
>
> This pulse train is prescaled for increased accuracy and gated by a digital timer. This precision timer allows the pulse train to pass to a counter where it is accumulated for a pre-set interval. At the end of the interval the count displayed represents the integral

$$C \int_{t_1}^{t_2} I_\nu \, dt = \text{displayed counts}$$

where C is a constant determined by a combination of the high voltage applied to the phototype (Gain) and ATTENUATOR setting, phototupe sensitivity, and optical geometry.

I_ν is the intensity of the light emitted from the sample, and t_1 and t_2 represent the initial and final times respectively of the integration period.

Reagents:

1. Buffer: Tris-buffer (Tris-(hydroxymethyl)-aminomethane, 0.02 M, pH 7.75) was used. After preparation, the tris-buffer was autoclaved and stored in stoppered bottles in a refrigerator. Once a flask was opened, it was used for one day.

2. Enzyme Preparation: as outlined in the JRB-ATP Photometer Instruction Manual (1971).

Sample preparation:

Approximately one litre of sludge sample is used. This sample is homogenized in a blender and a one-milliliter sample was immersed in 20 ml of boiling (100 °C) Tris-buffer. The samples is stored at - 20 °C.

Protein

A colorimetric determination of protein by the biuret test is used. The method is described in "Selected Analytical Methods for Research in Water Pollution Control" by Ramanathan et al., Oklahoma State University, Aug. 1968.

Carbohydrates

The Anthrone test for measuring the overall carbohydrate content is used. The method is described in "Selected Analytical Methods for Research in Water Pollution Control" by Ramanathan et al., Oklahoma State University, Aug. 1968.

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