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CHARACTERIZATION OF THE DEGREE OF STABILITY
OF WASTE WATER SLUDGES
LIME STABILIZED SLUDGES

Progress Report No. 3

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1. INTRODUCTION

In this progress report our work on possible methods for measuring stability of lime stabilized sludges is discussed.

The objective of this work is first of all to define what we mean when we say that a particular sludge is stabilized with lime and secondly how we should go about measuring the stability.

No effort has been made at the present time to measure the degree of stability of lime stabilized sludges. Hopefully this will be covered in a future progress report.

Different opinions exist whether or not lime stabilization should be considered as a true stabilizing process in the same way as anaerobic or aerobic stabilization. It is recognized by the authors that there is a major difference between lime stabilization and the biological stabilization methods. However, lime stabilization as a unit process has become widely used, and for this reason questions regarding this process should be dealt with through research.

2. LITERATURE REVIEW

DEAN et al. (1974) conclude in their work on disposal and recycling of sludges containing lime that if the pH is greater than 9, the sludges are resistant to putrefaction and will have improved dewatering properties.

TRUBNICK et al. (1958) found that the odor problems usually experienced during dewatering of primary sludge can be completely eliminated by adding lime prior to the exposure of the sludge to the atmosphere. They also state that if the dewatered sludge is disposed of on the ground, it does not become a nuisance regardless of the exposure to the elements.

FARRELL et al. (1974) investigated lime stabilization of primary sludges both in laboratory and full scale experiments. During the full scale experiments the sludge emitted obnoxious odors when pumped to a treatment tank, particularly when mixing air was turned on. After lime was added, the odor was masked by the ammonia that was stripped out of the sludge by the mixing air. The typical ammonia odor was reduced at the end of the mixing period, and when the sludge was placed on the drying beds, it quickly lost its ammonia odor. Only a humus-like odor was left.

TULLANDER (1972) is of the opinion that even though all the bacteria are not killed during lime stabilization, the sludge can be considered as stabilized. In this case he considers a sludge stabilized as long as it does not create odor problems during sludge handling.

PAULSRUD (1974) found that as soon as pH decreased below 11.0, this was usually followed by an increase in odor intensity from the sludge. It was therefore quite important to add enough lime during lime stabilization to prevent a pH drop below 11.0.

BUZZELL et al. (1967) made laboratory studies on removal of algal nutrients from raw wastewater with lime. Although the primary goal of their work was to gain knowledge on wastewater treatment, the sludge cakes produced during filtration were checked for putrescibility. The sludge cakes were placed in an air tight container and checked for the presence of any odor after a few days. Even though the putrescibility studies were of a preliminary

nature, it was found that after 4 to 7 days in an air tight container, sludges with a pH below 11.0 became strongly odorous. The odor of sludges with pH above 11.0 remained unchanged. This is in agreement with work at NIVA.

DOYLE (1967) conditioned sludges with both polymers and ferric sulphate plus lime during studies on destruction of pathogens in raw sludge filter cake. When he used polymers, he found a substantial odor from the filter cake. Changing back to ferric sulphate and lime the odor was eliminated. By greatly reducing the lime dosage, the odor was again induced, but disappeared with an increase in lime content.

Although many researchers mention the odor problems when discussing lime stabilization, very little work has actually been done on stability of lime stabilized sludges. The emphasis has always been on the lime quantities necessary and the change in dewatering properties and hygienic quality.

3. EXPERIMENTAL METHOD AND ANALYTICAL PROCEDURES

The equipment used for lime stabilization consisted of 8 cylindrical containers placed in a water bath at 20 °C. Each of them contained 20 liters of sludge.

Primary and septic tank sludge were used in this investigation. The lime dosages were 50, 100 and 200 g $\text{Ca}(\text{OH})_2$ per kg total suspended solids (TSS) for both types of sludge. Two of the units had no lime addition and served as control units.

The lime was added as a 20% slurry, using analytical quality $\text{Ca}(\text{OH})_2$. Mixing of the lime and the sludge was done manually. The sludges were stored in the open containers for 28 days without disturbance except thorough mixing prior to sampling.

In the following only those analytical methods that differ from the procedures described by the Standard Methods for the Examination of Water and Wastewater (1971) will be discussed.

Hydrogen Ion Concentration

A Radiometer, Type PHM, with a combined electrode type GK 2311C, GK 2303C was used to determine pH. The pH-meter was calibrated against Radiometer buffer solutions pH 6.50 and pH 9.00.

Total Suspended Solids

Total suspended solids was determined gravimetrically; a 40 ml volume was centrifuged in a Sorvall Superspeed Centrifuge, type SS-1, KSB-1 for approximately 10 minutes; the clear centrate was withdrawn from the centrifuge tube and the solids put in aluminium foil dishes and dried at 103 °C overnight. They were then placed in a dessicator and weighed. All tests were run in triplicate.

Volatile Suspended Solids

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

Specific Resistance to Filtration

The specific resistance to filtration was determined, using the method of COACKLEY et al. (1956). The filtration pressure was supplied by a vacuum pump via an equalization flask and measured with a pressure gauge.

A 200 ml sludge sample under constant vacuum of 49 kPa was used. The filtrate was measured in a graduated cylinder. Whatman filter paper No. 1 was used throughout the test period. A wire screen inside the 9 cm Buchner funnel supported the filter paper and the effective filtering area used was equal to the perforated area in the Buchner funnel.

Odor Intensity Index

The method recommended by the Standard Methods for the Examination of Water and Wastewater (1971) was used (identical to ASTM D1292). The method is based on dilution with odor free water until a dilution is obtained that has the least definitely perceptible odor. Three persons participated in the panel.

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 were filled with 50 ml of sludge. A strip of lead acetate paper was 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 was recorded.

Adenosine Triphosphate

The adenosine triphosphate (ATP) measurements were made using a JRB-ATP Photometer.

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 only used for one day.
2. Enzyme: Preparation as outlined in the JRB-ATP Photometer Instruction Manual (1971).

Sample preparation:

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

4. POSSIBLE METHODS FOR MEASURING SLUDGE STABILITY - RESULTS AND DISCUSSION

4.1 Change in Odor Intensity Index (OII) during Storage of Lime Stabilized Sludges

The change in odor intensity during storage of lime stabilized sludges was investigated during this project. An increase in odor intensity index was experienced for both types of sludges investigated regardless the amount of lime added. The increase was usually taking place during the first 8 days of storage. The odor intensity would then remain fairly constant during the rest of the storage period (see Figure 1). Based on our result, using the ASTM - D1292 method for measuring OII, there is no reduction of OII taking place during lime stabilization.

The intensity of odors from sludges is important, but the type of odor must be considered as well. Lime added to a particular sludge will transform the rotten offensive smell usually associated with raw sludges to an ammonia or manure odor. The odor after lime addition was less objectionable than the raw sludge odor, but it was still offensive. It should be recognized, however, that this reflects the opinion of the panel members.

The processes that the lime stabilized sludge goes through after lime addition, will undoubtedly also change the "nuisance potential" (i.e. release of odorous gases) of the sludge. Practical experience indicates that dewatered sludge can be stored much longer without causing odor problems than liquid sludges.

4.2 Change in pH as a Function of Lime Addition and Storage Period

Previous work at NIVA (PAULSRUD et al., 1974) and work by others (BUZZELL et al., 1967) have stated that as soon as pH in a lime stabilized sludge falls below 11.0, the odor will increase considerably. Therefore the use of pH or rather change in pH was investigated as a possible method for measuring stability of lime stabilized sludges.

Both the initial pH after lime addition and the rate of change in pH during storage will depend on the type of sludge and the amount of lime added. A typical example is given in Figure 2. High dosages will give a very low change in pH during storage.

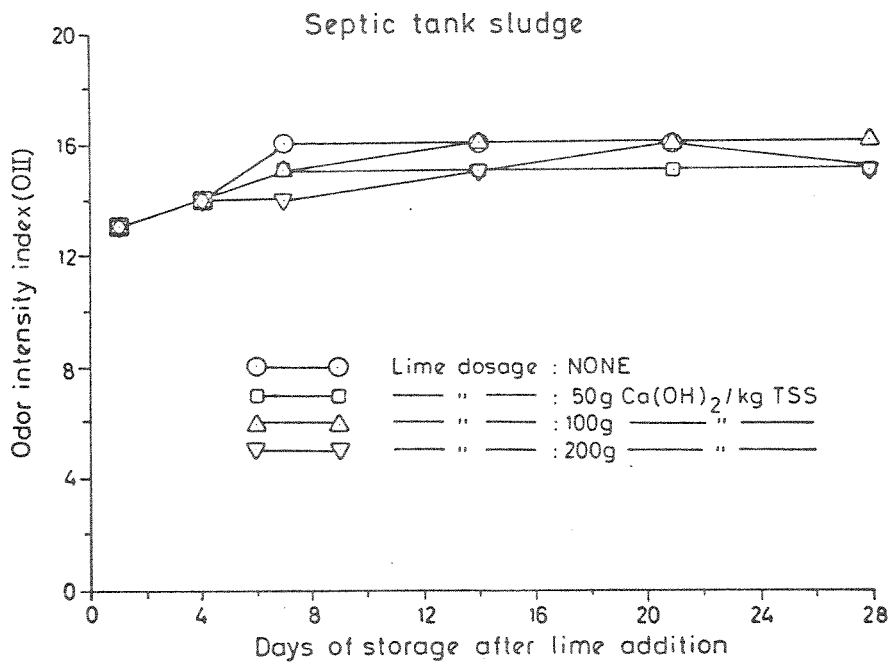
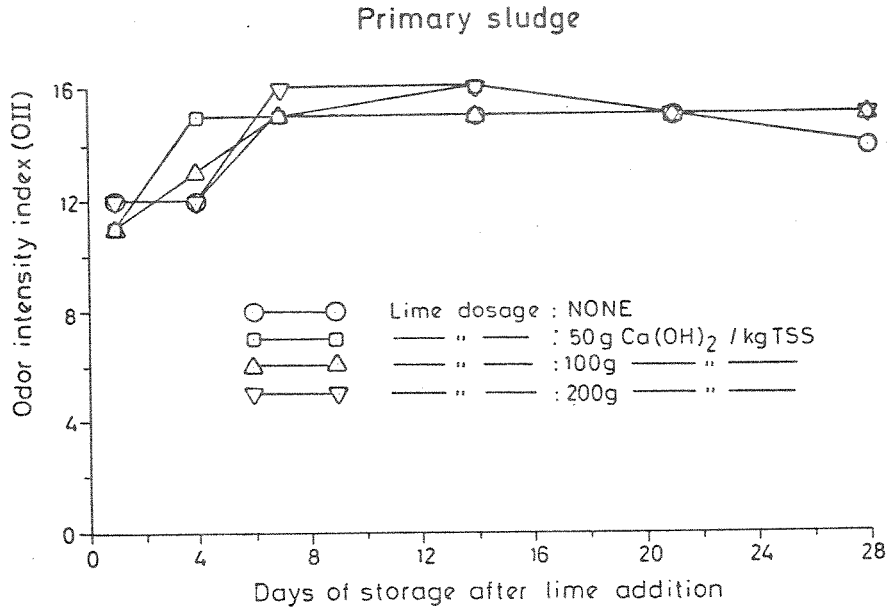


Figure 1. Change in odor intensity index (OII) during storage of lime stabilized primary and septic tank sludge at 20 °C.

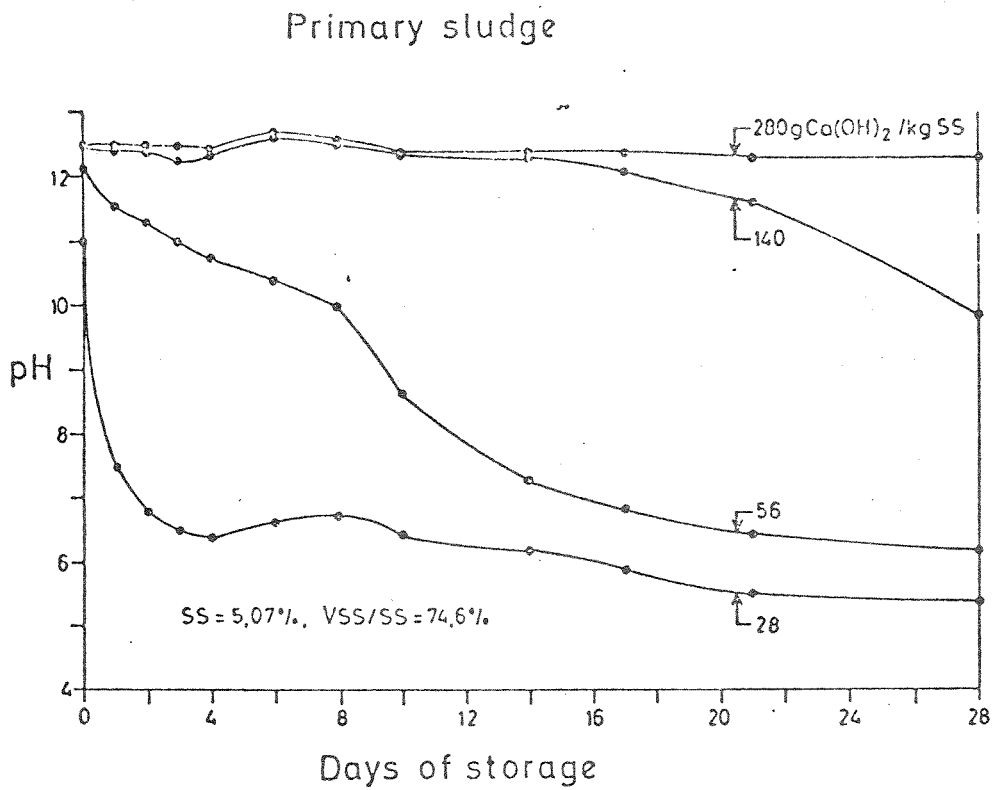


Figure 2. Change in pH during storage at 20 °C of primary sludge using different lime dosages. (Paulsrud et al., 1974.)

Similar result was obtained for other types of sludges (PAULSRUD et al., 1974).

Since a high pH will inhibit a biological break-down of the organic material in the sludges with subsequent release of offensive odors, the pH value during storage seems to be a useful parameter for measuring sludge stability. When we want to measure stability of lime stabilized sludges we are faced with the problem of relating the stability concept to a particular storage period and storage temperature. The authors of this report suggest that a pH above 11 during 14 days of storage at 20 °C would be sufficient to prevent major nuisance problems at most treatment plants. This should give the treatment plant operator ample time to process the sludge (dewater and haul it away for final disposal). In order to achieve this you would normally have to add enough lime to reach an initial pH of 12.0-12.6. This is shown in Figure 3. Since there is no reduction in odor intensity index (OII), but rather a change in type of odor during lime stabilization, the storage period is rather arbitrarily selected. At particular plants periods deviating from 14 days might be necessary.

Some of the primary-chemical treatment plants in Norway will use lime as the coagulant to remove phosphorus. This type of treatment plants will produce a stabilized sludge by just mixing the primary sludge and the calcium sludge together. It is also of interest to notice that even though this mixture has a lower initial pH (approximately 10-11) than usually experienced during lime stabilization of other types of sludges, there is no reduction in pH during storage.

4.3 Change in Adenosine Triphosphate (ATP) during Storage of Lime Stabilized Sludges

The adenosine triphosphate (ATP) content was considered as a possible method for measuring stability of lime stabilized sludges. Table 1 shows the ATP content of primary sludge and biological sludge before and at different time intervals after lime addition.

Table 1. Variation of ATP during storage of lime stabilized sludges.
(PAULSRUD et al., 1974)

Type of sludge	Lime added $\frac{\text{g Ca(OH)}_2}{\text{kg TSS}}$	ATP before lime addition ($\mu\text{g/l}$)	ATP after lime addition ($\mu\text{g/l}$)			
			$\frac{1}{2}$ hr	6 hrs	24 hrs	96 hrs
Primary sludge	28	1430	125	66	92	37
	56	1430	96	25	26	<1
	140	1430	52	<1	<1	<1
	280	1430	<1	<1	<1	<1
Biological sludge	44	2500	718	177	251	476
	88	2500	850	259	96	45
	220	2500	648	130	49	112
	440	2500	533	81	42	32

It is of interest to notice that some microbial activity was taking place in the biological sludge even 4 days after lime addition. This was not the case with the primary sludge. At the highest dosage added to primary sludge, no ATP could be detected 0.5 hrs after lime addition and no increase occurred during the 4 days test-period. It appears from the result given in Table 1 that there is very little difference in ATP content for the different dosages. This is especially true for the biological sludge. For this reason the ATP content will not be recommended as a parameter for measuring stability of lime stabilized sludge.

4.4 Change in Filtration Properties during Storage of Lime Stabilized Sludges.

No detailed discussion of the changes in filtration properties during storage of lime stabilized sludges will be carried out in this progress report. The work is not completed at the present time. However, the use of filtration and drainage properties as a measure of sludge stability will be discussed in general terms.

Lime added to the most common type of sludges will usually initially improve the specific resistance to filtration or capillary suction time (CST) values. This initial improvement will not remain unless the lime dosage is quite high. This is shown in Figure 4.

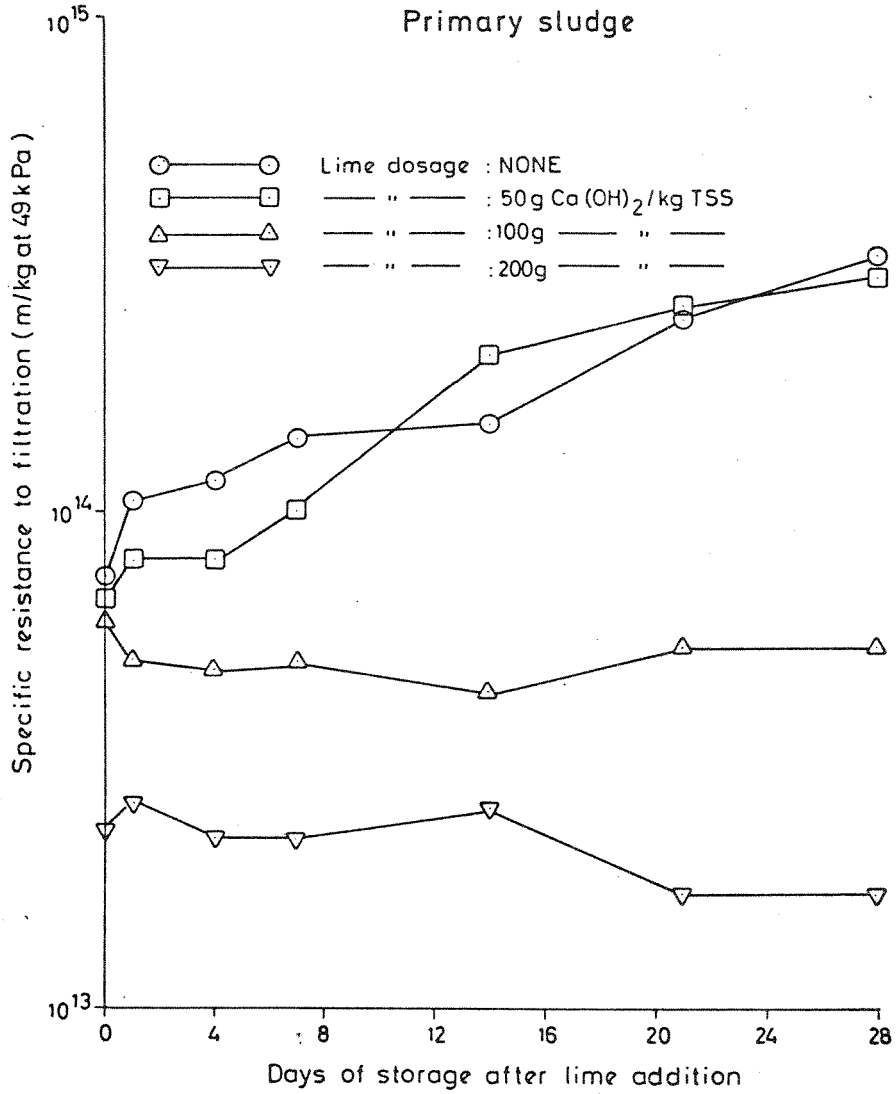


Figure 4. Change in specific resistance to filtration during storage of lime stabilized primary sludge at 20 °C.

At the present time there seems to be a correlation between the change in filtration properties during storage and the amount of lime added to the sludge. In other words, the change in filtration properties might be used to measure sludge stability, although further work needs to be done to clarify this.

4.5 Change in Nitrogen Forms during Storage of Lime Stabilized Sludges.

The different forms of nitrogen and possibly the total nitrogen content will change during lime stabilization. Due to the high pH after lime addition hydrolysis of complex organic material might take place and thus increase the ammonia gas, NH_3 , present in solution. The ammonium ions, NH_4 , present prior to lime addition will also be converted to NH_3 . Two factors were then investigated as a possibility for measuring the stability of lime stabilized sludges; first the reduction in total nitrogen content due to ammonia release and secondly the change in ammonia content in solution. Table 2 (see next page) shows the change in total nitrogen content in the sludge and the ammonia content in the sludge liquor.

Primary sludge indicated a slight reduction in total nitrogen. Biological sludge and sludge from secondary precipitation using Fe^{+3} salt to remove phosphorus did not show any reduction in total nitrogen. In other words, essentially no release of ammonia gas to the ambient air would take place. This would probably not be true if air was used for mixing lime with the sludge. The total nitrogen content in the sludge could therefore in no way be related to the amount of lime added (i.e. sludge stability).

Table 2. Change in nitrogen forms during storage of lime stabilized sludges.

Type of sludge	Parameter	Lime added g Ca(OH) ₂ kg TSS	Before lime addition (mg/l-N)	After lime addition (mg/l-N)			
				½ hrs	6 hrs	24 hrs	96 hrs
PRIMARY SLUDGE TSS=5.07% VSS/TSS = 74.6%	Tot-N (mg/l)	28	1238	1157	826	935	834
	in sludge	56	1238	873	986	1227	699
	in sludge	140	1238	922	944	1030	1038
	in sludge	280	1238	897	1100	1108	879
BIOLOGICAL SLUDGE TSS = 0.47% VSS/TSS = 71.5%	Tot-N (mg/l)	44	226	207	227	195	175
	in sludge	88	226	208	221	163	196
	in sludge	220	226	232	212	225	219
	in sludge	440	226	215	205	231	231
NH ₄ - N (mg/l)	in sludge	44	1.2	1.2	1.8	9.6	-
	in sludge	88	1.2	1.0	2.6	4.8	-
	in sludge liquor	220	1.2	0.7	0.1	2.3	14.6
	in sludge liquor	440	1.2	0.6	2.4	3.1	5.3
SLUDGE FROM SEC. PREC. WITH IRON TSS = 1.55% VSS/TSS = 45.7%	Tot-N (mg/l)	160	335	585	345	289	345
	in sludge	320	335	293	323	323	367
	in sludge	800	335	362	346	363	320
	in sludge	1600	335	358	326	336	336
NH ₄ - N (mg/l)	in sludge	160	11.5	17.1	9.6	12.4	18.6
	in sludge	320	11.5	0.1	9.1	14.9	13.6
	in sludge liquor	800	11.5	2.2	1.2	11.9	16.9
	in sludge liquor	1600	11.5	0.3	0.2	15.8	20.2

The NH₄-N content in the sludge liquor was not changed appreciably because of lime addition although there seemed to be an initial decrease and then a gradual increase with lime. This was true for all the dosages used. The changes in the nitrogen forms taking place during lime stabilization seem to be independent of lime dosages used in this study. The use of total nitrogen in the sludge or ammonia nitrogen in sludge liquor is therefore not recommended as an indicator of stability of lime stabilized sludges.

4.6 Rüffer's Lead Acetate Test

The use of Rüffer's lead acetate test as a measure of sludge stability was investigated in this project although to a limited extent.

Primary sludge and mixed primary-chemical (A1) sludge were used. A lime dosage of 150 g Ca(OH)₂/kg TSS was added to the primary sludge and

400 g Ca(OH)_2 /kg TSS was added to the mixed primary-chemical (A1) sludge. Samples were taken at different time intervals after the lime addition.

The lime stabilized primary sludge caused the paper strips to change colour within 2-4 days regardless of when the test sample was taken after lime addition.

The mixed primary-chemical (A1) sludge did not show any colour change in any of the test bottles.

Based on our result it has been decided not to investigate this method for measuring stability of lime stabilized sludges any further. The use of this method is therefore not recommended. This is in agreement with what has been found on aerobic stabilized sludges.

5. CONCLUSIONS

The following conclusions can be drawn from the result of this research.

1. An increase in odor intensity index (OII) is experienced during storage of lime stabilized sludges regardless of the amount of lime added.
2. Lime added to sludges will change the type of odor from the rotten offensive smell to the ammonia or manure type odor.
3. The use of change in pH during storage of lime stabilized sludges is a possible method for measuring sludge stability.
4. The ATP content of lime stabilized sludges is not recommended for measuring stability of lime stabilized sludges.
5. There seems to be a correlation between the change in filtration properties during storage and the amount of lime added to the sludge. High dosages of lime will normally be followed by a small change in filtration properties during storage.
6. The use of total nitrogen in the sludge or ammonia nitrogen in the sludge liquor is not recommended as an indicator of stability of lime stabilized sludges.
7. The Ruffer's lead acetate test is not recommended as a method for measuring stability of lime stabilized sludges.

6. RECOMMENDATIONS

It is recommended that a stable sludge from a lime stabilization unit should meet the following requirement:

The pH of the sludge must remain above 11.0 during 14 days of storage at 20 °C.

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