EFFECT OF ACIDIFICATION ON SLUDGE Dewatering properties

P. Texier
Water and Environmental Engineering; Department of Chemical Engineering

1. Abstract

The study was performed on digested sludge from Öresundsverket wastewater treatment plant in order to study the possible effect of acidification on the sludge’s dewaterability. A method developed by Kemira Kemi AB was used to evaluate the dewatering properties. It appears that adding sulfuric acid improves dewaterability. However, the acidification leads to a reaction which causes the formation of gas bubbles, and thus an increase of sludge’s volume. That must be avoided by not exceeding a limit pH or volume of acid. Sludge’s acidification causes also dissolution of struvite crystals, hence the increase of dissolved phosphate concentration in the reject water from the dewatering operations. This dissolution in the centrifuge (in full scale) could be negligible, as the retention time is too low (few seconds). However, because the Kemira method is long to apply, adding too much acid results in a high concentration of dissolved phosphate in the reject water (recycled in the inlet of the WWTP). Regarding the experiments, it appeared that the optimal pH or optimal amount of acid to get the highest Dry Solids content corresponded to the ones reached just before the increase of the sludge’s volume.

Keywords: dewaterability, digested sludge, sulfuric acid, struvite, phosphate

2. Introduction

Sludge disposal is a growing problem for all waste water treatment plants, as intensified wastewater processing to meet more stringent discharge limits leads to increased sludge production. Before being used for different applications, the sludge is transported, sometimes long distances, for ultimate disposal. The amount of produced sludge being very high, it is economically important to reduce its volume by removing as much water as possible in order to reduce the transport, handling and disposal costs.

Several techniques exist to dewater the sludge. Most of them are mechanical and use gravity forces or pressure forces. The one used at Öresundsverket WWTP is centrifugation. To evaluate the dewaterability behavior of the sludge, a simple method was developed by Kemira Kemi AB. This method was evaluated by Tastu (2007) for characterization of sludge dewatering properties. It is a two-step method where the sludge is successively filtered and pressed. It gives characterization of its filterability and compressibility. Tastu (2007) noticed that the method gave a good characterization of the compressibility for activated sludge and digested sludge. He saw that DS_press (Dry Solid content after pressing) was a good prediction of the full scale dewatering results. Although the lab-scale and the full-scale results were different, they both indicated a
similar trend. Moreover, according to Tastu’s finding, the filtration step could only be considered as a way to prepare the sludge before the pressing step.

Sulfuric acid has different effects on the digested sludge. Digested sludge contains extracellular polymeric substances (EPS), which are composed of proteins and carbohydrates. EPS is excreted from the bacteria. According to Dursun et al. (2006), the EPS content in the sludge is responsible for its gel-like behavior due to an extensive network of the macromolecules. The sulfuric acid could break the EPS structure. Digested sludge contains also heavy metals. According to Cheung (1989), acidification causes heavy metals elution in the sludge, transforming those solid heavy metals into soluble ones that are removed later by centrifugation. The elution rate depends on the type of heavy metal (Cd, Cr, Cu, Ni, Zn, Pb, etc). Moreover, the charge on sludge’s particles is strongly dependent on the pH. According to Gillberg et al. (2003), almost all solid particles have a negative charge. With decreasing pH, the number of positive charges increases and causes the surface charge of sludge particles approaching neutral. All those effects could modify the sludge’s particle size distribution and structure and have an influence on the centrifugal dewatering.

The objectives of this study are to evaluate the influence of acidification on digested sludge’s dewaterability. If results are positive, the sulfuric acid will be added in the pipe just before the centrifuge of the Öresundsverket WWTP.

Moreover, adding sulfuric acid causes dissolution of struvite, a white crystal produced in the digested sludge by the spontaneous degassing of carbon dioxide. Its composition being $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, it would lead to an increase of dissolved phosphate concentration which might cause a rise of the phosphorus load in the centrifuge’s reject recycling water, hence in the WWTP inlet. Pre-experiments have to be performed in order to prevent and avoid this phenomenon.

3. Material and methods

   a. Kemira method

   As mentioned previously, the Kemira method is a two step method where the sludge is successively filtered and pressed.

   About the filtration step, a sludge sample corresponding to 1 g of TS content is filtered by using vacuum filtration in a Büchner funnel. Two filter papers of 9 cm in diameter (Munktell No3) are used. The filtration time is 40 minutes to make the sludge cake sufficiently solid for the pressing step. The mass ($m_c$) of the cake after filtration can be calculated.

   Afterwards, two other filter papers of 9 cm in diameter are added on top of the sludge cake. Then, five bigger filter papers of 12.5 cm in diameter are placed on the top and five other papers of the same diameter are placed at the bottom. This assembly is pressed by a device developed by Kemira Kemi AB. The device is a metal press which applies a 20 kg weight on the filter papers-sludge cake assembly during 10 minutes. The cake weight ($m_f$) can be calculated after pressing.

   The sludge cake including the two closest filters and the two outer filters are then dried at 105°C in the oven. The weight of the dried sludge cake ($m_i$) can be calculated.
Eventually, the dry solid content of the sludge cake after filtration (DS\textsubscript{filtr}) and pressing (DS\textsubscript{press}) can be calculated: DS\textsubscript{filtr} = m_0/m_c and DS\textsubscript{press} = m_0/m_f.

b. Pre-experiments

The objective of the pre-experiments is to measure the time when the struvite dissolution occurs at each pH level. In fact, it allows to check if the whole time of dewatering step in full scale (centrifuge) and in lab scale (Kemira method) is sufficiently low to avoid a too high increase of dissolved phosphate in the water phase. The retention time in the centrifuge being very short (a few seconds), the problem could occur only at lab-scale. The diluted acid solution (sulfuric acid 95% diluted 10 times) was added in 300 mL of sludge and the pH was measured with a pH-meter. 4 different volumes were added: 4 mL (pH=6.56), 7 mL (pH=5.91), 9.5 mL (pH=5.02) and 11 mL (pH=3.55). Afterwards, at each level of pH, the sludge was sampled at different times. To obtain the evolution of dissolved phosphate versus time, each sample was filtered and the dissolved phosphate concentration in each corresponding supernatant was measured. To carry out the phosphate concentration measurements, the auto analyzer and the Dr Lange method were used on the samples respectively at pH between 3.45 to 5.91 and at pH 7.50 and 6.56. It is important to know that the vacuum filtration operation to obtain the supernatant was about 10 minutes long. So, the measured concentration of dissolved phosphate in the supernatant is an average between 0 and 10 minutes filtration.

c. Acidification experiments

The DS\textsubscript{press} and DS\textsubscript{filtr} were measured 5 times each at three different pH (7.62, 6.78, 5.95) to study the repeatability of the Kemira method. The volume of studied sludge was still 300 mL and the solution of acid was still sulfuric acid 95% diluted 10 times.

4. Results and discussion

a. Pre-experiments

Figure 1 is representing the evolution of dissolved phosphate in the supernatant according to the pH.

![Figure 1: Evolution of dissolved phosphate in the supernatant according to the pH.](image-url)
In Figure 1, at the initial pH of 7.50, the concentration of dissolved phosphate is 290 mg/L. It corresponds to the concentration at the initial time (t = 0 minutes). First of all, whatever the pH, the concentration of dissolved phosphate already increases at around 10 minutes. Concerning the two lowest pH levels, the concentration of dissolved phosphate at around 60 minutes is too high. Indeed, the concentration increases from 293 to 755 mg PO₄-P/L at a pH of around 3.55 and it increases from 293 to 588 mg PO₄-P/L at a pH of around 5.02. Thus, the Kemira method in those conditions cannot be used. About the two highest pH levels in the graph, the increase of concentration seems to be reasonable after 60 minutes as it increases from 293 to 490 mg PO₄-P/L at a pH of around 5.91 (7 mL of added acid) and from 293 to 362 mg PO₄-P/L at a pH of around 6.56 (4 mL of added acid).

However, it has been observed that when reaching the pH of 5.91, the level of sludge’s volume increased suddenly from 300 mL to approximately 500 mL. This could be due to a high release of gas during the reaction between the sulfuric acid and the digested sludge causing the formation of bubbles. This gas could be hydrogen sulfide and CO₂ (www.kappala.se). This phenomenon could cause serious damage in full scale, considering the centrifuge capacity. Comparing the 4 studied pH levels of Figure 1, the pH when the sludge volume starts to increase is situated between 5.91 and 6.56 (between 4 and 7 mL of added acid). To avoid a too high increase of dissolved phosphate and an increase of the sludge volume, this minimum pH or maximum volume of added acid should not be exceeded.

The retention time in the full-scale centrifuge is a few seconds and it was not possible for practical reasons to measure the concentration during the first seconds following acidification. Nevertheless, a very low concentration of dissolved phosphate in the reject water from the centrifuge should be expected, as the dissolution of struvite probably does not have enough time to occur.

b. Acidification

The digested sludge used for the following experiments was sampled from the WWTP one week after the digested sludge used for the pre-experiments. The temperature of the sludge was around 8°C (storage room temperature). The DS_press and DS_filtr were measured 5 times each at three different pH: 7.62, 6.78, 5.95. The pH 7.62 corresponded to the conditions without adding acid, 6.78 to an addition of sulfuric acid of 3 mL and 5.95 to an addition of 6.5 mL. The results are shown in Figures 2 and 3.
According to Figure 2, the $\text{DS}_{\text{press}}$ is higher in average by adding acid which means that the sludge is dewatering better by acidification. Concerning the acidification from a pH of 7.62 to 6.78 (3 mL of diluted acid), the $\text{DS}_{\text{press}}$ increases significantly from 27.5 to 30.3% representing a DS rise of 2.8%. Moreover, regarding Figure 3, adding acid has a strong influence on sludge’s filterability as the $\text{DS}_{\text{filtr}}$ increases significantly from 20.9 to 29.2%. This represents a DS rise of 8.3%. Concerning the sludge at a pH of 5.95, the applied filtration time was 30 minutes instead of 40 minutes. Indeed, a too long filtration could cause a reabsorption of the water from the filter papers to the cake during the pressing step (Tastu, 2007). The $\text{DS}_{\text{press}}$ at pH 5.95 is not significantly different from the ones at pH 7.62 and 6.78. That means that the $\text{DS}_{\text{press}}$ could be stable as well as it could decrease. But the results at pH 5.95 should not be taken in to account as the level of sludge increased from 300 mL to 400 mL. Nevertheless, the experiment confirmed that the filterability is better by adding acid. The $\text{DS}_{\text{filtr}}$ at pH=5.95 and at pH=7.62 are the same while the filtration time at pH=5.95 is lower than at 7.62. Moreover, this experiment confirms that the minimum pH or maximum amount of acid reached before the sludge’s volume increases is situated between 5.95 and 6.56 or between 4 and 7 mL. The optimal pH or the optimal amount of acid to get the highest $\text{DS}_{\text{press}}$ seems to correspond to the ones reached or added just before the increase of the sludge’s volume.

If it is assumed that the digested sludge during the whole year has the same behavior as the one used in the experiment, one can estimate a cost reduction with an improvement of $\text{DS}_{\text{press}}$ of 2.8%. After calculation, a 5% cost reduction can be achieved by adding acid.

After several experiments, it appeared that the optimal pH value can vary, which is assumed to be due to a change in the sludge quality.

5. Conclusion

It has been demonstrated that adding acid in the digested sludge before the centrifuge is a good way to improve the dewaterability. From the experimental results, the acidification can provide a cost reduction of about 5%.

However, the acid addition must be limited, as beyond a certain amount and a minimum pH, it causes an increase of sludge volume due to gas bubble formation. That could lead to serious problems with the dewatering process in full scale.

The optimal pH or optimal amount of acid to get the highest $\text{DS}_{\text{press}}$ seems to correspond to the ones reached just before the increase of the sludge volume. This optimal pH and acid volume appeared to vary along time which is assumed to be due to the change in sludge quality.

6. References

Y.Cheung, (1988), Acid treatment of anaerobically digested sludge: effect on heavy metal content and dewaterability, Pollution Research Unit, The University of Manchester Institute of Science and Technology, United Kingdom


Y.Tastu, (2007), Evaluation of sludge dewatering properties, Water and Environmental Engineering at the Department of Chemical Engineering, master thesis