Exploring Stabilization Alternatives for a Lime-Softening Sludge with a High Organic Content

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Abstract

Stabilization of the sludge originating from a water treatment plant, where a lime-soda softening of the creek water containing a high organic matter is employed, was investigated. Several stabilization alternatives, namely, aerobic stabilization, acid stabilization, base stabilization, lime stabilization and thermal stabilization were tested. Thermal stabilization outperformed among the others. It was observed that exposing the sludge to at least 375°C would render the sludge disposable into non-hazardous waste landfills. Aerobic stabilization did not work at all. Acid, base and lime stabilization processes, though resulted in the organic content decrease from 6 to 9% in the sludge, could not satisfy the leachate organic content criteria of 80 mg L^{-1} DOC, since, probably, the organic matters in the sludge became less adsorbable to the sludge and, hence, more leachable to the bulk solution.

Key Words: Lime-softening, organic content, sludge, aerobic stabilization, acid/base stabilization, lime stabilization, thermal stabilization.

Introduction

Sludge treatment is needed to reduce the water and organic content of the sludge and to render the solids suitable for reuse or final disposal. In this respect, stabilization and conditioning are the integral steps towards proper sludge handling and disposal, which involve biological digestion, chemical or thermal stabilization. Biological digestion is a sludge stabilization process in which organic solids are decomposed into stable end-products, in a way total mass of solids is reduced and pathogenic organisms are destroyed. Thermal stabilization basically involves the use of heat treatment process in order to breakdown the solid cell structure while reducing some of the water content. Likewise in chemical stabilization process, sludge is mixed with either organic or inorganic chemicals or both to achieve the same desired results (Foladori et al 2010).

In this study, the sludge generated in a water treatment plant (WTP) serving to a Natural Gas Combined Cycle Power Plant was considered (Fig. 1). This WTP receives raw water from a creek nearby via a screening device. The creek water reaching to the WTP is very high in suspended solids content (mostly organic by nature), and requires hardness (calcium hardness of carbonate form) removal (Table 1). Thus; the raw water withdrawn is subjected to lime softening process, for the removal of hardness and also for the co-removal of suspended solids, which employs precipitation and sedimentation followed by granular filtration. Sludge from the sedimentation tank that contains precipitated hardness and also settled suspended solids is sent to a thickener and then to a belt-press for dewatering. The dewatered sludge is to be landfilled. However, high organic matter content renders this sludge not suitable for disposal in non-hazardous waste landfills. According to the Regulation on Landfilling of Waste (EU Directive 1999/31/EC), the simulated leachate from a waste should have a dissolved organic carbon (DOC) content not exceeding the limit of 80 mg L^{-1} in order to be accepted to a non-hazardous waste landfill. As the disposal in the nearest hazardous waste landfill is a costly option, the plant managers are not willing to dispose of their wastes in this landfill. Instead, they consider the possible stabilization of the sludge for its possible disposal in a non-hazardous waste landfill as a low-cost option.

In the present study, alternative stabilization methods that would render the sludge disposable in non-hazardous waste landfill sites by reducing DOC release were searched. To that purpose, aerobic stabilization, asit stabilization, base stabilization, lime stabilization and thermal stabilization methods were evaluated.

Fig. 1 here

Table 1 here

Materials and Methods

Sludge Sampling

Sludge samples were taken from different locations along the sludge treatment facility of the WTP according to the stabilization alternative to be studied. Sludge samples to be used in acid stabilization, base stabilization, lime stabilization and thermal stabilization were dewatered sludge taken from the exit of belt press, whereas sludge samples to be used in aerobic stabilization were from the concentrated sludge line of gravity thickener.

As the sludge characteristics are highly variable depending on the river water quality, sludge sampling and charcterization were continued throughout the study. Where deemed necessary, composited sludge samples were prepared in order to account for the variation in the composition of the sludge.

Each sludge sample taken was analysed for its volatile solids (VS), total solids (TS), and total organic carbon (TOC) contents as well as leachate DOC.

Stabilization tests

Aerobic Stabilization tests were conducted in reactors (2.5 L) with a working volume of 2 L. Sludge samples placed in reactors were aerated using air pumps. Reactor temperature was kept at 20°C with the help of water bath and pH was maintained at 7 by acid-base addition, as required. Dissolved oxygen (DO) level was monitored using a DO probe. Stabilization of the sludge was monitored via VS and TS measurements in samples taken weekly.

Acid and Base Stabilization was performed, using H_2SO_4 (1 M) and NaOH (1 M), respectively. Sludge samples of 30 g (wet weight) were exposed to different volumes of (2, 5 and 10 mL) acid and base solutions (corresponding to about 0.13 , 0.36 and 0.78 mL acid (g dry solids)$^{-1}$ and about 0.13 , 0.35 and 0.80 mL base (g dry solids)$^{-1}$) for a reaction period of 1 h at room temperature. Following to the addition of acid or base, the samples were equally seperated into two, as to serve for parallel experimentations and aritmetic averages were taken during the evaluation of the results. At the end of reaction period, the sludge samples were subjected to leach test according to the method given in Annex 2 of EU Directive 1999/31/EC and leachate was analyzed for the DOC content. In addition, acid/base stabilized sludge samples were analyzed for their TOC, TS and VS contents.

During the *Lime Stabilization studies, s*ludge samples of 20-30 g were exposed to different lime doses (5 and 10% weight by weigth) for a reaction period of 10 d at room temperature. At the end of reaction period, the sludge samples were subjected to leach test according to the method given in Annex 2 of EU Directive 1999/31/EC and leachate was analyzed for DOC. In addition, lime stabilized sludge samples were analyzed for their TOC, TS and VS contents on a daily basis. Experiments were run in parallel with homogenized sludge samples and aritmetic averages of the results were considered.

Experiments on the *Thermal Stabilization* were run with 8 grab samples taken weekly in a 2 months period. Samples delivered to the laboratory were immediately brought to dry weight at 105°C. Then, they were heated to the temperatures of 200, 250, 300, 325, 350, 400, 550, 700 and 800°C for an hour, and followingly were subjected to VS, TS and TOC analysis. Like for the stabilization with lime and acid/base, stabilized sludge samples were subjected to the leachate tests.

Results and Discussion

Sludge Characterization

Sludge originating from the thickener of the WTP is unique in the sense that it is high in both organic and inorganic matter content; because the WTP receives creek water which is high in particulate organic matter (Table 1). Another specialty regarding the sludge is that backwash water from pressure filters of the cooling water system is directed to the thickener; therefore additional organic and inorganic particulate matter enters into the sludge. Fig. 2 depicts VS, TS and TOC content of the sludge samples taken throughout the study. As the creek water is highly variable in composition, weekly samples were taken and analyzed. TS content of the dewatered sludge samples was in the range of 44 to 65 %, with an average value of about 53%. VS content of the sludge sampled were quite variable, changing from about 3 to 17%, with an average value of 8.6%. In parallel to this, TOC content was also variable in the range of 45500 to 142000 mg kg^{-1}. Composite sample prepared with the first 10 samples exhibited TS, VS and TOC values of 53.9%, 3.7% and 80 620 mg kg^{-1}, respectively. Particulate organic matters per total solids on dry weight basis (as %VS/TS) are presented in Table 2 which also points the type of sludge samples used in the stabilization tests.

Fig.2 here

Table 2 here

Acid-Base Stabilization

Acid and alkaline stabilization is a form of chemical treatment where an acid and alkali, in respective orders, is added to sludge, through which an unfavorable environment for microbial growth is created and putrescibility of the sludge is reduced (Neyens et al 2003, USDE 1999).

Acid-base stabilization experiments were performed with dewatered sludge samples taken as grap as well as compozited sample. Results belonging to one grap sample are presented here. This sample was selected to present in this paper as it was representing the worst case.

As can be seen in Fig.3, acid application has resulted in a decrease in VS content of the sludge along with a decrease in sludge TOC. This finding indicates a reduction in organic matter content of the sludge due to acid hydrolysis which is not yet sufficient to meet the TOC criterion given in the Legislation. According to the regulation on landfilling of wastes (EU Directive 1999/31/EC), a waste should have a TOC below 50 g kg^{-1} in order to be landfilled in a non-hazardous landfill site. Acid treatment has produced a sludge with a TOC content of 65 to 71 g kg^{-1} depending on the acid dose applied. When these sludge samples were subjected to leachate tests, it was seen that acid treatment resulted in an increase in leachate TOC in comparison to the raw sludge (Fig. 3). This observation was attributed to easier release or sorbed organic matter from sludge solids after acidification. All these findings have indicated that acid stabilization is not a satisfactory pretreatment; although it decreases the organic matter content of the sludge itself; it causes an increase in organic matter relased into water when subjected to leachate test.

Fig.3 here

Experimental findings from base treatment of the sludge are presented in Fig. 4. As can be depicted from the figure, VS/TS ratio decreased from its original value of 11.5 % to around 9% with the addition of base. Also, both TS and VS contents of the sludge decreased from 57.2% to 43.9% and from 6.6% to 4%, respectively, as the amount of caustic addition increased. In line with this, TOC content of the sludge has decreased from 142000 mg kg^{-1} to 28000 mg kg^{-1} with the addition of 10 mL 1 M NaOH to 30 g sludge. This value is well below the limit set by the regulation. However, when the stabilized sludge was subjected to the leach test, leachate TOC, unexpectedly, increased to 503 mgL^{-1} from its original value of 104 mgL^{-1}. This finding indicates that organic matters in the sludge became less adsorbable to the sludge and, hence, more leachable to the bulk solution side. Therefore, base stabilization method was deemed inappropriate.

Fig.4 here

Lime Stabilization

Lime stabilization is basicly applied to increase pH (>10) of biosolids that may support the growth of pathogens to produce a very efficiently sanitized end product. This treatment is reported to provide a reduction in organic matter content and an increase in total solids content of sludge (USEPA 2003, Czechowski & Marcinkowski 2006, Samaras et al 2008). In the present study, this method of treatment was considered as an option as it is reported to cause a reduction in organic matter content.

As can be depicted from Fig. 5, reaction with lime proceeded quite rapidly, resulting in decrease in VS/TS ratio from 11.5% to around 7% within one day, for both lime doses applied. TOC content of the sludge reduced to 55000 mg kg^{-1} and 70000 mg kg^{-1} from the original value of 142000 mg kg^{-1}, with the application of 5 and 10% lime, respectively (Fig. 6). However, when the sludge obtained at the end of 10 day was subjected to the leach test, it was observed that leachate TOC value did increase to 153 and 175 mgL^{-1}, in respective orders for the lime applications, from the initial TOC of 104 mgL^{-1}. Similar to the acid-base stabilization cases, organic matters in the sludge became less adsorbable to the sludge and, hence, more leachable to the bulk solution side. Therefore, lime stabilization method was also deemed as inappropriate to consider for the stabilization of sludge.

Fig.5 here

Fig. 6 here

Thermal Stabilization

Thermal treatment of sludge consists of heating to moderate temperatures (up to 220°C or more), with contact times of minutes or hours. The produced effects in the sludge are breakdown of the sludge structure, sludge solubilization and bacterial lysis and in a way resulting in the decrease of the sludge amount and thus easier and cheaper to manage and dispose of. The input of thermal energy is achieved by heat exchangers or by the application of steam to the sludge (Foladori et al 2010).

Eight samples of sludge taken through 2 months were subjected to thermal stabilization experiments each lasting for an hour. Temperatures were screened from 300 to 800°C with 25°C increments. Results obtained are summarized in Table 3. As seen, as temperature increases, organic matter content removed from the sludge (as % VS/TS) increases, as expected. However, when the stabilized sludge samples were subjected to the leach test, an interesting pattern was observed for the variation of leachate TOC with temperature. Leachate TOC did increase from its original value of 159 mgL^{-1} to 216 mgL^{-1} and 215 mgL^{-1} at temperatures of 200°C and 250°C, respectively. This was attributed to the possible decreased tendency of some organic matters to remain attached onto the sludge matrix when temperature was increased from 105°C to 200-250°C. And, accordingly, this fraction of the organic matters was released from the sludge matrix to the bulk solution side. On the other hand, with further increase in temperature, leachate TOC declined to values below its original value (Table 3), possibly due to decrease in organic matter content in the system at all (i.e. both in the sludge matrix and the bulk solution side)at higher temperature applications. As also seen from Table 3, regulation value of 80 mgL^{-1} DOC was attained at 375°C. At this temperature, TOC content of the sludge was 33249 ±12619 mg kg^{-1} which was appropriate, being below the relevant regulation limit of 50000 mg kg^{-1}.

Table 3 here

Aerobic stabilization

Aerobic digestion or stabilization is known as extended aeration of biosolids whereby waste primary and secondary sludges are continually aerated for long periods of time. In the process, the microorganisms extend into the endogenous respiration phase, which is a phase where internal storage products in the cells are oxidized, with a reduction in the biologically degradable organic matter. The organic matter, from the sludge cells is oxidized to final end products carbon dioxide, water and ammonia. The ammonia is further converted to nitrates as the aerobic digestion process proceeds. Aerobic digestion provides not only a reduction in organic matter content but also odor removal and pathogenic microorganism removal (USEPA 2003, WEF-ASCE 1992). This method is, normally, considered for the stabilization of biological sludge. On the other hand, it has been applied to the mixture of biological and chemical sludge in a few Literature studies. For example, Eikuma et al. (1974) showed that aerobic stabilization can be successfully applied to the sludge originating from alum coagulation when mixed with the primary sludge of the wastewater treatment plant. Therefore, in this study, altough the sludge was not of biological wastewater treatment plant origin and therefore, was composed of different organic structure with relatively low content, aerobic stabilization was considered as one of the alternatives to investigate.

Aerobic stabilization experiments were conducted with the sludge originating from the gravity thickener. Aeration was provided by the air pumps, however, DO value could not be maintained at the desired level; droped down from 1.5 mgL^{-1} to zero within an hour. Attempts to increase the DO by using more air pumps did not solve the problem. To explore the reason for this, chemical characterization of the sludge was performed to understand if oxygen scavenging compounds, other than organics, such as sulfite, sulphide, chloride are abundantly present. Results obtained showed that COD, sulfite, sulphide, chloride concentrations of the sludge samples, on the average, were 6012 mgL^{-1}, 122 mgL^{-1}, <1 mgL^{-1} and 205 mgL^{-1}, respectively; indicating organic fraction of the sludge is superior over sulfite, sulphide, chloride contents. In another words, sulfite, sulphide, chloride contents were not so high to lead to such high DO consumption during the aerobic stabilization. Moreover, organic content, though quite high, is not considered to cause to such rapid DO drop within an hour. So, probably, other substances present in the sludge matrix could cause this. Nevertheless, it was deemed unnecessary to search about these possible factors, as it was obvious that, regardless of the real cause for the problem, the required oxygen could not be supplied to the reactors in practice. Therefore, it was decided not to continue to the aerobic stabilization experiments.

Conclusion

Stabilization of the lime-softening sludge with a high organic content was investigated. Results obtained are summarized in Table 4. Among the tested processes, base stabilization, acid stabilization, and lime stabilization ended in a considerable decrease in the organic content of the sludge. However, they were not satisfactory in meeting the regulation leachate DOC value of 80 mg L^{-1}, probably, as the organic matters in the sludge became less adsorbable to the sludge and, hence, more leachable to the bulk solution. Aerobic stabilization did not work at all for the sludge of concern. On the other hand, thermal stabilization produced acceptable results when the temperature was over 375°C with a leachate DOC of 56 mg L^{-1} while organic content of the sludge (as %VS/TS) was decreased from 11.5 % to 8.6%.

Table 4 here

Acknowledgement

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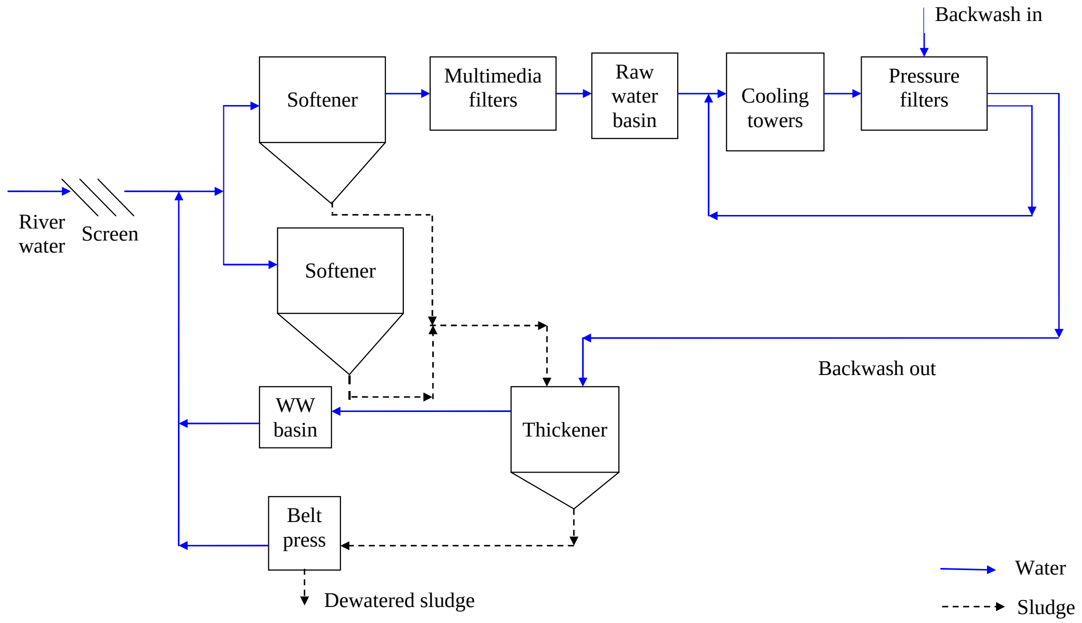


Figure 1. Water treatment plant flow diagram

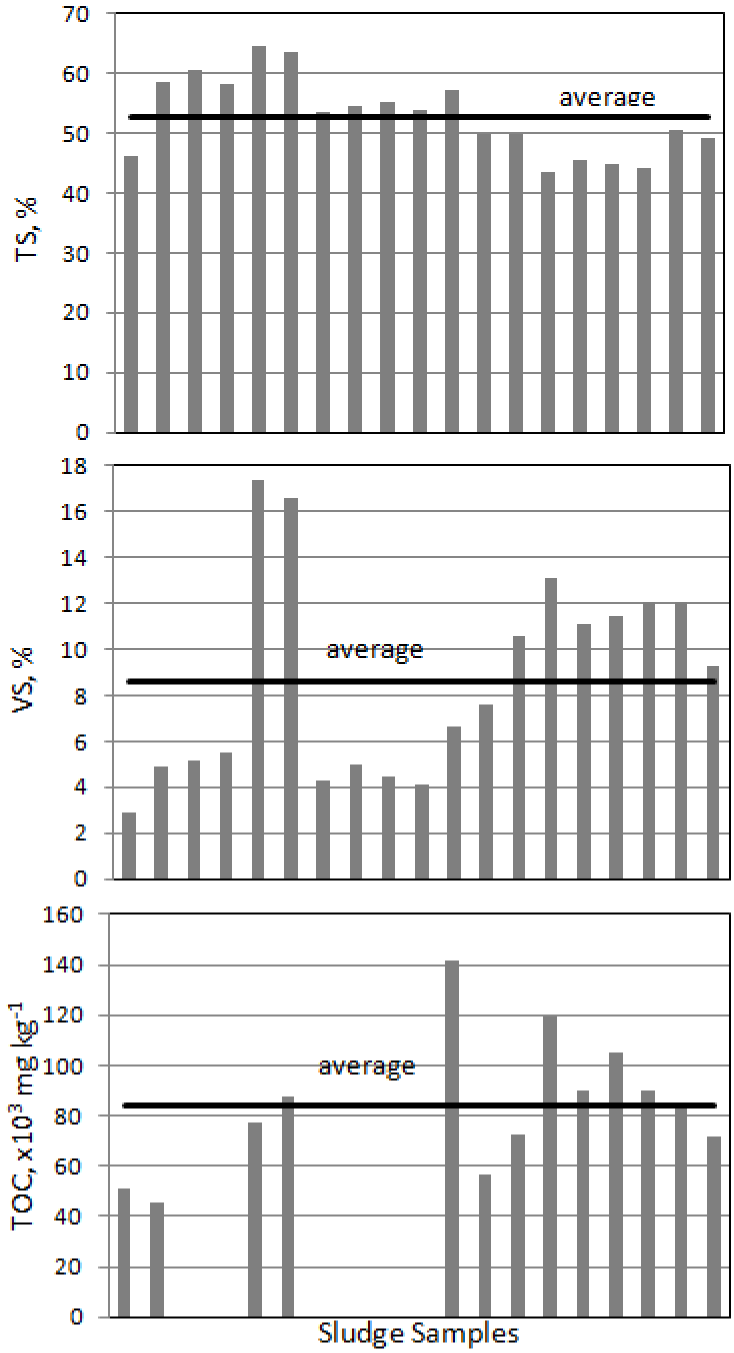


Figure 2. Variation in the TS, VS and TOC contents of the dewatered sludge samples.

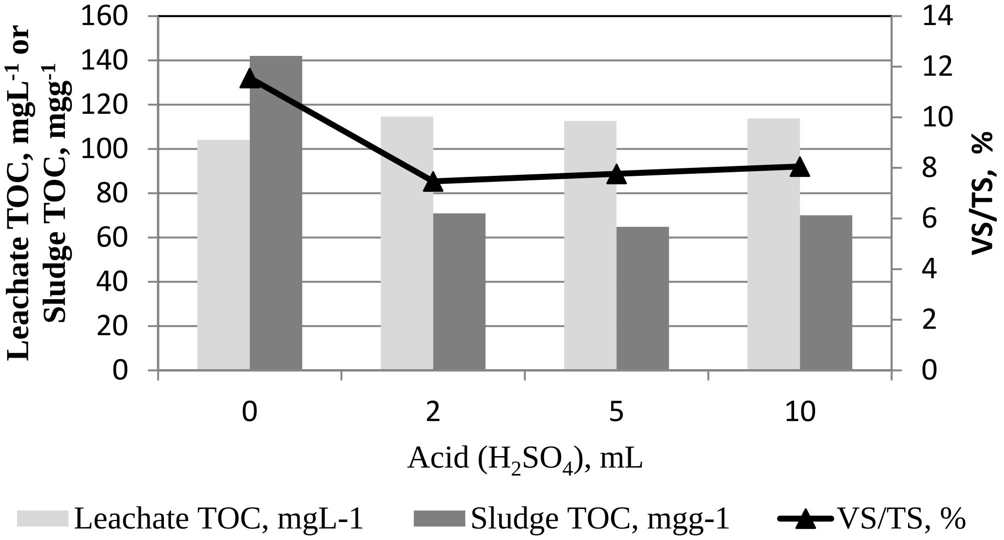
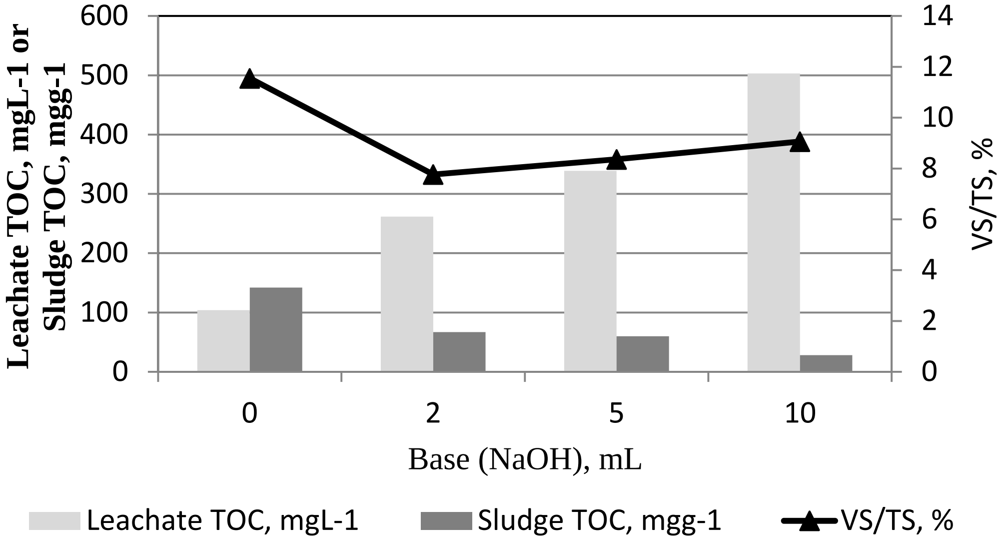


Figure 3. Effect of acid stabilization on TOC, VS of the sludge and on TOC of the leachate (Sludge sample: 30 g; stabilization duration: 1 h)



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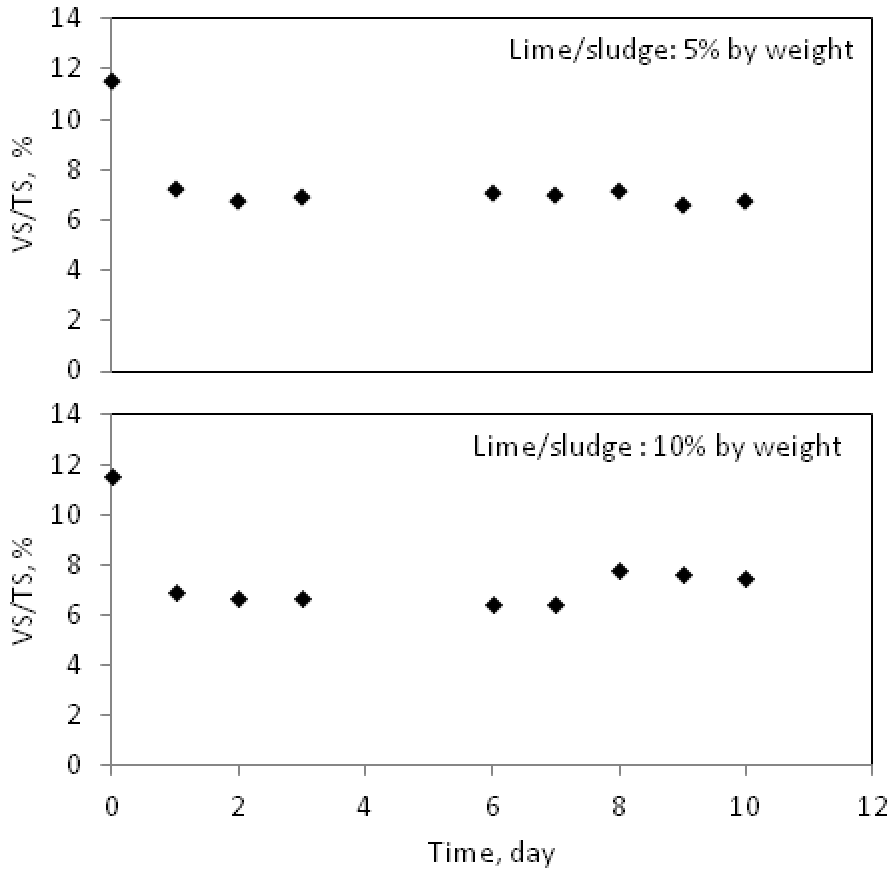

Figure 5. Effect of lime dose on VS/TS ratio

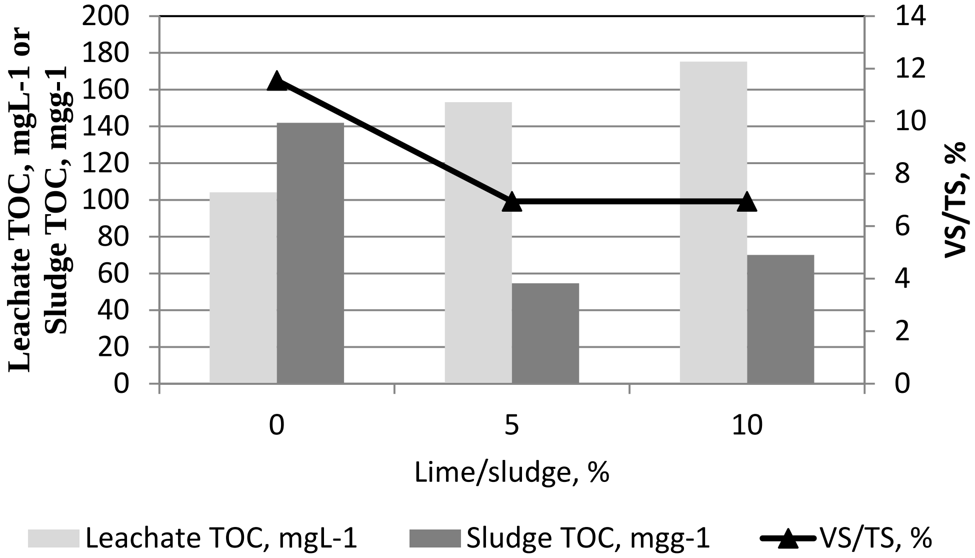

Figure 6. Effect of lime stabilization on TOC, VS of the sludge and on TOC of the leachate (Sludge sample: 30 g; stabilization duration: 10 d)

Table 1. Influent Creek Water Characteristics

Parameter	Value	Parameter	Value
COD, mgL^{-1}	154 (137[1],158[2])	Total hardness, mgL^{-1} $CaCO_3$	300
Soluble COD, mgL^{-1}	56 (60[1],69[2])	Total alkalinity, mgL^{-1} $CaCO_3$	340
DOC, mgL^{-1}	15.5 (15.2[1],20.5[2])	NH_4^+, mgL^{-1}	20
BOD_5, mgL^{-1}	60	Cl^-, mgL^{-1}	100
pH	7.8	$SO_4^=$, mgL^{-1}	130
Conductivity, μScm^{-1}	1200	Fe, mgL^{-1}	0.5
Suspended Solids, mgL^{-1}	400	Na, mgL^{-1}	110
PO_4^{-3}-P, mgL^{-1}	6	NO_3^-, mgL^{-1}	15

[1] Creek water after screen; [2] Lime-Softening influent.

Table 2. Sludge Samples and Their Characteristics

Sample Type	TS %	VS %	VS/TS %	TOC, mg kg^{-1}	Used in stabilization of
Dewatered sludge	46.2	2.9	6.3	51100	Acid, Base, Lime
Dewatered sludge	58.5	4.9	8.4	45500	
Dewatered sludge	60.5	5.2	8.6	-	
Dewatered sludge	58.4	5.5	9.5	-	
Dewatered sludge	64.5	17.3	26.6	77100	
Dewatered sludge	63.5	16.6	25.9	87400	
Dewatered sludge	53.4	4.3	8.1	-	
Dewatered sludge	54.7	5.0	9.1	-	
Dewatered sludge	55.2	4.5	8.2	-	
Dewatered sludge	54.0	4.1	7.6	-	
Dewatered sludge	57.2	6.6	11.6	142000	
Composited sludge	53.9	3.7	6.9	80620	
Sludge from thickener to belt-press*	134294	8510		-	Aerobic
Sludge from thickener to belt-press*	245092	17306		-	
Dewatered sludge	49.8	3.7	7.6	56813	Thermal
Dewatered sludge	53.4	5.6	10.6	72435	
Dewatered sludge	43.5	5.7	13.0	119756	
Dewatered sludge	45.4	5.0	11.1	90055	
Dewatered sludge	44.8	5.1	11.3	104767	
Dewatered sludge	44.1	5.2	11.2	90227	
Dewatered sludge	50.4	6.1	12.0	83068	
Dewatered sludge	49.2	4.6	9.4	71432	

*These samples are non-dewatered, so TS and VS values have a unit of mg L^{-1}.

Table 3. Effect of Thermal Stabilization on Organic Content Removal from the Sludge

Temperature, °C	200	250	300	325	350	375	400	550	*700*	*800*
Organic matter removal, % VS/TS										
Mean	4.2	4.0	6.5	7.1	8.0	8.6	8.8	10.7	13.0	28.3
STD	±0.1	±0.2	±1.6	±1.7	±1.4	±1.1	±1.1	±1.6	±5.4	±6.9
Leachate DOC, mg L^{-1}										
Mean	216	215	168	148	94	56	43	37	6.6	7.7
STD	±56	±41	±64	±25	±33	±14	±14	±9	±3.4	±4.5

Table 4. Organic Matter Removal by Different Processes

PROCESS	VS/TS %	LEACHATE DOC mg L^{-1}
Thermal Stabilization		
200°C	4.2	216
250°C	4.0	215
300°C	6.5	168
325°C	7.1	148
350°C	8.0	94
375°C	8.6	56
400°C	8.8	43
550°C	10.7	37
700°C	13.0	6.6
800°C	28.3	7.7
Base Stabilization (mL of 1 M NaOH/30 g wet sludge)		
2	7.8	262
5	8.4	339
10	9.0	503
Acid Stabilization (mL of 1 M H_2SO_4/30 g wet sludge)		
2	7.5	115
5	7.7	113
10	8.0	114
Lime Stabilization (Lime as % of TS)		
5	6.9	153
10	6.9	175