Solidification of Sludge from Waste Water Treatment

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Abstract

This paper is aimed to the stabilization/solidification of sludge from wastewater treatment. Wastewater arised from illegal handling with waste galvanic sludge contacted by the silage waters. Treated sludge contained high amount of heavy metals and dissolved organic substances and inorganic salts. Solidificates were leached according to standardized method ČSN EN 12457-4 and assessed in accordance with Decree no. 294/2005 Coll. High content of dissolved organic carbon content (DOC) and total dissolved solids (TDS), which is expected with regard to the character and origin of analyzed/processed sludge, were critical indicators. Required legislative limits were met only if the ratio of the binder to the sludge was sufficiently large, namely for the series of untreated sludge (K0) and pre-treated sludge
(K1, K2) this ratio was 80/20, for the sludge pre-treated by sludge filter press (N) 60/40. Heavy metals were stabilized with high efficiency were not critical in relation to the legislative limits. For the considered mixtures the costs were estimated.

Keywords: stabilization, solidification, sludge, leachate

Introduction

On the anonymous site the undesirable mixing of agricultural waste containing a large number of substances of predominantly organic origin, and galvanic wastewater contaminated with inorganic salts and heavy metals appeared. The total amount of such waste is 3000–3500 m^3.

A number of liquid waste treatment processes have been tested. However, none of them produced sufficient effect. Therefore, the solution will probably lead towards multi-step processing.

The pH value in the wastewater was around 2.2, due to the composition of the water, its acceptance to any waste water treatment plant (WWTP) was excluded without any prior treatment. Average composition of wastewater is presented in Tab. 1.

A collection of experiments have been carried out by Dekonta company. The work aimed to verify the possibility of using different technologies to treat the wastewater. In terms of meeting the criteria for receiving the analyzed water at WWTP, the combination of 2-step procedure (precipitation using Ca(OH)2 (1) and reverse osmosis (2) of the liquid phase after sedimentation) seems to be effective and the most acceptable.

At the same time, the possibilities of the concentrate handling after the reverse osmosis process are not completely solved. The concentrate will probably have to be stabilized together with the dewatered sludge and also could be partly recirculated to the reverse osmosis water input. The lime precipitation and the thickening of the sludge will be carried out within the treatment of the wastewater described above.

The main aim of this work is therefore the assessment of the possibility of the sludge stabilization/solidification (S/S) with different rate of its concentration including the standard leaching tests and the cost estimation of the selected recipes. Solidification and stabilization are treatment processes designed to either improve waste handling and physical characteristics, decrease surface area across which pollutants can transfer or leach, or limit the solubility or to detoxify the hazardous constituents (Wiles, 1987). It is a well-known and widely used waste treatment method that can easily reduce the leachability of undesirable components, thereby avoiding their possible emissions into the environment (Kuraš, 2014; Means, 1994). Solidification is a process in which materials are added to the waste to produce a solid. It may or may not involve a chemical bonding between the toxic contaminant and the additive. Stabilization refers to a process by which a waste is converted to a more chemically stable form. The term includes solidification, but also includes use of a chemical reaction to transform the toxic component to a new non-toxic compound or substance (Wiles, 1987). Topic of galvanic sludge S/S technology is solved in many studies (Bednarik, 2005; Cioffi, 2002; Luz, 2006; Marcinkowski and Banaszkiewicz, 2010) with respect to heavy metals.

Area description/Materials and methods

Original rising sludge from precipitation can be characterized as a smelly green-black material which releases after prolonged standing a yellow-colored,

Tab. 1. Characteristic of analyzed wastewater – selected parameters

Tab. 1. Charakterystyka ścieków – wybrane parametry

Parameter	Content, [mg/L]	Parameter	Content, [mg/L]
TOC	4570	Pb	12.4
Zn	2 560	Mn	60.7
Cd	1.38	Cr	236
Sr	1.50	Al	56.0
Ba	0.363	Cl^-	26 000
Cu	31.3	SO_4^{2-}	9 400
Ni	102	F^-	917

Tab. 2. Characteristics of sludges and liquid phase

Tab. 2. Charakterystyka fazy ciekłej I stałej

Designation of the material	Description	Dry matter content, [%]
F	Liquid phase formed after centrifugation and filtration	-
K0	Original untreated sludge	10.6
K1	Sludge K0 pretreated by centrifugation	16.7
K2	Sludge K0 pretreated by centrifugation	21.6
N	Sludge from the sludge filter press	25.5

clear liquid phase. Upon contact with air, the oxidation reaction with the metals (iron) presented in the sludge, the change of color occurs on the sludge surface.

Solidificates specimens were created by treating sludge with different pre-treatment methods. Description of sludge used are presented in Table 2. Together, the separated liquid phase from the sludge thickening step (F) has also been characterized.

By the formation of the testing specimens, the sludge was homogenized by means of a rod mixer, in some cases the drinking water was added to the sludge to ensure a suitable consistency of the paste of the resulting solidificate. Then cement was added into sludge. The resulting mixture was well mixed and allowed to age for 3 weeks at room temperature. The specimens were then subjected to leaching tests.

Screening analysis of original sludge was performed by X-ray fluorescence spectrometry. Based on the content of the heavy metals and the balance and in relation to the limits stated in the Decree no. 294/2005 Coll. the target metals were determined. These metals were further analyzed by the method of atomic absorption spectrometry in aqueous leachate. Heavy metals occured in very small content or under limit of quantification were not determined in the aqueous extract, respectively one-point determination on solidificated with the highest sludge load was performed. Priority metals were mainly Cr, Ni, Cu, Zn, Pb.

The leaching tests were carried out according to standard procedure (ČSN EN 12457-4, 2003).

The crushed matured solidificate material (optionally the sludge) after disintegration (particle size of waste less than 10 mm) was placed in a glass bottle and supplemented with distilled water to a ratio of 10/1 (L/S) based on dry matter. The bottle was placed on the headtoe shaker for 24 hours at a speed of 6.5 rpm. After this time, the content of the bottle was filtered through a 0.45 μm nylon filter. Used analytical equipment was: Carbon analyser Vario TOC Select (Elementar), Capillary electrophoresis CE7100 (Agilent Technologies), Atomic emission spectrometer 4200 MP-AES (Agilent Technologies).

Results and discussion

The following figures show the measured contents of selected parameters given by Decree (Vyhláška č. 294/2005 Sb., 2005). Although liquid phase (F) does not form a group of samples with sludges or solidificates, the value is incorporated into the following figures for illustration and comparison. The sludges and solidificates were analyzed in relation to the limits of leachability classes IIa and III referred in the cited decree.

pH value – a requirement for leachability classes IIa and III is a minimum pH value of 6.

The requirement has been met for all sludges and solidificates. The sludges, as well as the liquid phase (F), had a pH value of the leachate above 6. The solidificates had a pH value of the leachate higher, approximately 11–12, the value grew naturally in the direction of the increasing ratio of the cement in the mixtures.

Total dissolved solids (TDS) – parameter is showed in the Figure 1. The requirement for leachability class IIa is 8000 mg/L, for class III 10000 mg/L. The liquid phase (F) contained in the original sludge is characterized by a high concentration of dissolved substances (45000 mg/L). As the sludge drainage increased, the value of this parameter decreased significantly, but the limits were not met. From Fig. 1, it is evident that all solidificates met the limit set by Decree No. 294/2005

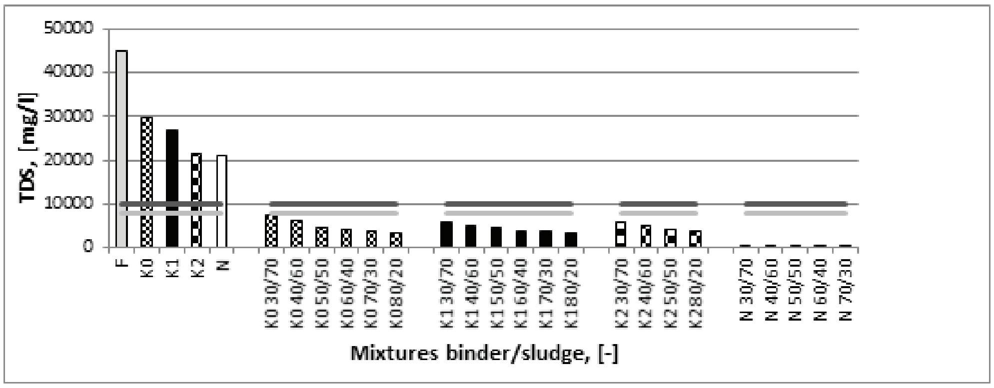

Fig. 1. Content of total dissolved solids in liquid phase (F) and leachates from sludges and solidificates

Rys. 1. Zawartość całkowita substancji rozpuszczonych (F) I odcieku z osadów

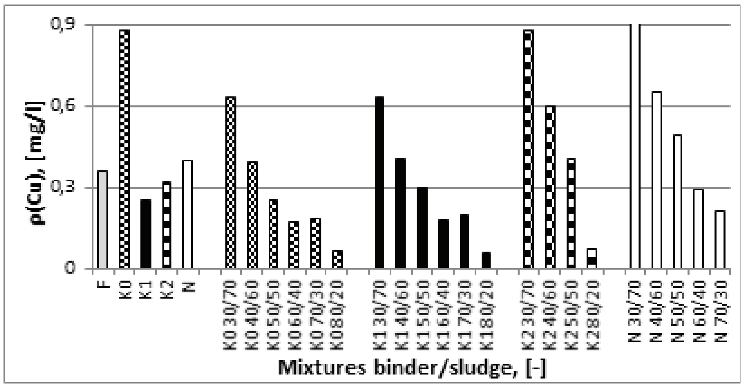

Fig. 2. Content of copper in liquid phase (F) and leachates from sludges and solidificates

Rys. 2. Zawartość miedzi w fazie ciekłej (F) i odcieku

Coll., both for the leachability class III and for the leachability class IIa. As the binder content increased and the sludge thicked, the content decreased. It is expected due to the fact that the residual liquid phase in the sludge is the dominant carrier of the dissolved substances subsequently found in the aqueous leachate of solidificates.

Copper (Figure 2) – For both leachability classes IIa and III, the limit is 10 mg/L. Copper concentrations in analyzed samples are below limit. However, due to the expected dramatic increase of pH value in the sludge/binder system, attention must be paid to this parameter, since there may be changes in the speciations, and Cu can be subsequently mobilized when the solidificate is leached. Within the ranges, the concentration of copper in the leachates decreased with increasing binder/sludge ratios, this indicate effective Cu stabilization with binder and also reduce the relative amount of Cu in the final material due to the greater relative binder quantity. As the sludge thickening increased, the amount of Cu in leachate increased. This trend can be explained by increasing copper complexing capabilities in an alkaline environment (increasing the thickening increases the alkalinity of sludge). There may be circumstances that have a contradictory effect. The content of copper in the leachates was greater after solidification than by sludge with varying degree of thickening. S/S process caused the metal mobilization, however, this parameter is not limiting in terms of comparison with the legislative reference values.

Nickel (Figure 3) - For leachability classes IIa and III the limit is 4 mg/L. Legislative limit of nickel content in leachate of sludge/pre-treated sludge was met only in the case of sludge K2 and N. The Ni concentration is much greater in the liquid phase F, indicating that the nickel compounds presented in the system are also contained in the residual liquid phase persisting in thickened sludges. The Ni content in sludge decreased considerably with increasing sludge thickening.

Legislative requirements for the content of Ni in solidificate extracts are met. As with copper, a superposition of phenomena is evident. As the binder/sludge ratio decreased, the Ni content increased, with the sludge thickening rate the Ni content in the leachate increased. However, the mass concentrations of Ni in the solidificate leachates decreased significantly compared to the leachate obtained from the sludge.

Dissolved organic carbon (DOC) (Figure 4) - requirement for leachability class IIa is 80 mg/L, for leachability class III 100 mg/L. It can be seen from the

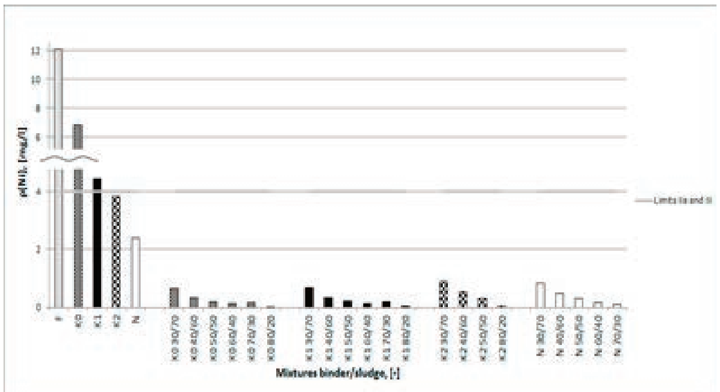

Fig. 3. Content of Nickel in liquid phase (F) and leachates from sludges and solidificates
Rys. 3. Zawartość niklu w fazie ciekłej (F) i odcieku

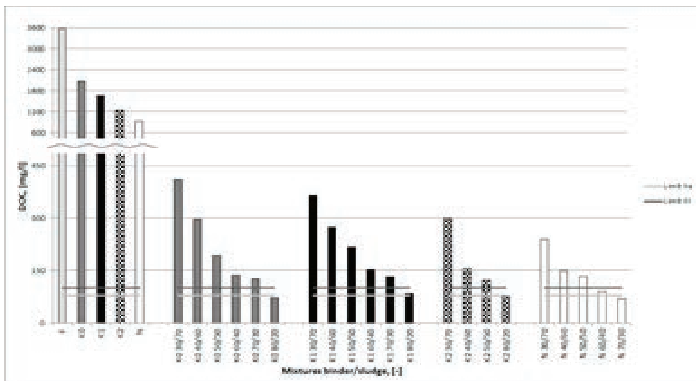

Fig. 4. Content of DOC in liquid phase (F) and leachates from sludges and solidificates
Rys. 4. Zawartość DOC w fazie ciekłej (F) i odcieki ze szlamów i brykietów

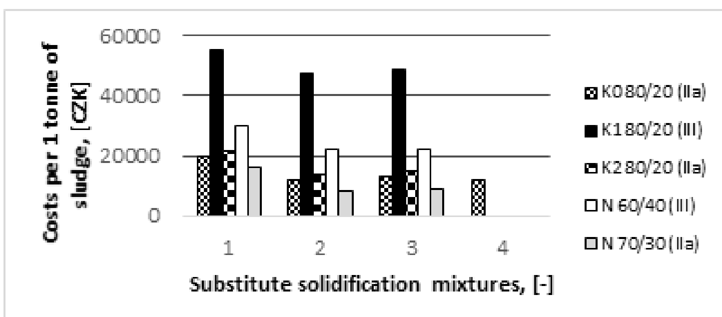

Fig. 5. Costs estimation for selected solidificate compositions (binders, landfilling)
Rys. 5. Szacunkowy koszt wybranych mieszanek do stabilizacji (spoiwo, składowanie)

figure that the DOC is the most problematic of any parameter with respect to susceptibility to exceeding the limits. In separated liquid phase (F), its content exceeded its limit value approximately 35 times. As the level of thickening of sludge increased (from K0 to N), the content of DOC in aqueous leachates decreased very slowly. In most cases, the limit IIa or III was exceeded. Based on awareness of the origin of the organic matter presented in the silage water after the neutralization and the precipitation with lime, it can be expected that their immobilization in solidificates will not be large.

The DOC represented the biggest problem in terms of the parameters and applicability of the S/S method and was therefore a critical limiting parameter. Legislative requirements were met only in case of very high binder/sludge ratios. Only mixtures of 80/20 (K0 and K2) and N 70/30 were suitable to meet the IIa limits. Limit III was complied with more tested ratios, namely mixtures of 80/20 (K0, K1, K2), N 60/40 and N 70/30.

As the binder/sludge ratio increased, the DOC value in solidificates aqueous extracts decreased very significantly. As the sludge thickening rised, DOC also de-

Tab. 3. Price of binders and its pretreatment (Strejc, 2015; Vejvoda, 2003)

Tab. 3. Koszt spoiwa i wstępnej obróbki (Strejc, 2015; Vejvoda, 2003)

Material	Price, [CZK/t of binder]	Pretreatment, [CZK/t of binder]
Portland cement	2700	0
Slag	230	50
Fluid fly ash	150	0
Energo-gypsum	100	800
Fly ash	120	0

Tab. 4. Description of binder mixtures composition

Tab. 4. Opis składu mieszanek spoiw

Mixture	Composition by weight (fraction), [-]				
	Portland cement	Slag	Fluid fly ash	Energo-gypsum	Fly ash
1	1	0	0	0	0
2	0.20	0	0	0	0.80
3	0.30	0.30	0	0	0.40
4	0.15	0	0.60	0.25	0

creased. The presented organic substances were contained in the residual liquid phase which was partially removed by pre-treatment. Considering the origin and nature of these substances, it can be said that solidificates matrix can them difficultly capture, they do not produce poorly soluble products, only marginally adsorption can be considered and the dilution process is mainly applied. It is generally known that organic compounds are poorly immobilized by inorganic binders (e.g., cement). It would be possible to test additives that effectively capture organic substances. In terms of practical applicability, however, this step did not bring meaning and realization.

At the end of this subchapter, it is necessary to summarize that S/S technology has achieved such binder/sludge compositions and solidificate qualities that the limits of the leachability class IIa have been gradually met in the various mixtures. However, it is a further investigation and consideration, in relation to the real application, whether this solution will be economically aviable.

This issue is briefly described in the following section in terms of the estimation of partial costs and the comparison of them in case of binder substitution.

Estimation of costs

When handling with raw materials and technologies, it is necessary to look at the system not only from a technological point of view but also from an economic conditions. An unreasonable attempt to improve technology can lead to costs increasing and refusal of its realization.

The objective of estimating the partial costs was to assess the possibility of reducing the cost of the binder materials and to select the waste stabilization/solidification method, which would be the cheapest and at the same time meeting the legislative requirements.

When the cost balance was carried out, only the material costs and the fee for the the landfilling were considered. No other operating costs were included as they are more or less similar for the cases considered, except of transport costs of the resulting amount of material (according to composition) to the landfill destination.

The costs considered for the binder materials are presented in Table 3. The cost for the disposal of hazardous waste is CZK 7900 per tonne. For the disposal of other waste at the landfill, the fee is CZK 1850 per tonne (Ceník, 2016).

From experience and on the basis of sludge characteristics and alternative binders, 3 alternative cement-based binder compositions have been proposed. The composition and designation of the selected compositions is presented in Table 4.

On the basis of the data above, an estimation of the costs for the preparation of solidificates complying with IIa or III limits and their subsequent landfilling was made. Cost items are a linear combination of pricing and representation of individual components. The resulting cost estimates are compared for the relevant mixtures in Figure 5. The mixture composition in the mixed binder corresponds to the numerical designation from Table 4.

Figure 5 shows that the cost of processing 1 tonne of sludge varies considerably depending on the type of binder used and the leachability class.

The most preferred variant of sludge stabilization/solidification is recepture N 70/30 with solidification composition no. 2. This variant meets the leachability class IIa, is based on the sludge pre-treated by sludge filter press, the binder/sludge ratio is 70/30, the cement is replaced by the binder mixture with cement/fly ash composition 20/80. For better consistency, drinking water is added to the mixture. The cost of processing 1 tonne of sludge in this way is CZK 8500. By replacing cement with less valuable materials, the costs has been reduced 1.5 times.

Due to the high consumption of binders and the high cost of the process, it is necessary to consider all the circumstances regarding the application of the waste process to a specific site and also to take into account other waste management options.

Conclusion

In this work, the process of stabilization/solidification of sludge from the treatment of waste water, which originated from the illegal treatment of galvanic sludge contacted with silage water, was studied. The sludge was formed in the process of precipitation of waste water by lime suspension.

The characterization of the sludge and its modifications resulting from the process of thickening (centrifuging and processing on filter press) was carried out in terms of leachability and a comparison was made with the reference limits of Decree no. 294/2005 Coll.

High content of chlorides, dissolved organic carbon content (DOC) and total dissolved solids (TDS), which is expected with regard to the character and origin of analyzed/processed sludge, was a critical indicator.

The results of the leaching test showed that the limits set by Dec. no. 294/2005 Coll. were met only if the ratio of the binder/sludge is sufficiently large, namely for the series K0, K1, K2, this ratio was 80/20, for the serie N-60/40.

Due to the relatively high cost of the binder used, it was decided to estimate the cost of the various binder mixtures in order to replace the used cement with other materials. The cheapest variant was a recepture with the sludge (N) with a binder/sludge ratio 70/30, with 80% cement replacing by fly ash. The cost of processing and landfill depositing calaculated per 1 tonne of input sludge is approximately 8500 CZK. By replacing cement with less valuable materials, the costs has been reduced 1.5 times.

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Zestalanie osadów z oczyszczania ścieków

W artykule przedstawiono wyniki badań nad stabilizacją (zestaleniem) osadów z oczyszczania ścieków. Ścieki pochodziły z nielegalnego zrzutu z galwanizerni. Poddany obróbce szlam zawierał duże ilości me-tali ciężkich i rozpuszczone substancje organiczne oraz sole nieorganiczne. Fazę stałą ługowano zgodnie ze znormalizowaną metodą ČSN EN 12457-4 i ocenione zgodnie z rozporządzeniem nr 294/2005 Coll. Wysoka zawartość rozpuszczonego węgla organicznego (DOC) i całkowitą ilością rozpuszczonej fazy stałej (TDS), które decydują o jakości osadu (szlamu). Limity określone w stosownym rozporządzeniu były spełnione tylko wtedy, gdy stosunek osadu do całkowitej objętości ścieków był wystarczająco duży, a mianowicie dla nieoczyszczonego szlamu (K0) i szlamu poddanego wstępnej obróbce (K1, K2) ten stosunek wynosił 80/20, dla szlamu poddanego wstępnej obróbce na prasie filtracyjnej (N) 60/40. Zawartość metali ciężkich ustabilizowała się na wysokim poziomie, wydajność nie przekraczała wartości krytycznych określonych w ustawie. Dla badanych osadów oszacowano koszty odwadniania i przeróbki.

Słowa kluczowe: stabilizacja, zestalanie, szlam, odciek