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Removal of heavy metals occurring in the washing water of flue gas purification

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ABSTRACT

Heavy metals are toxic for humans and the environment. Therefore it is important to limit the emission of these heavy metals in air, water and soil. An aqueous solution of sodium trimercapto-triazine, commercially supplied under the name TMT-15, is currently used for the removal of heavy metals occurring in the washing water from flue gas purification at the incineration plant of the Intercommunale Maatschappij voor Openbare Gezondheid (IMOG) located in Harelbeke (Belgium). This aqueous solution of sodium trimercapto-triazine belongs to a group of complexion agents which are expensive and a large dosage is necessary to obtain good effluent values.

Therefore an optimization study for the consumption of TMT-15 and an examination for the alternative products was performed. Key performance indicators were effluent quality and chemical consumption. The optimization study was realized based on a central composite experimental design (CCD) approach performed with the Design Expert software. The amount of complexion, coagulation and flocculation agent was used as input variable in this design, while the effluent heavy metal concentrations and the corresponding metal discharge levy were used as responses that needed optimization. Preliminary jar tests were used to determine the experimental boundaries, while the Design Expert software was used to determine the optimal complexion, coagulation and flocculation agent concentration.

Based on this approach a 19% reduction in chemical use could be achieved on lab scale and, because of safety precautions, a reduction of 10% was implemented in the actual plant. Further (cost) optimization of the installation was based on an alternative analysis which revealed that the same reagent supplied by a different supplier produced similar results, but was lower in cost price.

1. Introduction

In municipal waste incineration plants heavy metals volatilization occurs in the flue gas due to the high temperature combustion process. Without treatment these heavy metals would consequentially be released in the ambient air. This release causes great concern because of its risk of inhalation related diseases and its toxicity to the environment [1,2], especially in densely populated areas such as Flanders (the northern part of Belgium) were these municipal waste incineration plants are situated very close to domestic areas.

The volatile heavy metals can bind on dust particles and can be distributed in the atmosphere. Inhalation of air polluted with for example lead could damage the central nervous system. Long-term exposure of lead polluted air could result in a lag in intellectual development of children. These dust particles containing heavy metals can also deposit on vegetables and into surface waters. The intake of food polluted with heavy metal could lead to severe disorders of the reproductive system.

Several methods can be applied for the removal of these heavy metals from combustion or incineration systems [2,3]. At the incineration plant of the Intercommunale Maatschappij voor Openbare Gezondheid (IMOG) located in Harelbeke (Belgium) a wet two-stage gas washing process is used for flue gas treatment [4]. The heavy metals dissolve into the washing water which is further treated in a physical–chemical treatment plant.

In this gas washing process an aqueous solution of sodium trimercapto-triazine, commercially supplied under the name TMT-15 by Degussa (http://www.degussa.com) is currently used. Early studies have demonstrated the effectiveness of TMT-15 used for the waste water treatment in the automotive industry [5]. The advantages of this product are a very high efficiency for bivalent ions, limited sludge formation, no precipitation on piping and good precipitation by using a flocculant [6]. The disadvantages of this product are the high toxicity, the high sludge disposal costs, the cost price of the product itself and the inability to treat trivalent ions such as Fe^{3+}, Al^{3+} and Cr^{3+} [6].

As such the aim of this study was twofold. First the chemical use was optimized in view of the disadvantages. The aim was to minimize the use, taking into account the discharge limits, the plant reliability and the operational costs. Second an evaluation of differ-

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Nomenclature

AAS	atomic absorption spectrometry
AES	atomic emission spectrometry
ANOVA	analysis of variance
b	slope of the linear part of the dewatering curve
CCD	central composite design
EMS	residual mean square
H	levy for discharging waste water in surface waters
IMOG	Intercommunale Maatschappij voor Openbare Gezondheidszorg
MC-A	Metalclean
MLS	method of least squares
*N*2	contamination load caused by discharging heavy metals in surface waters
P	pressure
PE	polyelectrolyte
Qj	volume waste water discharged in the year precedent to the year of levy
R^2	determination coefficient
RMS	regression mean square
R_s	resistance against dewatering
T	uniform tariff
TMT-15	trimercapto-triazine
W	loading factor
Greek symbol	
μ	dynamic viscosity

ent alternative chemicals was performed in view of discharge limit requirements and operational costs. The design of experiments (DOE) technique was used to attain both aims. This DOE technique aims at obtaining as much information as possible about a process in a structured way with a limited number of experiments. With design of experiments, the performance of different process settings and applied chemicals can be compared. Experimental design has been used in several chemical engineering domains such as flue gas treatment [7], enzyme production [8], activated carbon production [9] and textile chemistry [10]. As such it was also used in this.

2. Methods

2.1. Description of the treatment plant

The physical–chemical treatment plant that treats the washing water containing the heavy metals consists of three reactors and a sedimentation tank as depicted in Fig. 1. In the first reactor the acid washing water (pH 0.5) is neutralized with lime milk (2%) up to a pH between 6 and 7. In the second reactor an aqueous solution of sodium trimercapto-triazine (TMT-15) and coagulant $FeCl_3$ (40%) are simultaneously added. The third reactor is a flocculation tank, where polyelectrolyte (PE), commercially available under the name Calflock (http://www.caldic.com) is dosed. After sedimentation the water is send to a pressure filter. The filtrate of this filter is discharged in the river Lys after passing through a cooling pond. The average influent flow rate to the plant is 3–5 m^3/h.

2.2. Applied chemicals

The aqueous solution of sodium trimercapto-triazine (TMT-15) is a sulphide that complexes the heavy metals which precipitated at a certain pH by the reaction mechanism [6] presented in Fig. 2.

Three alternative chemicals of TMT-15 were tested: a dithionite ($S_2O_4^{2-}$), commercially supplied by Brenntag (http://www.brenntag.be) under the name MC-A, sodiumdimethyldithiocarbamate commercially supplied by Caldic NV (http://www.caldic.com) under the name Metafloc and an alternative aqueous solution of sodium trimercapto-triazine also commercially supplied by Brenntag (http://www.brenntag.be) under the name Na3T. The active component in Na3T is also sodium trimercapto-triazine. The difference between Na3T and TMT-15 is that Na3T is an alkaline solution (pH 12) and TMT-15 is an acid solution (pH 3). As such, a difference between the two solutions can exist. Dithionite is known to be a strong reducer (redox potential = −0.651 V) that is able to transform metallic ions into the zero valent metal [11]. Therefore the advantage of dithionite (MC-A) is that the metals can be recovered in the sludge. Disadvantages are the toxic sludge and the high sludge disposal costs. The active compound in Metafloc is sodiumdimethyldithiocarbamate. By applying Metafloc, the metals will precipitate as sulphides. The most important disadvantage is that sodiumdimethyldithiocarbamate decomposes into toxic components. In Indianapolis an accidental discharge of waste water containing sodiumdimethyldithiocarbamate in the municipal sewage caused a massive fish death (117 tonnes) over a distance of 120 km [12]. In Fig. 3 the structural formulas dithionite, sodium trimercapto-triazine and sodiumdimethyldithiocarbamate are depicted.

2.3. Simulation of the physical–chemical treatment plant

The physical–chemical treatment plant was simulated by using jar tests [13]. Important parameters in this jar test are pH (similar to the actual process), stirring speed (determined by the velocity gradient), retention time (determined by the dimensions of the reactors) and the dosage sequence (similar to the actual process).

Each test was executed on a sample volume of 500 ml and temperature of 55–60 °C. The dosage of TMT-15 and PE was determined based on the amount used in the previous years as documented by the plant operators: TMT-15 and PE were added to obtain concentrations of 162.37 g/m^3 and 37.55 g/m^3, respectively. The dosage of $FeCl_3$ was determined by a preliminary experiment and set to a dosage of 345 g/m^3 [14].

2.4. Instrument analysis methods

The heavy metal concentration in the water samples was determined with AAS [15] (Thermo Optic Solar M-AAS) and Inductive Coupled Plasma AES [16] (Varian Vista – MPX). Due to its high volatility, mercury could not be determined with flame AAS. Using experimental design tools it was possible to optimize a measuring method based on electro thermal AAS with graphite furnace [14]. This optimization resulted in setting points for ash temperature (253.73 °C) and atomization temperature (647.26 °C) where an acceptable error (8.5%) was measured on a standard solution.

Solids content was analyzed according to standard methods [17].

2.5. Response Surface Design

With Response Surface Design [18] the influence of several parameters on a response can be examined and this response can be minimized, maximized or optimized. Further, the robustness of the process can be increased and interaction between different parameters can be determined. Interaction effects are important in the determination of the general conclusions over the experiment [18,19].

Response Surface Design was used to optimize the settings of the process under study. This type of design connects an output

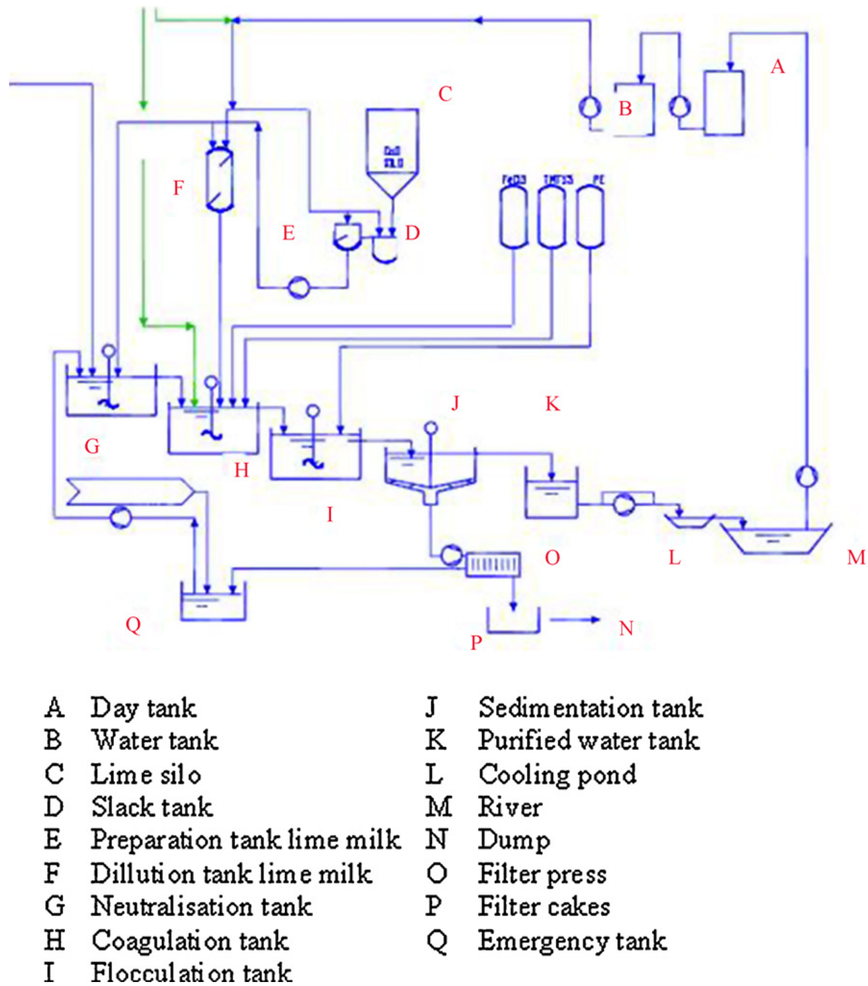

Fig. 1. Schematic representation of the physical–chemical treatment plant.

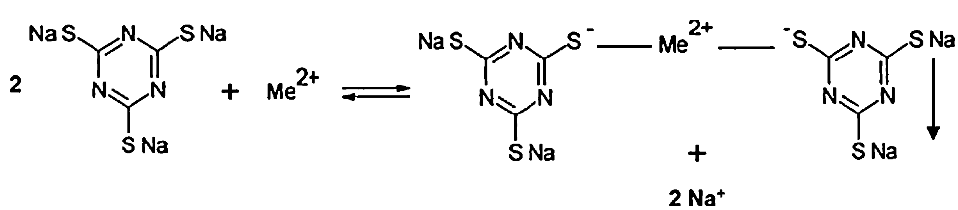

Fig. 2. Precipitation reaction mechanism of TMT-15.

variable or response (in this study heavy metal concentration as discussed below) to the input variables which have affected it (in this study the amount of complexion, coagulating and/or flocculating agents). It allows performing calculations at intermediate levels which were not experimentally studied, as well as performing predictions [20]. The connection between response and variables is done by selecting a functional relation or model which could be acceptable approximations of the responses. The different models used in this study are displayed with their equations in Table 1. In this study three input variables are used as explained below. As such models with three variables are given in the table. First-order polynomials model linear behavior, the second-order polynomial reveal two-component interactions, while more complex interactions can be modeled by third-order polynomials [10,20,21].

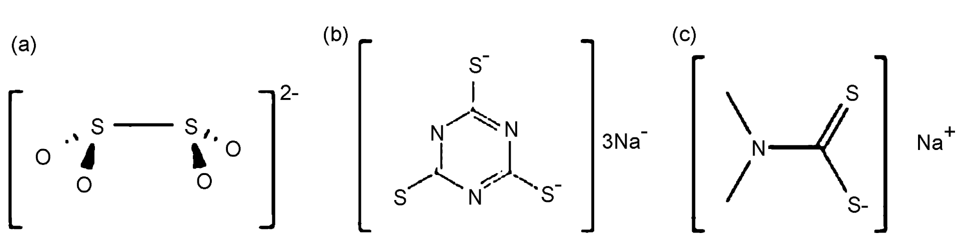

Fig. 3. Structural formula of dithionite (a), sodium trimercapto-triazine (b) and sodiumdimethyldithiocarbamate (c).

Table 1
Models with three variables and their equations.

Model	Equation
Mean	$Y = b_0$
Linear	$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3$
Quadratic	$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_1^2x_1^2 + b_2^2x_2^2 + b_3^2x_3^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3$
2FI	$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{23}x_2x_3 + b_{13}x_1x_3$
Cubic	$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_1^2x_1^2 + b_2^2x_2^2 + b_3^2x_3^2 + b_1^3x_1^3 + b_2^3x_2^3 + b_3^3x_3^3$

The experiments were designed by a central composite design (CCD) so that an optimum estimation of the regression coefficients (b_0, b_1, etc.) can be obtained [19–21]. The estimation procedure involves the method of least squares (MLS) to produce precise model coefficients as is described by Anderson and Whitcomb [20]. This method of least squares supposes that the random errors follow the normal distribution with zero as mean and an unknown variance.

By estimating the regression coefficients the response surface is determined. This response surface correlates the input variables to the responses and can be analyzed through analysis of variance (ANOVA) [20–22]. The significance of the regression surface is tested by calculating the *F*-value of a single *F*-test. A high F-value results in a significant response surface. The determination coefficient (R^2) is, next to the *F*-value, an important parameter in the analysis of variance. It shows in which amount the total variance is explained by the response surface. The value of R^2 varies between 0 and 1. If it approaches 1, the better the predicted model corresponds to the observed response. To examine divergence of the model, a lack of fit test is used by calculating a lack of fit *F*-value (FLOF). Low FLOF-values show that the lack of fit is not significant in comparison with the pure error. A non-significant lack of fit indicates that the predicted model matches the observed response.

When the experimental design is analyzed and each response is fitted to a predicted model, the response surface can be examined in search for optimal process conditions. For example, the minimal metal effluent concentration can be estimated as function of the complexion, coagulating and/or flocculating agents concentration as demonstrated below. Based on the proposed criteria the software formulates a compound desirability function between 0 and 1. A maximum desirability indicates an optimal model with corresponding setting points of the controllable variables [20].

In the Response Surface Design model applied in this study, the effluent concentrations heavy metals (Hg, Zn, Cu, Cd, Cr, Ni, Pb and Ag) were selected as responses. A minimization of effluent concentration was required. The levy for discharging waste water containing heavy metals is determined as response as well and also needed minimization. This levy (*H*) can be calculated as follows [23]:

$$N2 = \frac{Qj[40\text{Hg} + 10(\text{Ag} + \text{Cd}) + 5(\text{Zn} + \text{Cu}) + 2\text{Ni} + 1(\text{Pb} + \text{As} + \text{Cr})}{1000} \quad (1)$$

Table 2
Discharge limits for the different heavy metals.

Heavy metal	Discharge limit (g/m^3)
Zn	5
Cu	0.5
Cd	0.05
Cr	0.5
Ni	0.5
Pb	0.3
Hg	0.05
Ag	2

$$H = N2 \times T \quad (2)$$

with *N2*: contamination load caused by discharging these heavy metals in surface waters; *Qj*: volume waste water discharged in the year precedent to the year of levy; Hg, Ag, Cd, Zn, Cu, Ni, Pb, As and C: concentration of these heavy metals in the waste water expressed in g/m^3; *T*: uniform tariff rated at 28.61€/CU for the year 2006 [24].

The experimental design procedure was performed with the Design Expert software (http://www.statease.com).

2.6. The dewatering capacity of the sludge after optimization

After sedimentation, the sludge is filtered in a filter press by pressurized filtration. The filter press feed has a solid content between 0.5% and 5%. The solid content of the filter cake after filtration depends on the kind of sludge and varies between 30% and 75%. Filtration cakes consisting of metal hydroxides have a solids contents of 45–50%. By using laboratory equipment such as a filter press it is possible to determine important parameters such as the specific resistance against filtration (R_s). Values below 2×10^{12} m/kg suggest a good dewatering capacity [25]. This parameter can be determined by the dewatering graph which is experimentally determined by filtering a certain volume (100 ml) of sludge under pressure. The volume of filtrate in function of the time-to-volume ratio is represented in the dewatering graph. As such, the filter resistance can be calculated as follows:

$$R_s = \frac{2bA^2P}{\mu W} \quad (3)$$

with *P*: pressure (Pa); *b*: slope of the linear part of the dewatering curve; *A*: filtering surface (m^2); μ: dynamic viscosity of water (kg/(m s) while 1 kg/(m s) = 10 P); *W*: loading factor (kg/m^3).

3. Results and discussion

3.1. Evolution or determination of the heavy metals concentration in the influent

During a 13-day measurement campaign the evolution of influent heavy metal concentration was examined by taking grab samples of the influent on a daily basis. This allowed evaluating

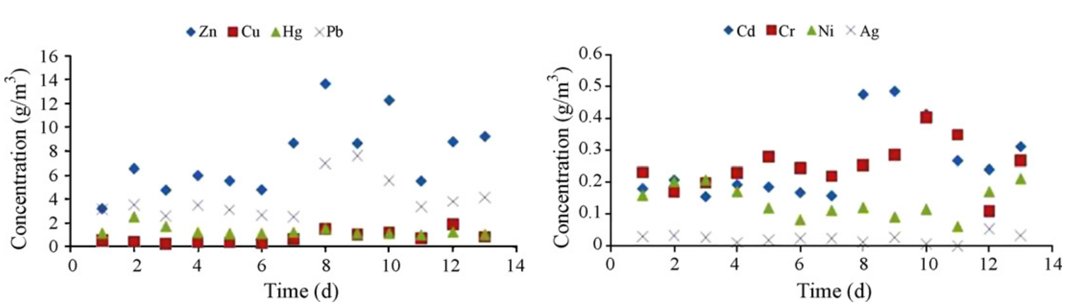

Fig. 4. Evolution of heavy metals in the influent.

Table 3
Experimental boundaries for the operational parameters.

Parameter	Min. (g/m^3)	Max. (g/m^3)
TMT	109.8	162.37
$FeCl_3$	230	345
Calflock	28	37.55

possible trends of heavy metal concentration in the influent. Fig. 4 demonstrates the obtained results.

The results show that the heavy metal concentrations only depend on the waste composition. No trend is visible. For each metal a certain minimum and maximum boundary was established based on Fig. 4 and personal communication with the plant operators. If the maximum boundary is not exceeded the quality of the effluent meets the discharge limits. These discharge limits are presented in Table 2. As such it can be concluded that the dosage of TMT-15 leads to satisfactory operation, although operational costs are rather high (as was also communicated by the plant operators).

3.2. Set-up and optimization of the physical–chemical treatment

The dosages of TMT-15, PE and $FeCl_3$ were determined as the operational parameters that needed optimization and were as such implemented as variables in the Response Surface Design model. The limits of each variable was determined based on preliminary jar tests by changing one variable at the time and measuring the effect on the heavy metals concentration and sedimentation performance. Based on these preliminary jar tests the boundaries presented in Table 3 were identified. In Table 4 the CCD set-up is illustrated, together with the results from the performed jar tests.

Table 5
Summary of the ANOVA for model TMT-15.

Response	Prob > F	Prob > FLOF	R^2-value	Model
Hg	0.9025	–	0.8030	Cubic
Zn	0.0482	–	0	Mean
Cu	0.2362	0.2001	0.7797	Quadratic
Cd	0.1070	0.1932	0.6598	Quadratic
Cr	0.2549	0.5466	0.7705	Quadratic
Ni	0.2624	0.6490	0.7669	Quadratic
Pb	0.0524	0.2890	0.7249	2FI
H	0.1083	0.3165	0.6586	2FI

A summary of the analysis of variance that was performed with the Design Expert software based on the experimental results presented in Table 4 is given in Table 5 for all the responses.

The summary shows that the model was not so successful because the calculated F-value is smaller than the tabulated value at a certain significance level. This F-value is expressed in the table by a probability. High values of Prob > F indicate that the model terms are not significant. For example the response of the metal Zn is 90% caused by background noise. This could be explained by the fact that the metal influent concentration was already very low, as some concentrations were close to the detection limit. Hence, large variations did not occur. It should further be noted that heavy metals such as Zn, Cu, and Cr are mainly removed by the neutralization process. The metal precipitant had no (or little) effect on these metals.

The constructed empirical model was nevertheless used to minimize the effluent heavy metal concentration and effluent levy. This optimization resulted in the values that are presented in Table 6.

Table 4
CCD set-up for the optimization of TMT-15 use, together with the results (indicated in grey) from the performed jar tests.

Run	TMT (g/m³)	FeCl3 (g/m³)	Calflock (g/m³)	Hg (g/m³)	Zn (g/m³)	Cu (g/m³)	Pb (g/m³)	Cd (g/m³)	Ni (g/m³)	Cr (g/m³)	Ag (g/m³)	N2 CU/m^3	H (€/m³)
1	147.93	345.10	32.00	0.0249	0.27	0.045	0.134	0.01	0.084	0.091	0.14	0.0045	0.1277
2	132.24	345.10	36.00	0.0229	0.266	0.044	0.06	0.008	0.125	0.037	0.184	0.0047	0.1355
3	132.24	230.06	28.00	0.0356	0.284	0.106	0.084	0.01	0.042	0.041	0.004	0.0037	0.1065
4	147.93	287.58	32.00	0.0056	0.328	0.132	0.052	0.006	0.025	0.034	0	0.0027	0.0779
5	109.83	172.55	28.00	0.0183	0.206	0.046	0.032	0.02	0.118	0.291	0.053	0.0033	0.0937
6	136.73	258.82	24.00	0.0398	0.172	0.042	0.12	0.012	0.1	0.265	0.021	0.0036	0.1023
7	136.73	258.82	32.00	0.0201	0.202	0.036	0.074	0.014	0.074	0.136	0.037	0.0029	0.0818
8	165.86	172.55	36.00	0.0178	0.314	0.071	0.05	0	0.091	0.07	0.03	0.0032	0.0927
9	134.48	258.82	32.00	0.0287	0.036	0.166	0.076	0.01	0.061	0.133	0.047	0.0031	0.0876
10	136.73	115.03	32.00	0.0065	0.374	0.043	0.042	0.018	0.136	0.033	0.013	0.003	0.0859
11	136.73	258.82	32.00	0.0058	0.456	0.04	0.084	0.016	0.042	0.029	0.015	0.0032	0.0922
12	136.73	258.82	40.00	0.0212	0.32	0.039	0.098	0.01	0.048	0.221	0	0.0032	0.0904
13	136.73	373.85	32.00	0.0051	0.372	0.042	0.04	0.006	0.081	0.197	0.013	0.0029	0.0819
14	96.38	258.82	32.00	0.0277	0.132	0.035	0.042	0.008	0.057	0.18	0	0.0024	0.0676
15	138.97	258.82	32.00	0.0064	0.174	0.035	0.078	0.002	0.067	0.075	0.016	0.0018	0.0505

Table 6
Optimal dosage of operational parameters.

Parameter	Dosage (g/m^3)
TMT-15	130.90
$FeCl_3$	253.07
PE	38

Table 7
Resulting effluent heavy metal concentrations, before and after the reduction in chemical use.

Heavy metal	Before (g/m^3)	After (g/m^3)
As	<0.019	<0.021
Cd	<0.00145	<0.00156
Cr	<0.0096	0.013
Cu	<0.019	<0.021
Hg	0.00112	0.00195
Pb	<0.024	<0.026
Ni	0.026	0.023
Zn	0.671	0.480

These values had an acceptable desirability (0.77). The optimized chemical use resulted in a 19% reduction in TMT-15 use.

Next to the tests at lab scale, the optimized settings were tested on the actual treatment plant. For safe operation of the installation only a 10% reduction of chemical use was implemented. The results of the analysis are shown in Table 7.

There was no significant difference between the new settings and the original settings (100%). As such the new settings were implemented and a 10% reduction in chemical use was obtained in the actual plant.

3.3. Dewatering capacity of the sludge after optimization

In order to determine changes in the dewatering capacity of the sludge because of the new operation, the dewatering curve was determined. This test was performed at 1.5 bar pressure and a sludge solids content of 2.39% at 100% dosage and 2.79% at 90% dosage. The filtrating surface was $0.005\ m^2$. In Fig. 5 the dewatering curves of both operational schemes are presented.

The specific resistance for filtration was calculated. At 100% dosage this gave:

$$R_s = \frac{2 \times 0.0087 \times 10^{12} \times 2.5 \times 10^{-5} \times 1.5 \times 10^5}{0.001 \times 44.8764} = 1.45 \times 10^{12} \quad (4)$$

At 90% dosage this gave:

$$R_s = \frac{2 \times 0.0136 \times 10^{12} \times 2.5 \times 10^{-5} \times 1.5 \times 10^5}{0.001 \times 54.233} = 1.88 \times 10^{12} \quad (5)$$

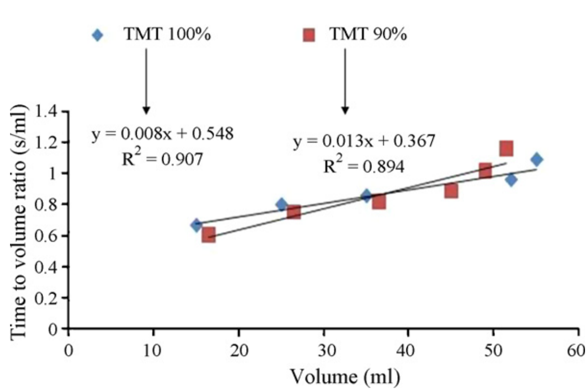

Fig. 5. Dewatering curve at 100% dosage and 90% dosage.

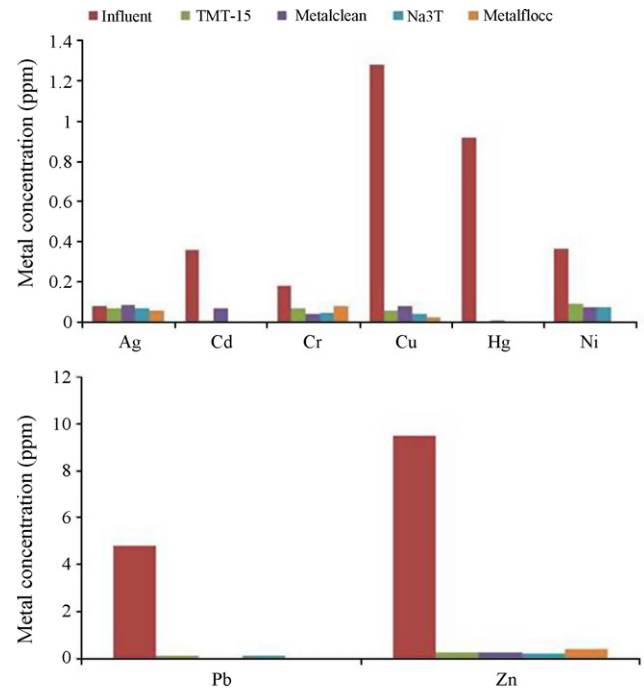

Fig. 6. Comparison of the efficiency of the alternative products.

Both values are beneath 2×10^{12}. As such, decreasing the dosage of TMT-15 does not have a negative influence on the dewatering capacity of the sludge.

3.4. Study of the alternative products

3.4.1. Effect of Metalclean, Na3T and Metafloc

This experiment was conducted to investigate the effect of the alternative products Metalclean, Na3T and Metafloc at pH 6–7. The products were dosed to the waste water, next to neutralization and the addition of coagulant and PE. The results (data not shown) indicated that the alternative products Metalclean, Na3T and Metafloc are able to remove metals such as Pb, Hg, Cd and Ni. The metals Cu, Zn and Cr are mainly removed by the neutralization process.

3.4.2. Comparative test between TMT-15 and alternative products

This experiment was conducted to investigate if the alternative products are an adequate alternative for TMT-15 when dosed under similar concentration conditions. The results are shown in Fig. 6.

Fig. 6 illustrates that Metalclean does not satisfy when it is dosed at pH 6–7. The Cd concentration exceeds the discharge limit of $0.05\ g/m^3$. The other products exhibit an equivalent removal of heavy metals. Selection of an alternative product will therefore be based on price considerations and minimal required process changes. As such Na3T seems the best alternative although both other alternatives need further investigation as discussed below.

3.4.3. Influence of pH on Metalclean

To examine the influence of the pH on Metalclean, experiments were performed at different pH levels. The results of these experiments are shown in Fig. 7.

The results show that the highest removal efficiency is obtained if Metalclean is dosed in the weak acid domain (pH 3–5). If it is dosed in the neutral domain, the heavy metal concentration is increased and the Cd discharge limit ($0.05\ g/m^3$) is violated.

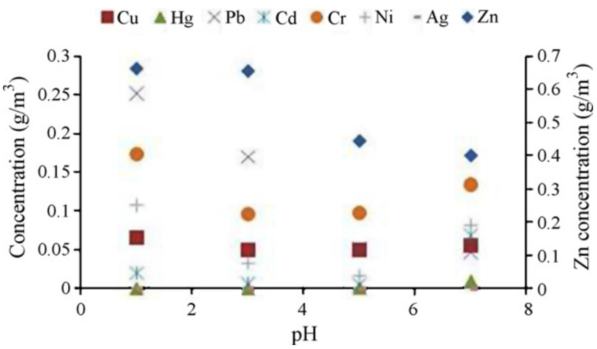

Fig. 7. Influence of pH on the removal capacity of Metalclean (applied influent concentrations are (expressed in mg/l): Zn: 6.6, Cu: 1.1, Cd: 0.26, Cr: 0.29, Ni: 0.26, Pb: 5.3, Hg: 0.93 and Ag: 0.076).

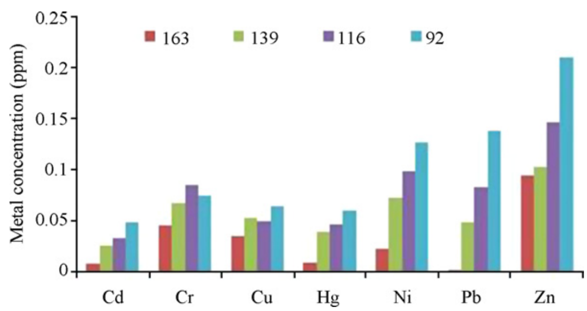

Fig. 8. The effect of reducing dosage Metafloc (expressed in g/m^3) on heavy metal concentration. Applied dosages are 163 g/m^3, 139 g/m^3, 116 g/m^3 and 92 g/m^3.

3.4.4. Study of the product Metafloc

This experiment was conducted in order to investigate the possible dosage reduction of Metafloc without losing effluent quality. The results of these experiments are shown in Fig. 8.

The results show that there is no reduction of the dosage possible. At 139 g/m^3 (85% of the original dosage) dosed a significant concentration increase occurred for Hg, Cd and Ni. Therefore the original dosage (163 g/m^3) should be maintained.

3.5. Optimization of physicochemical waste water treatment plant for alternative treatment chemicals

The above-performed experiments conducted with alternative products revealed that Na3T is the best alternative for TMT-15 because of price considerations and effluent discharge limits. Therefore the optimal dosing rate was determined based on experimental design with a Response Surface Design model implemented in the Design Expert software. Jar tests while changing one variable at the time resulted in the determination of the variables limits which are presented in Table 8.

The responses in this Response Surface Design model were the concentration of heavy metals and the levy due to the discharge of waste water. Table 9 gives a summary of the results. The optimization criteria were similar to the study with TMT-15. This resulted in a maximum desirability (=1) for 131 g/m^3 Na3T, 325 g/m^3 $FeCl_3$ and 27.4 g/m^3 PE. These values correspond with respectively 81%, 94% and 72% of the original dosage. Implementation of the new settings on jar tests allowed comparing the predicted concentrations versus the measured concentrations. The results of this analysis are displayed in Table 10. The results show little difference between the predicted and measured values. As such it can be concluded that the reduced dosage can be applied.

Table 8
Experimental boundaries for the operational parameters.

Parameter	Min. (g/m^3)	Max. (g/m^3)
Na3T	121.04	162.37
$FeCl_3$	172.55	345
PE	16	38

Table 9
Summary of the ANOVA for model Na3T.

Response	Prob > *F*	Prob > FLOF	R^2-value	Model
Hg	<0.0001	0.5706	0.9967	Quadratic
Zn	0.1285	0.11	0.9402	Cubic
Cu	0.1276	0.7190	0.3914	Linear
Cd	0.9293	–	0.5410	Cubic
Cr	0.1831	0.8982	0.8070	Quadratic
Ni	0.1771	0.6405	0.3494	Linear
Pb	0.0218	0.0277	0.9276	Quadratic
H	0.1708	–	0.9258	Cubic

Table 10
Measured versus predicted effluent values with the application of Na3T.

Metal	Predicted (g/m^3)	Measured (g/m^3)
Cd	0.0028	0.0019
Cr	0.0958	0.0128
Cu	0.0909	0.0742
Hg	0.0016	0.00367
Ni	0.1229	0.1216
Pb	0.0039	0.0033

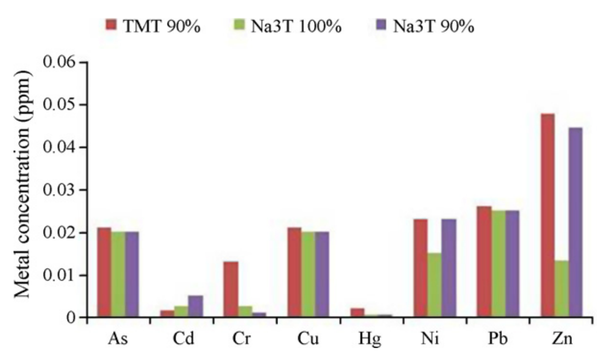

Fig. 9. Comparison of TMT-15 and Na3T implemented on actual installation.

Next to the tests at lab scale, the new settings were implemented on the actual installation. Again, for safe operation, only a 10% reduction was implemented. The results of the analysis are displayed in Fig. 9. This shows that the concentration of heavy metals with Na3T dosing at 90% of the original dosing are equal to those when TMT-15 was dosed. Therefore Na3T at 90% could be implemented on the actual installation.

In Table 11 an overview of the cost reduction with Na3T compared to TMT-15 is given based on the average water quantity treated over the past 2 years (35765 m^3/year waste water and 4907 kg TMT-15 used). The levy for discharging the same amount of waste water while using Na3T (146 g/m^3) is approximate 10% lower than while using TMT-15 (146 g/m^3).

Table 11
An overview of the yearly cost reduction with Na3T compared to TMT-15.

Product	Dosage (g/m^3)	Kg used	Price (€/kg)	Yearly cost (€)	Cost reduction (%)
TMT-15	162.35	5806	2.99	17361	–
TMT-15	146.11	5225	2.99	15624	10
Na3T	162.35	5806	2.69	15619	10
Na3T	146.11	5225	2.69	14056	20

4. Conclusions

Optimization of the physical–chemical treatment was necessary for the incineration plant, because the cost of the chemicals, more specifically TMT-15, was too high.

This study showed that a reduction of 19% in chemical use could be achieved for the product TMT-15 on lab scale. The settings were implemented on the actual installation, taking into account plant safety considerations. This gave a satisfying result for the plant operators: a reduction of 10% in chemical use was possible.

The study of the alternative products showed that towards consumption and chemical cost Na3T was the best alternative. Metalclean gave good results if it was dosed in the weak acid domain, which was not the case in this process. Changing the process would bring high costs so this product was not acceptable as an alternative. Metafloc gave in general good results, but the chemical cost is too high.

Optimization of the alternative treatment resulted in a reduction of also 19% for the product Na3T. This could be expected because TMT-15 and Na3T are the same products, but delivered by different suppliers. The tests on the actual installation showed that Na3T could be implemented at a significant cost reduction.

The tests for the dewatering capacity showed that changing the dosage of TMT-15 had no effect on the dewatering capacity. This was expected because this capacity is only influenced by the amount of PE.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2008.12.025.

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