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Effluents treatment plants sludge characterization in order to be used as solid fuels

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Abstract
The aim of this work is to study the characteristics of three types of WWTP residual sludge (urban and industrial) in order to be used as solid fuels. The tests focused on the physico-chemical characterization of each type of sludge (water content, organic matter, fuel fraction, ash), the assessment of their energy content (calorific value HHV, effect of moisture content on HHV) and the heavy metal content. The effect of adding lime to the sludge samples on different parameters (moisture and heating value) is also investigated.

Keywords: alternative fuel, higher heating value HHV, industrial waste, sewage, energy recovery.

Introduction

In Morocco, the treatment of wastewater generates the equivalent of 30-40 grams of dry matter (DM) per capita per day in the form of sludge. Representing an annual potential production of sludge estimated at 232 320 tones/year [1].The production of industrial sludge is estimated to75000 tones/year of dry matter [2].In addition, the national liquid sanitation program predicts an increase in sewage treatment rate up to 60% by 2015 [3] and so an increase in the production of urban sludge.
There is a wide variety of modes of treatment and recovery of WWTPssludge namely land spreading [3], composting [4] and energy recovery through incineration or co-incineration.
Sludge, being rich in organic matter (50% -70%) and thus having a relatively high energy content, is increasingly used in units that are energy intensive (cement, brick) as heat generating matter to replace conventional fossil fuels. [5,11] Co-processing of this type of fuel in the cement manufacturing for instance generates less gaseous pollutants due to the presence of atmospheric pollution treatment already integrated in the manufacturing process of the cement. The second advantage is that the use of this sludge constitutes a supply of mineral matter that will be incorporated in the raw material for the cement manufacture for example, [6, 7]. The American Society for Testing and Materials (ASTM 2006) had classified the waste fuel into seven major categories. The most common type used is conceived based on sewage sludge [5] after proper conditioning. Discussed in this work the formulationof solid fuels based on several types of sludge collected from three wastewater treatment plantsof municipal and industrial effluents. These are:

- Treatment plant of urban waste.
- Treatment plant ofindustrial effluents from a manufacturing facility of dairy products.
- Treatment plant of industrial effluents from a production unit of soft drinks.

The fuel formulated must have as characteristics a constant and convenient heating value approaching that of fossil fuels, a low ash and moisture content and a minimum low in inorganic pollutants [8].

2. Materials and methods:

2.1 Sampling:

Sampling is performed in a way to represent the two types of sludge usually encountered in wastewater treatment plants; including urban and industrial wastewater. Though they have different origins, all three types

of sludge have undergone the same tests in order to characterize and determine their ability to be used as fuels. A comparative study is conducted between these types of sludge.
Table 1 describes the types of sludge which were the subject of this study.

Table 1: Description of the types of studied sludge.

Type of sludge	Source	Treatment plant type/Processing	Level of sampling	Sludge nature	Production (t/day)
Industrial sludge 1 (LAI)	WWTP of Dairy industry	Activated sludge + prolonged aeration	At the aeration tank	Physicochemical thickened sludge	80
Industrial sludge 2 (BG)	WWTP of Soft drinks industry	Activated sludge	Basin of physicochemical treatment	Secondary sludge	-
Urban sludge (EU)	WWTP of urban effluents	Activated sludge + digesters	At the level of the digester	Primary sludge (thickened) + Secondary sludge (activated) >> digested sludge	150

The two types of sludge are collected during the final phase of treatment downstream of each of the three stations. The analysis in the state of samples is impossible due to their high water content. After measuring moisture content, samples are oven dried and milled in order to be packed for analysis.

2.*2 Thermogravimetric analysis:*
The thermo gravimetric analysis, which is a technique of thermal analysis consisting of the measurement of the loss on ignition depending on time for a temperature profile or a given temperature, is used to determine the moisture content of the sample, the combustible portion depending on the organic matter contentand the ash content. The apparatus used for this analysis is the TGA-2000.

2.3 Measurement of higher heating value:
The higher heating value (HHV) is a physical property of all fuels. It represents the actual amount of heat released in a combustion process (often expressed in kilocalories orkilojoules) of one kg or liter of fuel.
The measurement of the calorific value of the fuel is performed using an adiabatic calorimeter (figure 1)

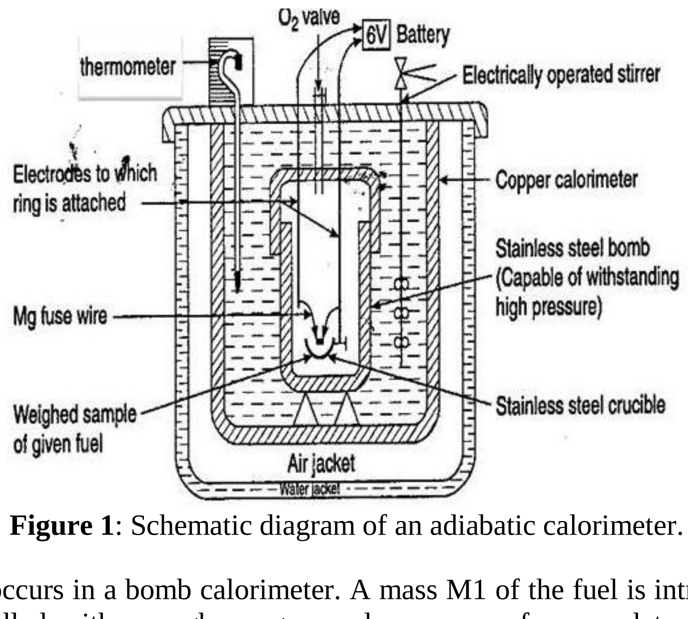

Figure 1: Schematic diagram of an adiabatic calorimeter.

The combustion reaction occurs in a bomb calorimeter. A mass M1 of the fuel is introduced (between 1g and 4 g weight) in the bomb filled with enough oxygen under pressure for complete combustion. The bomb is

immersed in a calorimeter containing a precise amount of water (V_w = 1.8l). Let the initial temperature Ti. After combustion, the temperature of the calorimeter increases and stabilizes in Te. The temperature variation is monitored by the Pod-Vu software Version: 2.0.50727.3603 (brand e-DAQ).
Let $Q_{(comb)}$ the heat of reaction. This heat is absorbed by the calorimeter and the whole reaction products present in the bomb. We neglect the influence of these products to the high mass of the calorimeter and the water contained.
The calorimetry relationship gives: $\Sigma Q_i = 0$.

$$Q_{(comb)} + (M * C_{(water)} + C_{(cal)})(t_e - t_i) = 0$$

$C_{(water)}$: calorific capacity of water
$C_{(cal)}$: calorific capacity of calorimeter
t_i : initial temperature
t_e : equilibrium temperature

Heat capacities are determined at constant volume. Solving this equation allows to determine $Q_{(comb)}$ for a given weight of the product.The calorimeter calibration is performed by carrying out the combustion of a product having a known [4] calorific value.
For tests related to the study of the influence of moisture, calorific value is determined for samples with different water contents.

2.4 Elemental analysis:
Elemental analysis of the samples, which will determine the composition of organic and inorganic chemical elements, is made by X-ray fluorescence spectrometer using a dispersion wavelength - Axios category. The sample is dried and conditioned in tablet form (¬ PROT ELE03-v01).

2.5 Analysis of heavy metals:
The heavy metal content in the collected samples is determined by atomic absorption spectrophotometry (Schimadzu brand 2000).

3. Results and discussion:

3.1 Analysis and characterization of sludge:
3.1.1 Elemental analysis:
Table 2 summarizes the results of analyzes by X-ray fluorescence for the three samples of the studied sludge.

Table 2: Results of XRF analysis

Element (%)	Sludge (LAI)	Sludge (BG)	Sludge (EU)
Al	1.8	1.4	0.1
P	2.9	1.8	0.4
Fe	0.9	4.1	0.2
Si	4.6	3.8	0.3
Ca	4.7	3.7	11.6
K	0.5	0.2	0.1
Cl	0.3	1.0	0.1
C	17.5	17.3	21.8
S	1.7	0.8	0.5

The examination of the table shows that the carbon is the most predominant chemical element (BG 17.3 - EU: 21.8%) and thus predominant over other organic elements whose content does not exceed for all three cases of samples 3%. The chlorine level recorded for each sample is less than 1.04%. Concerning the inorganic elements, silicon and calcium have high levels compared to other inorganic elements. The presence of metal components in the sludge is generally due to the addition, in the step of coagulation-flocculation process during the treatment

of effluents, coagulants (generally metal salts based on aluminum and iron) favoring the formation of agglomerates of sludge.
When it comes to incinerate waste such as sludge with unknown composition, it is essential to refer to the eligibility standards of waste to be incinerated. This is especially the case of components which are able to give toxic gases during incineration. Chlorine is an element which mass content must be minimal (generally between 0.4% and 1%) [9]. In the case of three samples of sludge LAI, EU and BG, the chlorine concentration is below the indicated level. This is also the case with sulfur content that should not normally exceed 2.5%[9]. It is true in all three cases studied sludge.

3.1.2 Analysis of heavy metals:
The analysis of metal elements in sludge is an important parameter when it comes to the treatment of this type of waste. In the case of co-incineration in cement kilns, sludge incineration is not only a source of energy but also a material input resulting from ash. The content of heavy metals should therefore not exceed the threshold concentrations indicated by the thermal treatment plants.
The results of heavy metalsanalysis of studied sludge are shown in table 3.

Table 3: Results of analysis of heavy metals in sludge samples

	Sludge type	**Elements**						
		Cd	Cr	Cu	Zn	Mn	Al	Fe
Concentration (mg/kg)	**Sludge(LAI)**	<1	16	661	1138	111	118	10
	Sludge(BG)	48	3447	425	369	539	2718	4511
	Sludge(EU)	22	1094	303	222	142	168	2830

Sludge issued from the treatment of liquid waste of dairy plant recorded high levels of copper and zinc compared to other elements. The high aluminum concentration compared to the iron concentration is probably due to the aluminum salt used as coagulant used in the treatment process. Unlike sludge issued from the WWTP treatment of urban wastewater where the value of iron concentration, exceeding the one of aluminum indicates that the coagulant used in this case is probably iron based , this is also seen in the hard aspect that sludge samples took in the dry state (hard sludge and rust colored) . Analysis of metals in sludge is also an indicator of the nature of the treated effluent. This is the case for example of sludge (EU) where it is noted that the chromium content is significant: in fact, this sludge is issued from a WWTP of a city where the tanning industry (producing high amounts of chromium) is highly developed.

3.2 Thermogravimetric analysis:
The curves obtained by thermogravimetric analysis are used to identify the phenomena that occur during rise of temperature and leading to decomposition reactions accompanied by the formation of gas or vapor:
• The dehydration reactions, decarbonisation, burning etc ... leading to weight loss.
• Oxidation reactions by air, hydration, carbonation leading to weight gain.
The graph below (figure 2) shows the evolution of weight loss of a sample of sludge (EU) depending on the temperature. The red curve shows the evolution of the mass of the sample. We note that the sample weight remains stable during temperature range (0-100 ° C).The mass loss begins to occur (blue curve) until 100 ° C, this can be attributed to moisture loss in the sample. Then the phenomena taking place in the combustion of organic materials under the effect of the temperature increase up to 910 ° C. Beyond this temperature the weight becomes constant.
The results of the thermogravimetric analysis used to evaluate the moisture content, the ash content and the rate of organic matter are summarized in table 4.
The three types of sludge in this study contain a relatively high moisture content (LAI: 76% - BG: 89% - EU: 80.2%), Industrial sludge from the soft drinks production industry contain the highest moisture content (89.2%) compared to the other two types of sludge. High moisture sludge rate represents constraints in storage since the presence of water promotes the proliferation conditions of microorganisms and risk of fermentiscibility and release of odors. A high moisture content also means a reduction of the calorific value, and so a decrease of the amount of heat generated during incineration of the sludge.

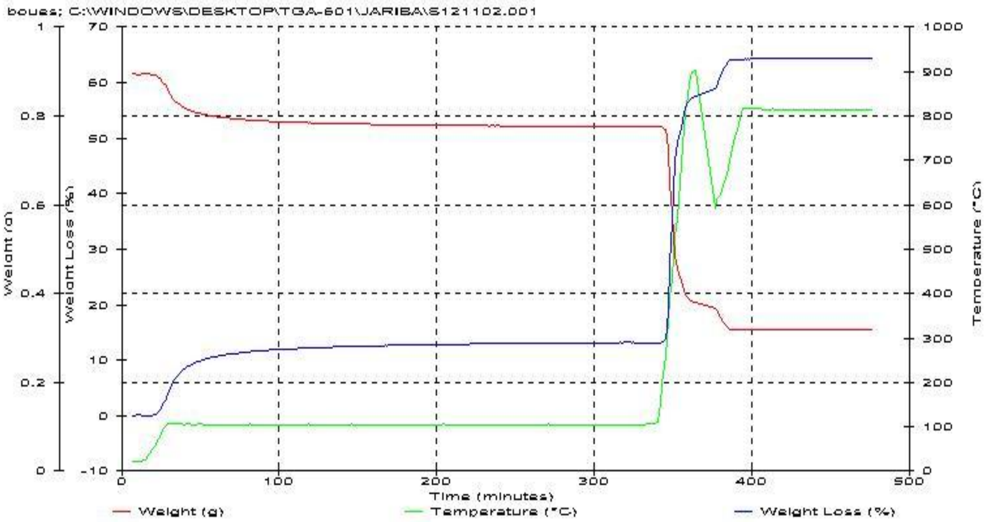

Figure 2: TGA curves for a sample of sludge (EU)

Table 4: Results of thermogravimetric and calorimetric analysis

	Industrial sludge (LAI)		**Industrial sludge (BG)**		**Urban sludge (EU)**	
	Raw	Dehydrated	Raw	Dehydrated	Raw	Dehydrated
Moisture content (%)	76		89,2		80,2	
Ash content (%)	1,1	4,6	3,7	34,6	6,5	32,8
Organic matter (%)	22,9	95,4	7,1	65,4	13,3	67,2

Concerning the rate of organic matter, it is noted that the three types of sludge record interesting values (65-95%). Dairy sludge have the highest level compared to the other two types of sludge and therefore the lowest rate of mineral matter content of organic matter. The organic matter content is the indicator of which depends the knowledge of the energy content of waste, which usually is quantified by the measurement of the calorific value. Many scientific studies have focused on techniques for determination of the combustible fraction of solid fuels and its relationship with the calorific value. It was actually proved that the correlation between these two parameters: the more the combustible fraction is important, the more the calorific content is important.

3-3 Determination of higher heating value (HHV) sludge:

Figure 3 shows a typical curve of evolution of temperature vs. time during the combustion process of a sludge sample. This curve is used to evaluate thehigher heating value (HHV) of the studied sludge. The evaluation results are summarized in table 5.

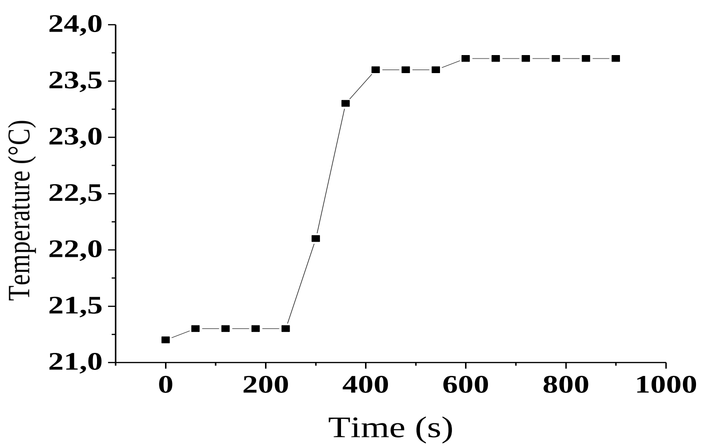

Figure 3: Example of temperature evolution with time during HHV determination.

Table 5 – Higherheating values of studiedsludge (dried basis)

	Industriel sludge (LAI)	**Industrial sludge (BG)**	**Urban sludge (EU)**
Higher heating value (Kcal/Kg)	5500	3897	3158

The higher heating values obtained experimentally vary between 3158 Kcal/Kg for urban sludge EU (dry)and 5500 Kcal / Kg for the first type of industrial sludge LAI (dry). The determination of the gross calorific value of the samples is impossible to achieve because of their high water content. The calorific value, which represents the amount of energy, is thus influenced by different parameters, namely the humidity and the organic content dependent on the combustible portion. So, it was necessary to evaluate the effect that can have the moisture content on this parameter. It was therefore necessary to study the evolution of HHV according to humidity.

3.3.1 Influence of moisture on the HHV of sludge:

The studies of the influence of moisture on higher heating value of sludge are presented on figures 4, 5 and 6 for the types of sludge.

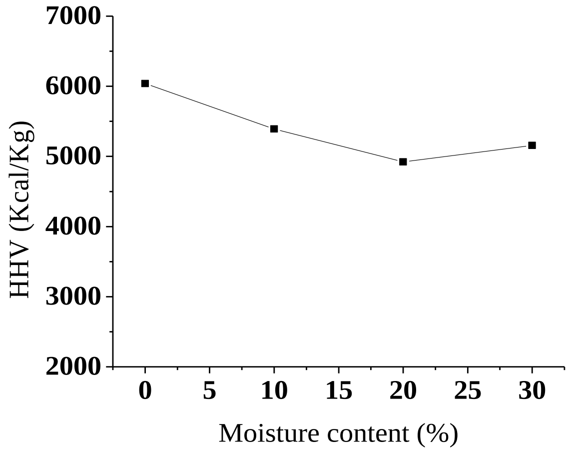

Figure 4: Effect of moisture content on the HHV of sludge (LAI)

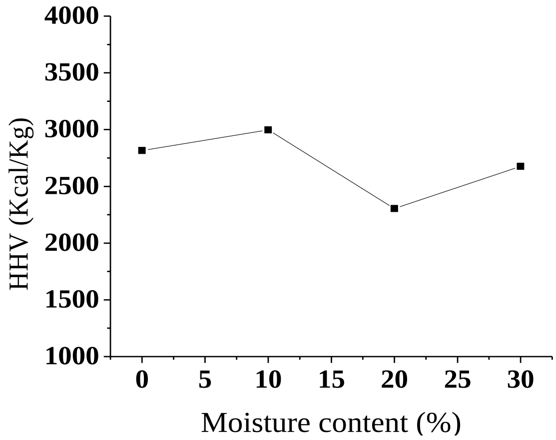

Figure 5 : Influence of moisture content on the heating value of sludge (BG)

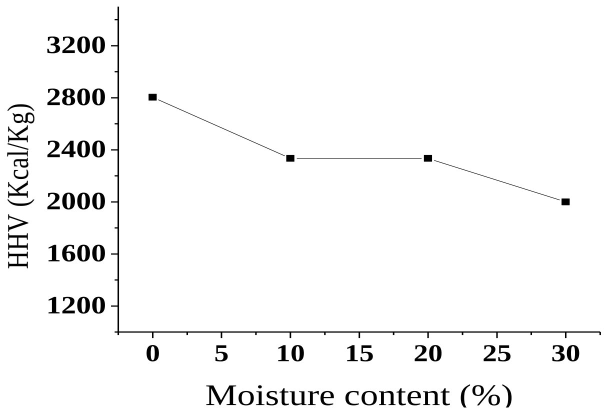

Figure 6 : Influence of moisture content on the heating value of sludge (EU)

In the case of the three types of sludge, the development of the HHV according to the moisture content represents a significant variation. We note that the three curves have similar paces. Indeed, when the humidity increases the HHV decreases: the decrease of heat can be attributed to the dissipated energy to evaporate the water contained in the sample.

This type of curves gives sufficiently precise evolution of a product's calorific value in terms of moisture through a mathematical representation. This will later be used to determine the calorific value of a sample once the humidity is known and without having to measure it experimentally.

3.3.2 Influence of lime on the moisture content and HHV of sludge :

It is proceededby adding different proportions of quicklime (CaO) in two samples of sludge (industrial sludge (LAI) and urban sludge (EU)) and monitored the effect on the HHV and moisture content. After addition of lime, it is noted that the sludge take a more compact and dense appearance. There is also a significant odors reduction. There for every ol factory disturbance is reduced.

Table 6 and figure 7 include the results of the influence of the addition of quicklime CaO on the moisture content of the two sludge samples (LAI) and (EU).

Table 6 – moisture values evolution with added lime percentages

Lime content (%)	0	5	10	15	20
Moisture content (LAI) (%)	75	70	63	58	52
Moisture content (EU) (%)	81	71	63	59	53

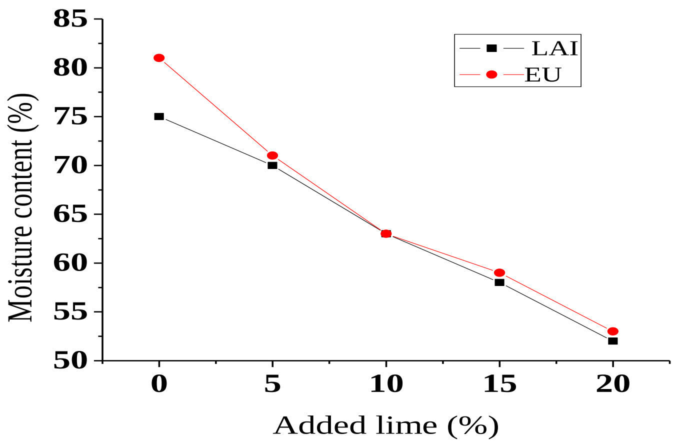

Figure 7: Influence of liming on the moisture content of the studied sludge

The two types of sludge have relatively high moisture content (LAI: 75% EU: 81%). The addition of lime reduces significantly the moisture content of the sludge samples. For example, humidity content decreases from 75% for a sample of raw sludge LAI to 52%when 20% of quicklime is added.

Indeed, the quick hydration reaction of quicklime with water in the sludge decreases the water content. The reasons are many:

- The chemical reaction of quicklime hydration needs quantity of water.
- Hydration reaction of quicklime is exothermic. The produced heat causes the evaporation of water. The alkalinity of the lime raises the pH of the sludge, making the environment not favorable to the proliferation of bacteria and therefore phenomenon of fermentation is inhibited. Consequently there is less release of odor and olfactory nuisance. This has advantages regarding the reduction of the moisture contained in the sludge.

In fact, liming reduces the water content by the effect of the hydration reaction according to the following equation:

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

A fraction of the water contained in the sludge will so react with the lime to give hydrated lime. This water fraction is transformed to incorporated water into the water-sludge mixture. In addition, the reaction of quicklime with water is exothermic, the heat generated will also be used to heat the sludge and consequently to evaporate water contained in the sludge.

It is known that the addition of lime increases the pH of the sludge and thus reduces the bacterial activity, which significantly decreases the release of foul odors usually sensed in sludge. The addition of lime also has the effect of fixing most metals as insoluble hydroxides in basic environment [10].

Concerning the influence of adding lime on the HHV, the results are shown on figure 8.

It appears that the addition of lime causes a decrease of the higher heating value of sludge which is due to the presence of non-combustible inorganic materials composing the added lime. A compromise must be found between a good sludge stabilization, partial dehydration and acceptable HHV.

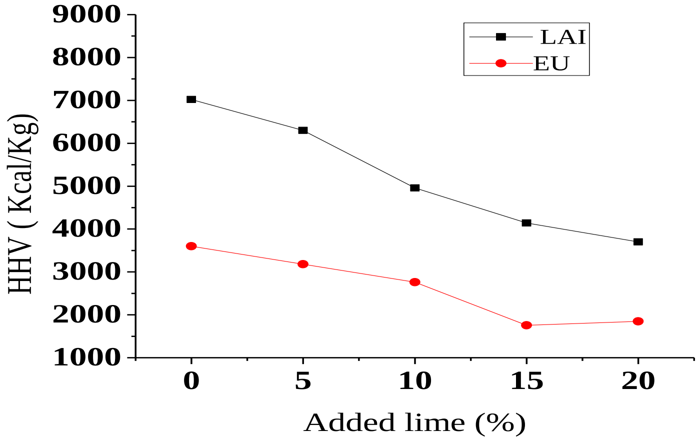

Figure 8: Influence of liming on the HHV of the studiedsludge

Conclusion

Sludge are of various types and composition due to their origin (industrial, urban ..). Their aspects represent different rheological and structural properties (pasty sludge, viscous, oily ..). The tests that were made on the sludge samples collected towards the final stage of the treatment process showed the following characteristics: The sludge have interesting content in organic matter and so a convenient HHV making them suitable for use as substitution fuels.However, the moisture content of sludge influences the HHV. The addition of lime to the sludge samples has lowered significantly the moisture content (up to 50%) while maintaining a proper HHV. Another advantage of the addition of lime relies in the rheological aspect of sludge that becomes more solid and so more easily handled. Analysis of the content of heavy metals shows that they may be in the sludge at various concentrations sometimes exceeding standards fuel.

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