ALTERNATIVE OF DESULFURATION IN ANAEROBIC DIGESTION OF URBAN WWTP BY USE OF IRON MINERAL SALTS (MIXTURE OF IRON OXIDES / HYDROXIDES OF NATURAL ORIGIN).

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Summary:

The public company Acosol SA (Costa del Sol, Málaga), manages the services of the Integral Water Cycle and, with regard to sanitation, collects the waste water from the municipal sanitation network and conduct them to the different Waste Water Treatment Plants of the coast. 4 of the 7 WWTPs that operate, have a sludge treatment and stabilization systems by anaerobic digestion and another one by biofiltration and anaerobic digestion of sludge, bringing a total of 5 out of 7 facilities with anaerobic digestion of sludge.

Anaerobic digestion operates in mesophilic (35-38ºC), using biogas itself as fuel in hot water boilers to raise the temperature of the reactors. Using biogas in boilers enforce the inspection of the emissions of boilers in the chimney to track parameters such as CO, NOx, SO_2, H_2S, opacity, etc. Due to the high concentrations of sulphur at the inlet (both in organic form and inorganic form-sulfates), outlet biogas has a high concentration of H_2S and this causes the non-compliance of the SO_2 flue emissions, limited at 200 mg/Nm^3 by decree. Current values are above this admissible limit if no type of desulfurization is carried out.

A test using iron oxides and hydroxides is planned at the Fuengirola WWTP, to desulfurize the biogas to levels that allow compliance with emissions decree. However, during the tests, other additional advantages were also verified compared to the use of conventional iron salts such as ferric chloride, which make this new reagent a good alternative for its use in urban WWTP digesters.

Keywords: Anaerobic digestion, biogas, hydrogen sulfide gas, sulfur dioxide, iron salts.

1. Introduction

Public company Acosol SA, depends on the Association of Municipalities of the Western Costa del Sol and manages the services of the Integral Water Cycle. Regarding to sanitation, Acosol collects the wastewater from the sewer collectors of the municipal networks from the boundary of the Torremolinos with Benalmádena to the district limit in Manilva. This wastewater is then conducted to the different Wastewater Treatment Plants of the Coast, where it is purified and regenerated for its new use in irrigation of golf courses and public green areas. Purified surplus is returned to the sea and comply with conditions of quality, flow, distance from the coast and depth that allow its total dilution in the medium.

Currently 7 WWTPs operate, of which 5 have sludge stabilization via anaerobic digestion. These WWTPs are in increasing order of population:

Facility	Zone	Population	Capacity (m^3/day)
WWTP Manilva	Manilva	60,000	15,000
WWTP Arroyo de la Miel (*)	Benalmadena	160,000	40,000
WWTP Cerro del Águila	Fuengirola	240,000	60,000
WWTP Víbora	Marbella	300,000	81,000
WWTP Guadalmansa	Estepona	400,000	100,000

(*) All with activated sludge technology except Arroyo de la Miel with biofiltration.

Below is the comprehensive sanitation map of the Western Costa del Sol.

2. The problem

All WWTPs with stabilization of sludge via anaerobic digestion work in a mesophilic regime with a stable temperature between 35-38ºC in anaerobic reactors to improve the activity of bacteria.

To heat the digesters, own biogas is as fuel, so that the use of external fuels such as natural gas or diesel is avoided. Methane concentration of this biogas is between 60-65% and therefore suitable for using it in a boiler with special designed burners needed for this type of fuel. Lower calorific value of biogas is around 6-6.50 kWh/Nm^3 (Natural Gas 10.83 kWh/Nm^3 and Diesel 10.28 kWh/L approximately).

Self-consumption of biogas results in an operating costs savings, but it must be treated appropriately before using it. Finally, any biogas surplus is burned in a safety combustion system or flare.

A typical composition of the WWTP biogas could be the following:

- Methane (CH_4): 55-70%.
- Carbon dioxide (CO_2): 30-45%.
- Hydrogen (H_2): 1-3%.
- Nitrogen (N_2): 0.5-3%.
- Hydrogen sulfide (H_2S): 0.1-0.5% (approx 1% = 10,000 ppmv).
- Water (H_2O): Traces

The particular composition of each biogas will depend on the substrate from which the biogas is obtained (wastewater type, other products in co-digestion), as well as the parameters of the digestion process (residence time, temperature, pH, etc.).

Sometimes, biogas contains high concentrations of pollutants that prevent its use if they are not previously eliminated. These pollutants, mainly, are:

- Hydrogen sulfide (H_2S)
- Siloxanes
- Ammonia
- Halogenated compounds
- Carbon Dioxide (CO_2)
- Water (It must be removed to avoid condensation)

In the case of urban waste water plants, where usually the biogas is self-consumed, the common pollutant is hydrogen sulfide (H_2S), where we can find concentrations of up to 5,000 ppm or higher in special cases.

Below is a photograph of a measurement carried out at the Víbora WWTP in Marbella, where a concentration of 0.31% or 3,100 ppmv can be verified.

Measurement of gas concentration in biogas WWTP Víbora (Marbella).

Hydrogen sulfide (H_2S) is formed by biological reduction of sulphates (SO_4) under anaerobic conditions. It is a gas, heavier than air, flammable, colorless, toxic, corrosive and odorous: its smell is that of decomposing organic matter (similar to the smell of rotten eggs). In addition, its combustion generates SO_2, which is one of the main causes of the acid rain phenomenon.

Below is a summary table with biogas production data and untreated H_2S concentration. In addition, the number and capacity of the digesters and the volume of thickened sludge fed daily to the reactors with the average dry matter (% DM) are indicated.

Installation	Digesters Volume (m3)	Mud (m3/day)	DM (%)	Biogas (Nm3/day)	H_2S (ppm)
Manilva WWTP	1x1.500	312,50	1,60	1.800	3.800
Arroyo de la Miel WWTP	2x2.990	118,75	4,00	1.710	3.800
Cerro del Águila WWTP	2x2.400+1x4.800	400,00	3,00	4.320	4.400
Viper WWTP	3x4.500	400,00	2,40	3.456	3.100
Guadalmansa WWTP	2x9.000	458,33	2,60	4.290	2.900

Depending on the type of biogas utilization to be carried out, some or all of the pollutants must be eliminated. In the case of the ACOSOL WWTP, hot water boilers are used.
To be used in boilers, the biogas must have a minimum methane content of 50%. In general, boilers are suitable for the use of biogas as fuel, but some operational conditions must be met; for example, the minimum boiler and operating temperature must be above the dew point.

It is recommended that the content of sulfur compounds in the biogas is less than 1,000 ppmv at the inlet of a boiler; otherwise, the biogas must be pre-treated to reduce it below this recommended concentration.
It was decided to carry out a test at the FUENGIROLA WWTP located on Camino Cerro del Águila, s/n in the municipality of Fuengirola (Málaga) because it is the facility with the highest load of hydrogen sulfide among other reasons.

2.1. SO_2 limitation in boiler emissions

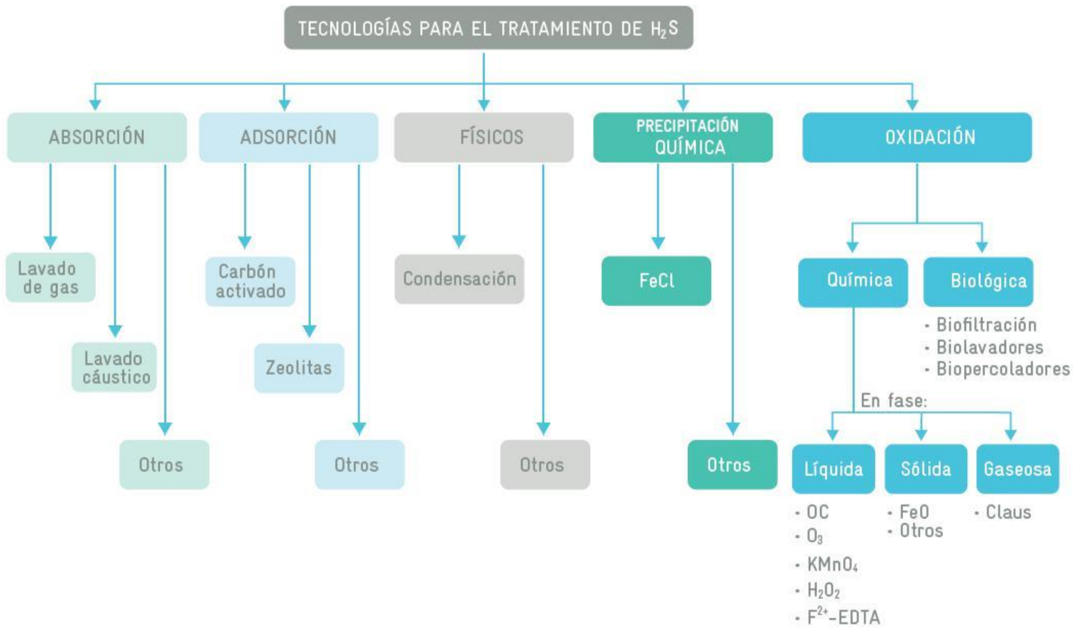
In addition to limiting the concentration of H_2S in biogas for use in boilers, there is a regulatory limitation for SO_2 emissions established at 200 mg / Nm3 (*) according to the emission limit values of Decree 239/2011, of July 12, which regulates the quality of the atmospheric environment and creates the Registry of Air Quality Assessment Systems in Andalusia.
(*) Value referred to 15 percent oxygen and in humidity-free conditions.
In the ACOSOL WWTP, due to the high concentration of H_2S two in biogas, these limits are exceeded if no type of desulfurization is carried out. That is why hydrogen sulfide reduction treatments are carried out in order to comply.

3. Objectives

The purpose of the tests carried out at the Cerro del Águila WWTP in Fuengirola is the implementation of a novel desulfurization reagent based on natural minerals of iron oxides and hydroxides. In addition, monitoring will be carried out to study the effects on the concentration of H_2S in biogas and SO_2 in boiler emissions, as well as a comparison with conventional ferric chloride reagents.
As a secondary objective, other possible beneficial contributions in the purification installation will be evaluated, such as the effect on the dehydratability of the sludge, deodorization and water lines. Although they were not originally contemplated objectives, they have been qualitatively valued (still to be contrasted) by observing different improvements on the operation of the WWTP.

4. Desulfurization systems

Hydrogen sulfide removal processes can be biological, chemical, or physical. The choice of treatment, or the combination of them, is made according to the use to which the biogas is going to be destined. When the removal of H_2S is not very restrictive (300-500 ppmv), desulfurization can be applied within the digester itself. When the required reduction is restrictive (<100-200 ppmv), a more complete external process or a combination of them is needed.

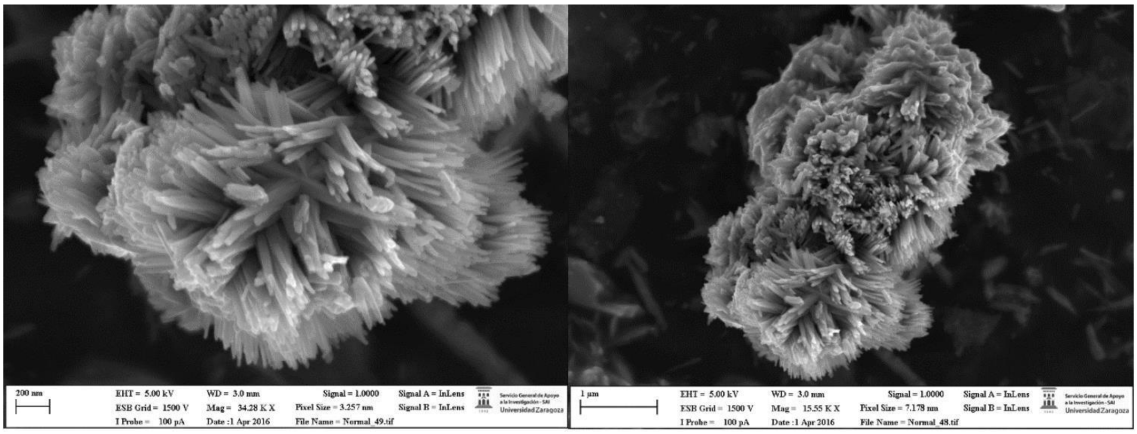


Source: Morgan Sagastume (2001). Technical guide for the management and use of biogas in wastewater treatment plants.

In our case, and given the gross reduction in the concentration of H_2S, the type of treatment is listed as physicochemical desulfurization by dosing of iron salts, being liquid format for conventional ferric chloride and solid format for the new reagent used in tests based on a mixture of iron oxides and hydroxides.

5. Characteristics of the solid mineral reagent

It is a product of natural origin, coming from our mineral deposits of iron hydroxides (FeOOH). It is supplied in powder form and is obtained after adequate mixing and micronization of the aforementioned raw materials.
Shown below are Scanning Electron Microscopy (SEM) images with the characteristic (acicular) crystallization of goethite mineral (FeOOH, or iron hydroxide).



Due to their crystallization system, these minerals are characterized by having a high specific surface, however, additionally, they are conveniently micronized to further increase the specific surface area and optimize their chemical reactivity.
Attached table shown typical technical data of the product:

DATOS TÉCNICOS INFORMATIVOS (valores orientativos)

Análisis Químico Típico *(ICP-OES)*

Óxidos	% en peso
$FeOOH+Fe_2O_3$	70-73
Fe *(total)*	44.0-45.8
SiO_2	13-15
Al_2O_3	4-6
MnO_2	2-3
MgO	1.5
K_2O	0.5-1.5
CaO	0.3-0.1
Na_2O	<0.05
Cr_2O_3	<0.005

Análisis Mineralógico *(DRX)*

Óxidos	Fórmula	% en peso
Goetita	FeOOH	63-65
Hematites	α-Fe_2O_3	7-10
Minerales micáceos	$(K,Na)(Al,Mg,Fe)_2[(Si,Al)_4O_{10}](OH)_2$	7-8
Cuarzo	α-SiO_2	8-9
Fase amorfa		13-15

Distribución granulométrica
(Difracción Laser)

Tamaño medio de partícula (µm): 2.00 (±0.20)
Tamaño máximo de partícula (µm): 10.00 (±0.10)

BET:
44.8 m^2/g

Micronox® ON16 has been the subject of extensive preliminary studies, with successful application in anaerobic biomethanization plants with the aim of reducing the levels of hydrogen sulfide in the biogas produced.
Iron hydroxide reacts with hydrogen sulfide generating ferric sulfide and water. The chemical reaction is as follows:

$$\mathbf{2\ FeOOH}(s) + \mathbf{3\ H_2S}(g) \longrightarrow \mathbf{Fe_2S_3}(s) + \mathbf{4\ H_2O}(w)$$

Therefore, as a result of the complete theoretical reaction of ferric hydroxide and hydrogen sulfide, ferric sulfide and water (liquid phase) are produced, both in very small percentages in relation to the volume of waste contained in the reactor, and always contained in the digestate and not in biogas. To be more precise: for every 1,000 kg of Micronox® ON16

(67% in ferric hydroxide) 272 kg of digestate water are produced and 386 kg of hydrogen sulfide are removed from the biogas.

Also, the reaction of the Micronox® ON16 does not generate CO_2 nor O_2. It only reduces the levels of hydrogen sulfide in the biogas, which is what it has been developed for. These data are confirmed both at a theoretical and experimental level in data obtained in plants that are currently dosing it.

With Micronox® ON16, the operators of biomethanization facilities have a product that enables the efficient and cost-effective reduction of hydrogen sulfide present in biogas.

5.1. Application sectors

Micronox® ON16 is particularly advantageously applicable, due to its optimal cost / effectiveness ratio, in the reduction of hydrogen sulfide in the biogas produced in anaerobic biomethanization plants from:

- Sludge from sewage treatment plants (WWTP)
- Organic Fraction of Urban Solid Waste (FORSU)
- Agricultural waste (slurry, manure)
- Agricultural and forestry waste (rape, corn, sunflower, beet, etc.)
- Food industrywaste (slaughterhouses, canneries, etc.)

Likewise, the Micronox® ON16 is applicable to different biomethanization technologies: dry technology (percentage of dry matter in the digester greater than 15%) and wet technology (percentage of dry matter in the digester less than 15%).
Hydrogen sulfide reduction occurs under both mesophilic and thermophilic digestion conditions.
Micronox® ON16 must be added together with the organic substrate in the feed to the anaerobic digester.
Depending on the characteristics of each plant, the most convenient points for dosing can be selected: in the mixer prior to feeding the digester, in the return of black water (bacterial flora) to the digester re-feeding, or by prior mixing in stocks of organic waste.

6. Cerro del Águila WWTP in Fuengirola

Fuengirola WWTP is the facility selected for tests with the new mineral reagent since it is the one with the highest hydrogen sulfide loads, among other reasons. The WWTP has the capacity to treat 60,000 m3 / day of wastewater, equivalent to a population of 240,000 inhabitants. The WWTP's treatment system is activated sludge type with stabilization of sludge via anaerobic digestion and dehydration via centrifuge. The treatment line is summarized below:

- Arrival work
- Pretreatment using thick and thin gratings
- De-sanding and degreasing
- Primary settling
- Anaerobic sludge reactors activated with aeration by rotors with anoxic selector
- Secondary settling
- Sludge line consisting of:
    - Sludge sieve
    - Gravity thickening for primary sludge.
    - Mechanical thickening with polyelectrolyte dosage for secondary sludge.
    - Mixed sludge tank for feeding to digesters. Anaerobic digesters.
    - Buffer tank for digested sludge.
    - Dehydration with centrifuges and addition of polyelectrolyte.

SLUDGE SCREENS: the sludge purge from the primary decanters and the excess of the biological is passed through a self-cleaning 3 mm sieve, the retained solids being pressed and sent to a container for management as waste.

THICKENING: It has two gravity thickeners for primary sludge with a diameter of 10 m and part of the excess biological sludge is pumped to rotary thickeners that transport the sludge, flocculated with polyelectrolyte, through a rotor with Archimedean screw geometry. The liquid is separated through a screen that is cleaned by means of a brush ramp with intermittent washing. The thickened sludge falls into a hopper to be pumped to the mixed sludge silos and storage and later sent to the digesters. The approximate average concentration of the thickened sludge is 3% (30 kg/m^3).

DIGESTION: The sludge from the sludge thickening is sent to anaerobic digesters, which are two closed concrete tanks, 2 of them with a capacity of 2,400 m^3 each and the third and new one of 4,800 m^3, with a conical bottom and cover. They have a retention time of approximately 30 days. The pumping to digestion is carried out by means of groups of 40 m^3/hour motor pumps. The mixing of sludge is carried out with 180 m3/hour motor-pump units.
To maintain the temperature of 35-38ºC in the digester sludge, two water boilers have been installed, heated by the biogas produced in the digestion. The gas produced is stored in a low-pressure gasometer with a capacity of 1,800 m^3.

DEHYDRATION: Drying is done by 3 centrifuges, being transported by pump to the 50 m^3 storage silo. To facilitate the dehydration of the sludge, they are mixed with a cationic polyelectrolyte.

The dosing point for the solid-mineral reagent has been the mixed sludge tank, where the primary and secondary sludge are mixed and agitated after being pumped to the different digesters. Currently the system works in parallel with a flow rate proportional to each of the digesters 100 m^3/day to each of the small digesters of 2,400 m^3, and 200 m^3/day to the digester greater than 4,800 m^3.

The reagent packaging is a 20 kg paper bag. For continuous operation, it can be done using an automatic dispenser or using a water-soluble bag that can be introduced directly into the sludge tank.

7. Work planning

Dosing tests are planned in 2 months (8 weeks) of treatment. It is decided to carry out the test in the months of October and November 2019, leaving December for data collection, analysis and conclusions.

The work plan at the WWTP is summarized below:

1. Previous audit of the treatment process of the sewage treatment plant: water line and sludge line.
2. Collection of sludge line operation data for the current full year from January 2019 to September 2019.
3. Reagent dosage calculations and simulation of results.
4. Start of tests with double dosage during the first week to speed up the process.
5. Daily dosage at 3 shifts.
6. Daily operation data collection (amount of sludge fed, sludge concentration, biogas flow, etc).
7. Weekly visit to measure concentrations in biogas (CH_4, CO_2, O_2, H_2S) as well as a review of the evolution of the process. With issuance of a report of results and actions to be carried out.
8. Occasional visits to measure gases in boilers (Tª, O_2, SO_2, NO, NO_x, and other parameters). A measurement is established at the beginning and another at the end of contrast. With issuance of a report of results and actions to be carried out.
9. Collection of final data, analysis and conclusions, with issuance of a final report.

Although the object of the tests originally only focused on the reduction of H_2S in biogas and SO_2 in boiler fumes, it is decided to expand the range of data to be collected and analyzed to see the effects on digestion and the rest of the sludge line and waters.

8. Calculation of the required dosage

INFORMACIÓN DE LA PLANTA DE GENERACIÓN DE BIOGAS					
UBICACIÓN DE LA PLANTA	ACOSOL - EDAR FUENGIROLA				
TIPO DE DIGESTOR	SMC	Nº DE DIGESTORES			3
TIPO DE SUSTRATO/S	LODOS EDAR URBANA				
MASA DE SUSTRATO TRATADO (tn/día)	400,00	DENSIDAD DEL SUSTRATO (tn/m3)			1,1
TIEMPO RESIDENCIA SUSTRATO (días)	35	SÓLIDOS TOTALES/VOLÁTILES (%)			3% / 80%
VOLUMEN DE BIOGAS (m3/día)	4.320,00	pH	7,2	Tª	35ºC
H_2S INICIAL (ppm)	4.400,00	H_2S OBJETIVO (ppm)			500,00
OTRAS OBSERVACIONES	Se cuenta con estudio detallado				

CALCULOS DE CONSUMO MX-ON16/DÍA				
PARÁMETROS DE FUNCIONAMIENTO				
H2Saq	1,00	Sulfuro de hidrogeno total disuelto		
fH2S	0,50	Porción de Azufre disuelto presente en fase acuosa		
H2Ss (Inicial)	4.400,00	Cantidad de sulfuro de hidrogeno inicial del biogas (ppmv)		
H2Sg (Objetivo)	500,00	Cantidad de sulfuro de hidrogeno objetivodel biogas (ppmv)		
AH2Sg	3.900,00	Cantidad de sulfuro de hidrogeno a reducir del biogas (ppmv)		
P_sustrate	1,10	Densidad del sustrato (t/m3)		
M_sustrate	400,00	Peso del sustrato (t/d)		
V sustrate	363,64	flujo del sustrato (m3/d)		
V biogas	4.320,00	Caudal de biogas (m3/d)		
P_H2S	1,36	Densidad de H2S (g/l)		
M_Fe	55,84	Masa atomica Fe		
M_S	32,00	Masa atomica S		
B	2,20	Factor sobredosis (1,7-5)		
CÁLCULOS DOSIFICACIÓN		DOSIFICACIÓN (SACOS/DÍA)		FEEDBACK
Fe(gr/d)	90.756,08	SEMANA 1	17	
Ley de Fe MX-ON16	52	SEMANA 2	9	
Gramos MX-ON16 equiva.	174.530,93	SEMANA 3	9	
Kg/d MX-ON16	174,53	SEMANA 4	9	
Sacos/dia	8,73	SEMANA 5	9	

Summary 180 kg / day = 9 bags x20 kg / bag.

NOTE: although the objective is to reach 1000 ppm of SH_2 in biogas, for calculation purposes a lower limit is established for safety.

9. Results

The average data obtained during the tests are indicated.

		September	October	November	December
Sludge Flow	**m3/month**	11.701,00	10.661,00	8.349,00	7.606,00
%total solids input	**%**	2,78	3,01	3,67	3,43
% volatile solids input	**%**	81,73	81,84	80,23	81,23
%total solids output	**%**	1,26	1,32	1,18	1,23
% volatile solids output	**%**	70,71	68,56	68,97	66,87
Retention time	**days**	24,61	27,91	34,5	39,13
kg volatile solids input	**kg/month**	265.550,09	262.477,35	245.854,99	211.946,45
kg volatile solids removed	**kg/month**	161.443,84	165.931,19	177.662,04	149.208,92
Biogas flow	**Nm^3/month**	105.214,00	114.918,00	116.485,00	136.867,00
% CH_4	**%**	61,50 (*)	61,50(*) /62,30	63,7	64,3
ppm H_2S	**ppmv**	4.400 (*)	4.384 (*) /1.505	858	593
RATIOS					
Biogas production	**Nm^3/kg SV**	0,652	0,693	0,656	0,917
Volatile solids removal	**%**	60,80%	63,22%	72,26%	70,40%

NOTE: Testing begins October 21, although contrast measurements are performed prior to reagent dosing.

(*) Before dosing ON16.

10. Conclusions

The main conclusions of the test are listed below as well as the next steps to be taken to contrast some unconfirmed results obtained.

- New mineral reagent based on iron oxides and hydroxides proves to have satisfactory results for desulfurization in mesophilic anaerobic digestion of urban WWTP sludge, reaching results below 1,000 ppm of H_2S in biogas and below 200 mg/Nm^3 of SO_2 in boiler fumes, thus fulfilling the objective of the tests (* 1).

- Dosage used during the tests was 9 bags per day (3 bags per shift) of 20 kg, which means a daily feeding of 180 kg of reagent to the digester. With this dosage it was possible to reach a H_2S concentration below 600 ppmv and SO_2 in boiler fumes below 30 mg / Nm3 or even undetectable. This supposes an approximate dosage of 0.45-0.50 kg reagent/Tn of sludge fed for the conditions of the Fuengirola WWTP (3% DM and 80% MV approximately). It is confirmed during the tests that the reagent has no negative effects on digestion; no inhibitions of any kind are detected. Noticed there is a dark brown coloration in the mud.

- The use of the reagent reports certain improvements to both the sludge line and the water line, the most important being the following:

  - Improvement of the biogas quality by increasing the concentration of methane
  - Improvement of the % or reduction of volatile matter
  - Improved sludge thickening and increased% DM at the inlet, thus reducing the amount of sludge fed and therefore reducing the amount to dehydration (* 2)
  - Improved sludge dehydrability (* 2)
  - Reduction of the polyelectrolyte dosage in dehydration (* 2)
  - Reduction in the amount of sludge generated due to the increase in the% DM in input and better dewatering, thus reducing the cost of managing them (* 2)
  - Reduction of odors in the sludge line (* 3)

(1) Previous experiences in other facilities show that it is possible to go down to 150-300 ppm by adjusting the dosage and improving the mixing in the digester.*

(2) These improvements have been qualitatively verified, since their follow-up was not programmed. Although it can be affirmed that these improvements arose after the reagent dosing, to be rigorous we cannot attribute them only to this event, so it is recommended to do a quantitative follow-up in future tests to be able to contrast.*

(3) This improvement has been assessed qualitatively and not quantitatively by official measurement. It is recommended to incorporate the studies in future trials to quantify their effect. We do find a justification for its effect, since the solid that remains in the unreacted sludge continues to adsorb SH2 particles while in contact with the air.*