WASTEWATERS SEWAGE SLUDGE DISPOSAL BY PYROLYSIS AND OXYCOMBUSTION TREATMENTS

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The feasibility to dispose wastewater sewage sludge through a two steps pyrolysis-vitrification process was studied. In the first step, the pyrolysis of the sludge takes place, with recovery of its energy content. In the second one, the solid residue of pyrolysis undergoes a vitrification process in an oxy-fuel fired furnace. The kiln offgas allow the heating of the pyrolysis reactor.

The research was firstly carried out by studying the pyrolysis of a sludge sample obtained from a municipal wastewater treatment plant. The pyrolysis was studied and monitored by thermogravimetric-mass spectrometric and thermogravimetric-gas chromatographic-mass spectrometric analyses. The sewage sludge mass loss, during the pyrolysis treatment, is 51.8% up to 600°C. Water, carbon mono- and di-oxide, several hydrocarbons (up to C5, both saturated and unsaturated) were the major detected species.

The stabilization of the pyrolysis process residue was obtained by vitrification in a pilot plant scale oxy-fuel fired furnace. The resulting material presents features of a totally inert vitreous matrix, showing excellent resistance against leaching of heavy metals ions, and it is suitable for commercialization in the ceramics field. The energy balance confirms the sustainability of the proposed disposal process.

Keywords: pyrolysis, oxy-combustion, sewage sludge, thermogravimetric-mass spectrometric analysis**.**

1. Introduction

Wastewater sludge is a solid waste which storage and degradation is a problem of great importance and complexity [1]. The high concentration of heavy metals, and the bacteria and viruses content do prevent the use of sewage sludge as fertilizer.

Landfill disposal of wastewater sludge should be avoided, because it involves the subtraction of soil from agricultural use. Moreover this choice implies the loss of sludge energy content [1-3]. Incineration appears a useful

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method, even if the costs of scrubbing of gaseous by-product up to acceptable limits, and ashes disposal cannot be disregarded [1].

Pyrolysis with gasification of organic compounds was studied as a plausible and viable option as an ecological way for sludge disposal, along with the exploitation of produced gas as an alternative energy source [1-5].

Although this process considerably reduces the sludge mass, it is not a complete solution for the disposal of the solid waste. Analogously to the ashes of incineration plants, the solid residue from the pyrolysis process must be stabilized.

For this purpose, vitrification is a reliable method [6]. Vitrification considerably reduces the environmental impact of the heavy metals, which are immobilized into a stable vitreous-matrix. Moreover, possible organic-chlorinated compounds are totally destroyed by the high temperatures of the process. The vitreous matrix presents high resistance to leaching, and high durability. Moreover, it doesn't need landfill disposal, and it may be used as sintering additive in the ceramics industry, or as roadbed, with considerable savings on raw materials.

Compared with traditional processes in air or with electric furnaces, the oxy-combustion process allows the drastic decrease of the off-gas volume and of the particulate content, a flame temperature higher than the one of a traditional combustion process, and a higher efficiency. Otherwise, the energetic consumption sensitively affects the cost of production, which is justified only if the final product presents higher quality, for remunerative applications. The oxy-combustion kiln is similar to the one used in glass industry, without the presence of regenerative heat exchangers.

The three fundamental aspects for the feasibility of the overall process are: (1) the characterization of the gas phase evolved from the thermal treatment in the pyrolysis reactor, which allows to define its heat of combustion, (2) the inertia of the vitreous matrix to heavy metals leaching tests, which allows its use in several fields, (3) the energy balance analysis of the overall process.

2. Results and Discussions

2.1. Characterization of the gas phase evolved from the pyrolysis process

TG-MS and TG-GC-MS were used to characterize the gas phase evolved from sludge thermal treatment under inert atmosphere. The first configuration allows the real time detection of the gaseous species released during the thermal decomposition of the solid sample, the second one allows the accurate qualitative and semi-quantitative gas phase analysis of released compounds, sampled in correspondence with the most significant thermogravimetric events. The instrumental interfaces, experimental procedure, and data processing adopted in this study were described elsewhere [7, 8].

Elemental analysis (C, H, N and S) and content of metals in the dried sewage sludge are reported in Table 1.

Table 1

Elemental analysis and content of metals in the dried sewage sludge

Element or species	C	H	N	S	SiO_2		
Amount / wt. %	36.0	4.5	5.6	0.5	10.0		
Element or species	Al	B	Ba	Bi	Ca	Cd	Co
Amount / $mg \cdot kg^{-1}$	$6.7 \cdot 10^3$	62	460	6	$52.2 \cdot 10^3$	< 4	4
Element or species	Cr	Cu	Fe	Ga	In	K	Li
Amount / $mg \cdot kg^{-1}$	130	240	$43.4 \cdot 10^3$	4	2.2	940	$1.34 \cdot 10^3$
Element or species	Mg	Mn	Na	Ni	Pb	Zn	
Amount / $mg \cdot kg^{-1}$	$3.88 \cdot 10^3$	128	780	24	16	540	

The thermal treatment of the sewage sludge, under inert atmosphere, shows a continuous mass loss (61.4%) up to 1000°C. The TG curve presents a first event in the 100–600°C range, with intensity of 51.8%, followed by a second lower mass loss (9.6%) in the 600–1000°C range. DTG curve shows an intense peak at 320°C, with a pronounced shoulder at 460°C, followed by two small overlapped bands centred at 705°C and 770°C respectively.

The mass spectrometric analysis of the released species (TG-MS measurement) shows a total ion current (TIC) plot which is characterised by two intense overlapping peaks at 325 and 470°C, followed by a small band at 700°C (Fig. 1). Mass spectra, in correspondence of the most significant TIC peaks, indicate main evolution of CO_2 and H_2O at 325°C, whereas at 470°C the simultaneous release of different compounds is observed. Finally, spectra recorded at 700°C show the evolution of CO, CO_2 and small amounts of H_2O.

TG-GC-MS analyses at 320°C confirm the presence of CO_2 and H_2O, with small amounts of acetaldehyde, acetonitrile, acetone and traces of other unidentified species. Gas samplings at 460°C indicate the evolution of several compounds: CO, CO_2, H_2O, alkanes and alkenes up to C5, toluene, and minor amounts of styrene and C8 and C9 hydrocarbons are the chemical species observed. Finally, gas sampling at 705°C confirms the evolution of CO and CO_2, with very small amounts of H_2O.

As observed by other authors [1], CO and CO_2 arise from pyrolytic decomposition of partially oxygenated organic compounds (lipids, carbohydrates, cellulose, lignin) and, to a lesser extent, from decomposition of inorganic salts such as carbonates. In an analogous way, acetaldehyde and acetone derive from oxygenated organic compounds. Cyano compounds may derive from proteins, nucleic acids and dead micro-organisms present in sewage sludge; they could be formed by dehydrogenation of amino groups [1].

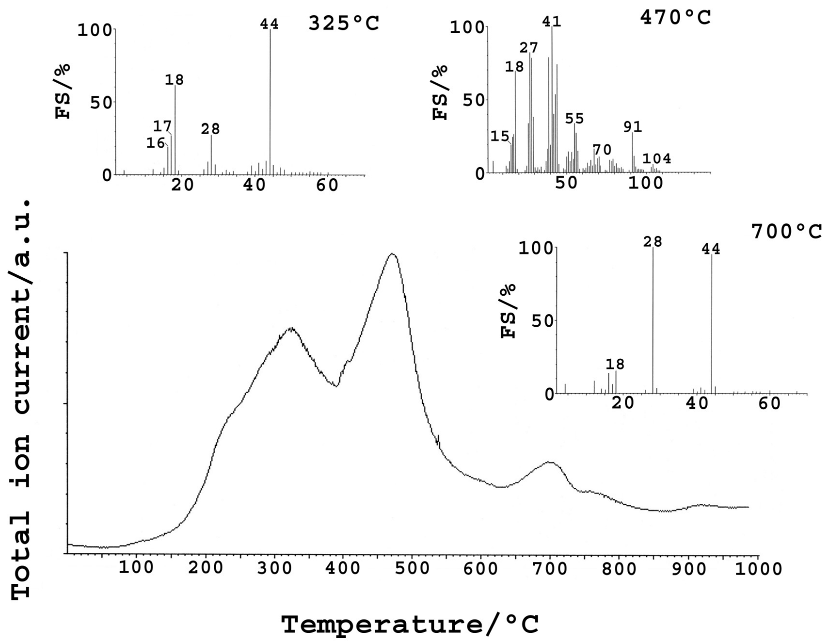

Fig. 1. TG-MS analysis of sewage sludge. In the insets mass spectra recorded corresponding to selected pyrolysis temperatures.

The evolved species monitoring, throughout the pyrolysis up to 1000°C, can be obtained by selecting an appropriate *m/z* signal, recalled from TG-MS data, suitable to identify a specific compound among the various released species [7]. Water evolution trend shows a maximum at 310°C, while CO_2 evolution trend presents two overlapping peaks at 240 and 320°C, followed by a shoulder at 430°C and by less intense peaks at 610 and 700°C. The release of hydrocarbons occurs mainly in the 350–550°C interval and gives rise to the most intense peak of the TIC curve.

A semi-quantitative evaluation of the pyrolysis process was estimated by comparison of experimental data concerning: (i) the chemical composition of the gas phase released at 460°C (TG-GC-MS analysis); (ii) the values obtained from the integration of appropriate *m/z* ion currents (TG-MS analysis); (iii) the elemental analysis of dried and pyrolyzed sludge samples.

Table 2 reports semi-quantitative evaluation of the evolved gas phase.

A nominal calorific value of the released gas mixture was calculated taking into account both the chemical composition of the gas phase (determined by TG-MS and TG-GC-MS measurements), and the ΔH° values of the combustion reactions of evolved compounds. A calorific value of 7850 kcal/kg was obtained.

Table 2

Mass balance of the compounds evolved during the pyrolysis process

Species	**CO**	**CO_2**	**H_2O**	**CH_4**	**C_2H_4**	**C_2H_6**	**C_3H_6**	**C_3H_8**
Mol %	15.4	17.3	14.5	1.8	0.7	3.2	4.7	3.8
Mass %	8.8	15.5	5.3	0.6	0.4	2.0	4.0	3.4
Species	**HCN**	**C_4H_8**	**C_4H_{10}**	**CH_3CN**	**C_5H_{10}**	**C_5H_{12}**	**C_6H_9**	**C_8H_{16}**
Mol %	1.4	8.3	3.5	3.4	4.1	2.7	5.3	2.2
Mass %	0.8	9.5	4.1	2.8	5.9	4.0	10.0	5.0
Species	**C_8H_{18}**	**C_8H_8**	**C_9H_{18}**	**C_9H_{20}**				
Mol %	1.6	3.4	1.3	1.4				
Mass %	3.7	7.2	3.3	3.7				

These results show that pyrolysis of this sewage sludge sample may represent a viable process option for its environmental treatment. The residual mass of pyrolyzed sludge is considerably reduced and the enthalpy content of the released hydrocarbons may be recovered as fuel gas.

2.2. The vitrification process; features of the vitreous matrix and leaching tests of heavy metals

The pyrolysis of sewage sludge bears a mass loss of 51.8% as volatile gas, which is suitable for fuel gas in neighbouring plants. The chemical composition of the pyrolysis solid residue (48.2% of the sludge mass) is reported in Table 3. The high percentage of SiO_2 allows a good vitrification of the solid residue. Moreover, the presence of a substantial amount of CaO, makes the resultant vitreous matrix resistant against leaching tests [9].

Table 3

Chemical composition and metals content in the pyrolysis solid residue treated up to 600°C in inert atmosphere

Compound	SiO_2	Al_2O_3	$CaCO_3$	$MgCO_3$	Fe_2O_3	Na_2O
Amount / wt. %	54	2	27	2	14	0.4
Compound	K_2O	Li_2O	Metals			
Amount / wt. %	0.2	0.1	0.3			
Metal	B	Ba	Bi	Co	Cr	Cu
Amount / $mg \cdot kg^{-1}$	78	640	6	6	68	380
Metal	Ga	In	Mn	Ni	Pb	Zn
Amount / $mg \cdot kg^{-1}$	6	4	200	32	52	18

The melted glass can be discharged from the kiln by gravity casting in water (glass frit), or through two cylindrical roller rotating in the same direction of the casting. In the glass frit, a pellet size material is obtained, useful for road bed or inert additive for mortars and plasters. In the second case, the vitreous matrix appears as solid scales with high mechanical resistance, and it is used as inert additive in concretes production.

Leaching tests show heavy metals concentration values which are lower than the limit values, determined by IRSA and US-EPA rules [10]. In most cases, these values are lower even of an order of magnitude. Table 4 reports the detected values of concentration of heavy metals, compared with their limits.

Table 4

Concentration values of heavy metals eluted from the vitreous matrix in the leaching tests, compared with their limit values

Metal	As	Cd	Cr	Hg	Ni
Detected value / $mg \cdot L^{-1}$	< 0.001	< 0.001	< 0.001	0.0006	0.007
Limit value / $mg \cdot L^{-1}$	0.5	0.02	2	0.005	2
Metal	Pb	Cu	Se	Mn	Zn
Detected value / $mg \cdot L^{-1}$	< 0.001	0.09	< 0.003	0.006	0.01
Limit value / $mg \cdot L^{-1}$	0.2	0.1	0.03	2	0.5

2.3. Energy balance analysis of the overall process

Fig. 2 displays the process diagram, developed on the basis of the wastewater treatment plant in Trento. After anaerobic digestion, the sludge (flow rate 350 m^3/day) presents a solid concentration of 25 kg/m^3, and undergoes belt-press filtration, where solid concentration is increased to 200 kg/m^3, resulting in a sludge outlet flow rate of 44 m^3/day.

This sludge is further dried in order to reach a solid concentration of 95%, corresponding to 1370 kg/m^3, being the concentrated sludge density 1443 kg/m^3. The dryer outlet flow rate is 6.4 m^3/day (9260 kg/day) of sludge at 100°C. In this unit operation 34.7 m^3/day of water are evaporated, requiring $27.8 \cdot 10^6$ kcal/day.

The resulting sludge is treated in a pyrolysis reactor; the inlet flow rate is 386 kg/h. Tacking into account that the dried sludge presents a 5.3 % w/w of water, an amount of 20.5 kg/h of water is evaporated from the sludge, requiring 880 kcal/kg, corresponding to 18.100 kcal/h.

The heating of the dried sludge (C_p=0.3 kcal/kg°C) up to the working temperature (600°C), requires 54800 kcal/h.

The pyrolysis reaction of the 365.5 kg/h of sludge requires an heat of reaction which ranges from 24500 to 41300 kcal/h, as deduced by a series of DSC analyses carried out on sludge samples. Thus, the comprehensive endothermicity of the pyrolysis process ranges from 97400 to 114200 kcal/h.

Considering an oxi-fired furnace of 30 t/day, the pyrolysis solid fraction corresponds to the 15% ca. of the raw materials. The remaining 85% can be constituted by incinerator ashes, polluted soils, industrial sludge with high content of inorganic compounds, asbestos ecc., which can be disposed by the same process, because the required composition for the obtainment of a vitreous material with satisfying properties, is: SiO_2 ~50%, Al_2O_3 10÷20%, and CaO 10÷12% [9].

Taking in consideration a heat of 640 kcal/kg for the melting of the glass mixture, and an efficiency of the furnace of 50 %, the heat required by the process result of 2.000.000 kcal/h.

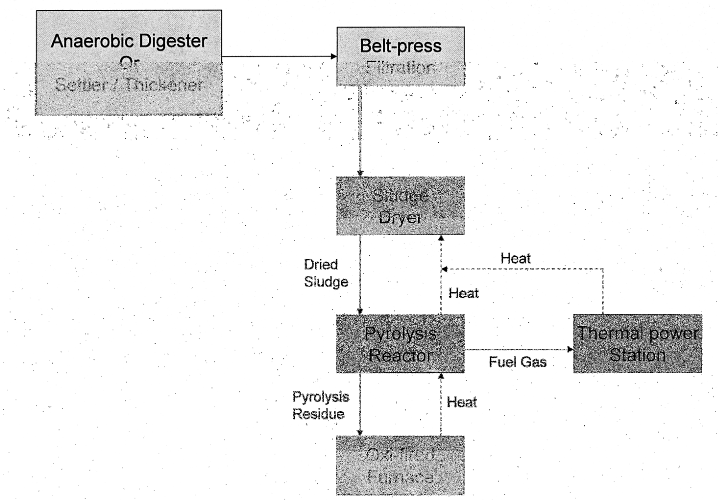

Fig. 2. Process diagram of the pyrolysis / oxy-combustion process.

Considering a furnace working temperature of 1400°C, the heat outgoing with the melted glass results 528000 kcal/h, whereas the one of the off-gas results 393450 kcal/h. The heating of the pyrolysis reactor can be carried out with the oxy-combustion off-gas heat. Considering a fumes inlet temperature of 1200°C, an outlet temperature of 670°C, and an energy loss of 40% into the heat exchanger, the heat available for the pyrolysis process results ca. 115000 kcal/h, satisfying the energetic demand of the endo-thermal process.

The sludge pyrolysis bears the evolution of the previously described gas phase, with an enthalpy of combustion of ca. 7.850 kcal/kg. Tacking into account the mass loss arising from the pyrolysis process (51.8%) and the percentage of hydrocarbons (79.2% w/w) ca. 256 kg/h of fuel gas mixture is developed by the thermal degradation of the sludge in inert atmosphere. The combustion of this fuel gas amount, produces a heat of 2.012.820 kcal/h, available for other neighboring plant devices.

3. Conclusions

The pyrolysis of the wastewater sewage sludge at 600°C bears a mass reduction of 51.8%, with the recovery of its energy content as fuel gas.

The stabilization of the solid residue (48.2%), with or without the presence of other waste, by vitrification in a oxy-fuel fired furnace, allows to obtain an inert vitreous matrix. This vitreous material shows excellent resistance against leaching of heavy metal ions, and it is suitable for many uses in more fields.

The energy balance of the overall process indicates that the heat of the oxy-combustion furnace off-gas satisfies the energy demand required by the sludge pyrolysis process. Moreover, the heat of the fumes outgoing from the pyrolysis reactor heating, and the ones developed by the combustion of the fuel gas obtained from the pyrolysis, can be used for the drying of the sludge after the belt-press filtration.

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