TINOS 2015
3rd International Conference on Sustainable Solid Waste Management
2-4 July 2015

ODORS AND GAS EMISSIONS DURING THE CERAMIC SINTERING OF SEWAGE SLUDGE. GUIDELINES FOR INDUSTRIAL IMPLEMENTATION

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SEWAGE SLUDGE FROM BIOLOGICAL PROCESS IN WASTE WATER TREATMENT PLANTS (WWTP)

- Typical production of sludge: about 25 - 50 ton/day (0.6 - 1 kg/inhabitant/day approx.)

CLAY BRICK PRODUCTION WITH A MAXIMUM OF 25% OF SEWAGE SLUDGE WITH 60% HUMIDITY

- Any conventional ceramic plant can be easily adapted to make products that include clays + sewage sludge.

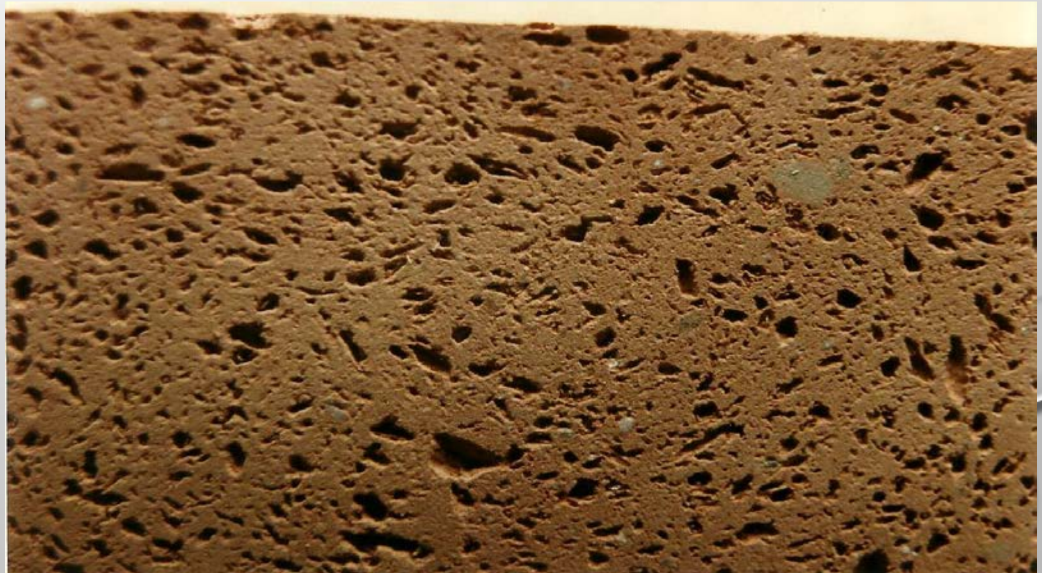
- Special care to handle hazardous wastes and treatment of washing and/or filtration of particles and gases in the sintering. In both cases it is not necessary to use extreme technologies.

IMPROVING SUCCESFUL TECHNICAL PROPERTIES

- Lightness (60% of weight compared to conventional clay brick)
- Ductility (low fragility, good for sailing races)
- Sound proofing
- Acceptable mechanical behavior for non-structural enclosures (compression resistance of 50 - 100 kg/cm^2)

SUCCESFUL ENVIRONMENTAL PROPERTIES

- Final zero waste (waste disposal)
- Final product without leachate. No toxicity to the user
- Thermal destruction of toxic and hazardous waste. Residence time in the oven = 20 hours (at 1000°C)
- Inerting by vitrification of heavy metals



WHAT IS THE PROBLEM IN THE INDUSTRIAL PRODUCTION?

- Emissions of odors and gases during sintering of sewage sludge in ceramic matrix

- Sewage sludges in ceramic matrix: thermal treatments possible

- Incineration, gasification or pyrolysis thermal process

  → **PYROLYSIS** (<<< gas emissions)

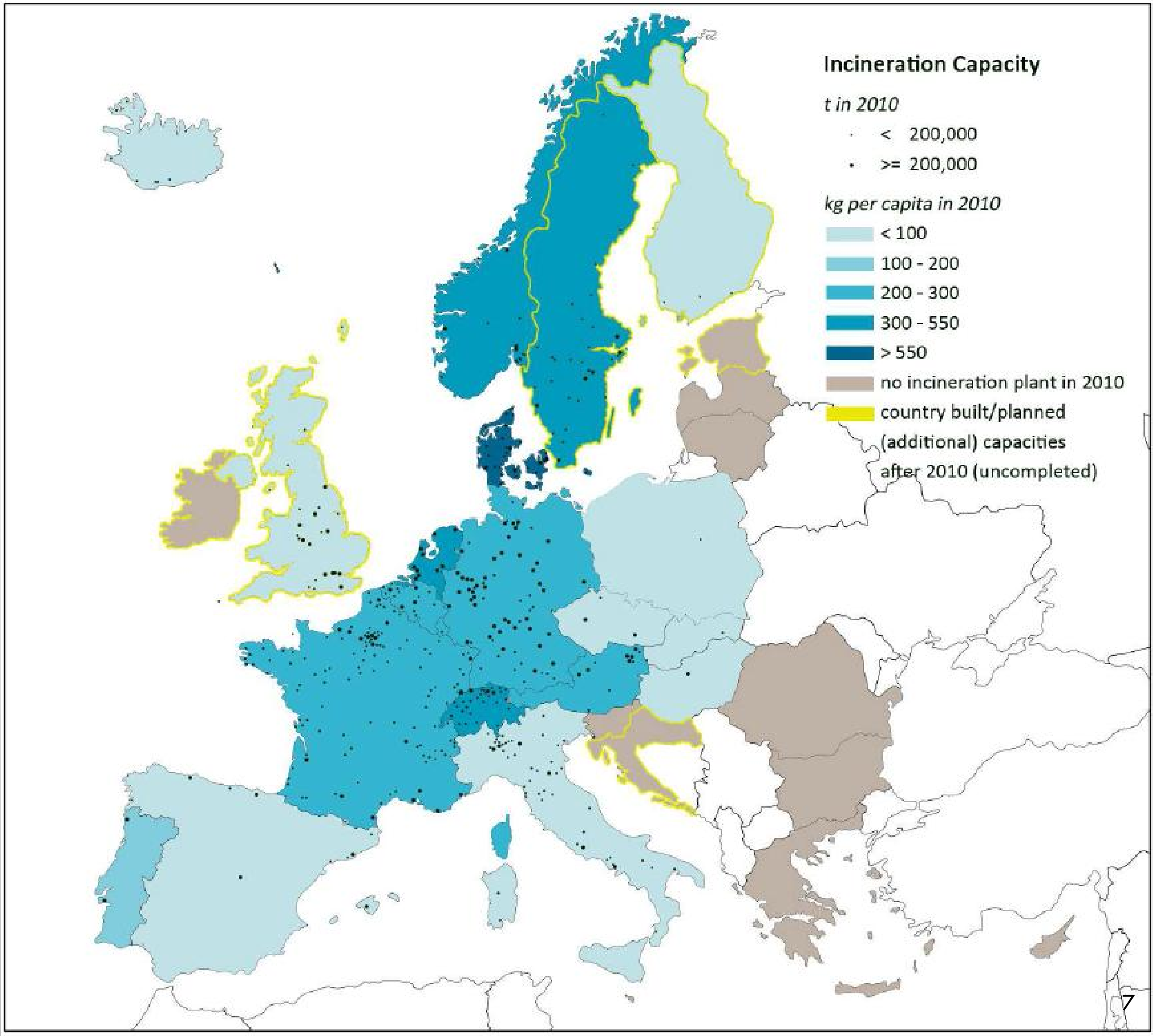
- *"Pyrolisys seems to be the optimal thermochemical option treatment compared to incineration and gasification (related sewage sludges)"*

  [M.C. Samolada, A.A. Zabaniotou. *Waste Management*, 34: 411-420 (2014)]

WHY NOT PYROLYSIS OF SEWAGE SLUDGE?

- Incineration is more hazardous or polluting than inerting sewage sludge in ceramic plants.

  See incineration plants in EU



EXPERIMENTAL LAB DATA OF GASES AND ODORS (1/3)

Table 1. VOC emitted during the firing process [a].

Family	VOC	Formula	Clay/sludge-brick firing emissions (µg m⁻³)	Clay-brick firing emissions (µg m⁻³)	TLV-TWA (µg m⁻³)	OD [b] (µg m⁻³)	OR [c] (µg m⁻³)
Chlorinated hydrocarbons	Trichlorofluoromethane	CCl_3F	0.0	571.9	5620		
	Chloromethane	CH_3Cl	536.5	0.0		20462	20462
	Dichloromethane	CH_2Cl_2	1846.7	0.0	174000	550008	790637
	Trichloromethane	$CHCl_3$	179.5	940.5			
Mercaptans	Methylmercaptan	CH_3SH	16.0	0.0	980	1.1	2.0
Sulfides	Carbon disulfide	CS_2	728.8	142.7	31000	1306.3	1306.3
	Dimethyl disulfide	$S_2(CH_3)_2$	68.4	0.0		7.7	
	Dimethyl trisulfide	$S_3(CH_3)_2$	0.0	0.0		5.2	
Thiocianates	Methyl thiocyanate	CH_3SCN	169.9	0.0			
Aliphatic ketones	Propanone	C_3H_6O	1142.4	0.0		147160	308561
	3-Methyl-3-buten-2-one	C_5H_8O	151.8	0.0			
Aliphatic aldehydes	2-Methyl propenal	C_4H_6O	303.5	0.0			
	3-Methyl butanal	$C_5H_{10}O$	305.6	0.0			
	Hexanal	$C_6H_{12}O$	104.7	0.0			
	Heptanal	$C_7H_{14}O$	183.8	0.0			
Aromatic aldehydes	Furfural	$C_5H_4O_2$	255.4	0.0	7900	2498.6	2498.6
	Benzoaldehyde	C_7H_6O	594.2	0.0			
	Hydroxybenzaldehyde	$C_7H_6O_2$	5.3	0.0			
Aliphatic nitriles	Acetonitrile	C_2H_3N	1688.5	0.0	67000		
	Benzonitrile	C_7H_5N	318.5	0.0			

EXPERIMENTAL LAB DATA OF GASES AND ODORS (2/3)

Aliphatic acids	Acetic	$C_2H_4O_2$	2533.8	0.0	25000	181.7	
	2-Methylpropanoic	$C_4H_8O_2$	32.1	0.0			
Aliphatic esters	Methyl acetate	C_3H_6O	238.3	0.0	606000	427238	
Aromatic amines	Pyrazine	$C_4H_4N_2$	160.3	0.0			
	Pyridine	C_5H_5N	454.2	0.0	16000	2133.7	2392.4
	4-Methylpyrazine	$C_5H_6N_2$	226.6	0.0			
	4-Methylpiridine	C_6H_7N	56.6	0.0			
Aliphatic amides	Acetamide	C_2H_5NO	237.2	0.0			
	3-Methylbutanamide	$C_5H_{11}NO$	0.0	0.0			
Monoterpenes	α-Pinene	$C_{10}H_{16}$	11.8	24.5		64	
Linear aliphatic hydrocarbons	N-nonane	C_9H_{20}	160.3	0.0	1050000		
	N-decane	$C_{10}H_{22}$	536.5	37.3			
	N-undecane	$C_{11}H_{24}$	0.0	37.3			
	N-dodecane	$C_{12}H_{26}$	89.8	0.0			
	N-tridecane	$C_{13}H_{28}$	361.2	0.0			
	N-tetradecane	$C_{14}H_{30}$	0.0	0.0			
	N-pentadecane	$C_{15}H_{32}$	0.0	0.0			
	N-hexadecane	$C_{16}H_{34}$	245.8	0.0			
Branched aliphatic hydrocarbons	2,2-Dimethylpentane	C_7H_{16}	5686.4	10693.3			
	Nonanes	C_9H_{20}	0.0	0.0			
	Decanes	$C_{10}H_{22}$	0.0	0.0			
	Undecanes	$C_{11}H_{24}$	0.0	0.0			
Polycyclic hydrocarbons	Decahydronaphthalene	$C_{12}H_{18}$	0.0	0.0			
	Methyl-decahydronaph-thalene	$C_{13}H_{20}$	0.0	0.0			
Monocyclic aromatic hydrocarbons	Benzene	C_6H_6	961.8	92.7	32000	194712	
	Toluene	C_7H_8	582.4	182.1	188000	6023.9	41414
	Ethylbenzene	C_8H_{10}	56.6	0.0	434000	2602.7	2602.7
	m+p –Xylene	C_8H_{10}	190.2	22.4	434000	86757.2	
	Styrene	C_8H_{10}	166.7	0.0	434000	85120.3	

[a] Units are referred to standard conditions: T = 25°C and P = 1 atm.

[b] Odour Detection Threshold.

[c] Odour Recognition Threshold.

EXPERIMENTAL LAB DATA OF GASES AND ODORS (3/3)

Table 2. Mean emission levels of selected major inorganic compounds during the firing process and maximum limits allowed in special wastes incinerators in Catalonia [a].

Pollutant	Units	Clay/sludge brick	Clay brick	Limit allowed [b]
Particles	mg Nm^{-3}	48.3	11.4	20
SO_2	mg Nm^{-3}	43	8.4	200
CO	mg Nm^{-3}	83	26	125
NO_x	mg Nm^{-3} NO_2	811	805	616
HCl	mg Nm^{-3}	112	0.7	60
HF	mg Nm^{-3}	1.2	1.6	4
Cd+Tl	mg Nm^{-3}	0.007	n.d.[c]	0.1
Sb+As+Pb+Cr+Co+ +Cu+Mn+Ni+V+Sn	mg Nm^{-3}	0.44	0.02	1

[a] Units are referred to normal conditions: T = 0°C, P = 1 atm, 11 v.% O_2 and dry gas.

[b] Decree 323/1994 of the Generalitat de Catalunya that regulates the facilities for waste incineration and determines their atmospheric emission limits. Values correspond to the strictest limits, i.e., those applicable to special waste incinerators (DOGC, 1994).

[c] "not detected".

GASES AND ODORS DATA IN AN INDUSTRIAL TEST

- VOCs obtained from an industrial test were not the same than in the lab (conditions were different).

- 57 compounds detected. The most significant ones were:
  - benzene (C_6H_6) : 1172 mg/Nm^3
  - dimethyl disulfide ($C_2H_6S_2$) : 1383 mg/Nm^3
  - toluene (C_7H_8) : 926 mg/Nm^3
  - 4-methylpentanenitrile ($C_6H_{11}N$) : 697 mg/Nm^3
  - benzonitrile + isociane-benzene ($C_7H_5N + C_7H_5$) : 1003 mg/Nm^3

- No dioxins or furans were detected due to a residence time of several hours at temperatures >1000 °C

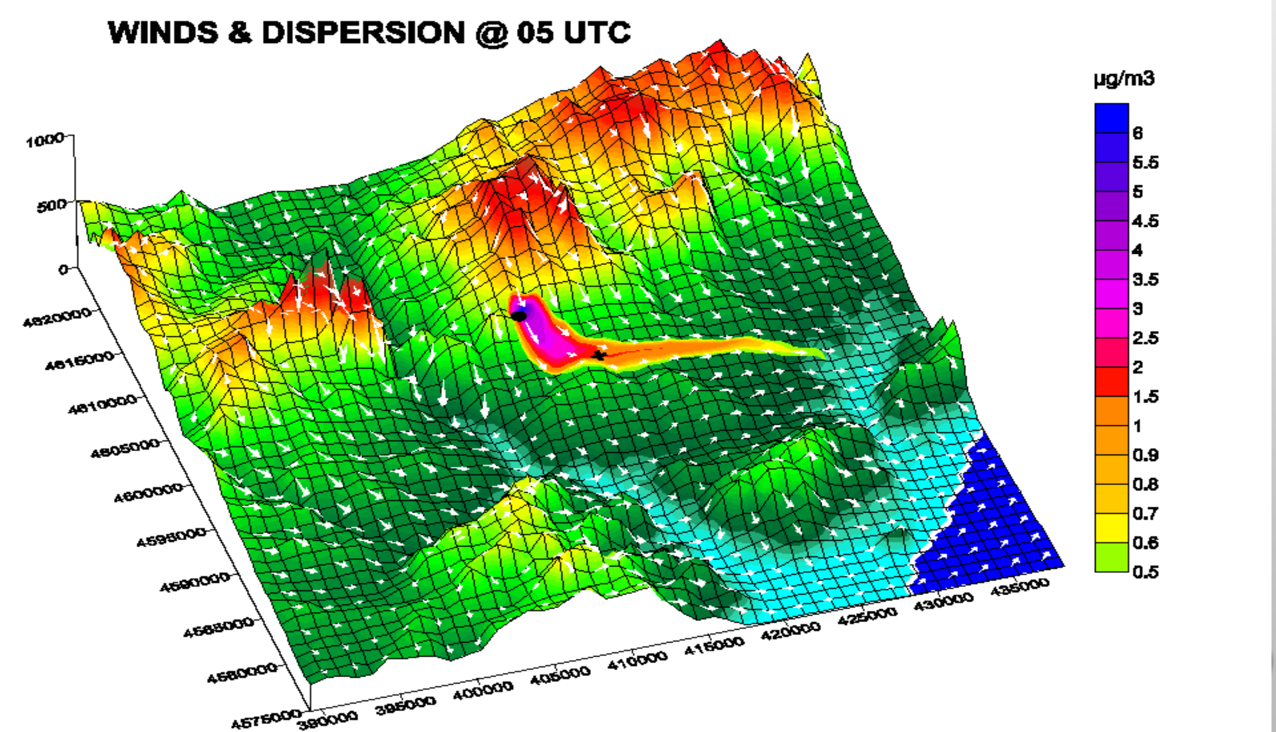
- Odors were similar to those in burning of textile materials (rags); in certain weather conditions must be corrected.

GUIDELINES (1/2)

- On the workplace : careful handling of wastes; use of mask and gloves; tower for washing gases; cyclones for removing particles; system of gas/gas exchanger and post-combustion cycle; biological filters or others for removing odors and other systems recomended by EPA and EU regulations.

GUIDELINES (2/2)

- Regarding the plant location (either new or adapted from a pre-existing one): simulation of air dispersion pollutants.
- Monitoring emissions/immissions (particles, SO_2, CO, NO_X, HCl, odors, etc).
- Information policy.



CONCLUSIONS

- Production of ceramic materials by inerting sewage sludge is a solution for removing pathogens and vitrifying heavy metals into ceramic matrix.
- Production of ceramic material for construction from clay/sewage sludge can achieve a double goal: *final and secure disposal of a hazardous waste and its valorization in a comercial product (clay bricks).*
- Compared to incineration or gasification thermal processes, *pyrolysis* in ceramic matrix may be the best option of valorization of sewage sludge.
- For the implementation of an industrial production, lab studies should be carried out, since sludges (as well as clays) have very varying characteristics depending of their site of origin. The application of the regulations of each country, as well as the existence of technologies avalaible for the treatment of gases, odors and particulates, would allow a clean production in accordance with legal standards.