WASTE MANAGEMENT THERMAL TREATMENT

Four main tasks for an air-pollution-control system:

- Dust / fly ash removal
- Neutralization of acid gases
- Removal and destruction of dioxins/organic pollutants
- Removal of Hg
- Removal of NO_x



Around the world: critical components

Typical concentration ranges and air emission limits (daily averages)

	Raw gas ^a	EU ^b	USA ^c	China ^b	Japan ^d
со	<10-30	50	100	150	50
TOC	1-10	10			
Dust	1000-5000	10	24	80	10-50
HCl	500-2000	10	25	75	15-50
HF	1-10	1			
SO ₂	150-400	50	30	260	10-30
NOx	200-500	200	150	400	30-125
Hg	0.1-0.5	0.05	0.08	0.2	0.03-0.05
Cd	0.1-0.5	0.05 ^e	0.02	0.1	
PCDD/F ^f	1-10	0.1	0.3	0.1	0.1

 $a mg/m^3$.

- ^b 273 K, 101.3 kPa, 11 vol% O₂.
- ^c 273 K, 101.3 kPa, 7 vol% O₂.
- ^d 273 K, 101.3 kPa, 14 vol% CO₂.
- e Cd + Tl.
- f ng(I-TE)/m³.

Around EU: critical components

	ma/m ³	European	Germanv ^b	The
		Union ^a		Netherlands ^c
	Daily average values based on on	-line meas	surements:	
	ТОС	10	10	10
	Dust	10	10	5
ſ	HCI	10	10	10
	HF	1	1	1
L	SO ₂	50	50	40
	NO _x	200	200	70
	CO	50	50	50
	Average values (sampling period	0.5-8 houi	rs):	
ſ	Cd+TI	0.05	0.05	0.05
	Hg	0.05	0.03	0.05
	Sb+As+Pb+Cr+Co+Cu+Mn+Ni+ V	0.5	0.5	
L	As+Cd+Co+Cr+benzo(a)pyrene		0.05	
	PCDD/F (ng I-TEQ/m ³)	0.1	0.1	0.1

New limits

Inquinante	BAT	BAT	D.Lgs. 152/06	D.Lgs. 152/06	Unità di misura
	Maggio 2017	Maggio 2017	(medie 10 minuti)	(medie giornaliere)	
	(medie semi-orarie)	(medie giornaliere)			
Polveri	30,00	5,00	-	10,00	mg/Nm ³
Cd+Tl	-	0,02	-	0,05	mg/Nm ³
sommatoria metalli	-	0,30	-	0,50	mg/Nm ³
HCl	60,00	8,00	-	10,00	mg/Nm ³
HF	4,00	1,00	-	1,00	mg/Nm ³
SOx	200,00	40,00	-	50,00	mg/Nm ³
NOx	400,00	180,00	-	200,00	mg/Nm ³
СО	100,00	50,00	150,00	50,00	mg/Nm ³
NH ₃		15,00	-	30,00	mg/Nm ³
TOC		10,00	-	10,00	mg/Nm ³
diossine		0,06	-	0,10	ng/Nm ³
diossine simili		0,08		0,10	ng/Nm ³
IPA		0,01	-	0,01	mg/Nm ³
Hg		25,00	-	50,00	$\mu g/Nm^3$

Combustion products

All elements are generally converted into oxides:

- C \rightarrow CO₂, CO, PAH or soot
- S -> SO₂
- N -> NO + small amounts of NO₂, N₂O
- CI, Br, F -> HCI, HBr, HF
- Volatile metals (Hg, Tl, Cd, but also As, Sb, Pb and Zn) evaporate as chlorides. When the temperature decreases (from >850 C to about 150-180 C), metals condense on fly ash particles (except Hg)

Air pollution from open burning





Air pollution from open burning



Source: US EPA and National Academy of Science

Aim of the lecture

Present an exercise in order to discuss:

- how waste composition and quantity influences the APC systems (PREVENTION);
- a consolidate sequence of treatments (Padua Plant);
- some criteria for dimensioning;
- the material flows from the systems (reagents, residual solids, etc.);

APC system



WM Thermal Treatment

Air Pollution Control

Process parameters for the treatment units

Which parameters for the dimension?

- Waste quantity and composition
- Temperature
- Retention time in reactors
- Quantity and typology of sorbants
- Drop preassure calculation
- Velocity of flue gas
- ph for chemical absorption process

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Brunner, P.H., Rechberger, H., 2015. Waste to energy - key element for sustainable waste management. Waste Manag. 37, 3–12. https://doi.org/10.1016/j.wasman.2014.02.003



Typical mass flows through a waste to energy facility equipped with dry (ESP) and wet air pollution control systems, in **kg per kg of MSW**. In addition to the flows presented in this figure, **about 5 kg of air** are required for combustion, increasing the amount of flue gas by the same extent

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Waste capacity	300,00 t/day
Lower heating values (LHV)	3.000,00 Kcal/kg
Moistere	30,00 %

1) Estimate the flow of Flue gas (Nm³/h)



- Chemical reaction
- C_xH_y +a (O₂+3.76 N₂)→ b CO₂+c CO+d O₂+e H₂O+ f N₂



Semiempirical relationship (as the Rosin-Fehling expression)

 $Vg = 0.89^{(LHV/1000)} + 1.65 (Nm^{3}/kg_{MSW})$

- Va = 1,01*(LHV/1000) + 1,65 (Nm³/kg_{MSW})
 - Similar plants

real volume of air: Vr = Va + Ve real volume of stack gas: Vf = Vg + Ve Where: Va= volume of stechiometric air Ve = volume of excess air (Nm3/kg); Vg = volume of gas (Nm³/kg); e% = Ve/Va * 100

The measured flow is 86630 Nm³/h

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6.000-10.00 Nm³/ton

APC system - INPUT



2) Estimate the flow at the reference conditions ($H_2O=U=0.0$ %; $O_2=11.0$ %)

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Flow at the reference condition

Actual condition

 $H_2O=U= 13.1\%$ $O_2= 8.47\%$

Dry condition

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H_2O=U= 0.0 \%

O_2= 9.75 \%

0_2 = O_{2,act}/(1-U_{act})
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O₂ =11% condition

H₂O=U= 0.0 % O₂= 11.0 %



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Flow at the reference conditions

Parameter	UNIT	Combustion chamber - OUT	Fabric filter 1 - IN	Fabric filter 1 - OUT	Fabric filter 2 - IN	Fabric filter 2 - OUT	Heating unit - OUT	SCR - OUT	Cooling unit - OUT	Flue gas from stack
Flow T=0°C, P= 1 atm	Nm3/h	86,630.00	88,630.00	89,671.00	92,171.00	93,150.00	93,150.00	93,669.00	93,669.00	93,669.00
Flow dry; 11% O2	Nm3/h	84,715.48	84,710.78	84,690.67	84,629.57	84,625.84	84,625.84	85,452.36	85,452.36	85,452.36
Flow at actual condition	m3/h	149,521.49	152,408.50	155,611.90	158,973.16	162,259.12	172,065.39	175,175.25	152,772.14	151,997.68

			Raw gas ^a
Concentration of HCl in raw gas	877,00 mg/Nm3	<u>co</u>	<10-30
% Cloro in waste	0,60 % (w/w)	TOC	1-10
		Dust	1000-5000
Concentration of SO2 in raw gas	258,00 mg/Nm3	HCI	500-2000
% S in waste	0,09 % (w/w)	HF	1-10
		30 ₂	200-500
Concentration of HF in raw gas	10,00 mg/Nm3	Hg	0.1-0.5
% F in waste	3,00E-04 % (w/w)	Cd PCDD/F ^r	0.1-0.5 1-10
Concentration of dust in raw gas	3.000,00 mg/Nm3	^a mg/m ³ .	

3) What happens if the composition of waste changes?

Assume an increase of 50% for Chloro in the weight mass of waste (more PVC plastics)
Assume an increase of 50% of Sulfur in the weight mass of waste (for example tyres treatment)

MSW composition	%	C, %	Cl, %	F, %	Н, %	0,%	N, %	S, %	Cd, mg/kg	Cr, mg/kg	Hg, mg/kg	Pb, mg/kg	ash, %	moisture, %	LHV, MJ/kg
Organic fraction	35.0	15.49	0.20	0.00	2.51	13.62	0.76	0.03	1.80	12	0.057	11	4.89	62.49	4.85
Paper	25.0	30.97	0.11	0.00	4.65	34.07	0.37	0.03	1.90	25	0.047	11	7.80	22.00	10.84
Glass	6.0	0.43	0.03	0.02	0.01	1.08	0.87	0.13	2.60	370	0.007	430	96.43	1.00	-0.02
Plastics	15.0	60.61	0.67	0.00	9.29	8.21	0.72	0.04	16.00	120	0.072	170	6.45	14.00	25.63
Metals	3.0	0.42	0.18	0.01	0.02	0.83	1.04	0.08	4.40	800	0.23	2300	96.43	1.00	-0.02
Aluminum	1.0	0.42	0.18	0.01	0.02	0.83	1.04	0.08	0.95	80	0.26	37	96.43	1.00	-0.02
Wood and textiles	4.0	39.32	0.05	0.00	5.14	33.16	1.53	0.08	2.25	197.5	0.027	220.5	2.74	18.00	14.92
Bulky waste and WEEE	11.0	21.97	0.52	0.00	3.56	16.74	0.94	0.14	57.00	630	1.8	460	23.63	32.50	8.06
TOTAL	100.0	26.29	0.27	0.00	4.03	17.78	0.73	0.05	10.2	152.7	0.3	186.7	17.0	33.9	9.7

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CI contained in the burned waste: $0.6\% \times 300/100 = 1.8$ ton/day HCI produced: $1.8 \times$ HCI/CI = $1.8 \times 36.5/35.5 = 1.85$ ton/day

The concentration of HCl in the flue gas, derived from solid mass balance, is $1.85 \times (10^9/24)/84715 =$ 910 mg/Nm³ (very closed to the real measured value= 877 mg/Nm³).

If we assume **an increase of 50%** for Chloro in the weight mass of waste (more PVC plastics), the Cl contained in the burned waste = $0.9\% \times 300/100 = 2.7$ ton/day and the concentration of HCl in the flue gas becomes 1365 mg/Nm³ (**1,5 times more!**).

Acid gas removal

Wet scrubbing systems in two stages:

- Acid scrubber
- Neutral scrubber
- (Fly ashes are typically removed before wet scrubbers)

Dry or semidry systems in one stage (Fly ashes are often removed after acid gas neutralization)

In dry and semidry systems, neutralization agent is sprayed into the flue gas and then removed in a later (fabric) filter.

- Typical reagents are:
 - CaCO₃ (calcium carbonate)
 - Ca(OH)₂ (calcium hydroxide; hydrated Lime; slaked lime)
 - NaHCO₃ (sodium bicarbonate)
- Dry process injects reagent as powder into flue gas
- Semi-dry process injects reagent as a slurry
- Neutralization processes mainly occur on filter surfaces

Neutralisation of acid gases

- \succ Ca(OH)₂ + 2HCl \rightarrow CaCl₂ + 2H₂O
- $\succ Ca(OH)_2 + 2HF \rightarrow CaF_2 + 2H_2O$

 $\succ Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$

4) Estimate the stechiometric quantity of $Ca(OH)_2$ (Calcium hydroxide or lime) in kg/h to neutralize SO₂, HCI and HF considering the following efficiency (E):

- HCl \rightarrow E=0,82
- SO₂ \rightarrow E=0,77
- $HF^{-} \rightarrow E=0,7$

5) Estimate the residual solid ($CaCl_2$ Calcium Chloride + $CaSO_4$ Calcium Sulfate+ CaF_2 Calcium fluoride) quantity from the gas neutralization

6) Why in your opinion the highest efficiency is for HCI removal?

7) Estimate the concentration of acid gases after the dust removal device

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Air Pollution Control

Unit "A". HCl reduction

Concentration of HCI in raw gas	877.00	mg/Nm3
Vg (dry condition; 11%O2)	84,715.48	Nmc/h
HCI emission	877*84,715.48*24/1000*1000=1,783.09	Kg/d
% reduction	0.82	%
Quantity of HCI to neutralize	1,783.09*0.82=1,457.78	Kg/d
MW CI	35.45	g/mol
MW HCI	36.46	g/mol
MW Ca(OH) ₂	74.09	g/mol
MW CaCl ₂ (Calcium Chloride - solid)	110.98	g/mol
The minimum amount of adsorbant $(Ca(OH)_2)$ for complete neutralization of HCl	0.5*(1,457.78/36.46)*74.09=1,481.17	Kg/d
Production of Calcium Chloride (CaCl ₂)	0.5*(1,457.78/36.46)*110.98=2,218.66	Kg/d

Unit "A". Dry injection - solution

4) Estimate the stoichiometric quantity of $Ca(OH)_2$ (Calcium hydroxide or lime) to neutralize SO_2 , HCI and HF considering the following efficiency (E):

- $\quad HCI \rightarrow E{=}0{,}82$
- SO₂ \rightarrow E=0,77
- HF \rightarrow E=0,7

Use the stoichiometric ratio from neutralisation reactions. For the real application, the dosage can be increseed considering problem as competitive reactions:

$$CO_2 (gas) + Ca(OH)_2 \rightleftharpoons CaCO_3 + H_2O$$

 $CO_2 = 400 \text{ ppm in air}$

Considering the approach used for the HCI removal, we obtain the following stoichiometric amount of adsorbants for the complete neutralization of acid gases:

- HCI \rightarrow 1,481.17 kg/d
- SO2 \rightarrow 465.57 kg/d
- $HF \longrightarrow 26.35 \text{ kg/d}$

The total amount is 1,973.09 kg/d.

Assuming a dosage ratio of 3 respect the stoichiometric quantity we obtain: 5,919.28 kg/d = 246.64 kg/h

Unit "A". Dry injection - solution

5) Estimate the residual solid ($CaCl_2$ Calcium Chloride + $CaSO_4$ Calcium Sulfate+ CaF_2 Calcium fluoride) quantity from the gas neutralization Considering only the stoichiometric ratio for the neutralisation, the quantity (waste) is 3.129,68 kg/d

6) Why in your opinion the highest efficiency is for HCI removal? Compare the pka of acid gas

- pKa HCI= -8
- pKa H₂SO₃= 1.9
- pKa HF= 3.17

7) Estimate the concentration of acid gases after the dust removal device Use the penetration factor ($P_t = 1 - \eta = 1 - E$)

- HCl \rightarrow E=0.82 \rightarrow Cout = 877 (1-0.82) = 160 mg/Nm3
- SO2 \rightarrow E=0.77 \rightarrow Cout = 258 (1-0.77) = 60 mg/Nm3
- HF \rightarrow E=0.70 \rightarrow Cout = 10 (1-0.70) = 3 mg/Nm3

A competitive process in dry injection, that we want to avoid, is represented by: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Considering the following information: Flow of flue gas = 86,630.00 Nmc/h (normal condition: P=1 atm; T=0° C) Flow of flue gas = 149,521 mc/h (actual condition: P=1 atm; T=195° C) Concentration of $CO_2 = 8.21 \% \text{ v/v}$

8) Estimate the flow of CO_2 (kg/h) in the flue gas

9) What will you suggest to enhance the neutralization of the acid gases?

8) Estimate the flow of CO_2 (kg/h) in the flue gas Referring to normal condition (P=1 atm; T=0° C), the flow of CO_2 is 7112 Nm³/h= 14134 kg CO_2 /h

9) What will you suggest to enhance the neutralization of the acid gases? The optimum removal efficiency occurs in restricted T ranges: 120-150 ° C. We work with a higher temperature, therefore the efficiency is not maximized. A solution could be to use bicarbonate that works better at 190° C, but it is more expensive.

10. Calculate the minimum pipe (or duct) **volume.**

Design a DSI – dry sorbent injection system - of an alkaline base in a flue gas duct. Are given the following data:

- Temperature at the injection point: T=200° C (approximated)
- Preassure: 1 atm (approximated)
- circular duct;
- duct residence time, t_r: 1.0 seconds;
- flue-gas velocity, v: 20 m/s.

Calculate the duct diameter (D) and the required duct length (L), that is the distance required between the injection point and the downstream particulate control device.





Because of short residence time - both for mixing and reaction - only fast reactions/processes can occur inside the reactor. The use of **fine solid particles** and **high temperature** is a good starting point.

A sufficient length of ductworks is necessary to ensure a sufficient residence time.

In order to increase the reaction volume, the one of FF could be used because most of it is empty

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Unit "A". Dry injection – high velocity

ADVANTAGES

- Small ducts, lighter ducts
- Less dust/particulate deposition

DISADVANTAGES

- Problem of noise
- Drop pressure increases $\Delta P \rightarrow v^2$
- Erosion due to the dust



The best point for the injection is the venturi (restriction) area. In venturi the velocity could be 100 m/s

Unit "A". Dry injection – high velocity

Reactor flow rate (normal condition)	86.630,00Nmc/h	
Temperature at the injection point Preassure	200,00°C 1,00atm	(Approximated) (Approximated)
Reactor flow rate (real condition) at T=200° (G)	150.095,20mc/h	
	41,69mc/s	
Duct residence time	1,00s	
Resident volume	41,69mc	
Flue-gas velocity (v)	20,00m/s	velocity: 10-20 m/s
Area (G/v)	2,08mq	
Diameter (A = π D2/4)	1,84m	
Lenght	20,00m	

11. Calculate the number of bags required for a pulse-jet baghouse with the following process information:

- $Q = 152,408.50 \text{ m}^3/\text{h}$
- Temperature of exercise: 190°-200°C
- Filtration velocity = 0.86 min/s
- Can velocity = 1 m/s

Bag characteristics: Bag diameter = 150 mm Bag height =6500 mm Fabric loading = 750 g/m² Material = Polytetrafluoroethylene (PTFE)



Vf= filtration velocity= 1m/min

With an high collection efficiency as a «given», baghouse design involves optimizing the filtering velocity to balance capital costs (baghouse size) versus operating costs (pressure drops).

Pressure drop and air-to-cloth ratio are the major design parameters in bag-house design.

Flow (qa)	152,408.50	m3/h	actual condition
	42.34	mc/s	
Temperature actual	191.00	°C	
Filtration velocity (v)	0.86	m/min	Reference 1 m/min
	0.01	m/s	
Filter surface	2,953.65	mq	2940 mq from project
Bag diameter	150.00	mm	
Bag height	6,500.00	mm	
Filtration area of one single bag	3.06	mq	
Number of bags	964.77	ad	960 from project

12. Calculate the total dust removed by the fabric filter



You have to consider the following fluxes:

- Emission dust (concentration= 3076 mg/Nm3)
- Calcium Chloride
- Calcium Sulfate
- Calcium Floride
- Excess of CaOH₂ (calcium hydroxide). Use a dosage ratio of 3.
- PAC (use the dosage of 100 mg/m³)

Flow (qref)	88.630,00 Nm3/h	
	84.710,78 Nm3/h	referred to dry condition and O2 concentration 11%
Concentration of dust in raw gas	3.076,00 mg/Nm3	concentration range: 1000-5000 mg/Nm3
Emission dust	260,57 kg/h	
Calcium Chloride	92,44 kg/h	
Calcium Sulfate	35,65 kg/h	
Calcium Floride	2,31 kg/h	
Excess of CaOH2	164,42 kg/h	
PAC	8,66 kg/h	
Total solid	564,06 kg/d	reagent + PAC + dust
Efficiency FF	99,50%	
Solid residual from 1° dry injection + FF	561,24 kg/h	
	13.469,78 kg/d	
Solid residual from 1 ton of waste incinereted	44,90 kg/ton-waste	

Unit "C". Dry injection with NaHCO₃

O ADVANTAGES

- reaction equilibrium more favorable with respect to lime: higher efficiencies, less required excess reagent
- easier operation with respect to lime
 - less difficulties of bicarbonate transport, movement and addition
 - no requirements of recycling separated product
- potential for reagent regeneration/recycle
- reduction of moisture effects due to higher temperatures at fabric filter inlet

O DISADVANATGES

- higher cost of reagent
- higher operating temperature required for reagent activation (170-190°C)

Unit "E". SCR DE-NOx



 $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O(i)$ $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O(ii)$ $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O(iii)$ **13.** Estimate the stoichiometric amount of ammonia for reducing NOx

- Considering a concentration of NOx equals to 400 mg/Nmc
- The removal efficiency is 83%.

Four **undesirable** oxidation reactions can also take place:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O(iv)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O(v)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O(vi)$$

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3(vii)$$
The oxidation of the equation of the equa

The oxidation of SO_2 is unwanted because SO_3 mists are harder to remove in FGD scrubbers than SO_2 gas

Unit "E". SCR DE-NOx

 NO_{χ} is represented by the 100% of NO_2 .

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6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O(ii)
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We can apply the approach seen into a previous lecture. We obtain a quantity of **57,68** kg/h in solution 24%W/W.

Cost of reagents

REAGENT	Qua	ntity	Price (*)	Total
	kg/h	kg/d	Euro/ton	Euro/d
Ca(OH) ₂ (calcium hydroxide)	246.64	5919.28	48.00	284.13
NaHCO ₃ (sodium bicarbonate)	55.00	1320.00	750.00	990.00
Activated carbon	18.00	432.00	240.00	103.68
NH_3 in solution 24% (w/w)	57.68	1384.43	140.00	193.82
TOTAL	1571,63			

Notes:

(*) Commercial value on 2019

Values calculated in the present exercitation

Pressure drop



Stack

$$\Delta h = \frac{V_s D}{u} \left(1.5 + 0.00268 PD \, \frac{(T_s - T_a)}{T_s} \right)$$



 $\Delta h =$ plume rise, m V_s = stack exit velocity, m/s D = stack diameter = 2 mu = wind speed = 4 m/sP = pressure = 1 atm T_s = stack gas temperature = **170**°*C* T_a = ambient temperature, K = **10**°*C*

14. Estimate using the Holland formula:

- The plume rise Δh (m)
- The effective stack height H (m)

Stack

$$\Delta h = \frac{V_s D}{u} \left(1.5 + 0.00268 PD \, \frac{(T_s - T_a)}{T_s} \right)$$



 $\Delta h = \text{plume rise, m}$ $V_s = \text{stack exit velocity, m/s}$ D = stack diameter = 2 m u = wind speed = 4 m/s P = pressure = 1 atm $T_s = \text{stack gas temperature} = 170^{\circ}C$ $T_a = \text{ambient temperature, K} = 10^{\circ}C$

Estimate using the Holland formula:

- The plume rise Δh (m) = 23.3 m
- The effective stack height H (m) = 103,3 m

APC System



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POSSIBLE CONFIGURATIONS

16. Why is it better to have SCR as final unit?



POSSIBLE CONFIGURATIONS



17. Is the present configuration correct?

POSSIBLE CONFIGURATIONS



Ultrafine (< 0.1 µm) particulates



Reference: Stefano, P., Michele, P., Consonni, P.S., Coghe, P.A., Apostoli, P. Pietro, Sperimentale, M., Bergamaschi, P.E., Medica, C., 2010. Emissioni di Polveri Fini e Ultrafini da impianti di combustione. Sintesi finale.

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Air Pollution Control