Recherche et Développement

Gas adsorption capacity of Municipal Solid Waste Incineration Bottom Ashes based materials

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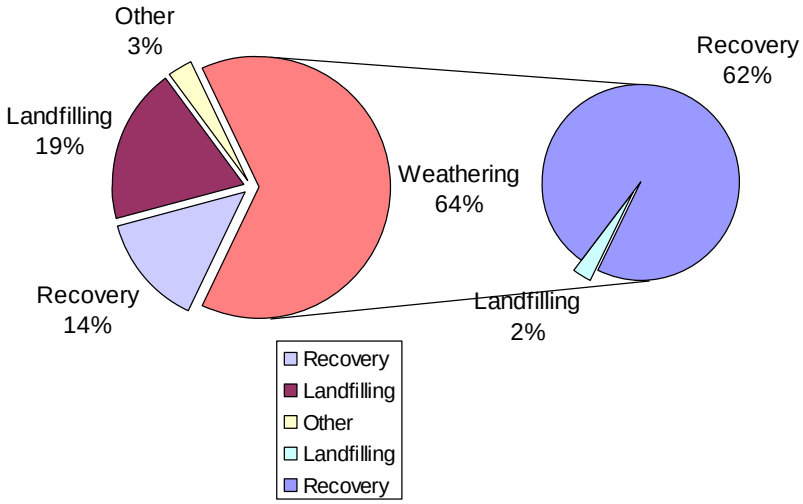
VEOLIA ENVIRONNEMENT

INTRODUCTION

- Municipal Solid Waste Incineration Bottom Ash : MSWI BA
- In 2007, in France (SVDU*) :
  - 2 400 KT produced MSWI BA
  - 80% valorized
  - 20% landfilled



- To improve the recovery and be able to adapt the MSWI BA recovery to new regulation: need of better knowledge of the residues' properties

* SVDU : Syndicat national du traitement et de la Valorisation des Déchets Urbains et assimilés (French Confederation of Waste-to-Energy Plants)

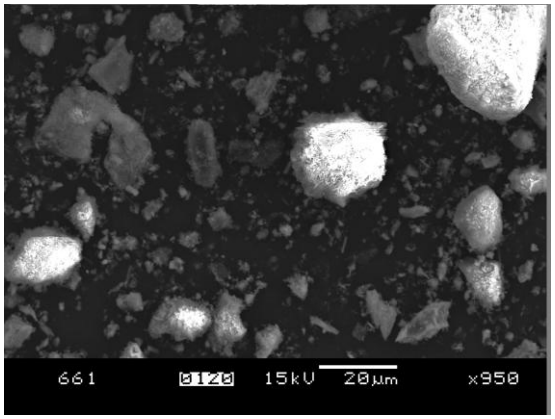
INTRODUCTION

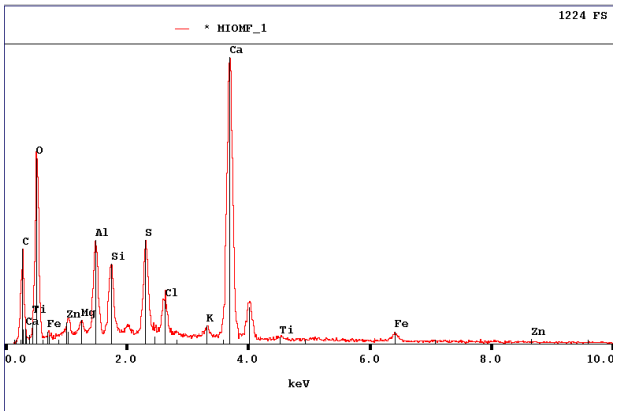
- Known properties of MSWI BA:
  - ➔ Geotechnical properties
    - Valorization in road construction
  - ➔ Gas adsorption properties
    - CO_2 (Rendek et al, 2006)
    - H_2S (Tirnoveanu, 2004)
- Presentation of a study focused on H_2S adsorption properties of BA-based materials
- Adsorption=process where molecules of a fluid are attached to the surface of a solid (physically or chemically)

MATERIALS and METHODS

- 2 materials based on MSWI BA (>80%)
- Added materials: wastes like sludge or ash
- Adsorption properties carried out in the lab GEPEA (Ecole des Mines of Nantes, France)

Methodology to evaluate the adsorption





- Physico-chemical characterisation:
  - ➔ Elemental and chemical compositions
  - ➔ Scanning electron microscopy coupled to energy dispersive X-ray spectrometry
  - ➔ Porosity determination (density, BET specific surface, porosity volume, porosity distribution)
  - ➔ And surface pH
- gas adsorption isotherms and kinetics performed in a static reactor:
  - ➔ Control of the gas initial concentration in air, temperature and relative humidity
- gas breakthrough test in fixed bed reactor:
  - ➔ to evaluate breakthrough time and capacities
  - ➔ Control of inlet concentrations of gas and water vapour and of a fixed air flow rate

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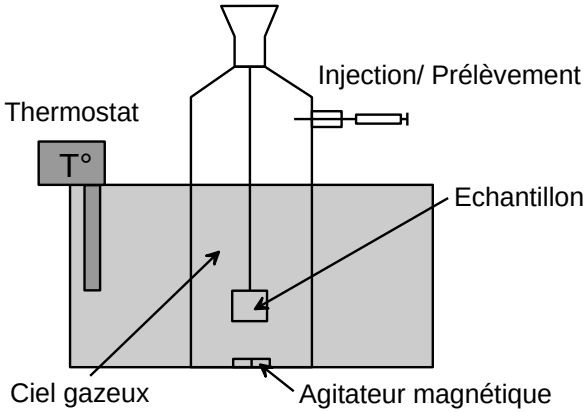

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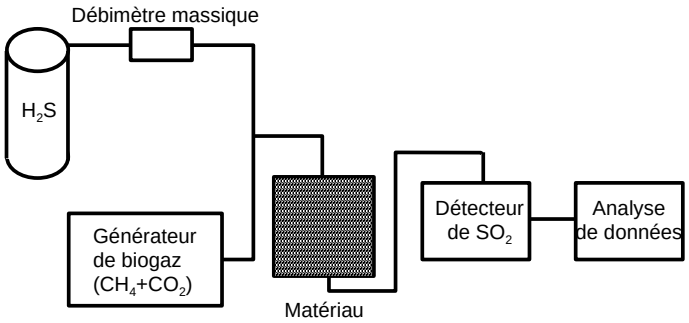

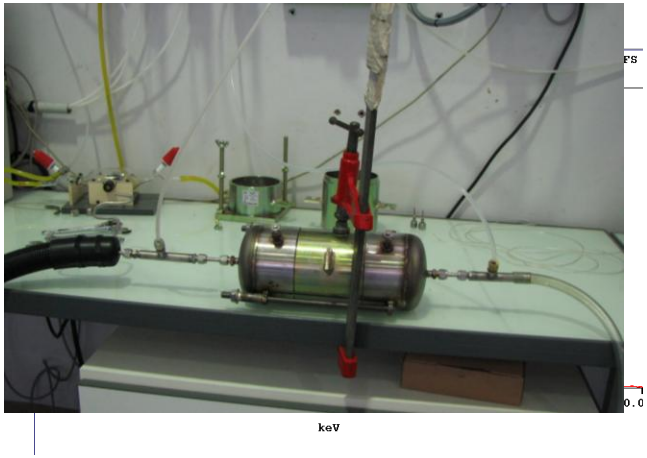

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RESULTS: Physico-chemical properties of MSWI BA-based materials

- Similar results for both materials in terms of average porosity properties, chemical composition and surface pH if compared with commercial adsorbents such as activated carbon commonly used for gas treatment
  - ➔ Small specific surface, macroporous materials
  - ➔ No CH_4 or VOC adsorption forecast (need of physisorption in micropore volume)
- Basic surface pH at around 11
  - ➔ can favour H_2S solubility with water and then adsorption/reaction with surface functional groups of tested materials

	S_{BET} (m^2/g)	V_{macro} (cm^3/g)	V_{meso} (cm^3/g)	V_{micro} (cm^3/g)	Surface pH
MSWI BA-A	7	0.19	0.016	0.002	11.3
MSWI-BA-B	19	0.13	0.038	0.005	11.3
Commercial GAC	1090	/	0.097	0.312	8

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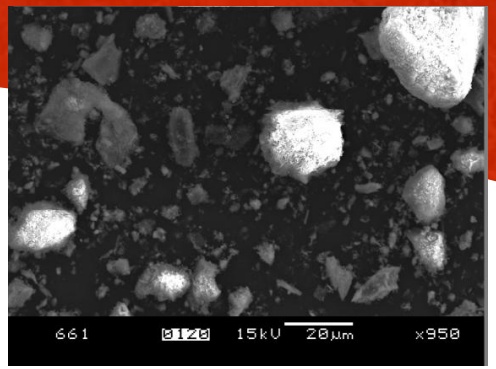


- Water content: 15-18%
- Mostly mineral (high ash content, low carbon content)
- Semi-quantitative elemental analysis of MSWI-BA materials performed using scanning electron microscopy coupled to energy dispersive X-ray spectrometry
  - ➔ available sites containing CaO or MgO (can be converted to their corresponding hydroxide chemical compounds (with water) and participate in hydrogen sulphide oxidation) – can be in competition with CO2
- Adsorption possibilities towards acid gas
  - ➔ Focus on H_2S

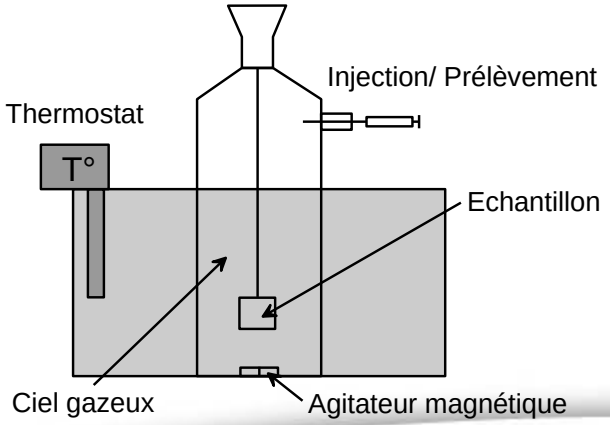
	% water content	%C	% H	% N	% $S_{inorganic}$	%O	% ash content
BA+A	15,6	4,04	0,82	0,10	n.d.	6,4	96,7
BA+B	18,4	4,42	1,09	0,19	0,97	7,7	89,8

RESULTS: static reactors

- Kinetics:
  - $C(t)/C_O=f(t)$
  - 80mg sample in a bottle filled with a controlled atmosphere (fixed temperature, moisture and concentration in $H_2S=C_0$). Gas sampling with time (t) to measure the H_2S remaining in the atmosphere (C(t)).
  - Contact time needed to adsorb the gas (t_c)

- Isotherm:
  - Qe=f(Ce)
  - a sample of a mass m is placed in a bottle filled with an atmosphere with a concentration C_0 of H_2S. After t_c, the concentration of H_2S at the equilibrium (Ce) is measured in the air and linked to the H_2S adsorbed quantity by the material at the equilibrium (Qe)
  - Material quantity needed to have a good adsorption

- Tested parameters
  - Air relative humidity (60%-100%)
  - With or without CH_4 (55% N_2 or CH_4)
  - Initial concentration of H_2S (2 to 5g/m^3)
  - Temperature (20-35°C)
  - Sample water content (optimum Proctor, 50%)



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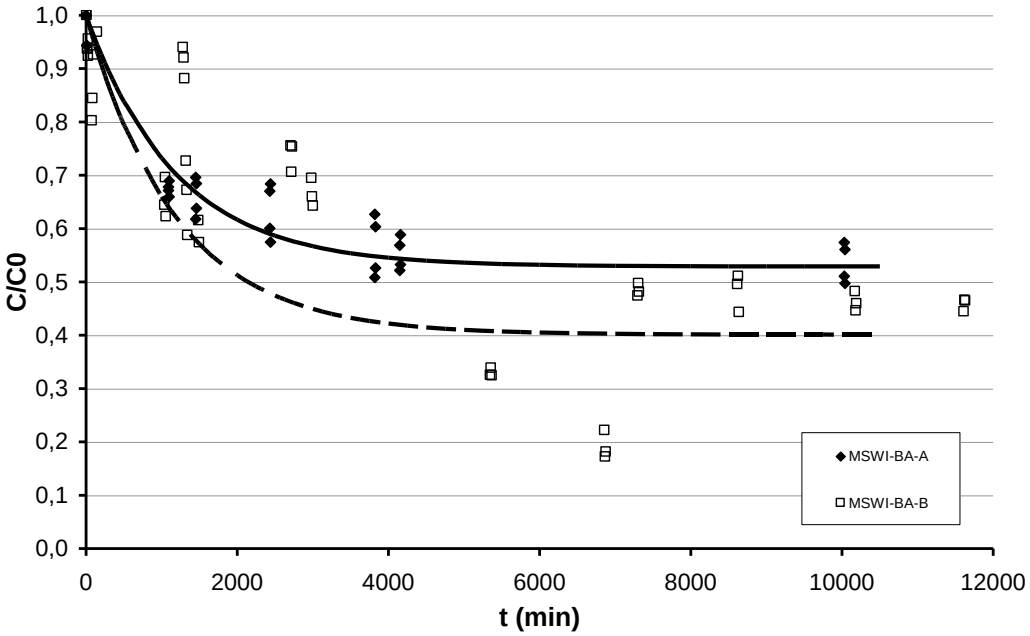

Gas composition: 45% CO_2 + 55% N_2, C_0=5000 mg/m^3, 60%HR, 35 C ; sample moisture: MSWI-BA-A = 18%wt, MSWI-BA-B = 26%wt

H_2S adsorption kinetic on studied MSWI-BA materials

- MSWI-BA-B material: slightly better performances regarding H_2S separation from gas (Qe=155mg/g instead of 129mg/g for A) due to a higher mesoporous volume
- Similar contact time needed (~19 hours)
- great influence of the global moisture: air humidity but mostly sample moisture, on H2S adsorption for both samples ;
- adsorption capacity similar to the one of some activated carbons but with necessary contact time much longer ;
- and confirmation that there is no competition between CH4 and H2S adsorption.

RESULTS: static reactors

	Water content	Air	C0 H_2S	Ce H_2S	Ce/ C0 H_2S	qe	Time constant
	% mass		mg/ m^3	mg/ m^3		mg /g	(hours)
BA+A	18,0	45% CO2, 55% N2, 60%HR, 35°C	5905	3124	0,53	129	19,33
BA+B	26,0	45% CO2, 55% N2, 60%HR, 35°C	5310	2130	0,40	155	19,17
BA+B	26,0	45% CO2, 55% **CH4**, 60%HR, 35°C	5100	2050	0,40	153	19,17
BA+B	50,0	100% air, **100%HR**, 20°C	4850	50	0,01	/	2,33
BA+B	50,0	100% air, 50%HR, 20°C	1978	400	0,2	52	1,50

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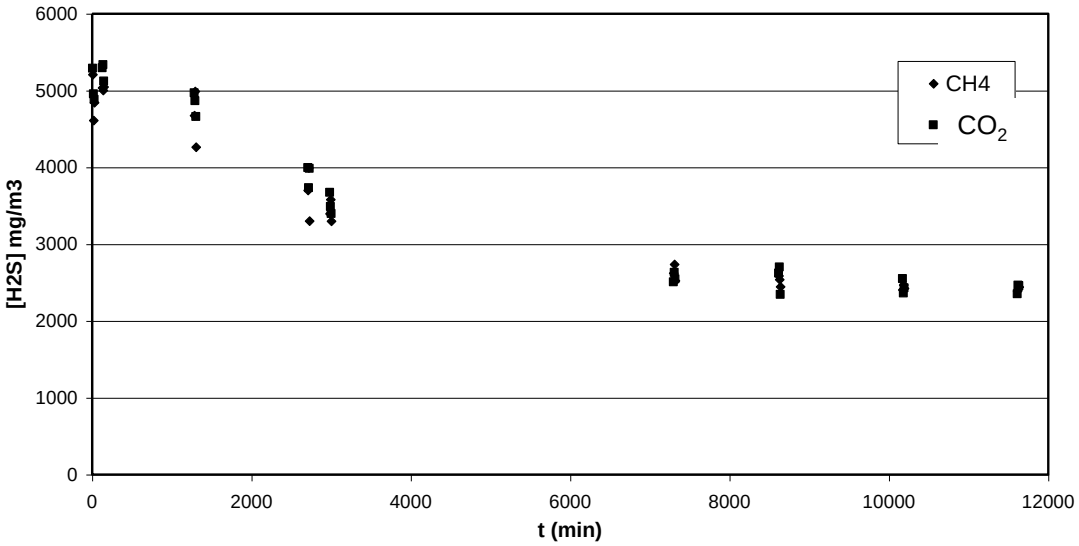

Gas composition: 45% CO_2 or CH_4 + 55% N_2, C_0=5000 mg/m³, 60%HR, 35 C ;
H_2S adsorption kinetic on MSWI-BA-B material containing 26%wt water

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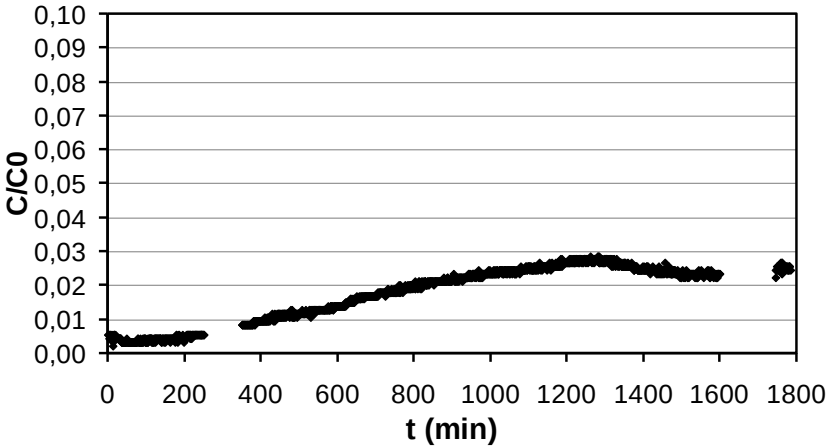
RESULTS: breakthrough tests

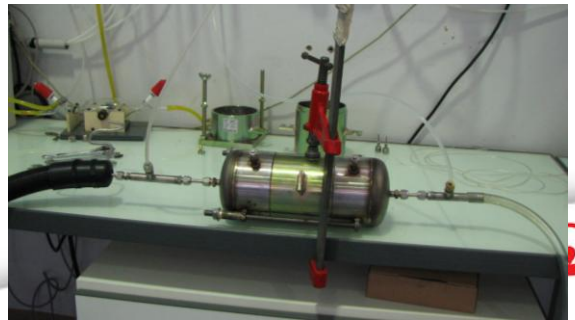


H_2S adsorption breakthrough curve on MSWI-BA-A material packed in a fixed bed (air flow: 0.017 m/s, C0=165 mg/m3, 60%HR, 25 C, 18%wt WC for the sample)

- Material MSWI BA+A compacted at the Proctor optimum in a column
- Air flow through the column and measurement of H_2S concentration at the outlet of the column during 30 hours
- High purification efficiency from the beginning but
- Residual H_2S concentration at the outlet of the gas treatment process

  ➔The MSWI-BA-A bed thickness is too low

➔ This MSWI-BA material exhibits very promising performances regarding H_2S removal from humid gas



Conclusions

- Good performances of MSWI BA-based materials to adsorb H_2S
  - ➔ Reduction of 99,5% of H_2S during the first 200min
- Long enough contact time needed
  - ➔ About 19h
- And presence of humidity in the material to allow chemisorptions
- Additional experiments could be performed with gas containing CO_2 to study the influence of CO_2 as competitor in involved chemical reactions