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Municipal waste pyrolysis (2)

Chlorine Capture by Addition of Calcium and Sodium-Based Sorbents

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ABSTRACT

Pyrolysis of municipal and industrial waste presently under development produces liquid, gaseous and solid fuels. Their utilisation as substitution fuels with regard to environment needs special attention and a strict control of the behaviour of chlorine content. Indeed, chlorine can be found either in pyrolytic gases or in the char. The aim of this paper is to analyse the different ways of entrapping the chlorine in the char in a leachable form by addition of sorbents during pyrolysis. Synthetic waste mixtures containing PVC and lead oxide are pyrolysed at laboratory scale with calcium and sodium-based sorbent. Mass and chlorine balances are presented using the different sorbents in various proportions. This article shows that 100% of the emitted HCl in the pyrolytic gases can be captured and leaching the char can capture up to 98% of the chlorine. Pilot scale runs with mixtures of wood, PVC and calcium carbonate or lime containing sludge confirm the interest of this approach. It is demonstrated that the chlorine elimination before energy valorisation of the pyrolysis derived fuels could simplify the flue gas cleaning devices.

1 INTRODUCTION

It is well known that, in municipal waste incinerators and in coal-based electric power plants, there is a need for sophisticated flue gas cleaning in order to eliminate contaminants such as solid particles, sulphur and nitrogen oxides, halogenated compounds and trace elements. Dry and/or wet alkaline processes are used, followed by an activated carbon treatment. These systems are well developed and discussed in literature [1–8]. However, with the environmental legislation being increasingly strict, the treatment processes are more complex so that operating costs become very expensive. In order to improve the overall plant performance, it is possible to reduce emissions by direct injections of sorbents inside the furnace before the gas cleaning steps. So, Endesa (Spain) added 30% of calcite to a high-sulphurous coal before burning in the fluidised-bed installation [9]. Adanez et al. [10] studied the sulfidation process of different calcium-based sorbents in an entrained-bed reactor. Courtemanche et al. [11] evaluated the capacity of sorbents such as calcium and magnesium carboxylic acid salts for the HCl capture during combustion. More recently, Fontana et al. [12] showed that selected additions during combustion and gasification of waste derived solid char could decrease heavy metals emissions. Therefore, it appears clearly that the role played by the alkaline sorbents during combustion and gasification is of prime importance.

Now, in the case of the municipal waste treatments, it is widely accepted that pyrolysis can be an attractive alternative to incineration, if the process is followed by an energy valorisation of the solid residue [13, 14]. Chlorine contained in wastes has a complex behaviour during pyrolysis. It evolves mostly as HCl under 350°C in the preliminary stage of the PVC thermal degradation [15]. Then competitive reactions take place and the chlorine can follow different paths, depending on the chlorine environment in the charge during pyrolysis [16]. We recently demonstrated that cellulose and lignin, usually present in municipal solid waste, interact differently with PVC during pyrolysis [17] and modify the chlorine distribution between the gaseous and solid phases. With a high lignin content in the waste, chlorine is entrapped in the char, but with a high cellulose content, chlorine concentrates in the hot pyrolytic gases.

It is important to guide the chlorine either in the gas or in the char outputs by selected additions, in order to fit with the requirements of the fuels end users. When the char during pyrolysis entraps the chlorine leachable form, it can be eliminated before further use. The effect on chlorine trapping by mixing alkaline reactants with waste during pyrolysis is studied.

Table 1 **Sorbent properties**

Sorbents	$CaCO_3$	$Ca(OH)_2$	Na_2CO_3	$NaHCO_3$
Supplier	Lhoist	Lhoist	Solvay	Solvay
Type	Lhocal EC90	Lhocal EH63	Light soda	Bicar
D_p (μm)*	< 90	< 63	< 250	< 45**
BET (m^2/g)	1–2	14–18		

* Size of sorbent particles (93–96%)

** Particles with Dp < 45 μm account for 90% – coated with 1% calcium stearate

2 EXPERIMENTAL

2.1 Materials

PVC was obtained by Solvay Company from recycled water bottles (particles size in the range of 1–5 mm): it contains 53% Cl (PVC chips with 56% Cl for pilot runs), 0.07% H_2O, 0.1% ashes with traces of 230 ppm Ca, 190 ppm Zn, 150 ppm Al, 150 ppm Si, 120 ppm Mg, 110 ppm Na, 37 ppm Sn and other minor elements. Four different powdered sorbents were tested in mixtures with PVC and their characteristics are given in Table 1. Fine granular quartz (60% withdiameter between 0.2 and 0.8 mm) from Merck Company was added to the charge for weight compensation.

Wood chips of a few millimetres contain about 37% water.

Sewage sludge from "Kläraranlage Schartsfeld, Germany" contains 122 kg/t of calcium and the water content is about 50%.

2.2 Pyrolysis experiments

2.2.1 Laboratory scale

All experiments were performed in a fixed-bed reactor [17] with the same amount of PVC (3 g) and with additions of different alkaline sorbents, in order to obtain different Ca or Na/Cl atomic ratios. Inert silicon dioxide was added in order to reach a total amount of charge of 15 g. Only the first experiment was made with PVC alone, in order to check the influence of quartz on the chlorine distribution.

The starting mixtures were heated at atmospheric pressure up to 500°C during 25 min (heating rate of 35°C/min).

The hot pyrolytic gases were carried out of the furnace by a nitrogen flow (0.4 dm^3/min). Condensable matter was recovered in cold

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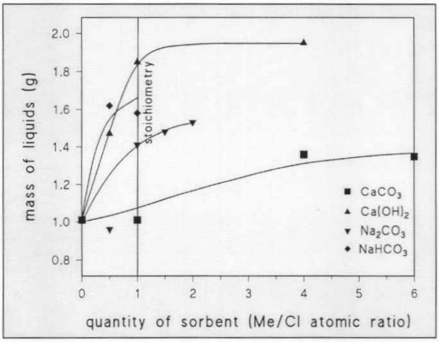

Fig. 1 Production of liquids during pyrolysis of PVC for different sorbent's additions

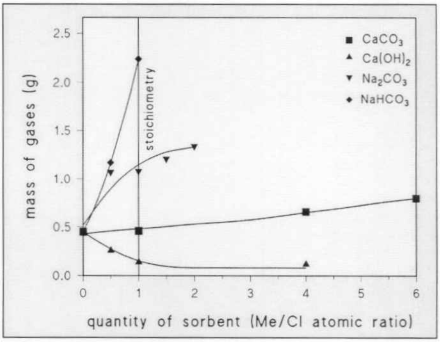

Fig. 2 Production of gases (excluding HCl) during pyrolysis of PVC for different sorbent's additions

traps and weighted. The uncondensed gases were washed (in water for HCl trapping) and collected for analysis. The mass of solid, condensable gases and hydrochloric acid were measured. The quantity of uncondensable gases was determined by difference.

2.2.2 Pilot scale

CUTEC pilot plant in Clausthal consists of the following main components:

- a 10 to 50 kg/h rotary kiln of a length over all of 5.8 m and a diameter of 300 mm (40 kW heated length of 3.6 m length),
- the pyrolytic residue is discharged through an electrically heated delivery chamber,
- the pyrolytic gas is directed from the kiln's delivery connection piece into a three-staged washing column filled with Raschig rings,
- the purified pyrolytic gas arrives after post cooling in the succeeding combustion chamber where it is burnt, along with natural gas for supporting the flame,
- the flue gas at 1200°C is cooled down and cleaned with sodium hydrogen carbonate and activated coal,
- the flue dust is separated by means of a cloth filter.

The material to be treated is delivered from the feeding shaft flooded with inert gas nitrogen into the kiln via a conveyor worm.

The operating conditions in the pilot plant rotary kiln can be varied among others by the following parameters:

- Composition of input material,
- Level and distribution of temperature,
- Residence time (mass flow, inclination and rotation),
- Mixing conditions,
- Variation of load,
- Insertion of additives.

At the hot gas output of the rotary kiln, a discontinuous gas sampling device is equipped with a so called-finger type cooler installed before a spiral cooler.

Another discontinuous gas sampling of the purified uncondensable pyrolytic gas is placed after the washing column.

Table 2 **Mass balance of PVC pyrolysis in presence of calcium and sodium based sorbents**

Samples	PVC g	Sorbent g	Quartz g	Char** g	Liquids g	Gases g	HCl g
PVC-alone	3.02	0	0	0.45	0.98	0.42	1.17
PVC-Q	3.03	0	12.01	0.41	1.01	0.45	1.16
$CaCO_3$ 1/2	3.06	2.27	9.73	2.95	1.01	0.46	0.91
$CaCO_3$ 2/1	3.01	9.01	3.04	9.79	1.36	0.66	0.21
$CaCO_3$ 3/1	3.00	13.51	0	14.36	1.35	0.80	0
$CaCO_3$ 2/1*	3.00	9.08	3.05	9.79	0.61	1.17	0.51
$Ca(OH)_2$ 1/4	3.00	0.83	11.17	1.62	1.47	0.26	0.48
$Ca(OH)_2$ 1/2	3.00	1.68	10.43	2.64	1.85	0.14	0.05
$Ca(OH)_2$ 2/1	3.01	5.41	6.65	6.35	1.95	0.12	0
Na_2CO_3 1/2	3.00	1.19	10.84	1.63	0.96	1.07	0.53
Na_2CO_3 1/1	3.00	2.38	9.62	2.63	1.41	1.08	0.26
Na_2CO_3 3/2	3.00	3.58	8.42	3.89	1.48	1.21	< 0.01
Na_2CO_3 2/1	3.00	4.76	7.24	4.89	1.53	1.34	0
$NaHCO_3$ 1/8	3.00	0.47	11.53	0.71	1.09	0.63	1.04
$NaHCO_3$ 1/4	3.00	0.95	11.05	1.05	1.39	0.73	0.78
$NaHCO_3$ 1/2	3.00	1.90	10.10	1.72	1.62	1.17	0.39
$NaHCO_3$ 1/1	3.00	3.78	8.22	2.96	1.58	2.24	< 0.01

* N_2 flow rate of 5 dm^3/min; ** Weight of solid residue after substraction of the quartz charge

2.2.3 Analyses

Leaching tests were performed on all residual solids: approximately 3 g of sample in 50 ml of water (10 g in 400 ml of water for pilot scale experiments) during 1 h at 50°C. Chloride anions were titrated in all solutions with silver nitrate (potentiometric titration).

Minerals present in the char before and after washing were determined by X-ray powder diffraction (XRD) on a Philips PW 1729 equipment (Cu Kα, 32 kV, 28 mA).

Ashes were analysed by a SEM Jeol JSM 820, coupled with an energy dispersion microanalysis device (EDAX 9100). The accelerating voltage was 20 kV.

Uncondensed gases were analysed on two Varian 3300 chromatographs (porapak Q and molecular sieve columns, catharometer detectors).

3 RESULTS AND DISCUSSION

3.1 Laboratory scale experiments

Without any additive, there are no significant differences between the results obtained for PVC and PVC-quartz mixtures neither on phase's distribution, nor on hydrochloric acid production (Table 2). Quartz is completely inert under these conditions. More than 70% of chlorine is recovered as hydrochloric acid. The remaining chlorine is probably in the condensable gas phase as organic chlorinated compounds (only traces of chloromethane and chloroethylene are observed in the uncondensable gaseous phase).

3.1.1 Phases distribution

The mass of pyrolytic solid, liquids, gases and HCl issued from the treatment of different PVC-additive mixtures are presented in Table 2 and illustrated in Figures 1 and 2 for the liquids and the gases (excluding HCl). For all experiments, the char fraction is given after subtracting the inert quartz mass.

For each sorbent used during pyrolysis of

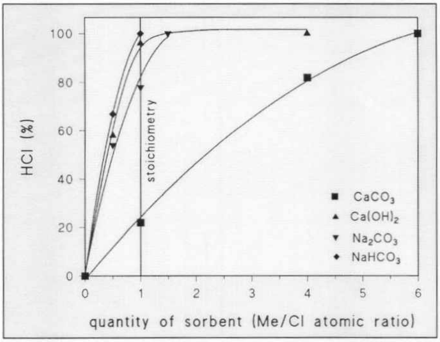

Fig. 3 HCl eliminated from the pyrolytic gases for different sorbent's additions

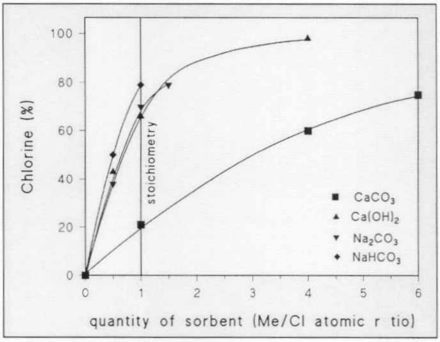

Fig. 4 Leachable chlorine from char for different sorbent's additions (% of chlorine input)

PVC, when the mass of the sorbent in the raw mixture increases, the mass of the char increases proportionally. This is due to the formation of the reaction products (calcium or sodium chloride) and to an excess of unreacted additives. Simultaneously, the liquid production also increases (Figure 1). The decarbonisation is enhanced when the presence of sorbent increases in the raw mixture.

For the uncondensable gases, the situation is quite different (Figure 2). $NaHCO_3$ and Na_2CO_3 produce a larger quantity of gases, because of the sorbent decomposition at a lower temperature than the other additives. With hydrated lime, a decrease of the gas production is observed, which is connected to the absence of CO_2 production and the formation of condensable water.

3.1.2 Chlorine capture

Chlorine has been determined as HCl in the pyrolytic gases and as leachable chlorine in the char (Table 3). The rest of the chlorine (18–28%) is distributed as non-leachable Cl in the char and as chlorinated compounds in the gases.

For the different sorbents, the percentage of chlorine found as hydrochloric acid in the hot gases is calculated from the HCl measured in the washing solution of the gases. By comparison with the 72% of chlorine found as HCl during pure PVC pyrolysis, the percentage of HCl eliminated from the pyrolytic gases is calculated and presented in Table 3 and Fig. 3 for different sorbents additions (various Ca/Cl or Na/Cl atomic ratios).

The leachable chlorine in the char is also included in Table 3 and presented in Fig. 4 in function of the quantity of sorbent.

With the use of sorbents, there is a significant decrease of the chlorine emitted as hydrochloric acid in the hot pyrolytic gases. The chlorine is found in a leachable form in the char. The quantity of chlorine bleeded from the char increases with the amount of sorbent added. The efficiency of the four sorbents added to PVC-quartz mixtures are discussed hereafter.

1. *$CaCO_3$*: for the stoechiometry of the reaction (Ca/Cl = 1/2), 56% of chlorine is still present as HCl in the gas phase (only 22% of chlorine has been eliminated from the pyrolytic gases). It is necessary to reach a ratio of about 3/1 (6 times the stoechiometry) to trap all the HCl. For this ratio, 75% of the chlorine input will be found in the char leachate. By increasing the nitrogen flow rate through the furnace from 0.4 up to 5 dm^3/min (simulating a humid input with large gas flow through the furnace), chlorine capture decreases drastically from 82 to 57% with a decrease of the leachable part of the char from 60 to 53%. Pre-drying the charge is useful to increase the efficiency of the sorbents.
2. *$Ca(OH)_2$*: for the stoechiometry of the reaction (Ca/Cl = 1/2), 96% of HCl in the hot pyrolytic gases is trapped, and 66% of the chlorine input is leachable from the char. With the ratio 2/1 (four times the stoechiometry), 98% of the total chlorine input is trapped in the char in leachable form.
3. *Na_2CO_3*: for the stoechiometry of the reaction (Na/Cl = 1/1), 78% of HCl in the hot pyrolytic gases is trapped, and 70% of the chlorine input is leachable from the char. It is necessary to add this sorbent in a ratio of 3/2 to trap all the HCl and to reach 79% leachable chlorine in the char.
4. *$NaHCO_3$:* for the stoechiometry of the reaction (Na/Cl = 1/1), 100% of HCl in the hot pyrolytic gases is trapped, and 79% of the chlorine input is leachable from the char.

3.1.3 Char characterisation

The observation of the chars by SEM confirmed that no more chlorine is present in the solid after the washing step. It can be concluded that 18 to 28% of the total chlorine input is present in the uncondensable gases, except for the $Ca(OH)_2$ addition in the ratio 2/1 where 98% of the chlorine has been eliminated by char washing. High-temperature ashes were obtained by fixed-bed combustion at 500°C during 8 h from the char produced by pyrolysis of PVC, quartz and $Ca(OH)_2$ (Ca/Cl

Table 3 **Chlorine distribution between HCl in pyrolytic gases and in the char leachate for different Ca/Cl or Na/Cl atomic ratios**

Sorbent type	Ca/Cl or Na/Cl atomic ratio	Shift from stoechiometry	Cl as HCl in pyrolytic gases, % of Cl input	Leachable Cl from char, % of Cl input	HCl eliminated from pyrolytic gases %
PVC without sorbent	–	–	72	0	0
$CaCO_3$	1/2	St	56	21	22
$CaCO_3$	2/1	4´St	13	60	82
$CaCO_3$	3/1	6´St	0	75	100
$CaCO_3$	2/1*	4´St	31*	53	57*
$Ca(OH)_2$	1/4	St/2	30	43	58
$Ca(OH)_2$	1/2	St	3	66	96
$Ca(OH)_2$	4/2	4´St	0	98	100
Na_2CO_3	1/2	St/2	33	38	54
Na_2CO_3	1/1	St	16	70	78
Na_2CO_3	3/2	1.5´St	0	79	100
$NaHCO_3$	1/2	St/2	24	50	67
$NaHCO_3$	1/1	St	0	79	100

* nitrogen flow rate of 5 dm3/min

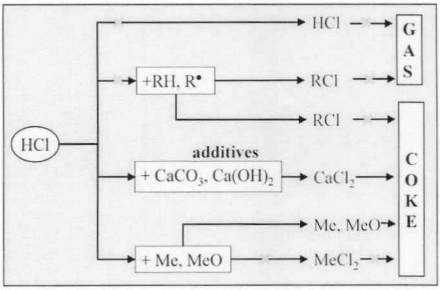

Fig. 5 Pathways for chlorine during pyrolysis (according to reference 16)

atomic ratio of 2/1). The analysis of this sample by XRD shows the presence of:

- quartz (SiO_2),
- hydrated lime ($Ca(OH)_2$),
- calcite ($CaCO_3$),
- larnite ($2CaO.SiO_2$),
- $CaCl_2.Ca(OH)_2.H_2O$.

3.1.4 Interpretation of results

It has been proved that the chlorine moves from the gas phase to the char in the form of calcium or sodium chloride [16], if alkaline sorbents are added during pyrolysis.

Large differences are observed between the efficiency of the sorbents at stoechiometric (Ca or Na)/Cl atomic ratios (Table 3, Figures 3 and 4). Among the calcium-based sorbents, hydrated lime reached the highest HCl trapping in hot pyrolytic gases (96%). Calcium carbonate clearly had the poorest behaviour (22%), which is probably due to low specific area (Table 1) and the formation of a calcium hydroxy-chloride layer. A large excess is needed to achieve the capture process (stoichiometry 6/1 to trap 100% HCl).

The efficiency of the sodium bicarbonate is close to that of the hydrated lime. This can be explained by the fact that $NaHCO_3$ when heated in the furnace decomposes according to the reaction:

$$2\ NaHCO_3\ (s) \Rightarrow Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g).$$

PVC and $NaHCO_3$ are in good contact in the crucible and their decomposition starts in the same temperature range. Thought in this case, the sodium carbonate becomes the reactant responsible for the HCl capture, the release of water and carbon dioxide increases the porosity of the particles, so explaining the good results (100% instead of 78%) obtained with bicarbonate under experimental conditions (Table 3).

Nevertheless, the use of sodium bicarbonate is not recommended as the stoichiometry of the reaction uses respectively 2.2 and 1.7 times the quantity of this sorbent compared to calcium hydroxide or sodium carbonate. Moreover, very fine granulometry could provide the blowing out by the gas stream of fine particles before the starting of the reactions. The best choice of chlorine sorbents would be between hydrated lime and cheap calcite. Beside material costs, a decrease of the amount of calcite is expected in rotating kilns by the fact that the abrasion of calcite particles could reactivate the sorbent during the process.

There is a significant shift for the chlorine from paths a and c to path d [16] (Fig. 5)

The results obtained at laboratory scale under static conditions are hereafter compared with pilot tests on a 20 kg/hr rotating kiln at 500°C.

3.2. Pilot scale experiments

The working program comprised the comparison of the behaviour of chlorine issued from the pyrolysis of PVC with wood and with calcium carbonate or hydroxide. The results are focused on mass balance and on chlorine trapping by char washing.

3.2.1 Preliminary tests at laboratory scale

Pyrolysis of 110 g of mixtures of wood chips / PVC (10/1) with and without limestone (Ca/Cl = 3:1) in a batch rotary kiln were carried out under a nitrogen flow (1.6 l/min) at 500°C during 1 hour. In both cases, only less than 0.5% of the chlorine input was present in the pyrolytic gases as HCl. It has been shown that in the presence of limestone, 24% of the chlorine was present as leachable calcium chloride in the char. In absence of limestone the chlorine was mainly entrapped in the char, with only 1.6% of leachable chlorine (path c).

3.2.2 Phases distribution and chlorine capture

As for lab-scale experiments, less than 0.5% of the chlorine input is present in the pyrolytic gases as HCl.

The pyrolysis of wood chips at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg of char, 20 kg of gas and 113 kg of condensable gas (oil and water).

The pyrolysis of a mixture of wood chips and PVC (10:1) at 20 kg/hr during 4.6 hours (92 kg) gives about 16 kg of char, 10 kg of gas and 66 kg of condensable gas (oil and water). Char washing can only leach out 2% of the chlorine input. Thought, examination of the char after leaching by scanning electron microscope coupled with energy dispersion analysis confirms the presence of chlorine (in non-leachable form).

The pyrolysis of the same mixture wood-PVC with additions of limestone (10:1:4.7) (i. e. Ca/Cl = 3:1) at 22.8 kg/hr during 6 hours (137 kg) gives about 61 kg of char, 14 kg of gas and 61 kg of condensable gas (oil and water). Examination of the char (SEM + EDAX) confirms the presence of chlorine associated with calcium before leaching. Char washing can leach out about 60% of the chlorine input.

The pyrolysis of the same mixture wood-PVC with additions of hydrated lime containing sludge (10:1:11) (i. e. Ca/Cl = 2:1) at 22 kg/hr during 5.5 hours (121 kg) gives about 38 kg of char, 13 kg of gas and 71 kg of condensable gas (oil and water). Char washing can also leach about 60% of the chlorine input out. Calcium is also associated with chlorine in the char. By pre-heating the mixture in the feeding worm and increasing the furnace temperature up to 700°C, the leachable chlorine in the char reached 86%.

The pyrolysis of wood contaminated with lead oxide (100:2) at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg of char, 20 kg of gas and 113 kg of condensable (oil and water). The lead is mainly present in the char as non leachable PbO.

If the same input contains PVC (100:2:10), the pyrolysis at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg of char, 20 kg of gas and 113 kg of condensable (oil and water). The lead is mainly present in the char as PbO, but with 16% in leachable $PbCl_2$.

By addition of limestone in the last input (100:2:10:50), the pyrolysis at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg of char, 20 kg of gas and 113 kg of condensable (oil and water). The lead is mainly present in the char as non leachable PbO.

INTERPRETATION OF RESULTS

The interpretations of the results are based on the chlorine distribution illustrated in Figure 5 [16].

The results obtained with the wood–PVC mixture are in accordance with the predictions made by the laboratory experiments on PVC-lignin and PVC- cellulose systems [17]: the chlorine is mainly adsorbed on the char (path c).

With limestone and sewage sludge additions to the wood-PVC mixture, the hydrogen chloride reacts preferentially with calcium to form calcium chloride (path d). At 500°C, the 60% leachable chlorine from the char obtained in both cases are slightly less than those at laboratory scale (see Figure 4):

- With limestone, for Ca/Cl = 3:1 (i. e. stoichiometry 6:1): 60% compared to 75%,
- with sewage sludge, for Ca/Cl = 2:1 (i. e. stoichiometry 4:1): 60% compared to 98%.

The behaviour of the lead is closely related to that of the chlorine. In absence of sorbent, part of the lead oxide reacts with hydrochloric acid to form lead chloride (path f). With limestone additions, the lead oxide stays in the char ashes (path e).

CONCLUSIONS

Depending on the nature of the waste (municipal or industrial waste, automobile shredder refuse, contaminated mud,...), it can be concluded that the chlorine can be entrapped in the char in a non-leachable form by wood [17]. By selected additions to the waste input, such as calcium or sodium-based sorbents, the majority of the chlorine can be eliminated before the energetic valorisation of the char. Indeed, when chlorine is stabilised as calcium or sodium chloride, washing the char before the energy valorisation can easily leach it out.

These basic additions can also stabilise heavy metals as oxides in the char ashes instead as volatile chlorides.

The elimination of a large part of the chlorine during pyrolysis can lead to substantial economies on the flue gas cleaning system after combustion of the pyrolytic gases.

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Municipal waste pyrolysis:
2. Chlorine capture by addition of calcium and sodium-based sorbents.

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Abstract.

Pyrolysis of municipal and industrial waste presently under development produces liquid, gaseous and solid fuels. Their utilisation as substitution fuels in respect with the environment needs special attention and a strict control on the behaviour of contained chlorine. Indeed, chlorine can be orientated either in pyrolytic gases or in the char. The aim of this paper is to analyse the different ways of entrapping the chlorine in the char in a leachable form by addition of sorbents during pyrolysis. Synthetic waste mixtures containing PVC are pyrolysed at laboratory scale with calcium and sodium-based sorbent. Mass and chlorine balances are presented using the different sorbents in various proportions. This work show that 100% capture of the emitted HCl in the pyrolytic gases can be reached and leaching the char can capture up to 98% of the chlorine. Pilot scale runs with mixtures of wood, PVC and calcium carbonate or lime containing sludge confirm the interest of this approach. It is demonstrated that eliminating chlorine before energy valorisation of the pyrolysis derived fuels could simplify the flue gas cleaning devices.

Keywords : pyrolysis, waste, wood, sludge, PVC, chlorine, $CaCO_3$, $Ca(OH)_2$., Na_2CO_3, $NaHCO_3$.

Introduction.

It is well known that, in municipal waste incinerators and in coal-based electric power plants, there is a need for sophisticated flue gas cleaning in order to eliminate contaminants such as solid particles, sulphur and nitrogen oxides, halogenetated compounds and trace elements. Dry and/or wet alkaline processes are used, followed by an activated carbon treatment. These systems are well discussed in the literature[12345678]. However the environmental legislation being more and more strict, the treatment processes are more complex so that the operating costs becomes very expensive. In order to improve the global plant performance, it is possible to reduce the emissions by direct injections of sorbents inside the furnace before the gases cleaning steps. So in Endesa (Spain), 30% of calcite is added to a high-sulphurous coal before being burned in the fluidised-bed installation[9]. Adanez et al.[10] studied the sulfidation process of different calcium-based sorbents in an entrained-bed reactor. Courtemanche et al.[11] evaluated the capacity of sorbents such as calcium and magnesium carboxilic acid salts for the HCl capture during combustion. More recently, Fontana et al.[12] showed that selected additions during combustion and gasification of waste derived solid char could decrease heavy metals emissions. Therefore, it appears clearly that the role-played by the alkaline sorbents during combustion and gasification is of prime importance.

Now in the case of the municipal wastes treatments, it is widely accepted that pyrolysis can be an attractive alternative to incineration, if the process is followed by an energy valorisation of the solid residue[1314]. Chlorine contained in some wastes has a complex behaviour during pyrolysis. It evolves mostly as HCl under 350°C in the preliminary stage of the PVC thermal degradation[15]. Then competitive reactions take place and the

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Municipal waste pyrolysis:
2. Chlorine capture by addition of calcium and sodium-based sorbents.

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Abstract.

Pyrolysis of municipal and industrial waste presently under development produces liquid, gaseous and solid fuels. Their utilisation as substitution fuels in respect with the environment needs special attention and a strict control on the behaviour of contained chlorine. Indeed, chlorine can be orientated either in pyrolytic gases or in the char. The aim of this paper is to analyse the different ways of entrapping the chlorine in the char in a leachable form by addition of sorbents during pyrolysis. Synthetic waste mixtures containing PVC are pyrolysed at laboratory scale with calcium and sodium-based sorbent. Mass and chlorine balances are presented using the different sorbents in various proportions. This work show that 100% capture of the emitted HCl in the pyrolytic gases can be reached and leaching the char can capture up to 98% of the chlorine. Pilot scale runs with mixtures of wood, PVC and calcium carbonate or lime containing sludge confirm the interest of this approach. It is demonstrated that eliminating chlorine before energy valorisation of the pyrolysis derived fuels could simplify the flue gas cleaning devices.

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chlorine can follow different paths, depending on the chlorine environment in the charge during pyrolysis[16]. We recently demonstrated that cellulose and lignin, usually present in the municipal solid wastes, interact differently with PVC during pyrolysis[17] and modify the chlorine distribution between the gaseous and solid phases. With a high lignin content in the wastes, chlorine is entrapped in the char, but with a high cellulose content, chlorine concentrates in the hot pyrolytic gases. It is important to guide the chlorine either in the gas or in the char outputs by selected additions, in order to fit with the requirements of the fuels end users. When the char during pyrolysis under leachable form entraps the chlorine, it can be eliminated before further use. The effect on chlorine trapping by mixing alkaline reactants with waste during pyrolysis is studied.

Experimental.

- Materials

PVC was obtained by Solvay Company from recycled water bottles (particles size in the range of 1-5 mm): it contains 53% Cl, 0.07% H_2O, 0.1% ashes with traces of 230 ppm Ca, 190 ppm Zn, 150 ppm Al, 150 ppm Si, 120 ppm Mg, 110 ppm Na, 37 ppm Sn and other minor elements. Four different powdered sorbents were tested in mixtures with PVC and their characteristics are given in Table 1. Fine granular quartz (diam. between 0.2 and 0.8 mm account for 60%) from Merck Company was added to the charge for weight compensation.

Wood chips of a few millimetres contain about 37% water.

Sewage sludge from "Kläraranlage Schartsfeld, Germany" contains 122 kg/t of Calcium and the water content is about 50% water.

- Pyrolysis experiments

1. *Laboratory scale.*

   Use of a fixed-bed reactor described elsewhere[15].

   All experiments were performed with the same amount of PVC (3g) with additions of different alkaline sorbent, in order to obtain different Ca or Na/Cl atomic ratios. Inert silicon dioxide is added in order to reach a total amount of charge of 15g. Only the first experiment was made with PVC alone, in order to check the absence of influence of the quartz on the chlorine distribution.

   The starting mixtures were heated at atmospheric pressure up to 500°C during 25 min (heating rate of 35°C/min).

   The hot pyrolytic gases are carried out of the furnace by a nitrogen flow (0.4 dm^3/min). Condensable matter is recovered in cold traps and weighted. The uncondensed gases are washed (in water for HCl trapping) and collected for analysis. The mass of solid, condensable gases and hydrochloric acid are measured. The quantity of uncondensable gases is determined by difference.

2. *Pilot scale.*

   CUTEC pilot plant in Clausthal consists of the following main components:

   - a 30 to 50 kg/h rotary kiln of a length over all of 5.8m and a diameter of 300mm (40kW heated length of 3.6m length),
   - the pyrolytic residue is discharged through an electrically heated delivery chamber,
   - the pyrolytic gas is directed from the kiln's delivery connection piece into a three-staged washing column filled with Raschig rings,

- the purified pyrolytic gas arrives after post cooling in the succeeding combustion chamber where it is burnt, along with natural gas for supporting the flame,
- the flue gas at 1200°C is cooled down and cleaned with sodium hydrogen carbonate and activated coal,
- The flue dust is separated by means of a cloth filter.

The material to be treated is delivered from the feeding shaft flooded with inert gas nitrogen into the kiln via a conveyor worm.

The operating conditions in the pilot plant rotary kiln can be varied among others by the following parameters:

- Composition of input material,
- Level and distribution of temperature,
- Residence time (mass flow, inclination and rotation),
- Mixing conditions,
- Variation of load,
- Insertion of additives.

At the hot gas output of the rotary kiln, a discontinuous gas sampling of the pyrolytic gas device is equipped with a so called-finger type cooler and behind it a spiral cooler. Another discontinuous gas sampling of the purified uncondensable pyrolytic gas is placed after washing column.

- Analyses

Leaching tests were performed on all residual solids: approximately 3 g of sample in 50 ml of water during 1 h at 50°C. Chloride anions were titrated in all the solutions with silver nitrate (potentiometric titration).

Minerals present in the char before and after washing were determined by X-ray powder diffraction (XRD) on a Philips PW 1729 equipment (Cu Kα, 32 kV, 28 mA).

Ashes were analysed by a SEM Jeol JSM 820, coupled with an energy dispersion microanalysis device (EDAX 9100). The accelerating voltage was 20 kV.

Uncondensed gases were analysed on two Varian 3300 chromatographs (porapak Q and molecular sieve columns, catharometer detectors).

Results and discussion.

Laboratory scale experiments

Without any additive, there are no significant differences between the results obtained for PVC and PVC-quartz mixtures neither on phase's distribution, nor on hydrochloric production (table 2). In consequence, the quartz is completely inert in these conditions. More than 70% of the chlorine is recuperated as hydrochloric acid. The remaining chlorine is probably in the condensable gas phase as organic chlorinated compounds (only traces of chloromethane and chloroethylene are observed in the uncondensable gaseous phase).

Phases distribution

The mass of the pyrolytic solid, liquids and gases (including HCl) issued from the treatment of different PVC-additive mixtures are presented in Table 2 (solid, liquid and gaseous fractions) and illustrated in Figures 1 and 2 for the liquid and the gases (excluding HCl). For all experiments, the char fraction in Table 2 is given after subtraction of the inert quartz mass.

For each sorbent used during pyrolysis of the PVC, when the mass of the sorbent in the raw mixture increases , the mass of the char increases proportionally. This is due to the formation of the reaction products (calcium or sodium chloride) and to an excess of unreacted additives. Simultaneously, the liquid production also increases (Figure 1). The decarbonisation is enhanced by the presence of sorbent increases in the raw mixture. For the uncondensable gases, the situation is quite different (Figure 2). For the sorbents $NaHCO_3$, Na_2CO_3 and $CaCO_3$ in a lower extent, the quantity of gas increases due to the sorbent decomposition and CO_2 production. With hydrated lime, a decrease of the gas production is observed, which is connected to the absence of CO_2 production and the formation of condensable water.

Chlorine capture

The chlorine is distributed between HCl in the uncondensable gas phase, chlorine in the condensable gas and in the char under leachable form (Table 3).

For the different sorbents, the percentage of chlorine found as hydrochloric acid in the hot gases is calculated from the HCl measured in the washing solution of the gases. By comparison with the 72% found in pure PVC pyrolysis, the percentage of HCl eliminated from the pyrolytic gases with each sorbent in various proportions is calculated. Figure 3 shows the influence of the different sorbents (in various Ca/Cl or Na/Cl atomic ratios) on the chlorine evolution as HCl in the gas phase.

Figure 4 shows the percentage of initial chlorine recuperated in the char leachate in function of the Ca/Cl or Na/Cl atomic ratio in each case.

With the use of sorbents, there is a significant decrease of the chlorine emitted as hydrochloric acid in the hot pyrolytic gases, the chlorine being entrapped in a leachable form in the char. The quantity of chlorine bleeded from the char increases with the amount of sorbent added. The results of the efficiency of four sorbents additions to PVC-quartz mixtures are discussed hereafter.

1. $CaCO_3$: for the stoechiometry of the reaction (Ca/Cl = 1/2), 56% of chlorine is still present in the gas phase (only 22% of chlorine has been captured). It is necessary to reach a ratio about 3/1 (6 times the stoechiometry) to trap all the HCl. For this ratio, 76% of the chlorine input will be found in the char leachate. Increasing the nitrogen flow rate through the furnace from 0.4 to 5 dm^3/min (simulating a humid input with large gas flow through the furnace), decreases drastically the chlorine capture efficiency (57% instead of 100%) with a decrease from 76 to 53% of the leachable part. Pre-drying the charge is useful to increase the efficiency of the sorbents.

2. $Ca(OH)_2$: for the stoechiometry of the reaction (Ca/Cl = 1/2), 96% of HCl in the hot pyrolytic gases is trapped, and 66% of the chlorine input is leachable from the char. With the ratio 2/1 (four times the stoechiometry), 98% of total chlorine input is trapped in the char in leachable form.

3. Na_2CO_3: for the stoechiometry of the reaction (Na/Cl = 1/1), 56% of HCl in the hot pyrolytic gases is trapped, and 70% of the chlorine input is leachable from the char. It is necessary to add this sorbent in a ratio 3/2 to trap all the HCl and to reach 79% leachable chlorine in the char.

4. $NaHCO_3$: for the stoechiometry of the reaction (Na/Cl = 1/1), 100% of HCl in the hot pyrolytic gases is trapped, and 79% of the chlorine input is leachable from the char.

Char characterisation

The observation of the chars by SEM confirmed that no more chlorine stays in the solid after the washing step. We can conclude that 18 to 28% of the total chlorine input is present in the uncondensable gases, except for the $Ca(OH)_2$ addition in the ratio 2/1. High-temperature ashes were obtained by fixed-bed combustion at 500°C during 8h of the char produced from pyrolysis of PVC, quartz and $Ca(OH)_2$ (Ca/Cl atomic ratio of 2/1). The analysis of this sample by XRD shows the presence of:

- quartz (SiO_2),
- hydrated lime ($Ca(OH)_2$)
- calcite ($CaCO_3$)
- larnite ($2CaO.SiO_2$)
- $CaCl_2.Ca(OH)_2.H_2O$.

The last compound is an intermediate layer formed between the sorbent and the calcium chloride produced during pyrolysis. When calcium carbonate is used as sorbent, a surface layer of $CaCl_2$ is formed, so that there is an inhibition of the sorbent an a large excess is needed to achieve the capture process.

By addition of alkaline sorbents during pyrolysis, there is proof that the chlorine has moved from the gas phase to the char in the form of calcium or sodium chloride[16].

Interpretation of results

Large differences are observed between the efficiency of the sorbents at stoechiometric (Ca or Na)/Cl atomic ratios (Table 3, figures 3 and 5).

Among the calcium-based sorbents, hydrated lime reached the highest HCl trapping in hot pyrolytic gases (96%) and calcite clearly had the poorest behaviour (56%), which is probably due to the formation of a calcium chloride layer associated with a low specific area (Table 1).

The efficiency of the sodium bicarbonate is very close to that of the hydrated lime. This can be explained by the fact that $NaHCO_3$ when heated in the furnace decomposes according to the reaction:

$$2\,NaHCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(g).$$

During the bicarbonate decomposition, the release of water and carbon dioxide increases the porosity of the grains. The sodium carbonate becomes the reactant responsible for the HCl capture. The results obtained with sodium carbonate show an efficiency about 20% less than with calcium hydroxide. This could be explained by the pore closure effects during or after the decomposition in carbonate before the chlorine capture[8]. The good result with bicarbonate in our experimental conditions are probably not subjected to such a phenomenon as PVC and $NaHCO_3$ are in good contact in the crucible and their decomposition starts in the same temperature range.

Nevertheless, the use of sodium bicarbonate is not recommended because the stoechiometry of the reaction uses twice the quantity of this sorbent compared to calcium hydroxide and sodium carbonate. Moreover, very fine granulometry could provide the blowing out, by the gas stream, of fine particles before the starting of the reactions.

The best choice of chlorine sorbents would be between hydrated lime and cheap calcite. Beside the material costs, a decrease of the amount of calcite is expected in rotating kilns by the fact that the abrasion of calcite particles could reactivate de sorbent during the process.

The results obtained at laboratory scale under static conditions are hereafter compared with pilot tests on a 20 kg/hr rotating kiln at 500°C.

Pilot scale experiments

The working program involves the comparison of the behaviour of chlorine issued from the pyrolysis of PVC with wood and with calcium carbonate or hydroxide. The results are focused on mass balance and on chlorine trapping by char washing.

Preliminary tests at laboratory scale

Pyrolysis of 110g of mixtures of wood chips / PVC (10/1) with and without limestone (Ca/Cl = 3:1) in a batch rotary kiln are carried out under a nitrogen flow at 500°C during 1 hour. In both cases, only less than 0.5% of the chlorine input is present in the pyrolytic gases as HCl. It has been shown that in the presence of limestone, 24% of the chlorine is present as leachable calcium chloride in the char, while in absence of limestone the chlorine is mainly entrapped in the char (only 1.6% leachable).

Phases distribution and chlorine capture

In all cases, only less than 0.5% of the chlorine input is present in the pyrolytic gases as HCl.

The pyrolysis of wood chips at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg char, 20 kg gas and 113 kg of condensables (oil and water)

The pyrolysis of a mixture of wood chips and PVC (10:1) at 20 kg/hr during 4.6 hours (92 kg) gives about 16 kg char, 10 kg gas and 66 kg of condensables (oil and water). Only 2% of the chlorine input can be leached out by char washing. Examination of the char by scanning electron microscope coupled with energy dispersion analysis confirms the presence of chlorine.

The pyrolysis of the same mixture wood-PVC with additions of limestone (10:1:4.7) (i.e Ca/Cl = 3:1) at 22.8 kg/hr during 6 hours (137 kg) gives about 61 kg char, 14 kg gas and 61 kg of condensable (oil and water). About 60% of the chlorine input can be leached out by char washing. Examination of the char (SEM + EDAX) confirms the presence of chlorine associated with calcium.

The pyrolysis of the same mixture wood-PVC with additions of hydrated lime containing sludge (10:1:11) (i.e Ca/Cl = 1:1) at 22 kg/hr during 5.5 hours (121 kg) gives about 38 kg char, 13 kg gas and 71 kg of condensable (oil and water). About 60% of the chlorine input can also be leached out by char washing. Calcium is also associated with chlorine in the char. By pre-heating the mixture in the feeding worm and increasing the furnace temperature up to 700°C, the leachable chlorine in the char reached 86%.

The pyrolysis of wood contaminated with lead oxide (100:2) at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg char, 20 kg gas and 113 kg of condensable (oil and water). The lead is mainly present as PbO.

If the same input contains PVC (100:2:10), the pyrolysis at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg char, 20 kg gas and 113 kg of condensable (oil and water). The lead is mainly present as PbO, but with 16% in leachable $PbCl_2$.

By addition of limestone in the last input (100:2:10:50), the pyrolysis at 22 kg/hr during 7.3 hours (160 kg) generates 27 kg char, 20 kg gas and 113 kg of condensable (oil and water). The lead is mainly present as PbO.

Interpretation of results

The interpretation of the results are based on the chlorine distribution illustrated in Figure 7[16].

The results obtained with the wood–PVC mixture are in accordance with the predictions made by the laboratory experiments on PVC-lignin and PVC-cellulose systems[17]: the chlorine is mainly adsorbed on the char (pathway e).

By limestone and sewage sludge additions to the wood-PVC mixture, the hydrogen chloride reacts preferentially with calcium with the formation of calcium chloride (pathway d). At 500°C, the 60% leachable chlorine from the char obtained in both cases are slightly less than those at laboratory scale (see Figure 4):

- By limestone, for Ca/Cl = 3:1 (i.e. stoechiometry 6:1): 60% compared to 75%
- By sewage sludge, for Ca/Cl = 2:1 (i.e. stoechiometry 4:1): 60% compared to 85%.

Conclusions.

Depending on the waste nature (municipal or industrial waste, automobile shredder refuse, contaminated mud,…), we can conclude that it is possible to trap the chlorine by selected additions into the waste input, such as wood[15] or as calcium or sodium-based sorbents, in order to eliminate the majority of the chlorine before the energetic valorisation step of the char. When chlorine is stabilised as calcium or sodium chloride, washing the char before the energy valorisation can easily leach it out.

The elimination of a large part of the chlorine during pyrolysis could lead to substantial economies on the flue gas cleaning system after combustion of the pyrolytic gases.

Captions of table and figure

Table 1 : Sorbents properties

Table 2 : Mass balance of PVC pyrolysis in presence of calcium and sodium sorbents (g)

Table 3 : HCl reduction (%) for different (Ca or Na)/Cl atomic ratios

Figure 1 : Production of liquids during fixed-bed pyrolysis of PVC with different proportions of sorbents (g)

Figure 2 : Production of gases (excluding HCl) during fixed-bed pyrolysis of PVC with different proportions of sorbents (g)

Figure 3 : Chlorine fraction evolved as HCl in the gases (weight %)

Figure 4 : Chlorine estimation in the chars obtained by leaching tests (weight %)

Figure 5 : Pathways for chlorine during pyrolysis (according to reference 16)

Table 1

Sorbents	$CaCO_3$	$Ca(OH)_2$	Na_2CO_3	$NaHCO_3$
Supplier	Lhoist	Lhoist	Solvay	Solvay
Type	Lhocal EC90	Lhocal EH63	Light soda	Bicar
D_p (μm)*	< 90	< 63	< 250	< 45**
BET (m^2/g)	1-2	14-18		

* Size of sorbent particles (93-96%)

** Particles with $D_p < 45 \mu m$ account for 90% - coated with 1% calcium stearate

Table 2

Samples	PVC (g)	Sorbent (g)	Quartz (g)	Char** (g)	Liquids (g)	Gases (g)	HCl (g)
PVC-alone	3.02	0	0	0.45	0.98	0.42	1.17
PVC-Q	3.03	0	12.01	0.41	1.01	0.45	1.16
$CaCO_3$ 1/2	3.06	2.27	9.73	2.95	1.01	0.46	0.91
$CaCO_3$ 2/1	3.01	9.01	3.04	9.79	1.36	0.66	0.21
$CaCO_3$ 3/1	3.00	13.51	0	14.36	1.35	0.80	0
$CaCO_3$ 2/1*	3.00	9.08	3.05	9.79	0.61	1.17	0.51
$Ca(OH)_2$ 1/4	3.00	0.83	11.17	1.62	1.47	0.26	0.48
$Ca(OH)_2$ 1/2	3.00	1.68	10.43	2.64	1.85	0.14	0.05
$Ca(OH)_2$ 2/1	3.01	5.41	6.65	6.35	1.95	0.12	0
Na_2CO_3 1/2	3.00	1.19	10.84	1.63	0.96	1.07	0.53
Na_2CO_3 1/1	3.00	2.38	9.62	2.63	1.41	1.08	0.26
Na_2CO_3 3/2	3.00	3.58	8.42	3.89	1.48	1.21	< 0.01
Na_2CO_3 2/1	3.00	4.76	7.24	4.89	1.53	1.34	0
$NaHCO_3$ 1/8	3.00	0.47	11.53	0.71	1.09	0.63	1.04
$NaHCO_3$ 1/4	3.00	0.95	11.05	1.05	1.39	0.73	0.78
$NaHCO_3$ 1/2	3.00	1.90	10.10	1.72	1.62	1.17	0.39
$NaHCO_3$ 1/1	3.00	3.78	8.22	2.96	1.58	2.24	< 0.01

* N_2 flow rate of 5 dm^3/min

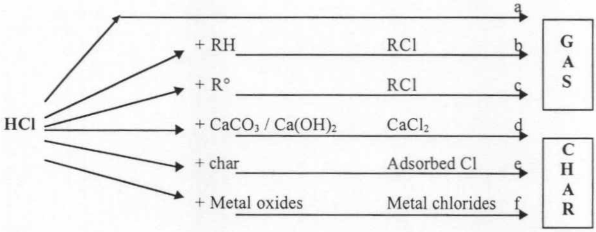
** Weight of solid residue after substraction of the quartz charge

Table 3

Sorbent type	(Ca or Na)/Cl atomic ratio	Shift from stoechiometry	Cl as HCl in pyrolytic gases (% of Cl input)	Leachable Cl from char (% of Cl input)	HCl eliminated from pyrolytic gases (%)
PVC without sorbent	----	----	72	0	0
$CaCO_3$	**1/2**	**St**	**56**	**21**	**22**
$CaCO_3$	2/1	4×St	13	60	82
$CaCO_3$	2/1*	4×St	31*	53	57*
$CaCO_3$	3/1	6×St	0	75	100
$Ca(OH)_2$	1/4	St/2	30	43	58
$Ca(OH)_2$	**1/2**	**St**	**3**	**66**	**96**
$Ca(OH)_2$	4/2	4×St	0	98	100
Na_2CO_3	1/2	St/2	33	38	54
Na_2CO_3	**1/1**	**St**	**16**	**70**	**78**
Na_2CO_3	3/2	1.5×St	0	79	100
$NaHCO_3$	1/2	St/2	24	50	67
$NaHCO_3$	**1/1**	**St**	**0**	**79**	**100**

* nitrogen flow rate of 5 dm^3/min

Figure 5


a
+ RH
RCl
b
+ R°
RCl
c
HCl
+ $CaCO_3$ / $Ca(OH)_2$
$CaCl_2$
d
+ char
Adsorbed Cl
e
+ Metal oxides
Metal chlorides
f
GAS
CHAR

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