

WP4: Exposures in test-plant under well-defined process conditions

General information about CUTEC pilot plant

Scheme and description of the pilot plant

Preliminary note: CUTEC owns several pilot plants with different reactor types; each for certain materials or processes. For this project only the grate system was used, so in the report "CUTEC pilot plant" every time stands for the described grate system.

The CUTEC pilot plant has a backward acting grate and three vertical passes and is build for a thermal capacity up to 950 kW. The grate and the first pass are constructed as a down-scale from big plants from the company MARTIN, so that the combustion is very similar to industrial plants. It includes also facilities for primary air preheating and flue gas recirculation. A scheme of the plant is shown in figure 1.

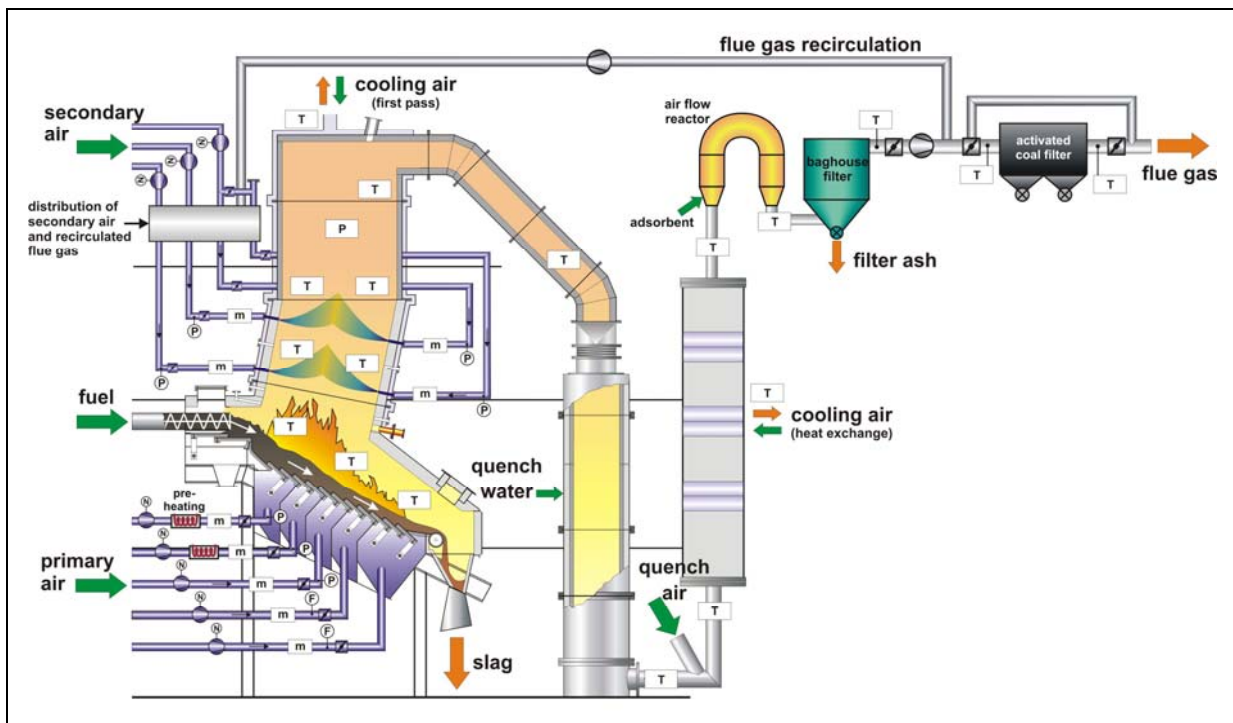


Fig. 1 Scheme of CUTEC pilot plant

Because of the big surface/volume-ratio the heat removal is made by cooling air behind a thin refractory layer. A further reduction of flue gas temperature can be done by quench with water or air in the second pass. After a short duct behind the second pass with several measurement ports there is an air-cooled heat exchanger which has four bundles and removes most energy of the flue gas. The two first bundles are comparable with super-heaters in a third pass of industrial plants. The flue gas cleaning is made by an adsorbent injection with an air flow reactor and a baghouse filter. After the fan there is an additional activated coal filter.

Photo and cross-section of the heat exchanger

The heat exchanger shall be shown more detailed, because several exposes and investigations about growth of deposits have been done in it or directly in front of it. Figure 2 shows a cross section and a photo of the lower half of the heat exchanger.

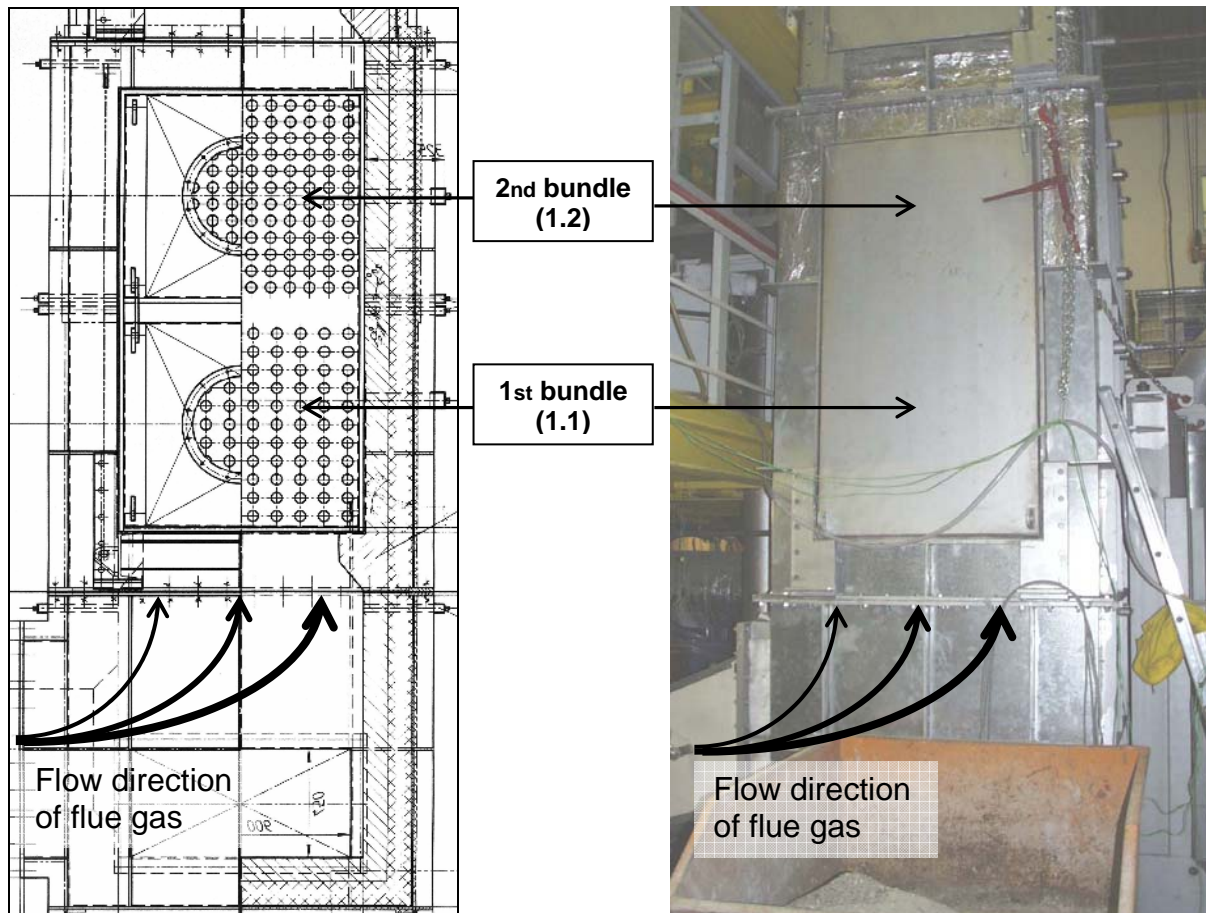


Fig. 2: Cross section and photo of the lower half of the heat exchanger

Unfortunately there were two properties which make the flue gas flow not being ideal for investigations in growth of deposits.

First the flue gas velocity in the heat exchanger with about 2 m/s is lower than in industrial plants which have velocities of about 5 m/s. This in most tests about growth of deposits has been compensated by smaller tube diameters, which cause a similar impaction like larger tube diameters at higher gas velocities in big plants.

Second there are two 90°-changes in flue gas flow direction instead of one 180°-change in industrial plants with vertical passes, which make an inhomogeneous flow of the flue gas, so that the conditions at different tubes or probes were similar, but not exactly the same.

Fuel types used and fuel conditioning

Biomasses and municipal solid waste were used for firing the pilot plant. Biomasses are homogeneous and available in small sizes. The mainly used biomass is wood. Residual materials from agriculture like sugar beets and wheat straw were also used in mixtures with wood. **Municipal solid waste** (msw) normally is inhomogeneous and contains also large pieces, which are unsuitable for feeding the pilot plant.

The basic material for tests using waste material was divided and homogenised msw, as shown in figure 3, from a mechanical conditioning facility. Because high caloric materials had been separated before cutting in order to produce refuse derived fuels (RDF), we had to add this high caloric RDF to obtain a typical municipal solid waste. In one plant operation week also the influence of the lower caloric value was examined. In this week one mixture with a normal and one mixture with a high quota of RDF and an increased lower caloric value were used.



Fig. 3: Cut msw with a reduced quota of high caloric materials

Starting and heating up the plant in the first hours as well as the shut down in the last hours of plant operation is generally done by firing with wood.

Process data from CUTEC pilot plant

Measuring values from about 165 instruments are transmitted to the control room and mostly visualized and logged. The components and the structure of the process control system are shown in figure 4.

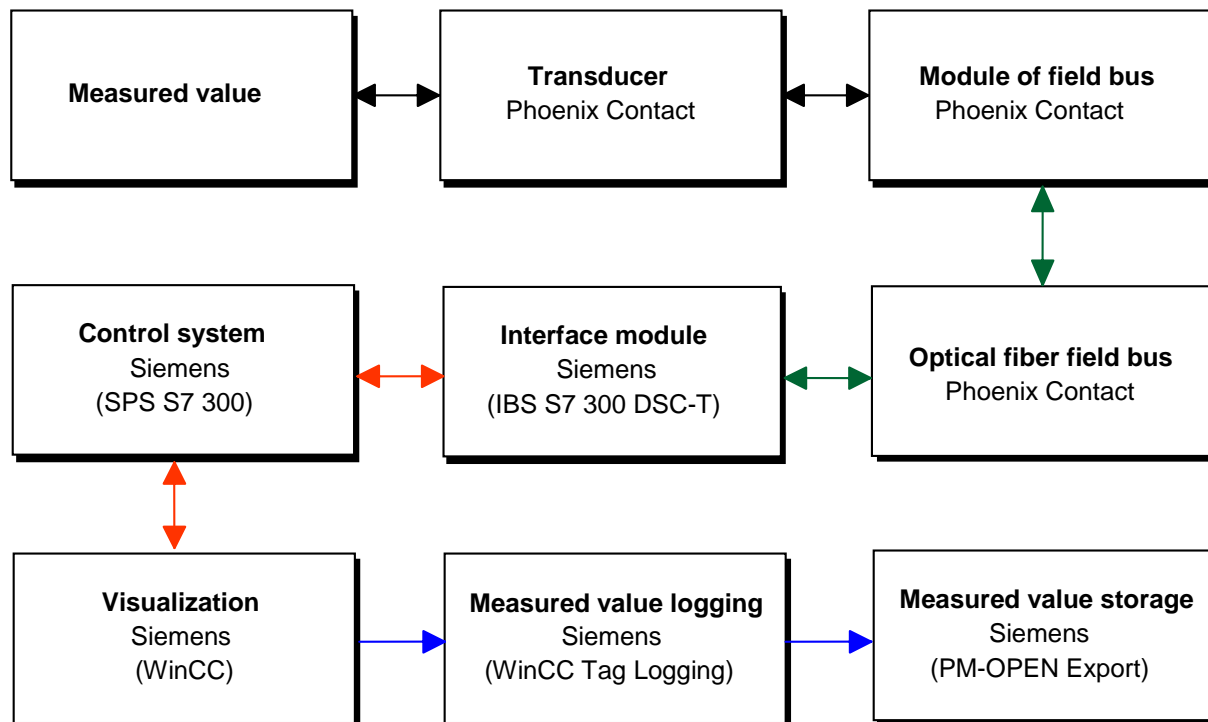


Fig. 4: Structure of process control system of CUTEC pilot plant

Large-scale plants have a higher thermal capacity and a larger grate area. Local events on the grate in this case are not or hardly visible in measurement values like flue gas temperature or oxygen-content, because they only affect a small part of the grate area and fuel. Because the grate of the CUTEC pilot plant is much smaller, here local effects can be seen clearly in measurement values.

Plant operation weeks for Biowas and its results

Table 1 gives an overview about all plant operation weeks, the variations in operation conditions and carried out investigations. Exposures and exposes were done.

Overview about operation of CUTEC pilot plant as well as exposures and other investigations				
Operation of pilot plant in calendar week	Fuels used; fuel and other variations in plant operation	Exposure of materials from project partners*1	Investigations in growth of deposits*2 by CUTEC	Other investigations by CUTEC
48 / 2004	Municipal solid waste	Plates from Inasmet were installed in 1st pass	Three identical tubes in three different levels in the heat exchanger	High-temperature-endoscopy in entrance of heat exchanger
15 / 2005	Normal ("low caloric") municipal solid waste	No materials were send from the partners for exposure	Three tubes with different diameters in similar positions and one tube in a different position in the heat exchanger	
	High caloric waste (by adding rdf)			
	Pure wood chips			
	Wood with co-firing of rdf			
42 / 2005	Pure wood chips (100 %)	Rings and sheets from KIMAB were installed in heat exchanger	Three tubes with different diameters in similar positions and one tube in a different position in the heat exchanger	
	80 % wood + 20 % wheat straw (pellets)			
	80 % wood + 20 % sugar beets (pellets)			
25 / 2006	Municipal solid waste	Inasmet: plates installed in 2nd pass	Three tubes with different diameters in similar positions in front of the heat exchanger and one tube in the heat	Expose of pre-oxidated and not pre-oxidated tubes which were installed in front of the heat exchanger
	Variations in primary air ratio (but constant total air ratio)	KIMAB: rings/sheets in heat exchanger		
*1 Materials were exposed for whole week and afterwards send back to the partners for material analysis				
*2 This investigations were made for every fuel used and every plant adjustment (see 2nd rift)				

Tab. 1: Overview about plant operation weeks

A plant operation normally is done from Monday morning till Friday afternoon. The operation periods are denoted by the number of the calendar week in the year (for example 48/2004).

The materials of the project partners for exposure were installed considering the wishes of the partners. After exposure the materials were sent back to the partners for material analyses. Deposits were collected and analyse with **X-ray fluorescence analysis (XRF)** disposed by CUTEC. This results and also data about exposure conditions were sent to the partners.

XRF analysis the elements and its quantities in a sample; the elements are as usual declared in there oxide form (except chlorine), although XRF gives no information about there chemical bounding.

At CUTEC investigations about growth of deposits on test tubes the samples were in principle only collected from the wind-ward side of the tubes.

Plant operation and investigations in week 48/2004

In week 48/2004 the first week of plant operation took place, with several investigations of deposits and corrosion. The plant was fired with finely divided and homogenized municipal solid waste. Only the running up and down of the plant was performed using wood chippings. An analysis of the waste material can be seen in table 2. The lower calorific value of 9.6 MJ/kg was in a normal range for waste incineration plants. The progress of the main operating parameters can be seen in figures 5 and 6.

content	C	H	O	N	S	Cl	water	ash
[%]	25.3	3.7	14.2	0.48	0.16	0.32	36.2	19.7

Tab. 2: Composition of the waste material used

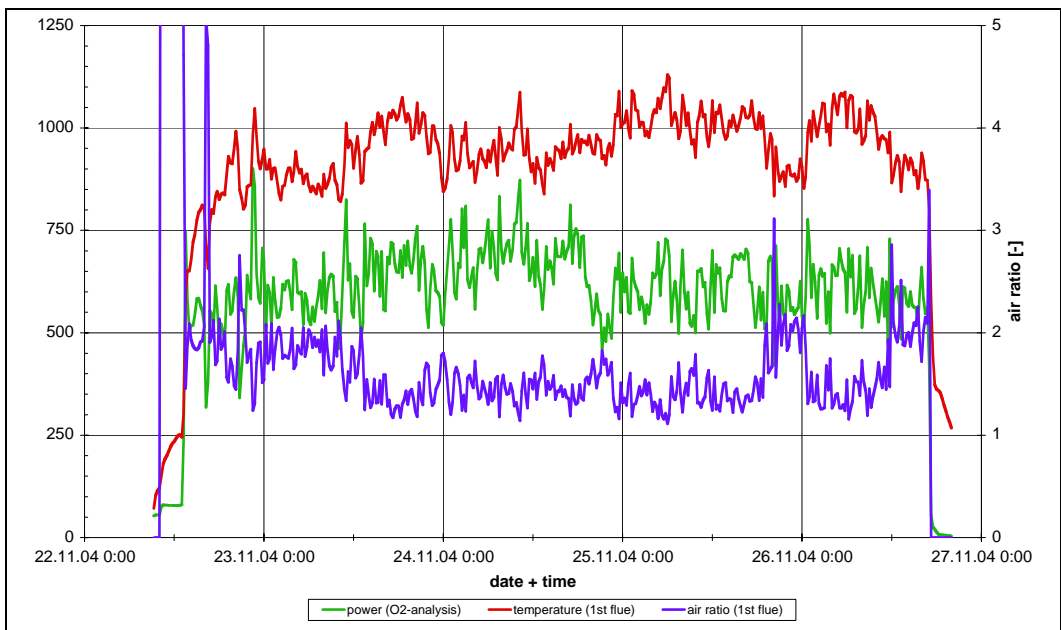


Fig. 5: Progress of the main operating parameters (1st flue)

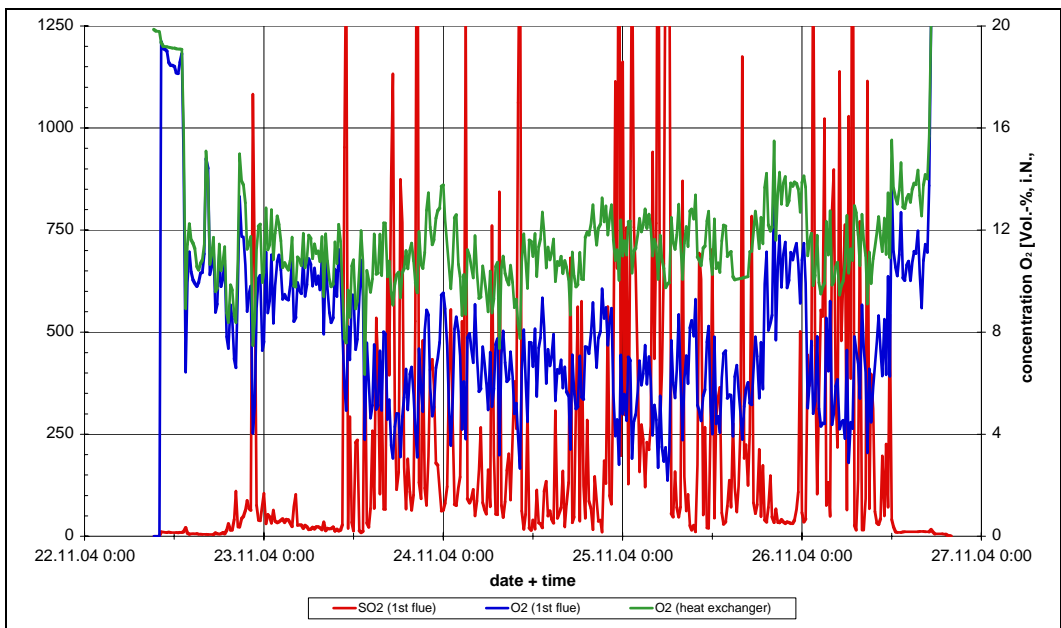


Fig. 6: Progress of the flue gas composition

Exposure of coated plates from Inasmet in week 48/2004

CUTEC received four coated plates from Inasmet which were to be exposed to flue gas temperatures of about 900°C without any cooling of the material. These plates were fixed at the top of the first pass by inserting a tube through a hole drilled in the plates. Figure 7 shows the exposed plates after one week of plant operation. The dust was surprisingly loose, and almost all of it fell off when the plates were removed. In order to carry out the planned material investigations the plates were sent back to Inasmet.

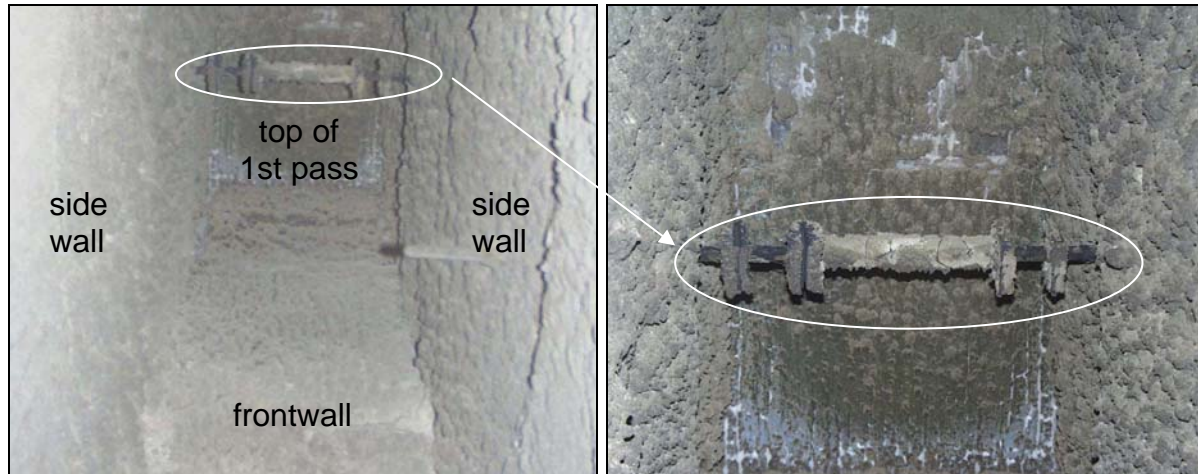


Fig. 7: Coated plates from Inasmet after one week of plant operation

Tubes for sampling of deposits in week 48/2004

Three identical tubes were installed in different levels of the heat exchanger (shown in fig. 2). The tube “above” was installed at the end of the lower half of the heat exchanger between the bundles 1.2 and 2.1.; tube “middle” was installed between the two first bundles; tube “below” was installed in front of the first bundle (1.1). On the tube designated “above” there were very few deposits, so that no reliable analysis could be done. On the “below” tube a white coating developed on the surface of the tube, on which a greyish layer built up (see figure 8). This two-layer development of coatings is known in principle from deposits in large-scale plants. The two layers of deposits were, as far as possible, removed from the tube separately and then individually analysed.

In the tube “below” air cooling was used to produce a material temperature of around 340 °C in the middle, as found in an initial superheater. The tube “middle” was held at around 390 °C material temperature, which is roughly similar to a typical final superheater with 400 °C. The temperature difference of the flue gas between the two positions can only be influenced to a very limited extent. The flue gas temperature at the tube “below” is, with around 700 °C, relatively high for an initial superheater, and at the “middle” tube, with around 520 °C, it is a little low for a final superheater.

The temperatures, quantities and composition of the deposits are shown in table 3. The deposits were taken only from the wind side of the tubes. The composition of the deposits was determined using X-Ray Fluorescence Analysis (XRF) and, as is usual, are given mostly in oxide forms.

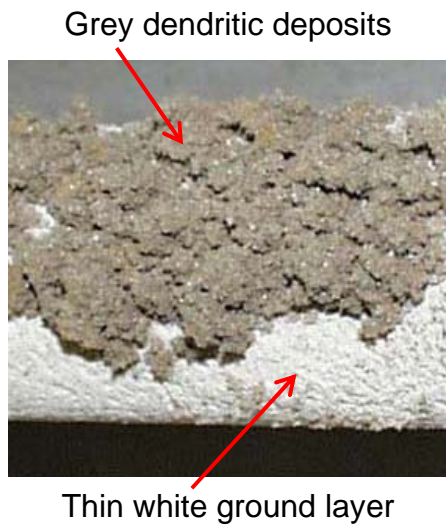


Fig. 8: Two-layer deposit

tube position		"middle"	"below"	"below"	"below"
part of deposits		all	all	"white"	"grey"
material	[°C]	387	338	338	338
flue gas	[°C]	520	703	703	703
mass	[g]	2.0	10.0	4.2	5.9
Na ₂ O	[%]	12.9	11.1	13.4	9.1
MgO	[%]	0.5	0.7	0.4	0.9
Al ₂ O ₃	[%]	1.4	2.9	1.2	4.4
SiO ₂	[%]	5.4	5.7	4.8	7.0
P ₂ O ₅	[%]	0.6	0.8	0.5	1.1
SO ₃	[%]	38.9	34.8	39.4	29.7
Cl	[%]	2.5	7.1	5.8	8.7
K ₂ O	[%]	16.7	18.3	22.2	14.5
CaO	[%]	9.7	14.4	7.4	20.8
TiO ₂	[%]	0.5	0.8	0.4	1.1
Fe ₂ O ₃	[%]	2.5	1.4	1.4	1.4
ZnO	[%]	1.3	0.7	0.9	0.6
PbO	[%]	1.4	0.7	1.4	0.1

Tab. 3: Quantity and composition of the deposits

In the comparison of the deposits from the different tubes, the significantly higher quantity of deposits (about 5x) and the higher chlorine content (about 3x) on the lower tube are especially noticeable. A heavier build-up of deposits and increased chlorine content on the first tube bundles are also known from large-scale plants. In those plants, however, it is hard to make a quantitative analysis of the growth of deposits due to the online cleaning procedure used.

The chlorine content in the grey outer layer of the tube "below" is higher than the chlorine content in the inner white layer. Exactly the opposite has been observed with deposit samples from large-scale plants. The samples taken from large-scale plants during periods of non-operation are, however, considerably older. Both chlorine contents ("white" and "grey" layer) are relatively high in comparison to chlorine contents of normally less than 5 % in deposits from superheaters in industrial plants.

Interpretation of above shown results:

As a result of chemical reactions, especially sulphating, the composition of deposits can shift during the operation time of a plant. The growth of deposits varies the conditions for further deposit growth. It is assumed that

- the chlorine contents in both layers are relatively high because the time for sulphating reactions was much shorter than in industrial plants (few days instead of several months).
- the chlorine content in the outer grey layer is higher than in the inner white layer, because the grey layer was build later and so had an even shorter period for sulphating, and it has a dendritic structure, which separates more very small particles with high chlorine-contents.

High temperature endoscopy (hte) in week 48/2004

In contrast to large-scale plants, the heat exchangers of the CUTEC research plant are not cleaned during operation. This has the advantage that the build-up of deposits can be observed in an unhindered manner. Figure 9 shows a selection of static pictures made with hte which show deposits growth at the windward side of the second bundle (1.2). The tubes are numbered from the entrance side.

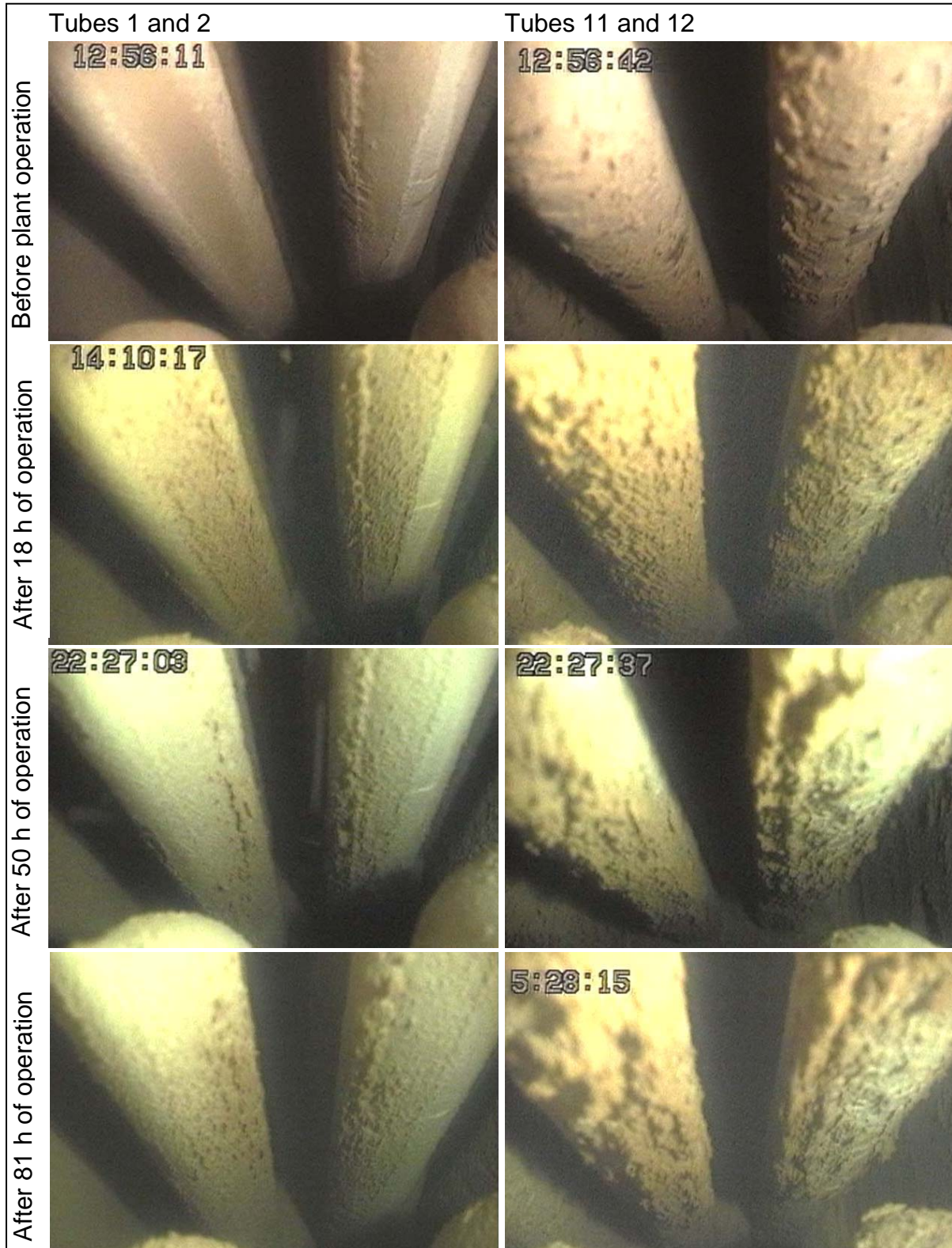


Fig. 9: Growth of deposits on tubes 1+2 and 11+12 (at windward side)

The progress of growth of deposits during the operation time in the absence of any intermittent cleaning process can be seen in vertical succession.

It can be seen that the build-up of deposits increases towards the outer, high-numbered tubes. Significantly increased flow rates in the outer areas, caused by the change of direction, seem to be present as far as the second bundle.

Plant operation and investigations in calendar week 15/2005

The aims of the plant operation in week 15/2005 were to study the influence of the fuel, especially changes by adding RDF, and of the tube diameter on the amount and composition of the deposits. The mixtures and compositions of the four fuels used are shown in table 4.

		"low caloric" waste	high caloric waste	pure wood	wood + rdf
waste (cutted; high caloric fraction separated)	%	83	60		
rdf (= high caloric fraction)	%	17	40		10
wood	%			100	90
water	%	20.0	23.2	30.0	29.8
ash	%	34.4	27.6	0.3	1.4
volatiles	%	39.3	41.8	58.2	57.5
fixed carbon	%	6.4	7.4	11.5	11.4
lower caloric value	MJ/kg	10.0	11.9	11.1	11.8
carbon	%	24.69	27.55	34.60	34.82
hydrogen	%	2.98	3.49	5.10	5.10
oxygen	%	16.18	16.47	29.79	28.62
nitrogen	%	0.83	0.76	0.15	0.19
sulfur	%	0.52	0.45	0.008	0.04
chlorine	%	0.43	0.48	0.011	0.08
fluorine	%	0.030	0.021	0.000	0.000
sulfur/chlorine-ratio		1.22	0.94	0.73	0.47

Tab. 4: Composition of the fuels used in week 15/2005

The basic material for tests using waste material was cut and homogenised municipal solid waste (msw) from a mechanical conditioning facility. Because high caloric materials had been separated before cutting in order to produce refuse derived fuels (RDF), we had to add this high caloric RDF to obtain a normal or "low caloric" waste. For getting a high caloric waste the quota of RDF was increased.

The in comparison "low caloric" waste has a lower caloric value of 10.0 MJ/kg. This is not a low but a typical value.

The trend of the main process data is shown in figure 10. In order to sample deposits, some tubes, which were cooled to nearly 400 °C, were installed at the inflow of the heat exchanger at flue gas temperatures of about 600 °C. Because wood contains less ash than waste and so should cause a slower deposit growth the time for sampling deposits was increased (12 instead of 8 hours at burning waste).

Figure 11 shows the temperatures about 0.45 m above the grate and the flue gas temperature at the end of the 1st pass.

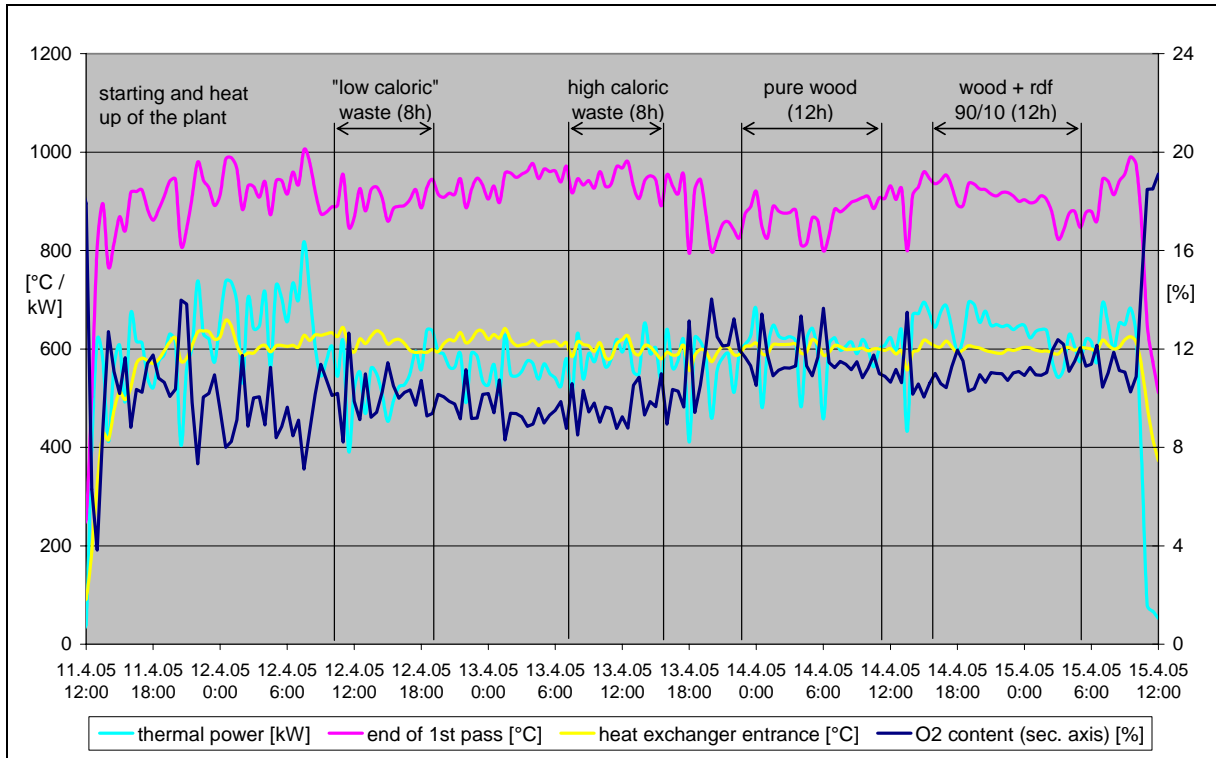


Fig. 10: Main process data during plant operation

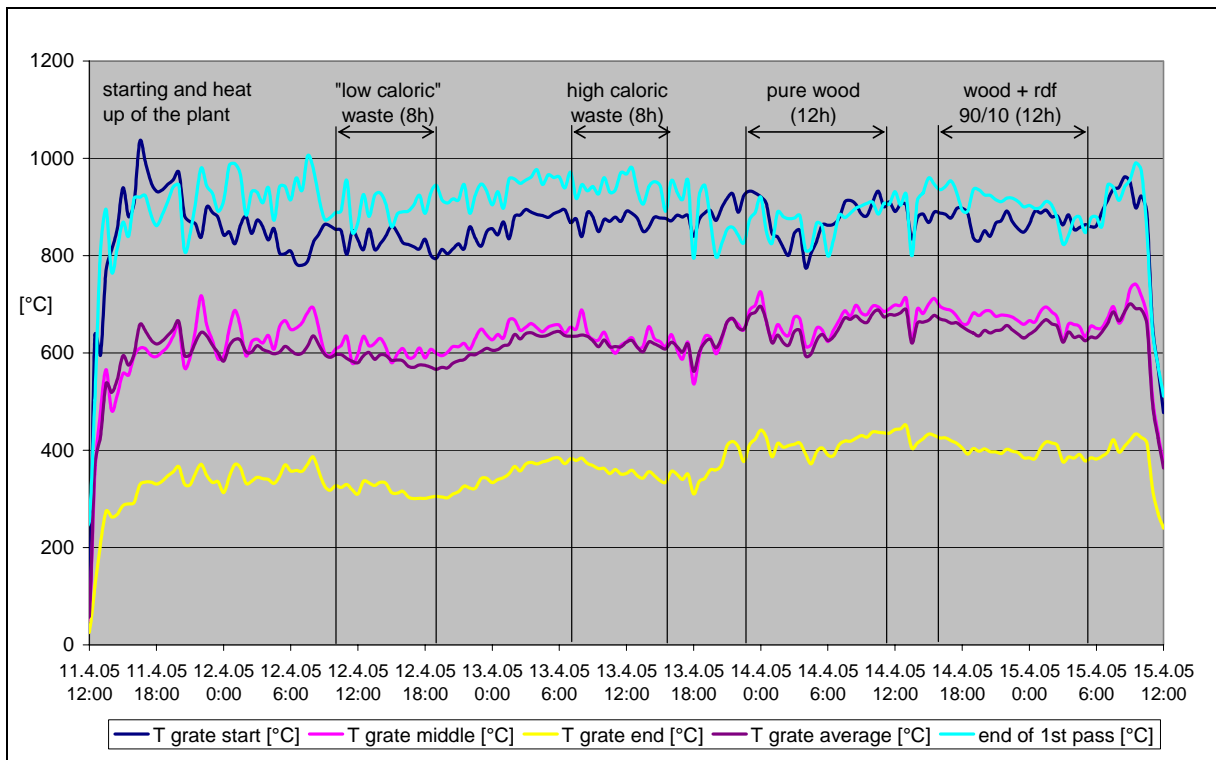


Fig. 11: Gas temperatures in 1st pass

In relation to the selection of the tube diameters some fundamentals about the building of deposits need to be explained.

A very effective mechanism for the building of deposits is the impaction of particles. The building of deposits by particles is a product of the amount and size of the particles in the flue gas, the probability of impaction, and the probability of adhesion. The amount, size and composition of the particles depend in principle on the fuel and

the combustion conditions (the combustion conditions, i.e. air ratio, were the same for all the fuels used). The impaction is proportional to the “Stokes” number and “Stokes” is proportional to the gas velocity divided by the tube diameter. This means that with small tube diameters there is a higher probability of impaction of particles. The probability of adhesion depends on material properties which are not yet known. Typical data for waste-to-energy-plants include gas velocity of 5 m/s and tube diameter of 40 mm. The gas velocity in the heat exchanger of the pilot plant is about 2 m/s. This means that we had to install a tube with a diameter about 16 mm to have similar conditions for impaction. In order to study the influence of the tube diameters 10, 15 and 21 mm tubes were chosen. All three tube diameters were installed at the entrance of the heat exchanger from the hall side (this means on the right-hand side in fig. 2); another 15 mm tube was installed from the framework (FW) side. The temperature of the tubes was measured using thermocouples and adjusted by cooling with compressed air inside. The deposits were collected from the windward side of the tubes over a length of 300 mm.

Analysis (mass and composition) of the sampled deposits from week 15/2005

After plant operation with low caloric waste and high caloric waste, there were enough deposits on all test tubes, so that the mass could be determined and the chemical composition could be analysed by XRD. After burning pure wood and wood with RDF, even after a longer time (12 h instead of 8 h) only the smallest tubes had enough deposit material on them to obtain reliable information.

The amount of deposits on different tube diameters after operation with waste is shown in figure 12. As expected, there is a decreasing mass from the smaller to the larger tube diameters. This decrease is even greater if you consider the mass related to the surface area. There is no great difference between deposits build during firing low caloric and high caloric waste.

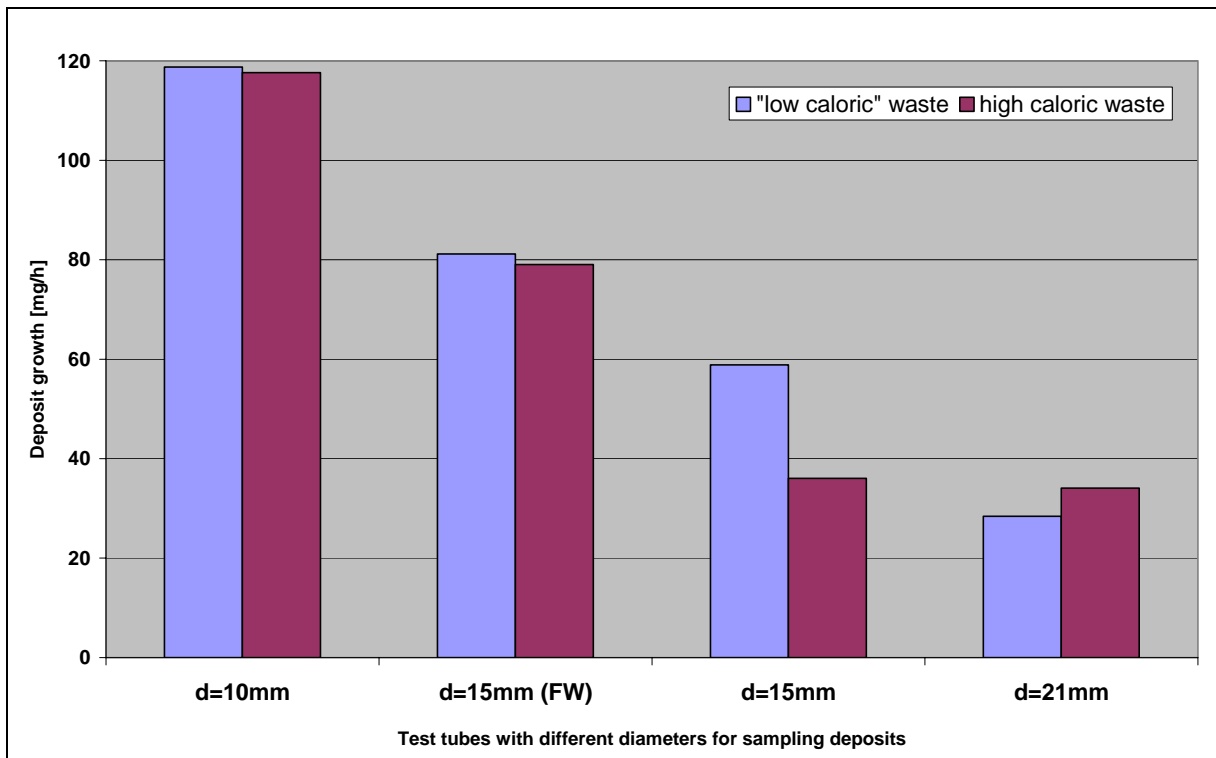


Fig. 12: Growth of deposits on different tube diameters during operation with waste
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The composition of the deposits and the mass of chlorine on different tube diameters is shown in figures 13 and 14 for operation with both waste fuels; they are very similar too. The fuel composition and sulphur/chlorine-ratio differ only slightly. There is no indication for a different release of ash components following different conditions in the fuel bed due to the different caloric values.

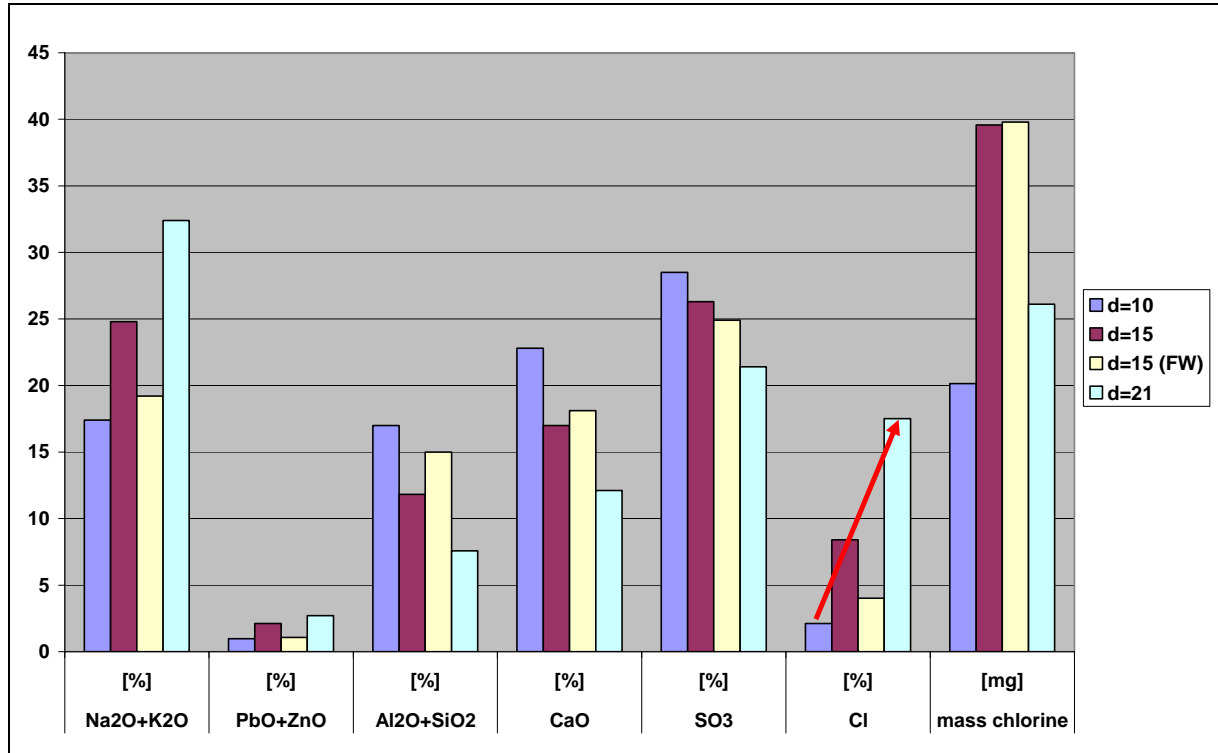


Figure 13: Deposits on different tube diameters after burning "low caloric" waste

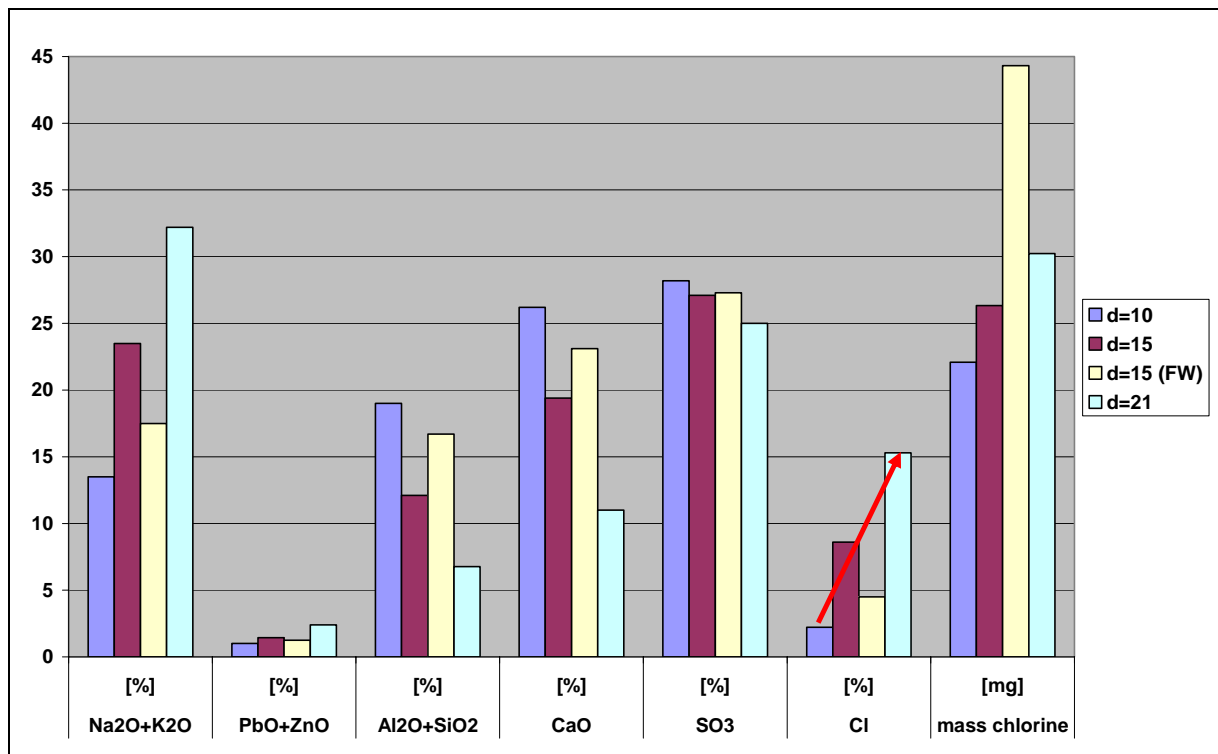


Figure 14: Deposits on different tube diameters after burning high caloric waste

The increase in the chlorine-content of the deposits from the smaller to the larger tube diameters is at first notable and surprises, because this is contrary to results obtained by us in another project.

Figures 15 and 16 give a hint, that this might be a result of the dilution by not themselves sticking elements. They show a decrease of soda, potassium and chlorine to higher specific amounts of deposits. It is assumed that these elements have build up a sticking ground and were diluted by other elements. More explanations are given at the results of the next plant operation week.

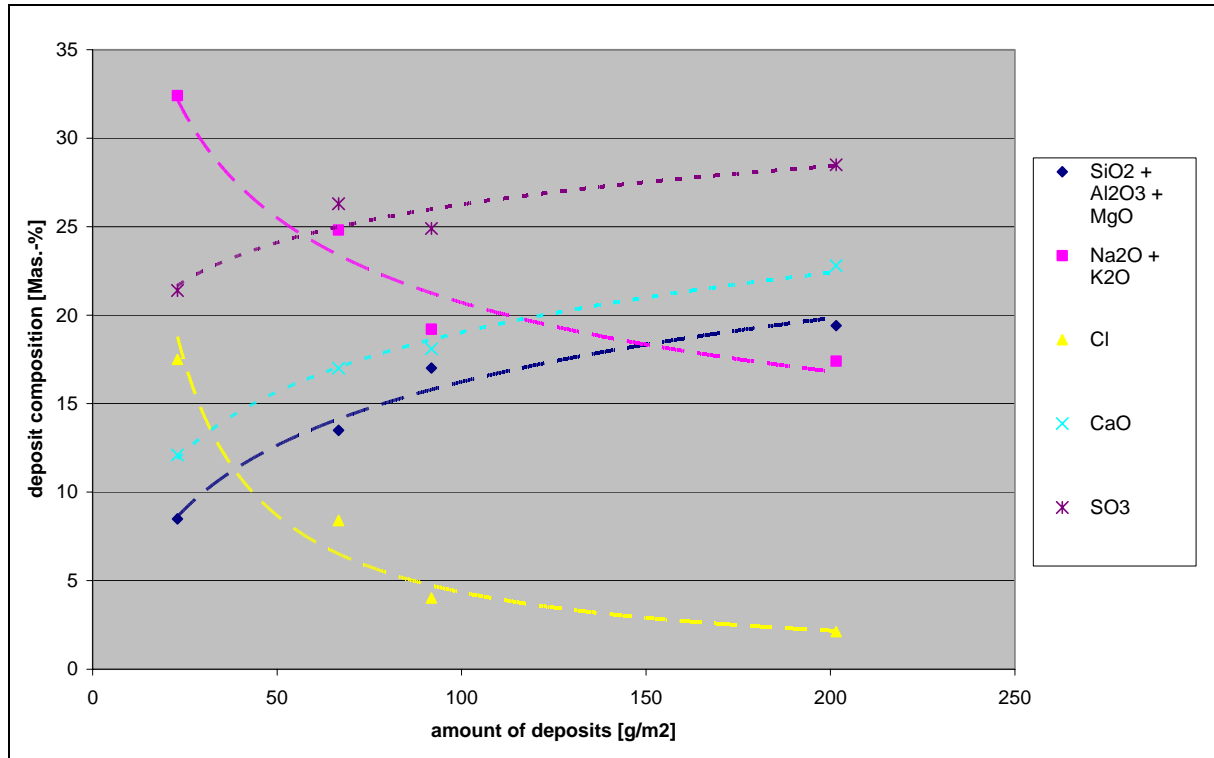


Fig. 15: Composition of deposits from burning "low caloric" waste

In figure 17 the deposits from the 10 mm tubes are compared for all four fuels. As similarly shown in figures 9 to 11 there is no great difference between the deposits from low and high caloric waste. While burning wood and wood with RDF the growth of deposits was slower; this corresponds with the low ash content of both materials. Although pure wood contains much less chlorine, the content of chlorine in the deposits was a little higher than in deposits from burning waste. The reason assumed is the sulphur content, which is also very low and inhibits a complete sulphating of alkali-chlorides. By adding RDF to wood the content of ash and chlorine (table 4) in the fuel increased. Therefore the increasing growth of deposit and the increasing chlorine content in the deposits is not surprising.

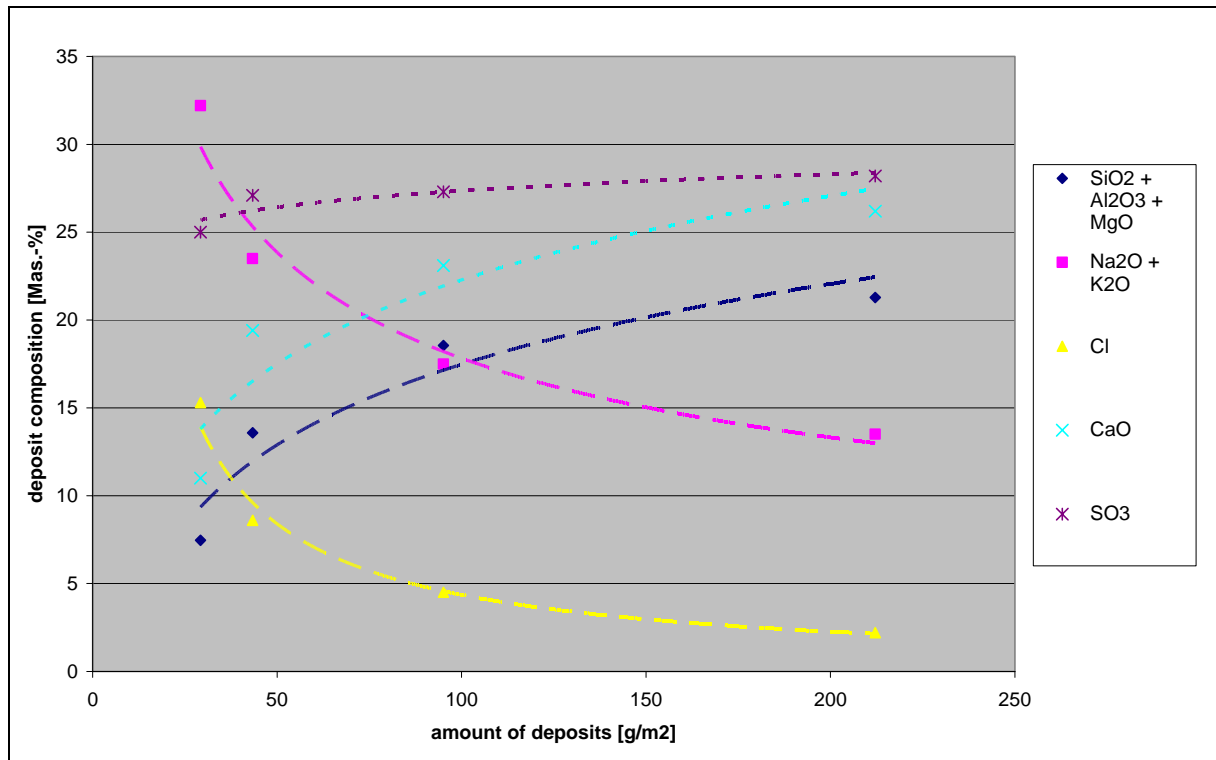


Fig. 16: Composition of deposits from burning high caloric waste

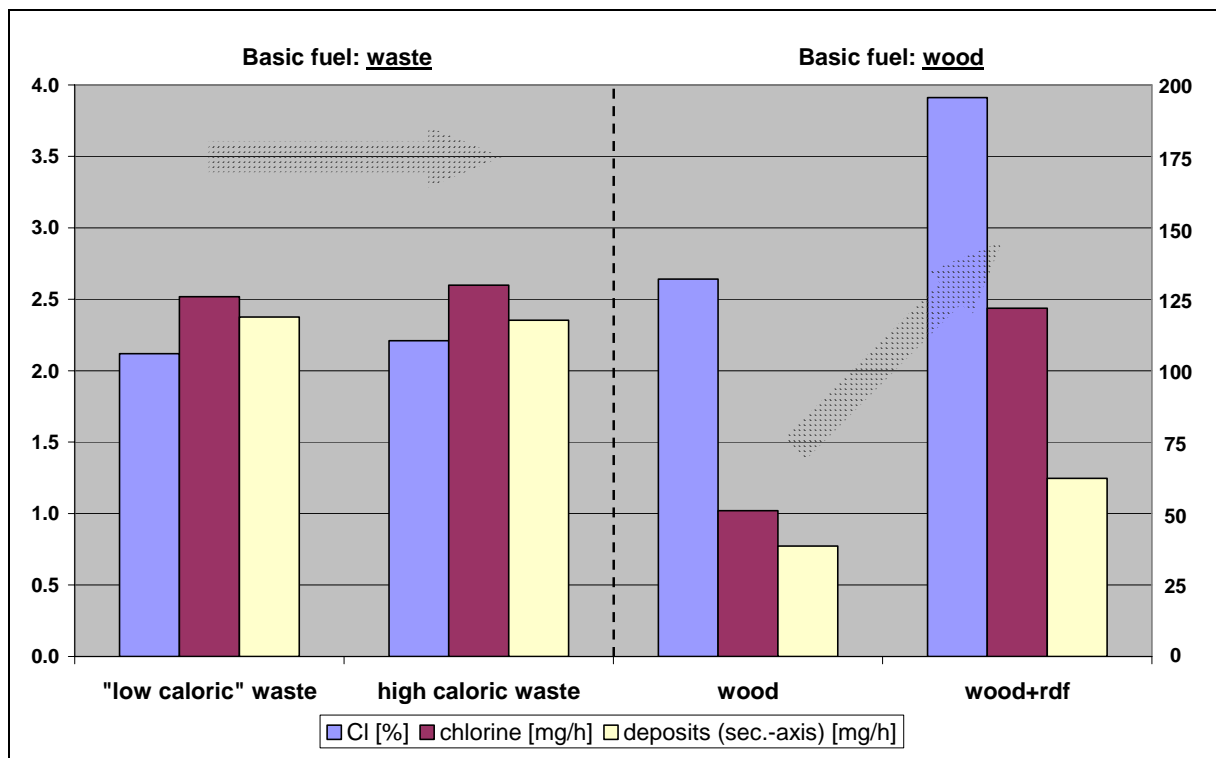


Fig. 17: Comparison of deposits from all four fuels used

Plant operation and investigations in week 42/2005

In week 42/2004 the third week of plant operation took place, with several exposures and investigations in growth of deposits. The plant was fired with wood and mixtures of wood with wheat straw and sugar beets, which are residues from agriculture. Wheat straw and sugar beets have been used in pellet form. An analysis of the different fuel mixtures used can be seen in table 5. The amount of ash and important components of the ash are marked in a yellow and the main variations in comparison to pure wood in an orange colour.

			100 % wood	20 % wheat straw & 80 % wood	20 % sugar beets & 80 % wood
water	w	Ma.-%	19.9	17.5	18.2
ash	a	Ma.-%	0.4	1.1	1.1
volatiles	V	Ma.-%	66.6	67.3	67.5
fixed carbon	C _{fix}	Ma.-%	13.1	14.0	13.2
lower caloric value	H _u	MJ/kg	13.1	13.7	13.3
carbon	C	Ma.-%	39.6	40.7	40.7
hydrogen	H	Ma.-%	5.8	5.9	5.8
oxygen	O	Ma.-%	34.1	34.4	33.7
nitrogen	N	Ma.-%	0.167	0.243	0.391
sulfur	S	Ma.-%	0.009	0.026	0.026
chlorine	Cl	Ma.-%	0.013	0.045	0.012
S/Cl-ratio			0.7	0.6	2.2
soda	Na	Ma.-%	0.013	0.014	0.017
potassium	K	Ma.-%	0.053	0.336	0.118
calcium	Ca	Ma.-%	0.088	0.115	0.221

Tab. 5: Composition of the biomass fuels used

The mixture of wood and wheat straw in comparison with pure wood contained more ash, sulphur and chlorine, but had nearly the same sulphur/chlorine-ratio. The mixture of wood and sugar beets contained more sulphur and had a higher sulphur/chlorine-ratio.

Figures 18 and 19 show the main process data of the firing in the first pass and at the entrance of the heat exchanger were the investigations about building of deposits have been done. The process conditions for all three measuring periods were about the same.

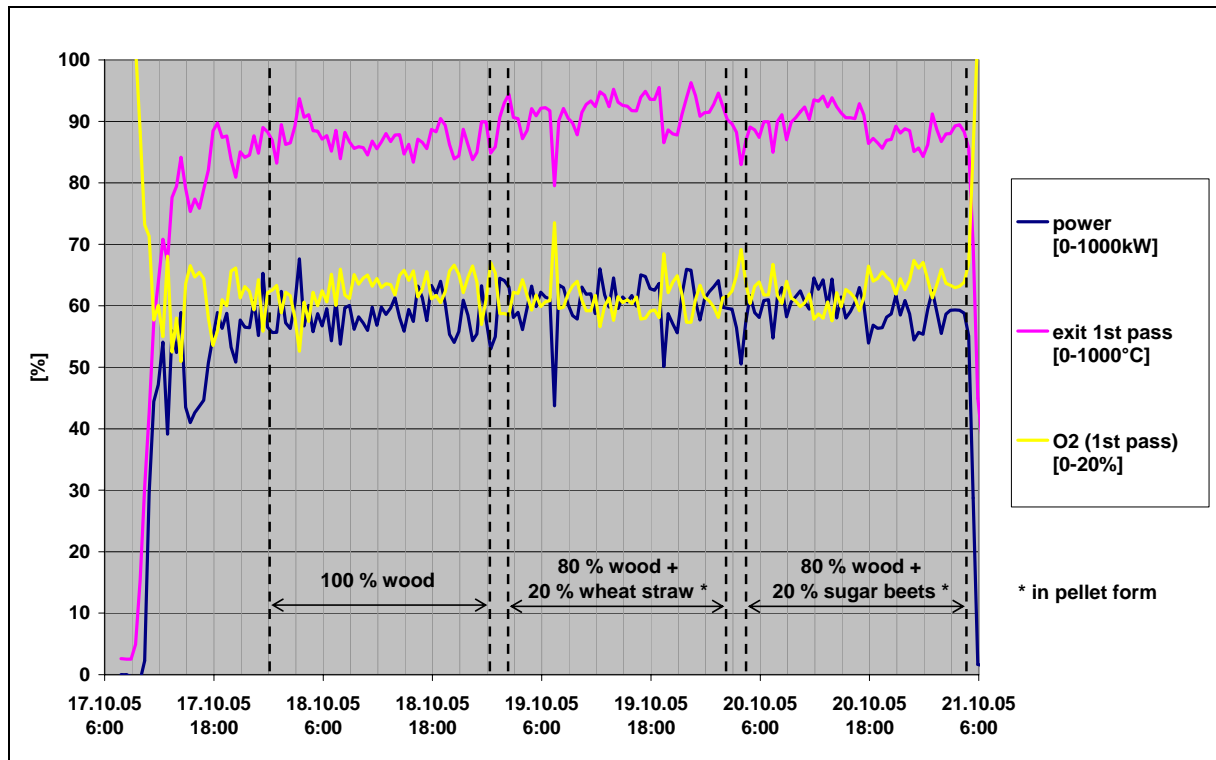


Fig. 18: Progress of the main operating parameters in 1st pass

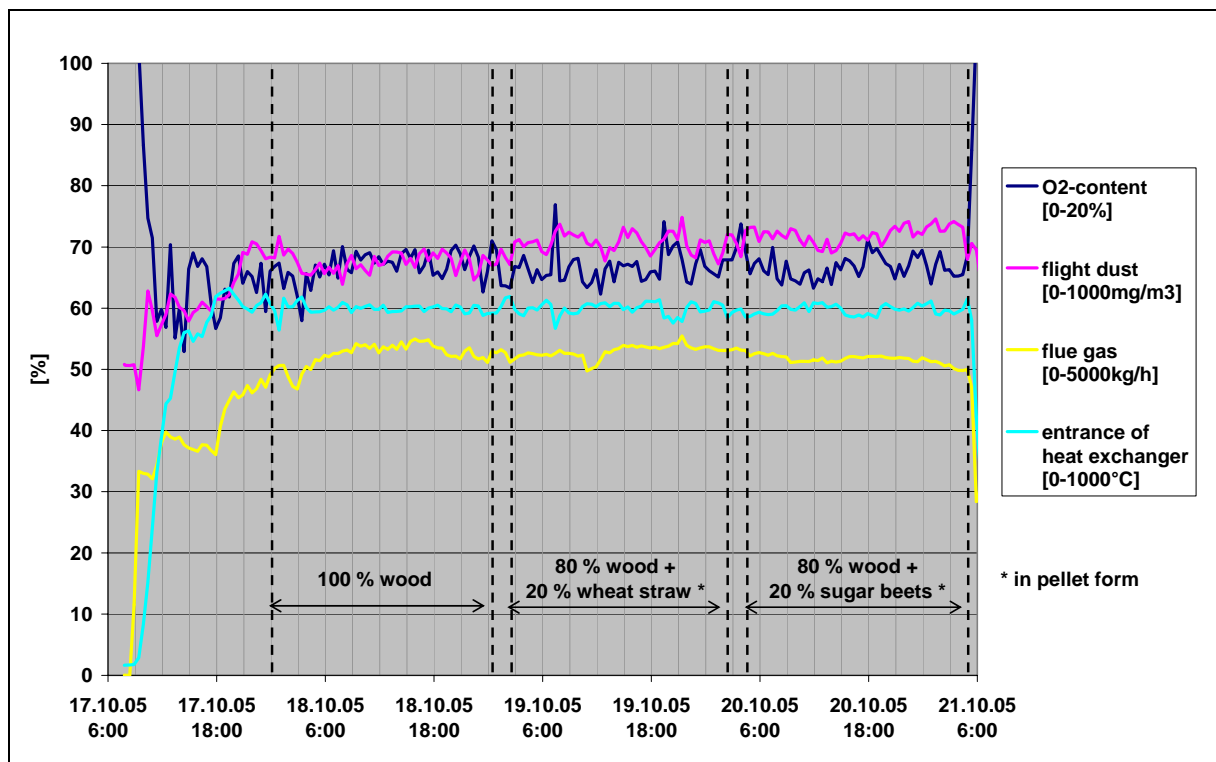


Fig. 19: Progress of operation data at the entrance in the heat exchanger

Exposure of sheets and tube probes from KIMAB in calendar week 42/2005

CUTEC received two sheets and three ring probes from KIMAB for an exposure at about 600 °C without any cooling. The materials have been installed at the entrance of the heat exchanger and have been exposed over the total operation time with all biomasses used. The materials are shown in figure 20 before and after exposure. They have been sent back to KIMAB for analyses. The loose dust has been analysed and the results have been send to KIMAB too.

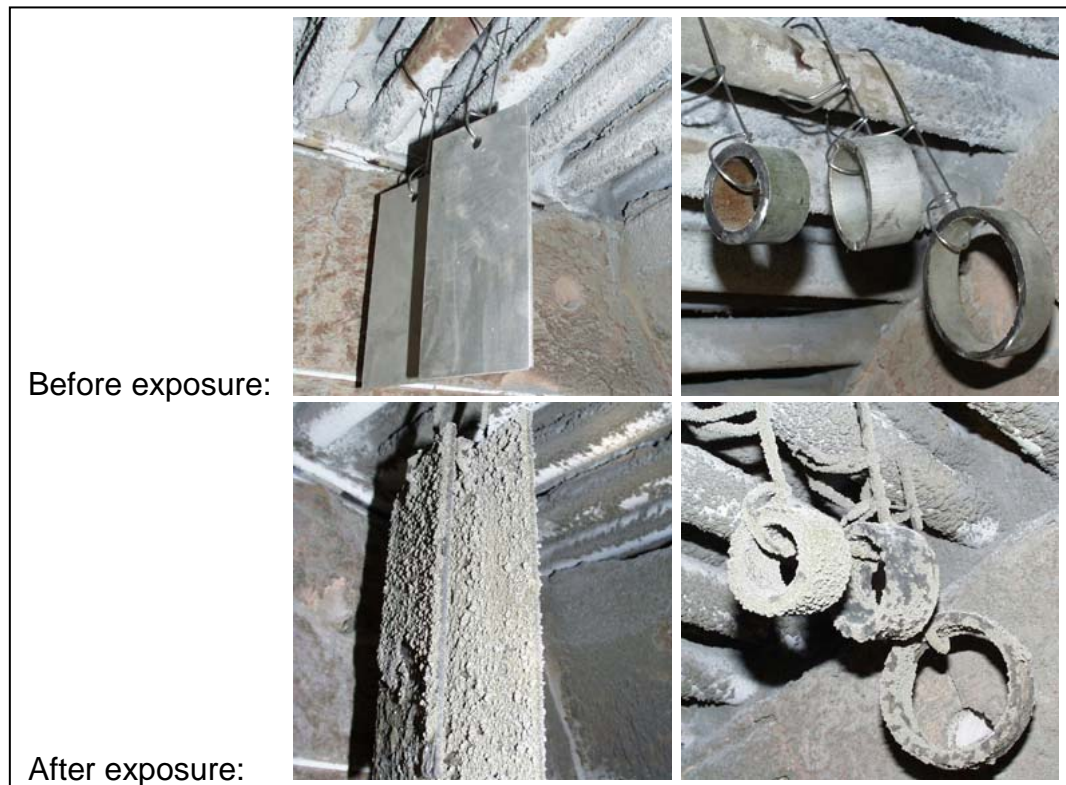


Fig. 20: Test materials from KIMAB before and after exposure

Investigations in building of deposits in week 42/2005

Like in former periods of plant operation there have been used several air-cooled tubes with different diameters to examine the growth of deposits. The flue gas temperature was about 600 °C and temperature of the tube material has been about 400°C.

The specific amounts of deposits build in 24 hours of plant operation are shown in figure 21 separate for each tube diameter and fuels. It is noticeable that in comparison to pure wood

- by adding wheat straw the amount of deposits increased for all tube diameters to roughly one level
- by adding sugar beets the amount of deposits increased too, especially for the smallest tube diameter; this is an indication for the impaction of small particles.

Both mixtures of wood with wheat straw and wood with sugar beets have nearly the same ash content, which is factor 3 higher as for pure wood. So the average increase of the deposits is in the estimated range.

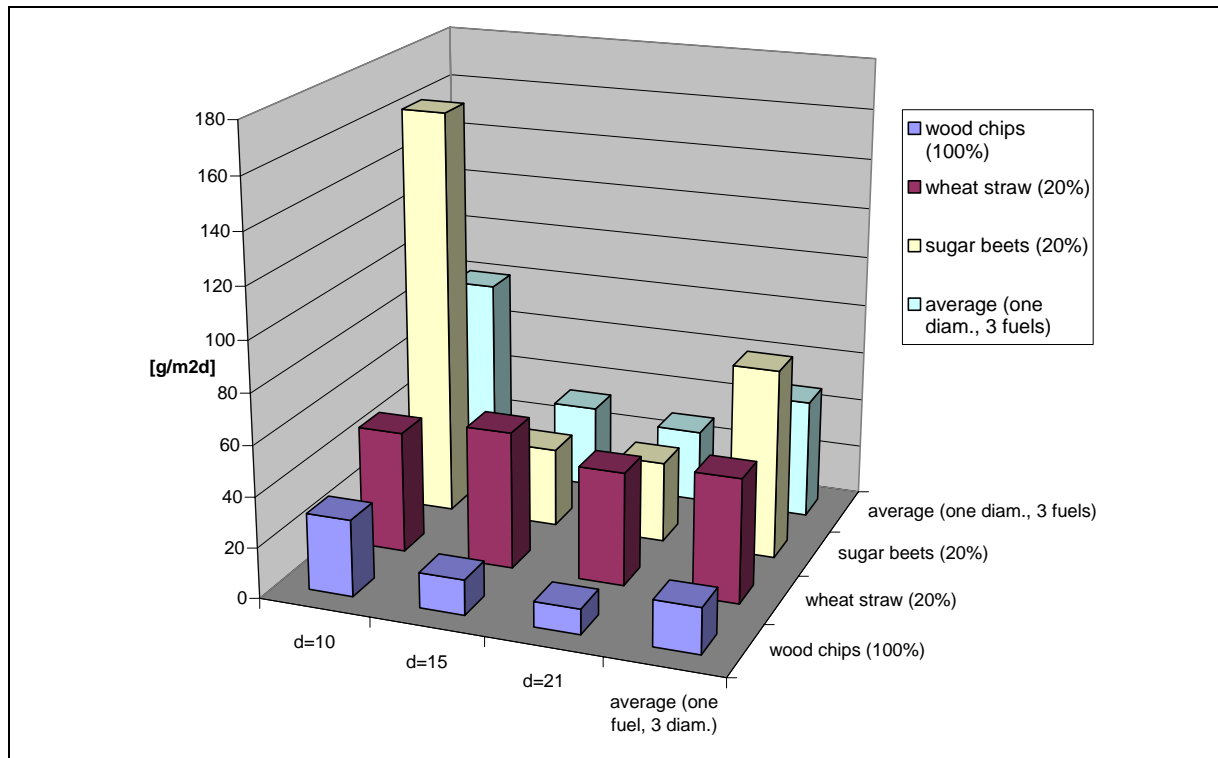


Fig. 21: Specific amount of deposits

The composition (only main components) of the deposits is visible in figure 22. There was a high content of potassium in the mixture of wood and wheat straw. This corresponds with the high content of alkali in the deposits. The deposits from burning wood and sugar beets contain only less chlorine. The higher sulphur/chlorine-ratio seems to produce a good sulphating of alkali-chlorides.

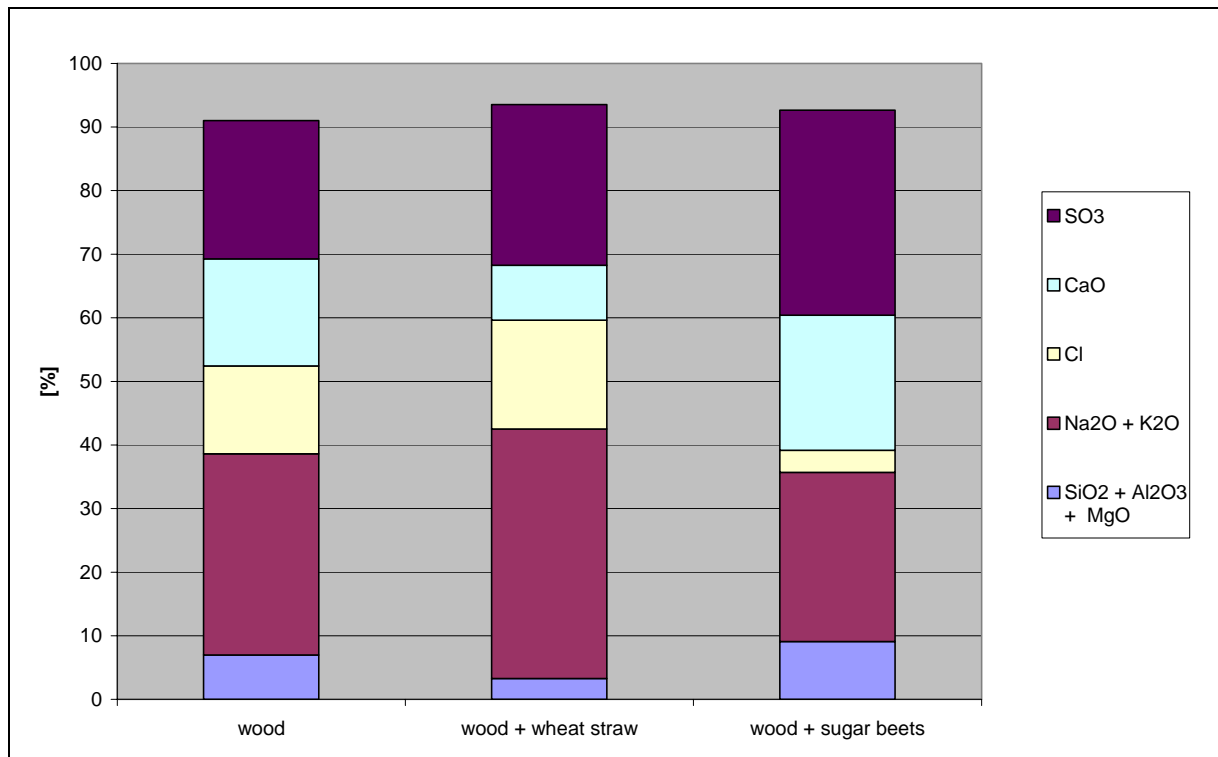


Fig. 22: Main components of deposits from different fuels (over all tube diameters)

There is an established critical value of 2 for the sulphur/chlorine-ratio in fuels. At an undercut - this rule says - there is a risk of (chlorine-) corrosion. The correlation between the chlorine-content of the sampled deposits and the sulphur/chlorine-ratio in the used fuels is shown in figure 23.

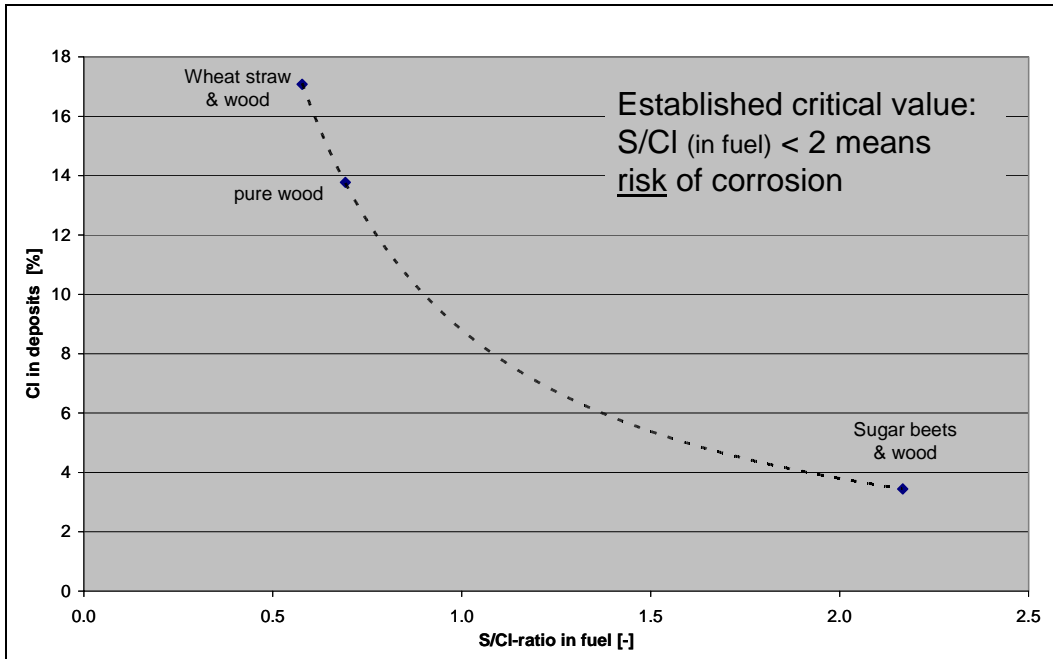


Fig. 23: Cl-content in deposits versus S/Cl-ratio in fuel (over all tube diameters)

The progress of the composition of deposits over the installed tube diameters is shown in figures 24 to 26 for each fuel used. The elements were analysed with XRF and are given in their oxide-form.

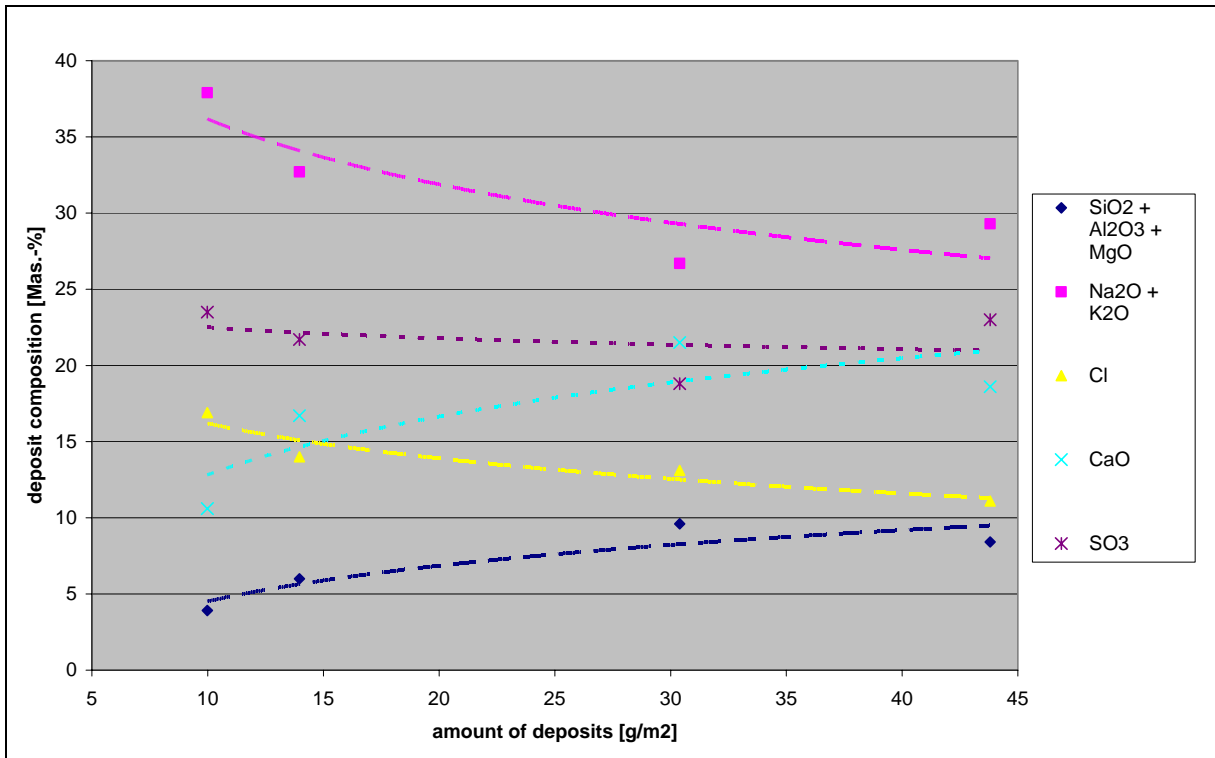


Fig. 24: Composition of deposits from burning pure wood

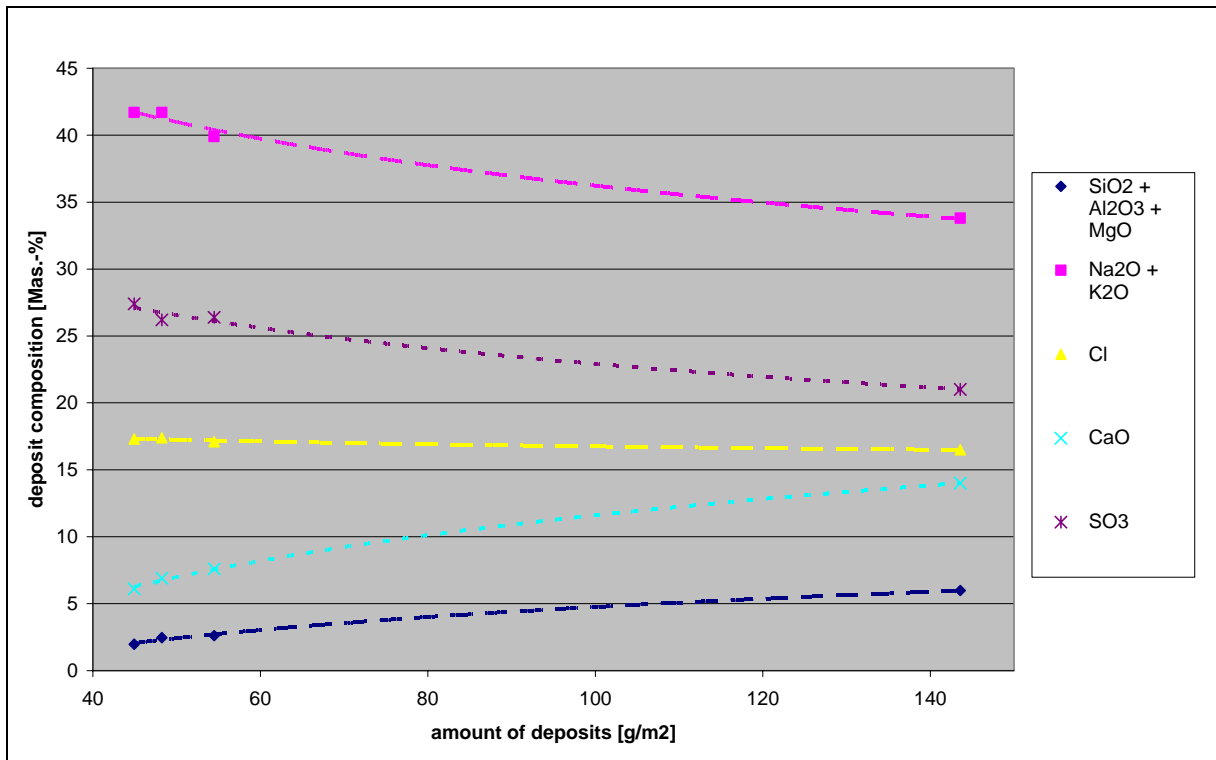


Fig. 25: Composition of deposits from burning wood and wheat straw

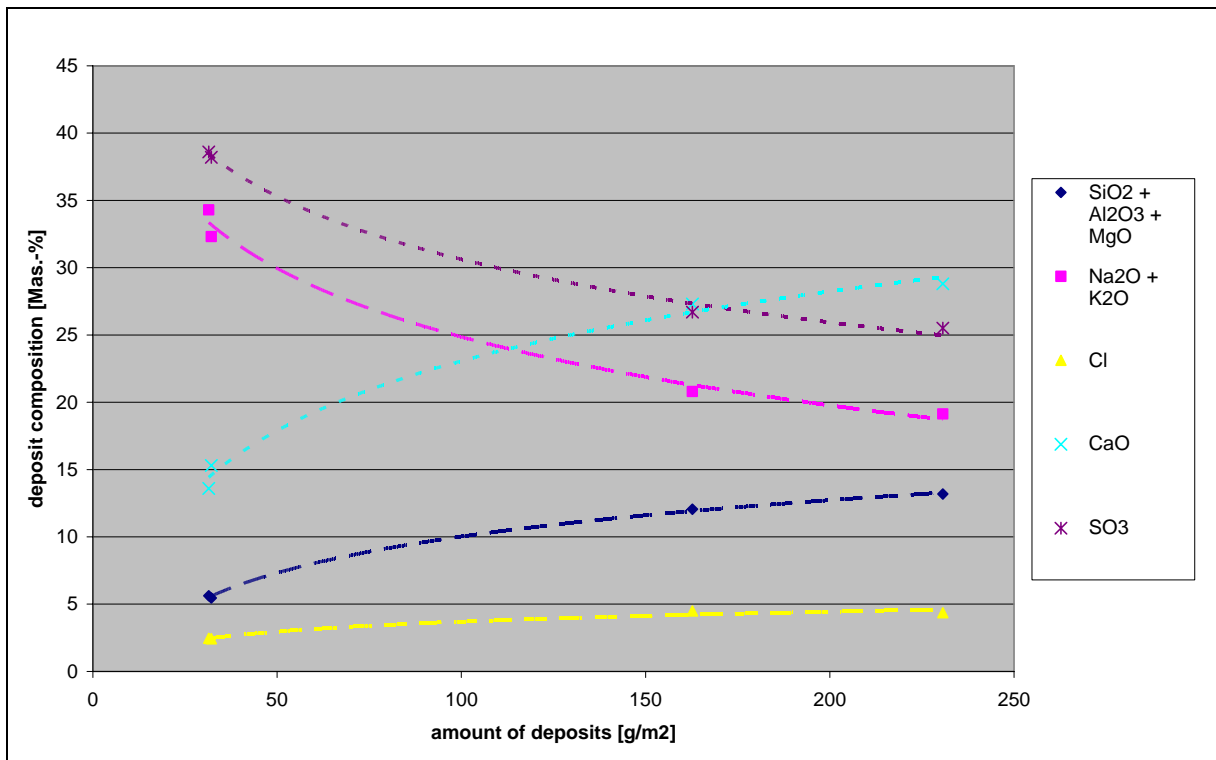


Fig. 26: Composition of deposits from burning wood and sugar beets

The building of deposits depends on the components in the flue gas, their transportation to the tube surface and also the probability of sticking. Sticking of particles on a tube surface can be caused by the features of the particle and also by the ground surface.

In the deposits from all fuels used there was an increasing content of soda and potassium and also sulphur to the higher amounts of deposits.

Especially soda and potassium are so called "sticking" elements which can exist in phases with relatively low melting points, so that particles can stick, and which can de-sublimate from gas phase too. When a sticking ground layer has been build, also particles which are not sticking by themselves, can stick on the surface. This means that the "sticking elements" are diluted by "not (by themselves) sticking elements".

This mechanism of dilution is assumed to be the reason for the decrease of soda and potassium to high amounts of deposits.

Sulphur in deposits mainly exists in form of calcium-sulphate, alkali-sulphate or mixtures of them. Figures 24 to 26 show a similar progress of alkalis and sulphur. So in this cases sulphur seems to exist mainly in form of alkali-sulphate and to vary with the alkalis.

At every fuel used the content of silicone, aluminium, magnesium and calcium in deposits increased to higher amounts of deposits.

These elements mainly exist in mineral phases which have high melting temperatures and are not sticking by themselves.

It is assumed that these elements were integrated in the deposits, when a sticking ground layer has been build up before.

The progress of the chlorine-content once shows a decrease (pure wood), once nearly no variation (wood & wheat straw) and once an increase (wood & sugar beets) to higher amounts of deposits. In this list the maximum amount of deposits has increased (up to 45, 145, 235 g/m²).

Alkali-chlorides are sticking compounds, so that a decrease by dilution has to be expected. But at higher amounts of deposits there is not only a flat deposit layer on the surface; at the windward-side there were also dendritic structures of the deposits. These very small barriers have a very high probability for impaction of small particles. It is known that the smallest particles have the highest chlorine-content.

This effect is assumed to be the reason for compensation of the decrease and change it to an increase of the chlorine-content at the highest amount of deposits.

Plant operation and investigations in week 25/2006

In week 25/2006 the fourth week of plant operation took place, with several investigations in deposits and corrosion of exposed materials. The grate was fired with cut and homogenised municipal solid waste from a mechanical conditioning facility. Because high caloric materials had been separated before cutting in order to produce refuse derived fuels (RDF), we had to add this high caloric RDF to obtain a normal caloric waste with about 9.5 MJ/kg.

One aim was to determine the influence of the primary air ratio on the building of deposits. This is expected by a changed release of components from the grate. There are two main effects for release of components from the grate. Small solid particles can be blown up with primary air into the flue gas. And volatile substances can vaporise and get gaseous into the flue gas.

Therefore the mass of primary air has been varied. Figure 27 shows main process data in first pass during process operation. To get a similar total air ratio and similar flue gas temperatures at the end of the 1st pass and the following parts the secondary air has been adjusted too. There were also short-term variations of secondary air, because this was part of an oxygen-control. It was planned to operate the plant with primary air ratios 1.0, 1.2 and 1.4. These are all in a normal range, so that exposures would be under normal conditions. By variability of thermal power and by infiltrated air especially through the feeder the real primary air ratios differ from the planned ones. The real primary air ratios were afterwards calculated from masses of flue gas, primary air, secondary air and the oxygen content in flue gas to 1.05, 1.29 and 1.42. In the period with a designated primary air ratio of 1.2 the thermal power was a little bit to low, and therefore the deviation of the real primary air ratio is the biggest one.

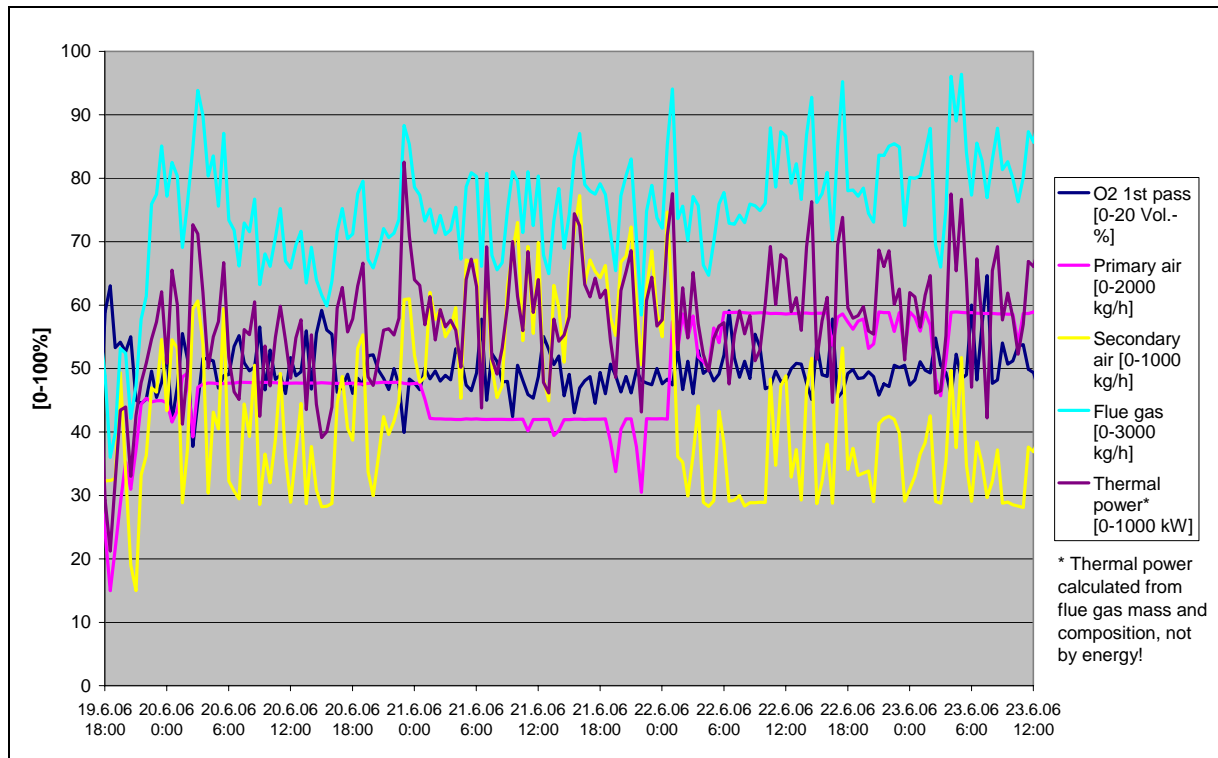


Fig. 27: Progress of main operation data in first pass

Table 6 shows average values of main operation data in 1st pass.

λ prim. air	Primary air*	Flue gas	Flue gas temper.	O ₂ - content	λ total	Thermal power
[-]	[kg/h]	[kg/h]	[°C]	[%]	[-]	[kW]
$\lambda=1.05$	948	1689	881	9.7	1.88	591
$\lambda=1.29$	1091	1622	864	9.9	1.93	554
$\lambda=1.42$	1260	1736	891	9.9	1.91	595
average	1100	1682	878	9.9	1.91	580

* including infiltrated air especially through the feeder

Table 6: Average values of main operation data in first pass

The effect of the different masses of primary air on the gas temperatures directly above the grate and on a level below secondary air injection is shown in figure 28.

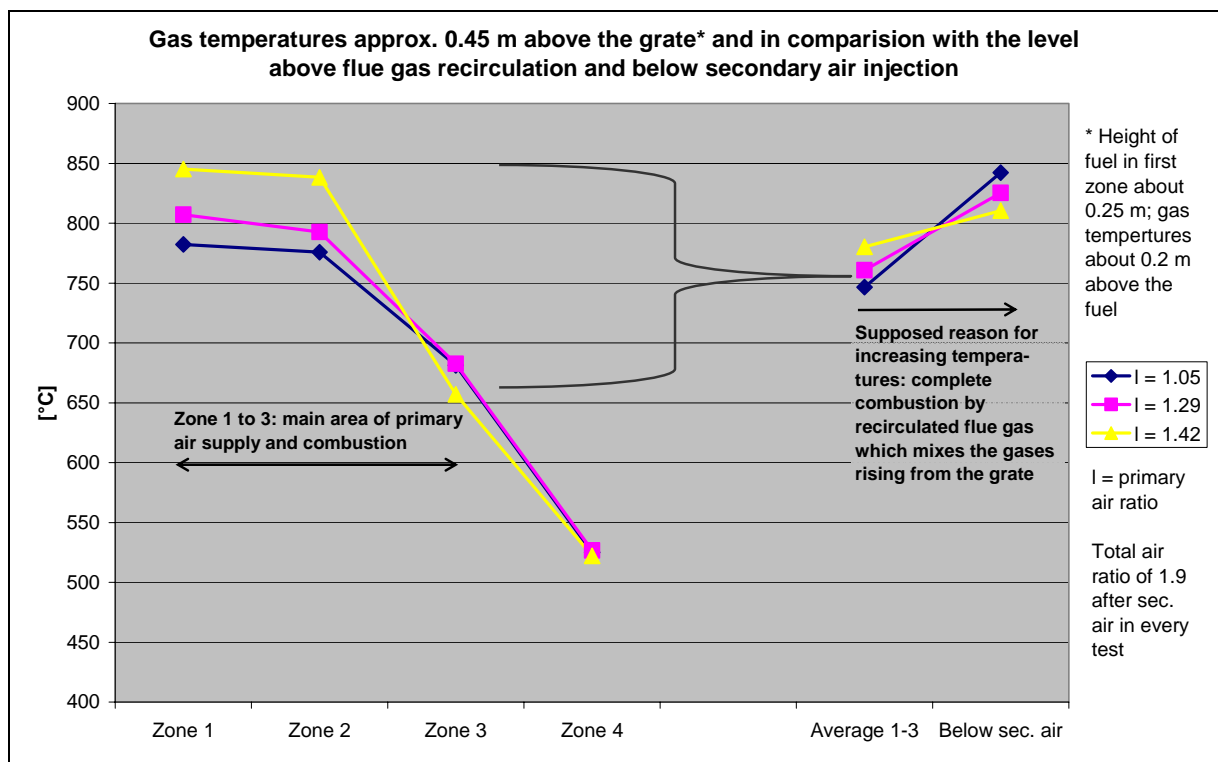


Fig. 28: Effects of different primary air ratios on temperatures in 1st pass

The flue gas temperatures at the top of the first pass in every period of primary air adjustment were about the same (see figure 29) because the total air ratio was nearly constant.

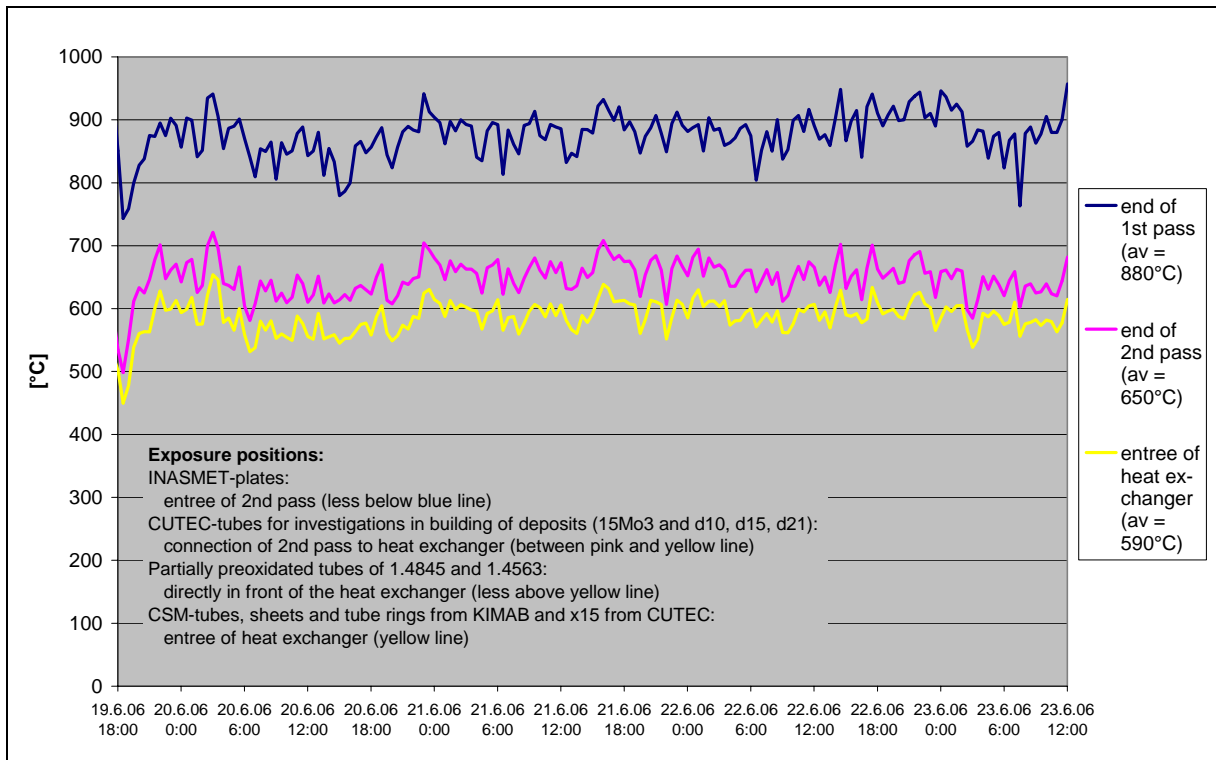


Fig. 29: Progress of flue gas temperatures at different positions

Exposure of samples from Inasmet, KIMAB and CSM in week 25/2006

From Inasmet two coated plates (HC276 and INCONEL 625 by SMAW) were sent to CUTEC for exposure. In our first test week in 2004 plates were installed at the top of the first pass. Now plates were installed in the upper part of the second pass at flue gas temperatures of about 850 °C at a side wall. As visible in figure 30 the plates showed a clear difference in ash adhesion. The composition of the deposits was very similar (table 7).

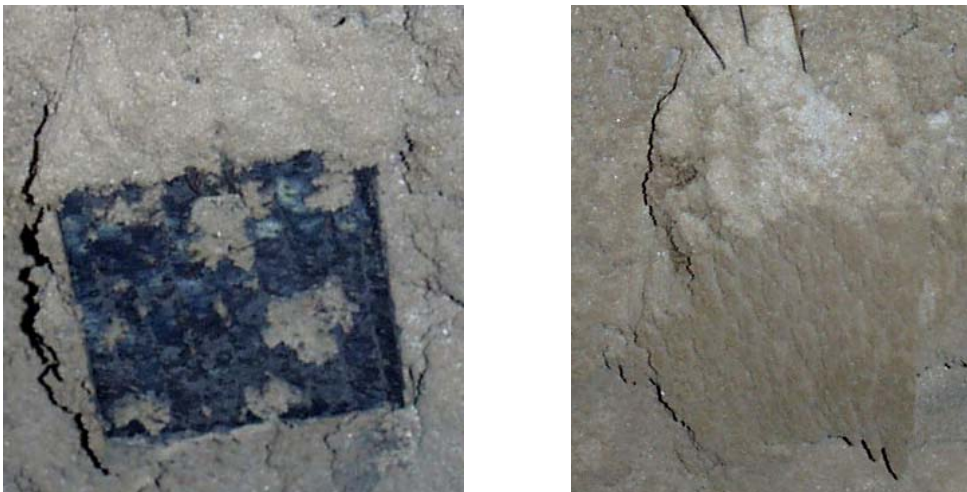


Fig. 30: Ash adhesion on HC276 (left) and INCONEL 625 (right)

In the third test week (42/2005) with biomass fire two sheets and three tube rings from KIMAB were exposed. In this week with waste fuel new samples of the same materials have been exposed in the same way. They were fixed at the first tubes of the heat exchanger at flue gas temperatures of about 580 °C without any cooling.

Both coated tubes of CSM (one with coatings "A"+"B"; one with coatings "C" + "D") were installed also in front of the first tubes of the heat exchanger at flue gas temperatures of about 580 °C. By cooling with water and pressurized air a material temperature of about 400 °C has been realized.

All samples were sent back to the project partners for material analysis. Deposit analysis with X-ray fluorescence analysis was made by CUTEC and the results were also sent to the partners. Important data for deposit growth and compositions of deposits from the exposed samples of the partners and on some test tubes from CUTEC are shown in table 7. The elemental composition is as usual given in oxide form (exception: chlorine), although the chemical bounding in not known.

The progress of deposit composition on the way of the flue gas flow is shown in figure 31. The plates from Inasmet in the 2nd pass without cooling as well as cooled and not cooled tubes in the entrance of heat exchanger have rather similar deposits compositions.

All these materials have been exposed over the whole operation time with three adjusted primary air ratios, which in average had a usual value of 1.25.

Partner	Inasmet	Inasmet	CUTEC	CUTEC	CUTEC	KIMAB	KIMAB	CSM	CUTEC
Material	Inconel 625	Hastelloy C-276	1.4571* ¹	15Mo3* ¹	1.4845 / 1.4563 * ²	B2+B4 (average)	B1,B5,B6 (average)	coating "C"	1.4571* ¹
Form	plates	plates	d=21mm	d=34mm	d=33mm	sheets	rings	d=34mm	d=15mm
Flue gas [°C]	850	850	640	640	610	580	580	580	580
Sample [°]	850	850	388	507	427	580	580	425	424
Position	2nd pass		duct: 2nd pass - heat exchanger			entree of heat exchanger			
Gas flow	parallel to surface		horizontal gas velocity (4-5 m/s)			lower gas velocity (on average)			
Na ₂ O [%]	3,8	3,8	5,3	7,0	5,6	3,5	4,2	5,0	4,1
MgO [%]	2,2	2,3	1,9	1,2	1,3	1,8	1,8	1,8	1,8
Al ₂ O ₃ [%]	4,4	4,4	4,2	3,0	2,8	4,2	4,0	4,0	4,2
SiO ₂ [%]	14,4	16,5	10,9	6,8	10,0	14,2	12,4	12,5	12,5
P ₂ O ₅ [%]	1,8	2,2	1,2	0,9	1,0	1,4	1,3	1,4	1,2
SO ₃ [%]	31,0	27,4	28,4	32,8	37,0	33,1	35,1	30,7	33,2
Cl [%]	0,5	0,8	5,3	8,8	1,4	1,0	0,8	2,1	1,4
K ₂ O [%]	5,9	5,9	7,6	12,5	11,4	4,4	5,9	6,9	6,4
CaO [%]	30,0	30,2	28,9	21,5	23,8	30,4	28,7	30,0	29,9
TiO ₂ [%]	1,0	1,0	1,0	0,6	0,7	1,2	1,0	1,0	1,1
Fe ₂ O ₃ [%]	2,6	2,5	2,5	2,5	2,3	2,5	2,3	2,2	2,1
ZnO [%]	0,6	0,6	0,7	0,9	0,9	0,6	0,6	0,7	0,7
PbO [%]	0,0	0,0	0,0	0,1	0,2	0,1	0,2	0,3	0,1

*¹ Tubes for investigations in building of deposits; no material analysis was done

*² Tubes were produced from Sandvik Germany and sent to MPIE for material analysis

Table 7: Conditions for growth of deposits and deposit compositions

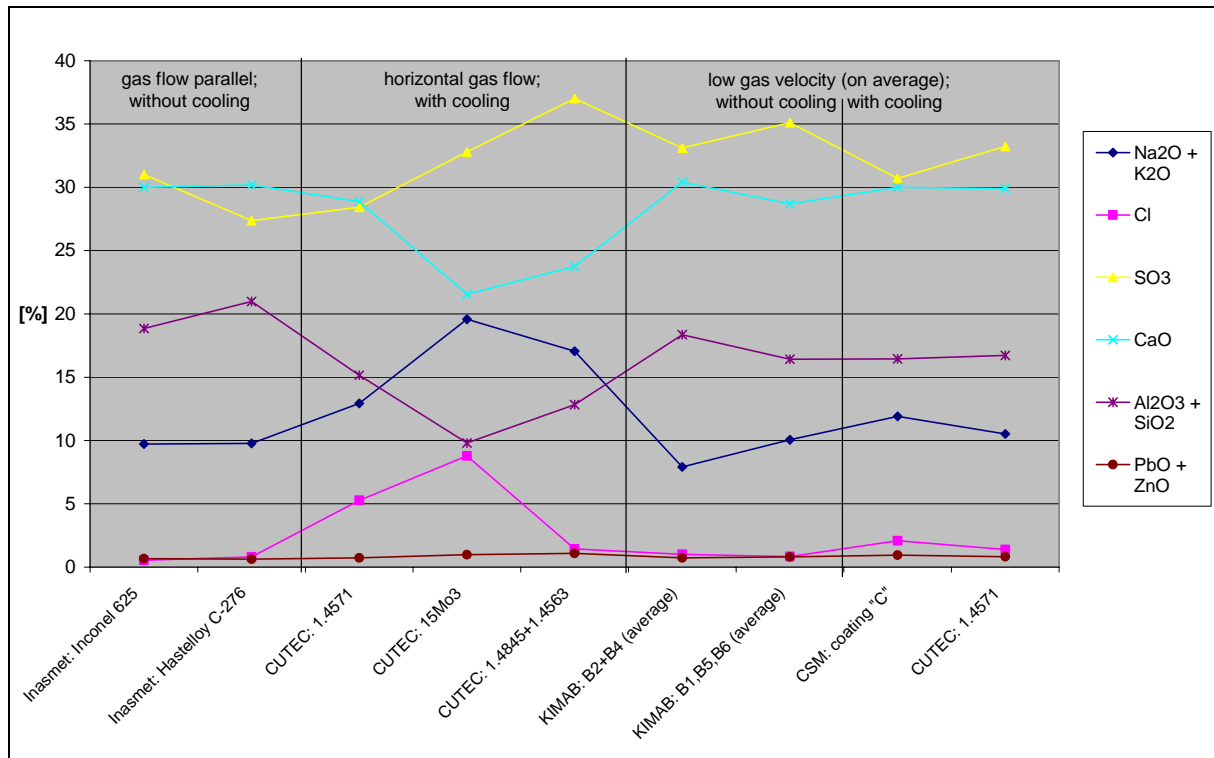


Fig. 31: Progress of deposit composition on the way of the flue gas

Test of pre-oxidized materials in week 25/2006

For investigations of the influence of pre-oxidation tubes of 1.4845 (25 % Cr, 20 % Ni) and 1.4563 (27 % Cr, 31 % Ni, 3.5 % Mo) have been used in this week. The same materials have also been used for pre-oxidation by project partners. Figure 32 shows both materials with and without pre-oxidation for 4 hours at 450 °C before their exposure.

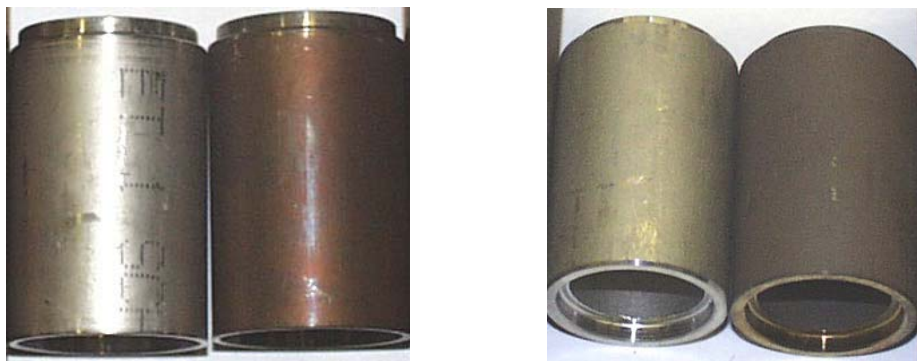


Fig. 32: 1.4563 without/with pre-oxidation

1.4845 without/with pre-oxidation

Both segments of one material have been done on the same lance directly next to each other. Both lances have been installed in front of the heat exchanger at a flue gas temperature of about 610 °C also next to each other. They have been cooled by pressurized air to a material temperature of about 425 °C. Unfortunately there was a short failure in the pressurized air supply which was used for cooling. Thereby the material temperature of the tubes for a very short time had increased to about 500 °C. After plant operation these tubes have been sent to MPIE for material analysis.

Figure 33 shows two segments after exposure. Micrograph sections of the windward-side, flank and lee-side from all four segments are shown in figure 34. From all shown micrograph sections SEM/EDX – analysis have been done. In figures 35 and 36 the maps for the main elements are shown exemplary for two micrograph sections: The windward-side of 1.4563 without pre-oxidation and the lee-side of 1.4845 with pre-oxidation.

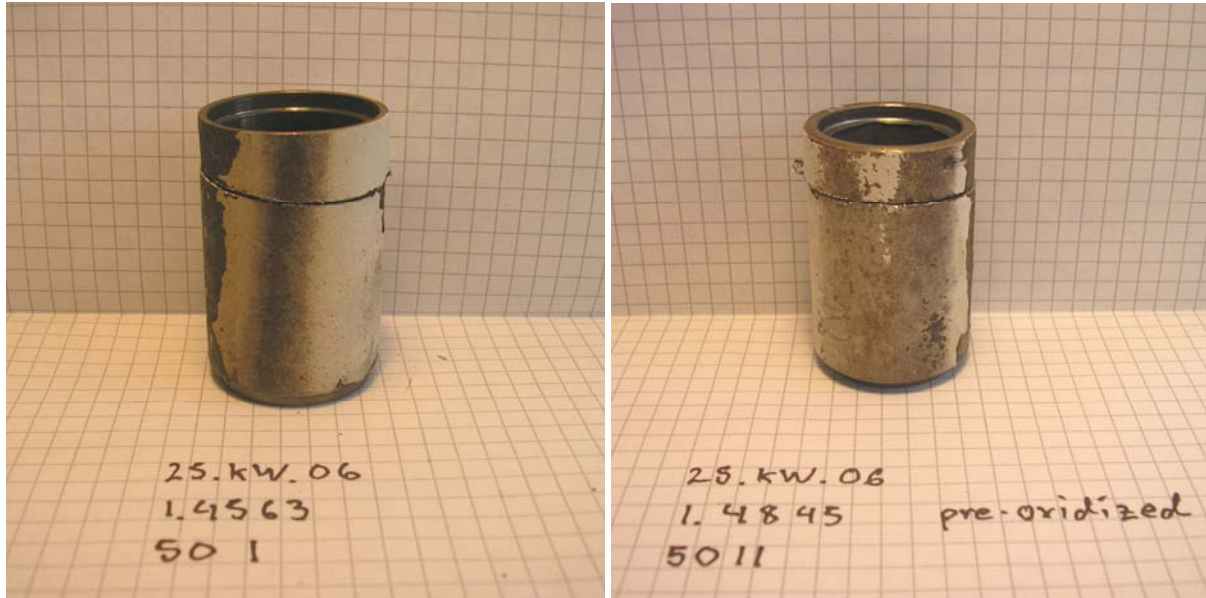


Fig. 33: Windward-side of 1.4563 without and lee-side of 1.4845 with pre-oxidation

1.4563		1.4845		
				windward-side
				flank
				lee-side
without pre-ox.	with pre-ox.	without pre-ox.	with pre-ox.	

Fig. 34: Polished micrograph sections of all segments (windward-side, flank, lee-side)

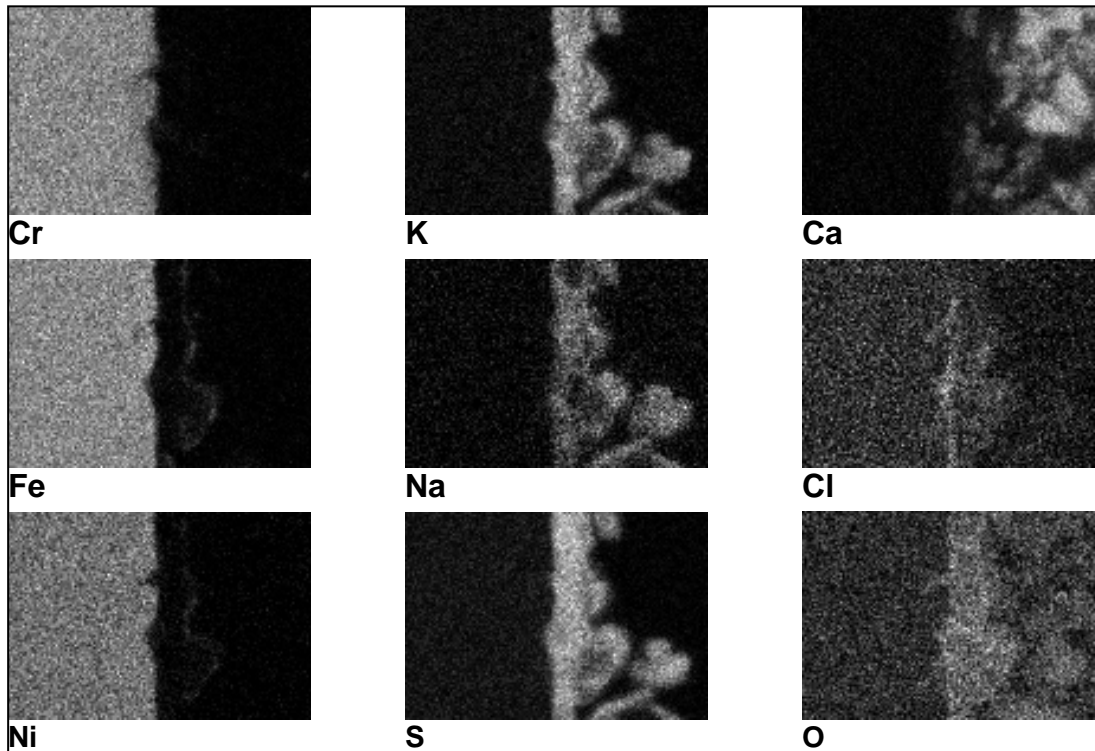


Fig. 35: SEM/EDX-analysis at windward-side of 1.4563 without pre-oxidation

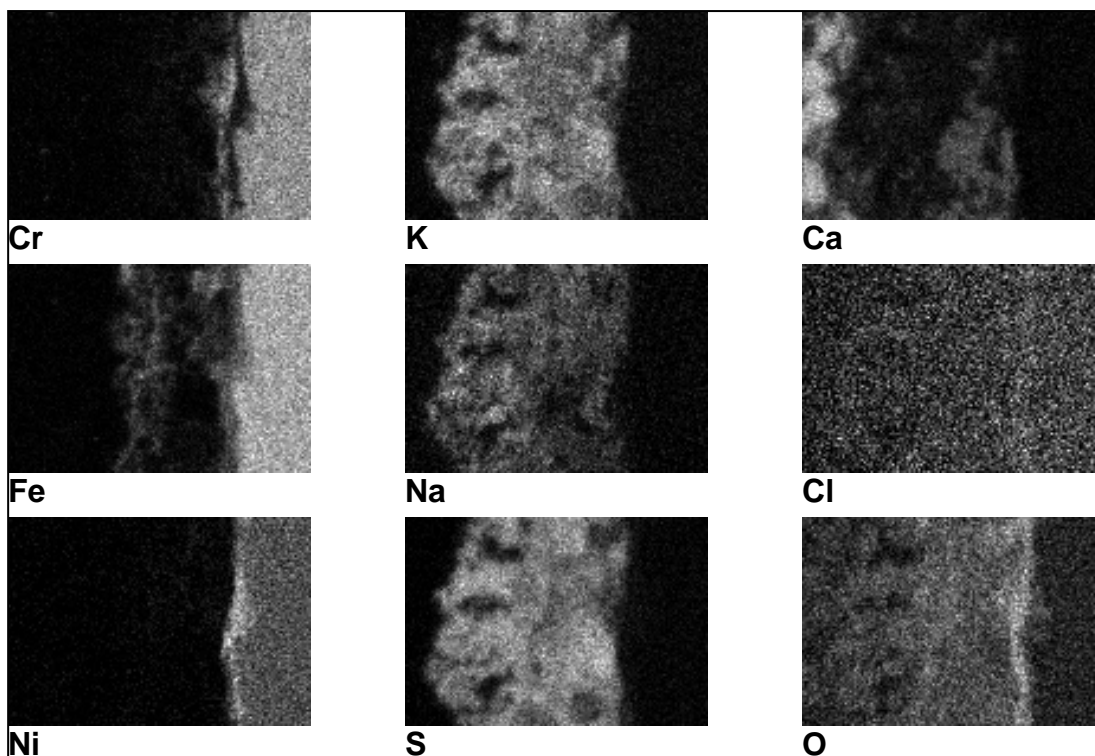


Fig. 36: SEM/EDX-analysis at lee-side of 1.4845 with pre-oxidation

The analysis show following results:

- The main deposit on all samples is $(\text{Na,K})_2\text{SO}_4$ (s)
- There is only less chlorine in deposits and also at the deposit/oxide interface
- Only minimal corrosion can be seen (corresponds with less chlorine-contents)
- In these tests neither pre-treatment nor material or position on tube shows a clear correlation to deposit composition or thickness of corrosion zone.

Investigations in influence of tube diameter and primary air ratio on growth and composition of deposits in week 25/2006

Like in former periods of plant operation several air-cooled tubes with different diameters have been used to examine the growth of deposits. It was not possible to use all the same ports for this investigation like in the two plant operation weeks before, because they partially were taken for exposure of CSM-tubes. Therefore the three different tube diameters (10, 15 and 21 mm) have been installed in the duct between the 2nd pass and the heat exchanger. An additional tube with a diameter of 15 mm has been installed in the entrance of the heat exchanger, which is named X15 for differentiation.

All these tubes have been taken out after each period with an adjustment of the primary air ratio (λ_p or "l p" in diagrams) to collect the deposits.

The flue gas temperature at tubes d10, d15 and d21 was about 640 °C and at X15 about 580 °C. The intended material temperature was 400°C, which in average was achieved. Table 8 shows masses and compositions of the deposits from different tube diameters and periods with different primary air ratios. The highest chlorine-contents are marked yellow. Masses and chlorine-contents for the different primary air ratios are also pictured in following diagrams.

	average (d10, d15, d21)			X15 (in heat exchanger)			average ($\lambda_p=1.0$, $\lambda_p=1.29$, $\lambda_p=1.42$)			
	$\lambda_p=1.05$	$\lambda_p=1.29$	$\lambda_p=1.42$	$\lambda_p=1.05$	$\lambda_p=1.29$	$\lambda_p=1.42$	d10	d15	d21	X15
Na ₂ O [%]	5.2	5.6	5.1	3.8	4.9	3.6	5.3	5.3	5.3	4.1
MgO [%]	1.8	1.7	1.9	1.8	1.6	2.0	1.7	1.8	1.9	1.8
Al ₂ O ₃ [%]	4.2	3.8	4.2	4.4	3.5	4.6	3.9	4.2	4.2	4.2
SiO ₂ [%]	11.0	11.3	10.3	13.0	11.9	12.7	10.6	11.1	10.9	12.5
P ₂ O ₅ [%]	1.2	1.0	1.4	1.2	1.0	1.5	1.2	1.2	1.2	1.2
SO ₃ [%]	30.9	28.8	31.8	33.3	33.6	32.8	32.3	30.8	28.4	33.2
Cl [%]	3.2	5.1	3.8	0.7	1.8	1.7	3.2	3.6	5.3	1.4
K ₂ O [%]	8.1	8.7	7.2	5.6	9.0	4.7	8.5	7.8	7.6	6.4
CaO [%]	28.1	28.0	28.9	30.5	28.1	31.1	27.9	28.3	28.9	29.9
TiO ₂ [%]	0.9	0.9	1.0	1.1	0.9	1.3	0.9	0.9	1.0	1.1
Fe ₂ O ₃ [%]	2.5	2.5	2.1	2.2	2.0	2.1	2.2	2.5	2.5	2.1
ZnO [%]	0.7	0.7	0.6	0.7	0.9	0.6	0.7	0.7	0.7	0.7
PbO [%]	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.0	0.0	0.1
mass [g]	9.8	5.2	9.3	3.4	0.6	3.4	4.0	7.0	13.4	2.5

Tab. 8: Compositions and masses of deposits

As visible in table 8 on the largest tube diameter there was the highest chlorine content and also the highest mass of deposits. The mass of deposits increases also in relation to the surface to larger diameters. But according to the following reasons both facts can not be allocated exclusively to the tube diameter.

In this operation period there was a faster growth of the deposits on the test-tubes like in earlier tests. As in figure 37 can be seen the form of the deposits on the test tubes was widely developed (also on the biggest tube as shown at the small photo).



Fig. 37: View at windward side of test tubes (d10, d15, d21) with deposits

Thickness and shape of deposits influence the further depositing as well as erosion of particles, which together give the net-growth rate. After a longer time on tubes with a larger diameter there can be more deposits although the deposit growth rate in the beginning was slower. The small tube diameter earlier reaches a status where erosion increases and reduces the net growth rate. This is schematically shown in figure 38. In this case main parts of the deposits on the small tube are older than the deposits on the tube with larger diameter and had a longer time for reactions like sulphating. Therefore also the compositions can not be compared directly.

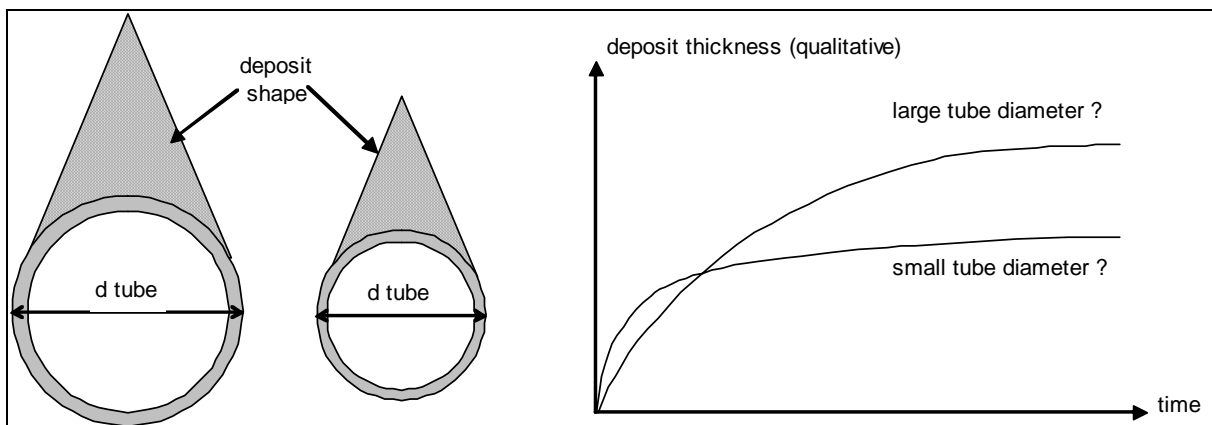


Fig. 38: Sketch of typical deposit shapes and sketch of possible deposit growth

So in this operation period unfortunately secondary effects inhibit a reliable interpretation of the test results with different tube diameters.

This restriction is valid only for the comparison of different tube diameters and not for following comparison and interpretation of results from periods with different primary air ratios.

In the operation time with a medium primary air ratio (1.29) the lowest mass of deposits on the test tubes was observed as shown in figure 39. In the same period there were the highest chlorine contents in the deposits (fig. 40).

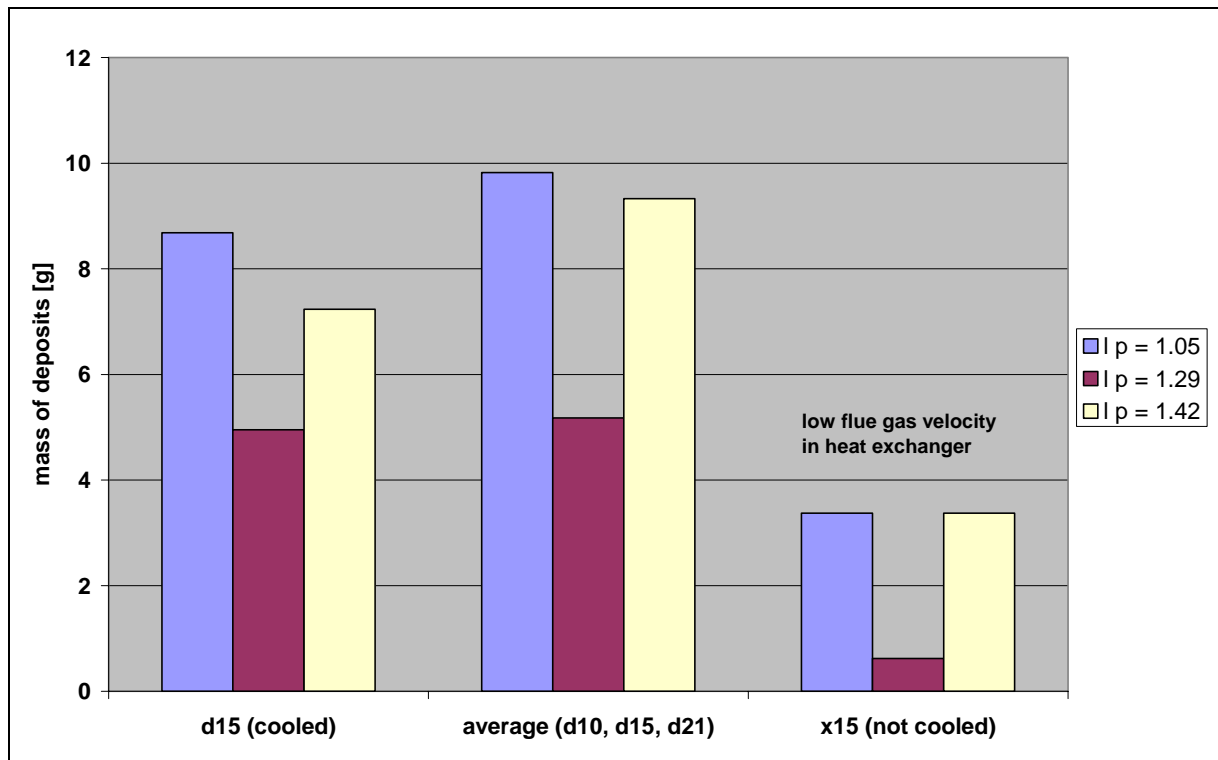


Fig. 39: Masses of deposits at different primary air ratios from several probes

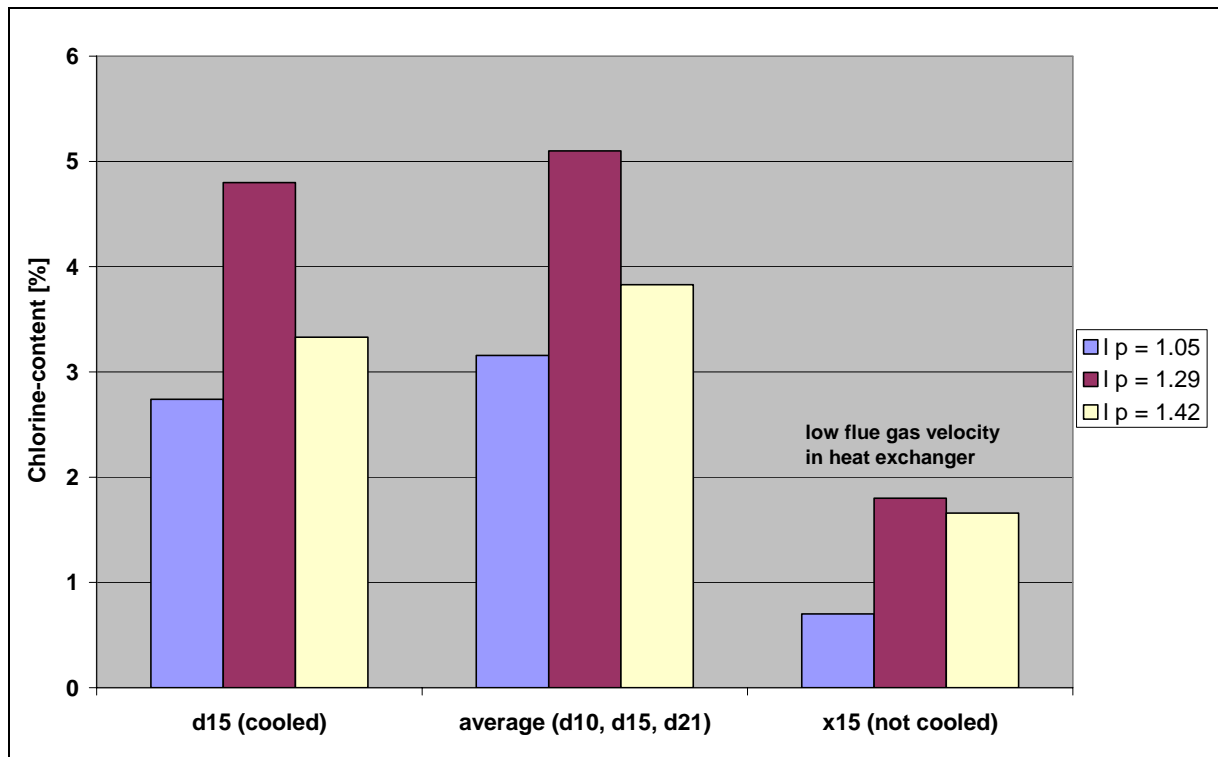


Fig.40: Chlorine content of deposits at different primary air ratios from several probes

In every period of adjusted primary air ratio the conditions for gas flow behind secondary air were very similar. Also the conditions for growth of deposits on the test tubes were nearly the same for every period. So the observed results indicate that the chlorine-release is less influenced by the primary air ratio as release of other deposit components.

In the operation time with the highest primary air ratio there were the highest temperatures above the fuel and must have been the highest gas velocities. This explains an increasing amount of deposits.

A minimum of deposits at a medium primary air ratio with an increase also to the lowest primary air ratio indicates a second mechanism. The reason is not really known by now. It seems that more volatile compounds have been formed in the reducing atmosphere.

Summarisation and interpretation of results from the CUTEC pilot plant

Exposure of materials from the partners

An overview about all exposures in the CUTEC pilot plant is given in table 1 at the beginning of the previous main chapter. Because the materials have been sent back to the project partners for material analysis the results will be presented in their chapters.

Summarisation of CUTEC investigations about growth of deposits

Thick deposit layers and severe corrosion are normally found only on the windward-side of tubes. Impaction, which is a very effective mechanism for growth of deposits, only affects on this windward-side. So the analysis of deposit was in principle done only at windward-side of tubes.

Fundamentals

The growth of deposits is a result of

- Composition of fuel which contains deposit components
- Release of these components from the firing bed on the grate
- Transport (macroscopic) with flue gas with simultaneous chemical reactions
- Microscopic transport through the boundary layer to a surface
- Sticking conditions/probability of components on surface

There are two mechanisms for the release of deposit components from the fuel in the firing bed. First, solid particle can be entrained by the arising primary air. Second, a couple of components can volatilise at high temperatures on the grate and get gaseous into the flue gas. Volatilisation in the fuel bed depends on temperature and also on chemical bounding which can change with kind of atmosphere (oxidising or reducing). Solid and gaseous components are transported with the flue gas flow in following boiler passes. With the decrease of the flue gas temperature gaseous components condensate or de-sublimate. A very effective mechanism for the building of deposits is the impaction of particles. The impaction depends on the Stokes number which is proportional to the gas velocity divided by the tube diameter. This means that with small tube diameters there is a higher probability of impaction of particles. Relatively big particles have a high probability of impaction (up to 100 %); with increasing Stokes-Number due to smaller tube diameters also small particles impact. When a particle hits on a surface it can rebound or stick. For sticking the kinetic energy must be transformed by a deformation of the particle or of the surface. Such a plastic deformation is possible especially at partially liquid or viscous materials. Especially chlorides and alkali can exist in compounds with low melting points and therefore chlorine is a so called sticking element. Aluminium, silicon and also calcium exist in compounds with high melting points and therefore are "not sticking" elements. On bare surface of a tube only particle capable of plastic deformation will be able to stick. When a deposit layer is built, which can be deformed, also rigid particles can stick. With increasing thickness of deposits the temperature and therefore the fraction of liquid phases on the deposit surface increases, too. This can cause a sticking ground for rigid non sticking particles. As a result in outer deposit layers the "sticking elements" can be diluted by "non sticking

elements". The term non-sticking element is used for rigid particles which do not stick on their own on a bare tube. Of course they can stick on a suitable surface.

Inevitable difficulties in interpretation of test results about deposit growth by above mentioned mechanisms:

For investigations following indirect influence parameters can be chosen: fuel, firing conditions and the position of the sample in the plant, which gives the flue gas temperature and velocity. These parameters produce a load of compounds in the flue gas at the sample position; mass and composition of flight dust can be measured; but the particle sizes and chemical bounding are not or hardly measurable at the existing conditions and not known. (Annotation: In 2005 first results of particle size and composition measurements have been published by a consortium of several companies. They together have developed the measuring equipment in a rather big project during years. These measurements are very complex, very expensive and NOT state of the art!)

As direct influence parameters the tube diameter (barrier dimension) and material temperature can be chosen. These are the starting parameters for the growth of the first deposit layer (first μm). But a thicker deposit layer (about one or more mm) is needed to get enough deposit material for a reliable analysis. By the growth of deposits itself the shape of the barrier, the structure, composition and temperature of the surface are modified. Like explained above, this influences the microscopic transport and the sticking conditions and therefore the following growth of deposits. So the starting parameters for growth of deposits can be chosen and measured, but not their course. Furthermore existing deposit layers surely make chemical reactions (sulphating for example) with gases.

Normally only one parameter is changed between two tests or two samples; but at this tests by changing one direct influence parameter automatically further indirect parameters have been varied. Especially the not known alteration of surface properties by growth of deposits and for further growth of deposits makes the interpretation of test results very difficult.

Influence of different fuels on growth and composition of deposits

In week 15/2005 four different fuels have been used in similar operation conditions: normal "low caloric" waste, high caloric waste, pure wood and wood with RDF. Following results for growth of deposits were found:

- There was no relevant difference in mass or composition of deposits from burning normal and high caloric waste.
- In comparison to deposits from waste during burning wood less deposit were build; this direction corresponds with the lower ash content in the fuel; there was a slight increase of the chlorine-content in deposits; this corresponds to the slight decrease of the sulphur/chlorine-ratio in the fuel.
- By adding RDF to wood the mass of deposits and also the chlorine-content in the deposits increased significant. This in principle matches to the higher ash content and lower sulphur/chlorine-ratio of wood.
- During burning wood with 10 % RDF the deposit growth was lower but the chlorine content in the deposit was even higher than in deposits from burning waste. This in principle matches to the lower ash content and the lower sulphur/chlorine-ratio in the mixture of wood and RDF.

Pure wood chips and wood in mixture with residues from agriculture have been used for firing in week 42/2005. 20 % of wood have been substituted by sugar beets respectively wheat straw in pellets form. The changes in comparison to firing pure wood were the following:

- By adding wheat straw the ash content of the fuel was about tripled as well as the chlorine und sulphur content. So there was only a little decrease of the sulphur/chlorine-ratio. This corresponds very well to a tripled mass of deposits and a little increase of the chlorine-content in the deposits.
- By adding sugar beets the ash and sulphur content was nearly tripled, too. But the chlorine-content did not change significant in comparison to pure wood. So the sulphur/chlorine-ratio was tripled. This also corresponds very well to the chlorine content in the deposits, which was only about a quarter of the chlorine content in deposits from burning pure wood. The mass of deposits increased as it was expected by the increasing ash content.

Comparison of deposits from different tube diameters, different deposit layers and different specific deposit masses

In week 48/2004 there were deposits with two clearly distinguishable layers on a test tube. The outer grey layer contained more chlorine and also more aluminium, silicon and calcium than the inner thin white layer.

- It is assumed that the higher chlorine content in the outer layer was caused by a shorter time for sulphating and a more effective deposition of small particles by dendritic deposit structures.
- The higher contents of aluminium, silicon and calcium in the outer layer are a hint for a sticking effect of deposits at higher temperatures in the outer areas.

Four different fuels have been used in week 15/2005. But only during burning of normal "low caloric" and of high caloric waste enough deposits have been built up on all tube diameters for reliable analysis.

- The mass of deposits increased to smaller tube diameters, as it was expected from the principles of impaction.
- The decrease of the chlorine content to smaller tube diameters was surprising. It must be assumed that this is a result of a dilution by non-sticking particles in outer layers of the deposits.

In week 42/2005 three mixtures of biomasses were burned.

The trends of deposit masses in dependence of tube diameter were the following:

- When burning wood chips there was an increase of deposits to smaller tube diameters; this corresponds to the fundamentals of impaction.
- During burning wood with wheat straw there was a similar growth of deposits on all tube diameters used. This might be a hint for relatively big particle sizes.
- Burning wood and sugar beets caused a very strong growth of deposits on the smallest tube diameter. This is a hint for impaction of small particles.

The following trends of deposit composition were found in deposits from all the fuels used:

- Increasing contents of calcium, silica, aluminium and magnesium (so called not sticking elements) to higher amounts of deposits. Assumed reason: Sticking on a deposit layer of other components.

- Decreasing contents of soda and potassium (so called sticking elements) to higher amounts of deposits. Assumed reason: Dilution by so called not sticking elements.

The chlorine-content once showed a decrease (pure wood), once nearly no variation (wood & wheat straw) and once an increase (wood & sugar beets) to higher amounts of deposits. In this list the maximum amount of deposits has increased (up to 45, 145, 235 g/m²).

Chlorides exist in so called sticking compounds, so that a decrease by dilution has to be expected. But at higher amounts of deposits there is not only a flat deposit layer on the surface; at the windward-side there were also dendritic structures of the deposits. These very small barriers have a very high probability for impaction of small particles. It is known that the smallest particles have the highest chlorine-content.

This effect is assumed to be the reason for the unexpected increase of the chlorine-content at the highest amount of deposits.

Results of other variations and investigations in CUTEC pilot plant

Deposit growth at different levels of the heat exchanger (week 48/2004)

At the second bundle there were fewer deposits with lower chlorine content than at the first bundle. The same result is normally found in industrial plants. Deposition seems to be most efficient at the first bundle(s). The higher difference between flue gas and tube temperature and also the rough surface at thick deposits seem to cause a higher chlorine-content.

High-temperature-endoscopy in heat exchanger (week 48/2004)

The growth of deposits at the windward side of the second bundle of the heat exchanger was shown in figure 9. The stronger growth at the positions with a higher gas velocity due to deflected flow shows the relevance of impaction for deposit growth.

Growth of deposits at different primary air ratios (week 25/2006)

In calendar week 25 of 2006 the plant was operated with three different primary air ratios to examine the influence on release of deposit forming components from the burning bed. The calculated real primary air ratios were 1.05, 1.29 and 1.42. Increasing temperatures after injection of re-circulated flue gas indicate local reducing atmospheres above the grate, although all primary air ratios were major one. The total air ratio in every case was about 1.9. So the flow conditions in the flue gas were in principle the same.

There was a minimum of deposit growth and maximum of chlorine-content in the deposits at the medium primary air ratio. This suggests that two different mechanisms were active. With the highest primary air ratio there were the highest temperatures above the fuel and must have been the highest gas velocities. This explains an increasing amount of deposits. With low primary air it is assumed that more volatile compounds have been formed in larger areas with local reducing atmospheres.

Comparison of pre-oxidised and not pre-oxidised tubes (week 25/2006)

Two high alloyed materials (1.4563 and 1.4845) were tested; each with and without pre-oxidation. On all four segments and in all tube positions there was only little chlorine in the deposits and little corrosion. So in these tests neither pre-treatment nor

material or position on tube shows a clear correlation to deposit composition or thickness of corrosion zone.