

Ash related Issues in Biomass Combustion

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September 21, 2006 Marriot Hotel, Glasgow, Scotland



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Programme

Location: ThermalNet conference, Marriot Hotel, Glasgow

Chairpersons: Bill Livingston and Sjaak van Loo

9:10	Opening and welcome, Sjaak van Loo, IEA Bioenergy Task 32 and ThermalNet Combnet
9:20	Overview of biomass ash characteristics/ Thermalnet WP2D Bill Livingston, Mitsui Babcock, UK
9:50	Ash related problems when cofiring biomass with coal in PF burners, Rob Korbee, ECN, Netherlands
10:10	Test rig and ash deposit characterisation for biomass cofiring Fraser Wigley, Imperial College, UK
10:45	Coffee break
11:00	Biomass ash deposition and corrosion processes, Bill Livingston, Mitsui Babcock, UK
11:20	Ash related problems in wood fired boilers and effect of additives, Håkan Kassman, Vattenfall Power Consultant AB, Sweden
11:40	Experience with ash deposition in poultry litter boilers David Bowie, Mitsui Babcock, UK
12:00	Experiences with wood/sludge cofiring in Sweden Claes Tullin, SP, Sweden
12:20	Discussion and conclusions, Bill Livingston, Mitsui Babcock, UK
12:30	Closing

Opening and welcome - Sjaak van Loo, IEA Bioenergy Task 32

Sjaak van Loo welcomed all participants to this workshop, which was co-organised by ThermalNet and IEA Bioenergy Task 32. Most of the practical organisation was arranged by Bill Livingston of Mitsui Babcock.

Overview of biomass ash characteristics -Bill Livingston, *Mitsui Babcock, UK*

Bill Livingston provided an overview of the major ash related issues in biomass combustion. Within ThermalNet, WP2D particularly focuses on ash related issues in biomass combustion. A key deliverable is a report summarizing the issues, which is currently available in draft for comments.

In the ash one can distinguish inorganic components contained in the biomass, as well as extraneous inorganic material such as sand. Inside a boiler, ash is related to various issues such as the formation of fused or partly-fused agglomerates and slag deposits, accelerated metal wastage of furnace and boiler components due to gas-side corrosion under ash deposits, and due ash particle impact erosion or ash abrasion of boiler components and other equipment. Ash may also result in the formation and emission of sub-micron aerosols and fumes, and have various impacts on the performance of flue gas cleaning equipment. Finally, ash contained in biomass has consequences on the handling and the utilisation/disposal of ash residues from biomass combustion plants, and of the mixed ash residues from the co-firing of biomass in coal-fired boilers.

Ash related problems when cofiring biomass with coal in PF burners - Rob Korbee, ECN, Netherlands

Rob Korbee explained the major ash related issues in biomass cofiring. In the Netherlands there is already significant experience with cofiring several types of biomass with pulverised coal. Following the agreement between the Dutch government and the power sector, cofiring biomass should lead to avoidance of some 3.2 Mton CO₂ by 2012, which is equivalent to 475 MWe biomass capacity.

Power plants have plants to cofire up to 35% on mass basis; when applied in combination with ultra super critical (USC) boilers this poses great ash related challenges on boiler operation. When compared to coal ash, biomass ash typically contains more chlorine and alkalines but less sulphur, minerals and total ash.

An experimental study on ash formation and deposition from various types of biomass and coal was performed at ECN. Major inorganic elements are mineral and organic calcium as well as potassium in salt and mineral forms. Biomass ash components that evaporate to over 80% are Na, K, Cl, S, Zn, Pb; other inorganics such as Ca, Mg, Mn, P, Ti are released for 20-50%. The release of minerals from coal however is much less in absolute terms, and also largely determined by the mineral composition (predominantly S and Cl).

The deposition chemistry of devolitalised ash elements may pose significant challenges for reliable boiler operation. Fuel preparation, quality control and blending may be needed to avoid problems. Such measures can be applied in combination with smart cleaning of membrane walls and superheaters, using a water jet that is controlled by a heat flux sensor.

Test rig and ash deposit characterisation for biomass cofiring - Fraser Wigley, Imperial College, UK

Fraser Wigley presented an assessment of ash deposits, produced on temperature controlled coupons by combustion of Miscanthus, palm kernels and Russian coal and at various process conditions in a combustion test facility of RWE npower.

The tests showed that the deposits with Miscanthus were slightly thicker and stronger than the deposit from Russian coal. The deposits with palm kernel were smoother, and significantly denser and stronger. At higher temperatures, deposits from all three fuels became denser, stronger and CCSEM analysis confirmed a significant increase in degree of sintering with increased temperature. This is particularly true for palm kernel, which increases the rate of sintering significantly if cofired with coal.

It was interesting to see that bulk iron oxide concentration in deposits from all three fuels increased with increasing temperature, especially for the deposits with palm kernels. Both the concentration of iron oxide in the aluminosilicate deposit material and the proportion of more iron-rich material in the deposit increased. This was probably caused by the biomass component in the ash creating a 'stickier' deposit surface – retaining more impacting iron-rich particles, increasing the iron content of the deposit and causing a further reduction in deposit viscosity.

Biomass ash deposition and corrosion processes - Bill Livingston, Mitsui Babcock, UK

Bill Livingston explained the mechanisms of ash deposition and corrosion on heat transferring surfaces, ash melting in the fuel bed and the consequences for the design and operation of biomass combustors and boilers.

In general, biomass materials and their ashes tend to be less erosive and abrasive than more conventional solid fuels. However, slag formation may significantly increase in comparison to coal, leading to less heat transfer and increased flue gas temperatures downstream of the superheater in the convective section, which may then cause unexpected ash deposition there. Increased formation of hard deposits and subsequent shedding may in turn lead to damage to grates and boiler ash hoppers.

Severe boiler fouling may occur on the surfaces of superheater, reheater and evaporator banks at flue gas temperatures less than around 1000°C. If formed at temperatures around 600-700°C, these deposits are relatively easy to remove, however for higher temperatures these deposits may be difficult to remove on-line or off-line. Fouling may also result in increased flue gas temperatures and boiler efficiency losses.

Corrosion of relatively hot heat exchanging tubes when cofiring biomass is often a result of high alkali metal and chloride contents of biomass. This can for example be mitigated by introducting sulphur. Higher chrome alloys are also more corrosion resistive.

Although there are online monitoring and cleaning (sootblowing) systems available commercially today, the key to avoidance of serious deposition and corrosion in biomass combustion plant is in the design phase. It can be very difficult to compensate for poor design after the plant is built. The designer of the combustion equipment and boiler plant must have the appropriate fuel assessment and design tools.

Ash related problems in wood fired boilers and effect of additives - Håkan Kassman, Vattenfall Power Consultant AB, Sweden

Håkan Kassman of Vattenfall Power Consultant AB presented the effect of additives on ash related problems in wood fired boilers. It is well known that K and Cl in biomass may cause KCl in deposits, leading to accelerated corrosion. Additives in the fuel or gas phase may either

- 1. reduce the release of gaseous KCl, e.g. by adding Al₂O₃ or SiO₂ K-alumino silicates are formed, and/or
- 2. react with KCl in the gas phase and form less corrosive components, e.g. by adding sulphur, potassium sulphates may be formed and Chloride removed as HCl.

In the strategy of Vattenfall, the concentrations of KCl, NaCl and SO_2 in the flue gas are monitored online using an In-situ Alkali Chloride Monitor (IACM). This information is used to inject a sulphur containing additive (ammonium sulphate, brand name ChlorOut \mathbb{R}) to obtain the latter effect. Ammonium may also lead to reduced NO_x emissions.

The effect of ChlorOut was successfully demonstrated at various biomass fired power plants, varying from grate, BFB and CFB. These demonstration showed that ChlorOut could effectively reduce deposit growth and Cl contents in deposits. At the same time, NOx could also be reduced using the ammonium in the additive.

Experience with ash deposition in poultry litter boilers -David Bowie, Mitsui Babcock, UK

David Bowie of Mitsui Babcock shared some results on the operating performance of a 40.6 MW_{th} chicken litter fired BFB installation and particularly the ash related impacts. Several severe operational problems were experienced in this installation, such as agglomeration of fuel ash in the bed, fouling of furnace walls, primary and secondary superheaters, the convective section and economiser. It appeared that the deposition of ash on superheaters led to higher superheater exit temperatures, and increased entrance temperatures to downstream convective and economiser sections. Since the ash deposits become more hard and difficult to remove using installed sootblowers at elevated temperatures, manual cleaning was frequently required, resulting in plant availability of 80%, vs. 90% as design availability.

Design changes have been proposed for the installation, including elimination of refractory slopes, extended support firing at start-up, on-load water washing of the furnace, large platen superheating surface and increased tube pitch.

Experiences with wood/sludge cofiring in Sweden - Claes Tullin, SP, Sweden

Claes Tullin explained the results of combustion trials where wood waste was cofired with sewage sludge. Sewage sludge contains relatively high concentrations of S, Al, Si, Fe, Ca and P, which may help in preventing the formation of alkali chlorides formed from relatively high concentrations of alkali metals in the wood.

While deposit formation increased when adding ZnO to wood fuel (as present in waste wood), adding sludge substantially reduced deposit growth and reduced corrosive alkali chloride concentrations in the deposit as potassium is sulphated. Adding sewage sludge also lead to reduced emission of aerosols (< 1 μ m), this is explained by transportation of mainly KCl and K₂SO₄ in aerosols to larger particles.

Discussion and conclusions

In the discussion that followed, it was concluded that ash related issues such as deposition and chloride based corrosion are important for reliable operation of biomass fired boilers. Particularly when biomass is used in a boiler that is originally designed for another fuel, availability may be seriously hampered. The challenges increase with more challenging fuels and steam conditions.

It is therefore essential that proper fundamental understanding exists of the ash chemistry in a boiler, and that particularities of a fuel are taken into account seriously when designing or modifying a new boiler.

Annex 1. Overview of biomass ash characteristics -Bill Livingston, Mitsui Babcock, UK

Biomass ash

- **Opening and welcome**, • 9:10 Sjaak van Loo, IEA Bioenergy Task 32 and ThermalNet Combnet
- 9:20 **Overview of biomass ash characteristics** Thermalnet WP2D Bill Livingston, Mitsui Babcock, UK
- 9:50 Ash related problems when cofiring biomass with coal in PF burners, Rob Korbee, ECN, Netherlands
- 10:10 **Characterisation of CTF Deposits from coal-biomass** combustion. Fraser Wigley, Imperial College, UK
- 10:45 **Coffee break**





Workshop programme

- 11:00 **Biomass ash deposition and corrosion processes**, Bill Livingston, Mitsui Babcock, UK
- 11:20 Ash related problems in wood fired boilers and effect of additives, Håkan Kassman, Vattenfall Power Consultant AB,
- 11:40 Experience with ash deposition in poultry litter boilers David Bowie, Mitsui Babcock, UK
- Experiences with wood/sludge cofiring in Sweden 12:00 Claes Tullin, SP, Sweden
- 12:20 **Discussion and conclusions**, Bill Livingston, Mitsui Babcock, UK
- 12:30 Closing







Biomass ash characteristics and behaviour in combustion systems

W R Livingston IEA Task 32/Thermalnet Workshop Glasgow September 2006



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Introduction **Thermalnet WP2D**

- A key deliverable of WP2D is a review report on the current 'state of the art' on the characteristics of biomass ash materials and their impact on the design, performance and integrity of combustion, gasification and pyrolysis process.
- The combustion and gasification sections are now available in Draft form for comment.
- The documents will be placed on the Thermalnet website after this meeting.





Agricultural products	Forestry products	Domestic and municipal wastes	Ene
Harvesting residues	Harvesting residues	Domestic/industrial	
Straws Corn stalks	Forestry residues	MSW/RDF Scrap tyres Wood wastes Sewage sludges	Willow/ Poplar Cottonwo
Processing residues	Primary process residues	Urban green wastes	Gr
Rice husks Sugarcane bagasse Olive/palm oil residues Fruuit residues	Bark Sawdusts Offcuts	Leaves Grass and hedge cuttings	Switch g Reed ca Miscanth
Animal wastes	Secondary process wastes		
Poultry litter Tallow Meat/bone meal	Sawdusts Offcuts		



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Wood
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Biomass ash fractions

- The **inherent inorganic material**, exists as part of the organic structure of the fuel, and is most commonly associated with the oxygen, sulphur and nitrogen-containing functional groups.
- Inorganic species can also be present in very fine particulate form within the organic structure of some of the fuels, and to behave essentially as an inherent component of the fuel.
- The **extraneous inorganic material**, which has been added to the fuel through geological processes, or during harvesting, handling and processing of the fuel.
- Biomass fuels are commonly contaminated with soil and other materials, which have become mixed with the fuel during collection, handling and storage.



	Class 1 - water soluble			
	Compound	Formula	Sha ele	
Na, K	Nitrates and chlorides	Na,KNO ₃ , Na,KCI		
Ca, Mg	Nitrates, chlorides, phosphates	Ca,Mg(NO ₃)2 Ca,MgCl ₂ CaMg ₃ (PO ₄) ₂		
S, P, Cl	Sulphate, phosphate and chloride ions	SO ₄ , PO ₄ , CI		
	Class 2 - organi	cally associated		
Ca, Mg	macromolecules			
Fe	Organic complexes			
S, P	Sulpholipids, amijno and nucleic acids, proteins		Ň	
	Class 3 precipitated	as pure compounds		
Са	Calcium oxalate	CaC ₂ O ₄ .nH ₂ O		
Si	Phytolite	SiO ₂ .nH ₂ O		



Biomass	Forestry residue	SRC willow	Cereal straw	Oil seed rape straw	Olive residue	Palm kernel
Ash (%)	2	2	5	5	7	4
Analysis (mg kg ⁻¹)						
ΑΙ	-	-	50	50	1,500	750
Са	5,000	5,000	4,000	15,000	6,000	3,000
Fe	-	100	100	100	900	2,500
Κ	2,000	3,000	10,000	10,000	23,000	3,000
Mg	800	500	700	700	2,000	3,000
Na	200	-	500	500	100	200
Ρ	500	800	1,000	1,000	1,500	7,000
Si	3,000	-	10,000	1,000	5,000	3,000





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General types of biomass ashes

- High silica/high potassium/low calcium ashes, with low fusion temperatures, including many agricultural residues,
- Low silica/low potassium/high calcium ashes, with high fusion temperatures, including most woody materials, and
- High calcium/high phosphorus ashes, with low fusion temperatures, including most manures, poultry litters and animal wastes.





The most important ash-related issues in biomass combustors and boilers

- The formation of fused or partly-fused agglomerates and slag deposits at high temperatures within furnaces and stoves,
- The formation of bonded ash deposits and accumulations of ash materials at lower temperatures on surfaces in the convective sections of boilers,
- The accelerated metal wastage of furnace and boiler components due to gas-side corrosion under ash deposits, and due ash particle impact erosion or ash abrasion of boiler components and other equipment,
- The formation and emission of sub-micron aerosols and fumes, Biomass ash impacts on the performance of flue gas cleaning equipment, and
- The handling and the utilisation/disposal of ash residues from biomass combustion plants, and of the mixed ash residues from the co-firing of biomass in coal-fired boilers.





Biomass ash characterisation techniques

- Chemical analysis S and CI contents and the major and trace elements,
- Ash fusion tests Melting curves and Ash Fusion Test **Equilibrium Phase Diagrams**
- Slagging and Fouling Indices ranking methods based on the chemical analysis and Ash Fusion Test data.
- Chemical fractionation techniques water, buffer and acid solutions.
- Mineralogical and microscopic techniques using both optical and electron microscopy.





An example of a melting curve for alkali metal salt mixtures









Summary data from chemical fractionation tests









The key biomass mineral transformations in flames

- The fusion or partial fusion of quartz and silica particles and, at high temperatures, interactions to form alkali and alkaline eath metal silicates,
- The fusion or partial fusion of alumino-silicates,
- The decomposition of carbonates, oxalates, chlorides, etc. and other inorganic salts,
- The volatilisation of alkali metals and some heavy metals,
- Particle fragmentation by thermal shock and the rapid release of gaseous species from particles, and
- The coalescence of intra-particle mineral particles.







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Principal types of biomass combustor

- Grate combustors are generally employed for the small and medium sized industrial/commercial applications,
- Fluidised bed combustors, of the bubbling bed and circulating types, are commonly employed for the medium to large industrial/commercial and utility applications,
- Pulverised fuel combustors, which are employed for large industrial and utility applications, i.e. for the cofiring of biomass materials in large coal-fired boilers, and for 100% biomass firing (relatively rare).





A schematic diagram of biomass ash behaviour on a grate









The fate of biomass ash material during combustion processes.

Release Mechanisms

- 1. Vaporization
- 2. Inorganic Reaction
- 3. Organic Reaction

Residual Ash 1. Fragmentation

- 2. Coalescence
- 3. Chemical Transformations









Conclusions

- The mineral and other inorganic components of biomass materials are very different chemically, mineralogically and microstructurally from those of the more conventional solid fuels
- There has been significant R&D and other technical work on these subjects, and there is increasing industrial experience with biomass processing and co-processing with more conventional fuels.
- The industrial experience is principally with combustion and co-combustion systems, but also with gasification and pyrolysis processes.
- Many of the process problems in operating biomass plants have been ash-related.
- The ash characterisation and testing methods are largely in place and the processes are reasonably well understood.
- There are, however, still significant ash-related design and operational problems at industrial scale.



Annex 2. Ash related problems when cofiring biomass with coal in PF burners - Rob Korbee, ECN, Netherlands



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Ash: what happens when biomass is co-fired with coal ? - Rob Korbee -







Everything changes,

and it can be controlled !

. . .

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Biomass co-firing maturing in the Netherlands

 Concrete 2002 agreement with government to reduce 3.2 Mton CO₂ by 2012, equivalent to 475 MW_e biomass capacity:

Coal plants	Expected (2000) capacity (MW _e)		
Gelderland 13	74		
Hemweg 8	77		
Maasvlakte 1+2	128		
Amer 8+9	147		
Borssele 12	49		
	Coal plants Gelderland 13 Hemweg 8 Maasvlakte 1+2 Amer 8+9 Borssele 12		

- Capacity realised in 2002: 177 MW_e, of which 147 co-firing without any other thermal pre-processing [Raven, 2005]
- Main fuels used: wood pellets, food industry residues, mixed waste pellets, MBM, paper sludge, waste wood (gasification)
- Projects between 1 July 2003 and 18 August 2006 supported by subsidies up to 9.7 ct per kWh of renewable energy; new initiatives uncertain !

Ambition (MW₀) new plant new plant new plant 250 160



New challenges to address

- High biomass shares, up to 35% (m/m) for conventional PF plants and 30⁺% (e/e) for future high efficiency plants
- Fuels with higher ash content and more ash complex chemistry (ref. wood), e.g. residues from households, industrial or agricultural activities
- New high efficiency, low emission technologies, such as ultra supercritical boilers producing 750 °C steam, or oxygen enriched combustion with flue gas recirculation
- Combinations of the above possibilities



Ash forming elements in biomass vs coal



olive residue

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Ash related issues to consider for a 'typical' biomass

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Ash forming species in coal

Pulverised coal sample in electron microscope

- typically mineral particles
- minerals mostly non-volatile
- minerals quantified by CCSEM

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particles ion-volatile ed by CCSEM

Ash forming species in biomass

Biomass (bark) sample in electron microscope

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reactivity


Experimental study of ash formation



Lab-scale PF combustion facility

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Burner Area

Furnace Exit





Experimental study of ash deposition



Lab-scale PF combustion facility

Energy research Centre of the Netherlands

Burner Area

Furnace Exit





Ash formation test program

- Single fuel combustion tests with bark, wood chips, waste wood, saw dust, olive residue, straw, coal
- Analysis: proximate, ultimate, elemental composition, CCSEM (coals)
- Method developed to determine release of inorganic matter (excl. Si, Al, Fe) in Lab-scale pf Combustion Simulator
- Release determined as *any* inorganic matter released from fuel particles, being gaseous (volatile) or liquid/solid (non-volatile) species with a size $\leq 1 \, \mu m$
- Release determined under same conditions for all fuels as a function of time in the range 20-1300 ms, covering devolatilisation to burnout



Ash release results – top-4 elements



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Comparison of ash release between fuels



Release biomass very different from coal:

- total release biomass 30-55% (incl. S and CI)
- total release coal 0.3-2.6% (excl. S and Cl) or 8-36% (incl. S and Cl)

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Ash release - conclusions

- Release different wood fuels very similar, in range 49-51%; release bark, straw and olive residue 30%, 40% and 55% respectively; a typical coal releases ~8% (S)
- Huge difference in absolute release; measurements ranging from 1350 to 27600 mg / kg dry material (~8000 mg / kg for typical coal)
- Release is time dependent; significant release observed already at 20 ms, 70-80% release observed around 200 ms, additional release observed into burnout phase up to 1300 ms
- Release kinetics of individual elements believed to depend on their speciation
- Generalisation of data across biomass fuels results in three element groups:
 - Si, Al, Fe: negligible release (exceptions may exist for specific mineral fragmentation)
 - Ca, Mg, Mn, P, Ti (waste wood): 20-50% released
 - Na, K, Cl, S, Zn, Pb: 80-100% released, with Na and K at lower end of range
- Release from coal largely determined by mineral composition
 - Release dominated by S and CI (nearly completely released)
 - Up to 50% release of Na observed when not bound to clay in coal





General understanding of fuel interactions

(example element potassium)



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Interaction demonstrated in ash deposition



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What does it mean ? (intermezzo)

- Biomass not necessarily problematic
- Solutions possible
- Perhaps even opportunity for improvement of operation (synergy)

It also means:

Bulk analyses biomass inorganics such as Ash Fusion Test insufficient



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Ash deposition – how to avoid problems ?

Preventive

- Appropriate fuel analysis to determine speciation or even specific thermal behavior
- Produce fuels with better properties, e.g. through torrefaction
- Blend fuels to reduce problems like strong thermal insulation, sintering, low-T melts, or high-CI compositions; requires knowledge / predictive tools

Control

- On-line monitoring of ash deposition combined with 'smart' cleaning
 - Membrane walls: heat flux measurement + water cannons (Clyde Bergemann)
 - Super-/reheaters: section-wise evaluation using cleanliness factors (ratio of actual vs theoretical heat transfer rate)



Smart cleaning

Membrane walls

Clyde Bergemann system

Super-/reheaters e.g. ABB system



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Ash deposition – how to avoid problems ?

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So, what else do we need ?

- 1. Data to quantify interactions and their impact on ash deposition
- Technology for direct monitoring of super-/reheater fouling 2.



Ongoing developments

Parametric ash deposition studies

- Lab-scale testing
 - parameters: fuel types, p_{SO2} (0-1000 ppm), biomass share (0-50%), surface temperature (450-750 °C), high-T alloys
- Full-scale testing & verification
- Thermodynamic calculations
- Model development

Technology development

- Heat flux measurement convective area
 - access, wiring issues
 - signal interpretation
- Novel sensor systems



deposit structure, bonding chemistry & initial corrosion: SEM-EDX deposition rate in g/m²s heat flux in W/m²K



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Concluding remarks

- Ash from biomass and coal differ (a lot) in terms of formation and behaviour
- Low shares and clean biomass successfully handled
- Different biomass, or higher shares and more extreme conditions could also be handled, provided that fuel interactions can be predicted
- Ash formation of main-stream fuels has been mapped, providing essential input (knowledge) to deal with ash related issues
- Focus now on experimental quantification of fuel interactions to be used for deposition and related corrosion control
- Combination of predictive modelling and on-line monitoring key to successful management of ash behaviour



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Thank you !

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Annex 3. Test rig and ash deposit characterisation for biomass cofiring - Fraser Wigley, Imperial College, UK

Imperial College London

Characterisation of CTF deposits from coal-biomass combustion

Fraser Wigley and Jim Williamson Imperial College London **Gerry Riley RWE** npower





Introduction

Co-firing of biomass with coal is now common at UK power stations, and levels of replacement of coal by biomass are steadily increasing. The impact of the inorganic component of the biomass on ash behaviour in the boiler is a cause for concern.

Although biomass typically has a lower inorganic content than coal, the biomass ash has a very different chemical composition from the coal ash – the alkalis in the biomass could change the properties of the mainly aluminosilicate coal ash.

Coal and biomass samples

	Russian	S. African	Misc.	Olive	Palm	SF
Ash	12.6	12.1	2.3	5.7	4.2	2
SiO ₂	60.1	54.1	57.0	32.1	15.1	17
AI_2O_3	24.0	33.5	2.4	6.6	3.2	Z
Fe_2O_3	6.0	3.1	3.4	4.9	5.3	3
CaO	4.1	4.1	10.0	12.4	10.7	33
MgO	1.1	1.3	3.1	12.2	12.0	8
K ₂ O	3.0	0.7	18.2	18.9	9.7	13
Na ₂ O	0.4	0.1	1.1	0.4	0.3	
TiO ₂	1.2	1.7	0.2	0.2	0.1	(
MnO	0.1	0.0	0.4	0.0	1.0	(
P_2O_5	0.0	1.4	4.2	12.2	42.7	17

RC Sawmill 2.4 2.5 7.3 40.7 8.1 4.4 3.8 3.8 3.3 28.6 4.1 3.6 8.8 6.8 1.0 1.1 0.3 1.1 3.6).4 7.0 2.1

Experimental procedure

A typical UK power station coal (Russian) was combusted alone and with 15wt% biomass replacement (Miscanthus and palm kernel) on the 0.5MW Combustion Test Facility (CTF) at RWE npower.

Deposit samples were collected on mullite substrates, under normal (and low oxygen) conditions, at a range of temperatures.



RWE npower Combustion Test Facility



ThermalNet Glasgow, 21 Sept 2006 © Imperial College London

Why use test facilities?



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CTF test programmes (examples)

Drax coals (slagging) **Emulsion tests** NOx control (air staging/coal reburn) South American study South African coal study **MBM/Tallow** Pet Coke for Aberthaw Blending **Co-firing Pet Coke** Slagging projects

DTi NOx/Burnout Ash re-firing Flame Stability Wood pellets Liquid Biofuels Indonesian coal Biomass tests (PKE) **Energy Crops** (Miscanthus/SRC) High Burn Biomass MinorTop (impact of air staging)



RWE npower Combustion Test Facility



ThermalNet Glasgow, 21 Sept 2006 © Imperial College London

Tallow 1995 Sawdust 2001 **PKE 2004** Palm Oil 2003

Photographs of CTF deposits on coupons

Russian coal

+ Miscanthus

+ palm kernel



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Deposit structure

Compared to the deposit from Russian coal, the deposits with Miscanthus were slightly thicker and stronger. The deposits with palm kernel were smoother, and significantly denser and stronger.

Deposits from all three fuels became denser and stronger at higher temperatures.



Sample preparation and characterisation

Each deposit sample was photographed.

Representative deposit material was removed and ground for X-ray diffraction (XRD).

Deposits were impregnated with epoxy resin. Circular sections were cut through the coupons and attached deposits. The circular sections were mounted in epoxy resin and prepared as polished cross-sections, then analysed by CCSEM.

CCSEM facility

Computer-Controlled Scanning Electron Microscope

An SEM with integration, under automatic control, of:

- sample movement,
- electron beam positioning,
- image acquisition,
- image processing,
- chemical analysis,
- data storage

e of:

CCSEM analytical technique for deposits

At multiple magnifications, and for multiple positions on the sample:

- acquire a high-quality digital BSE image
- locate analysis points by thresholding the BSEI
- analyse each point chemically by EDS

Process and interpret data and create standard reports using a database.

Output consists of both numeric data and images. CCSEM analysis is built from the bottom up.



BSE images from CCSEM analysis of deposit



Image side 800µm

Image side 160µm

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Cross-sections of CTF deposits from **Russian coal**

1050°C 1075°C 1100°C 1125°C 1150°C





8mm

800µm

Cross-sections of CTF deposits from Russian coal with 15% Miscanthus

1050°C 1075°C 1100°C 1125°C 1150°C



Cross-sections of CTF deposits from Russian coal with 15% palm kernel

1100°C 1050°C 1075°C 1125°C 1150°C



8mm

800µm

Cross-sections of CTF deposits



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Porosity of CTF deposits



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Effect of temperature on deposit microstructures

All three series of deposits showed a significant increase in degree of sintering with increased temperature. At higher temperatures the microstructures showed:

- fewer isolated ash particles
- more necks between adjacent ash particles
- greater evidence of particle coalescence
- larger clumps of particles
- a higher proportion of matrix material
- a lower abundance of quartz grains



Cross-sections of CTF deposits, aligned



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Effect of biomass on deposit microstructures

Co-firing with Miscanthus produced a deposit with a degree of sintering comparable to a pure Russian coal deposit about 25°C hotter.

Co-firing with palm kernel produced a similar microstructure and strength to a pure Russian coal deposit about 75°C hotter.

The rate of increase of sintering with temperature appeared to be higher for the Russian coal with palm kernel.





CaO-Al₂O₃-SiO₂ chemical distributions from Russian coal with palm kernel

Chemical distributions reflecting ash particles (derived from parent coal minerals) were steadily replaced by more uniform deposit matrix chemical compositions at higher temperatures.



Bulk chemical compositions for deposits at 1100°C

	Russian	+ Misc.	+ palm
SiO ₂	57.1	60.3	52.7
AI_2O_3	20.1	17.3	18.0
Fe_2O_3	8.4	8.6	11.9
CaO	6.3	6.2	6.4
MgO	1.2	1.1	1.8
Na ₂ O	0.5	0.4	0.5
K ₂ O	2.2	2.4	3.2
TiO ₂	2.0	1.6	1.6
P_2O_5	1.0	0.8	2.4
Mn ₃ O ₄	0.8	0.8	1.1
SO ₃	0.5	0.5	0.4

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Fe₂O₃ content of CTF deposits



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Abundance (wt%) of chemical types in deposits from Russian coal with palm kernel

Temp (°C)	1051	1077	1099	1124	1150
Alsil	47	44	47	44	48
Ca+Fe	10	13	11	14	14
Ca+alsil	5	6	4	1	1
Ca-rich	0	0	0	0	0
Fe-alsil	11	12	8	26	21
Fe-rich	0	1	1	1	1
non-CFAS	3	3	4	2	2
Si-alsil	16	15	16	8	10
Si-rich	8	7	8	4	4



Chemical composition (wt%) of 'alsil' chemical type in deposits from Russian coal with palm kernel

Temp (°C)	1051	1077	1099	1124	1150
SiO ₂	52.9	53.0	53.6	53.6	54.2
AI_2O_3	26.9	25.6	25.3	24.1	23.9
Fe_2O_3	4.6	4.6	4.7	5.5	5.8
CaO	4.7	5.6	5.5	5.8	5.6
MgO	2.1	2.3	2.2	2.4	2.2
Na ₂ O	0.4	0.5	0.4	0.5	0.5
K ₂ O	3.5	3.4	3.3	3.1	3.1
TiO ₂	1.4	1.3	1.3	1.2	1.3
P_2O_5	2.7	3.0	2.9	3.0	2.8
Mn ₃ O ₄	0.4	0.4	0.4	0.4	0.4
SO ₃	0.3	0.2	0.3	0.3	0.2

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XRD spectra of CTF deposits from Russian coal with palm kernel



ThermalNet Glasgow, 21 Sept 2006

Intensity

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Deposit chemistry

The small differences in chemical composition and distribution between the deposits from the three fuels reflected the differences in ash chemistry and mineralogy between the fuels.

At higher temperatures chemical distributions reflecting ash particles derived from parent coal minerals were steadily replaced by more uniform matrix chemical compositions, especially for the deposits with palm kernels.



Deposit chemistry – Iron oxide

Deposits from all three fuels showed an increase in bulk iron oxide concentration with increasing temperature, especially for the deposits with palm kernels. Both the concentration of iron oxide in the aluminosilicate deposit material and the proportion of more iron-rich material in the deposit increased.

The higher iron content was probably caused by the biomass component in the ash creating a 'stickier' deposit surface – retaining more impacting iron-rich particles, increasing the iron content of the deposit and causing a further reduction in deposit viscosity.

Summary

The ash deposition behaviour of coal-biomass mixtures has been investigated using a combination of rig-scale combustion tests and CCSEM analysis of deposits.

The relatively minor contribution of the biomass to the fuel ash has been shown to have a significant impact on the microstructure and chemistry of the deposits, enhancing the rate at which the deposits consolidate and strengthen with increasing temperature.

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Further work

Deposits collected under 'low oxygen' conditions will be characterised, to investigate the effect of over-fire air on boiler ash deposition from coal-biomass combustion.

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Annex 4. Biomass ash deposition and corrosion processes - Bill Livingston, Mitsui Babcock, UK

Biomass ash deposition, erosion and corrosion processes.

W R Livingston IEA Task 32/Thermalnet Workshop Glasgow September 2006



Stoker-fired boiler





Circulating fluidised bed boiler





Pulverised fuel boiler





Furnace slag formation

- The **partial fusion and agglomeration of ash particles** in the fuel beds of stoker-fired and fluidised bed-fired combustion equipment, can lead to poor combustion conditions, de-fluidisation of fluidised beds, and problems with ash removal and downstream ash handling equipment,
- The deposition of ash materials on **burner component and divergent quarl** surfaces in large pulverised fuel furnaces can result in interference with burner light-up, operation and performance,
- The deposition of fused or partially-fused ash deposits on furnace heat exchange surfaces reduces furnace heat absorption, and leads to increased gas temperatures both within the furnace and at the furnace exit.
- **Excessive furnace deposition** can lead to increased ash deposition and high metal temperatures in the convective sections of boilers, and it may be necessary to reduce load or to come off load for manual cleaning.
- The accumulation and subsequent shedding of large ash deposits on upper furnace surfaces can lead to damage to grates and to furnace ash hoppers, and to the defluidisation of bubbling fluidised beds.



Boiler fouling

- The formation of fouling deposits on the surfaces of superheater, reheater and evaporator banks occurs at flue gas temperatures less than around 1000°C,
- This is a much slower process than slag formation, with ash deposits growing over a a number of days.
- Convective section fouling is one of the most troublesome biomass ash-related problems, because of the relatively high alkali metal content, and hence the high fouling potential.
- Fouling reduces the heat absorption in the convective banks, and results in increased flue gas temperatures.
- Increased fouling also increases the gas-side pressure drop across the banks, and can eventually lead to ash bridging between the tubes.
- Ash deposits on economiser surfaces at low flue gas temperatures tend to be relatively weakly bonded.



Slag formation mechanisms

- Ash particle inertial impaction is the dominant process in high temperature slag formation, and for larger ash particles. The rate of deposition by impaction is a function of the particle flux, and of the deposition efficiency.
- The condensation of volatile inorganic species, in vapour or fume form in the flue gases, on cooled surfaces, is of particular importance for biomass materials because of the relatively high levels of volatile species in these fuels,
- **Chemical reactions** occurring within the deposits, and particularly oxidation, sulphation and chlorination processes.
- **Thermophoresis,** the transport of small, gas borne, ash particles to cooled surfaces by the effects of the local gas temperature gradients, is only important for very small, sub-micron particles and particularly during deposit initiation.



Convective section fouling

- Convective section ash fouling is largely driven by the deposition of **volatile inorganic species** in the ashes, principally the alkali metals, and in some cases phosphorus compounds, by a volatilisation-condensation mechanism.
- The volatile species will condense on any cooled surface, initiating deposit growth and acting as a bond between the non-volatile, non-fused ash particles which adhere to the deposits.
- On deposition, there is also a tendency for the alkali metal compounds and other inorganic species to **sulphate**, a reaction with the sulphur oxides in the flue gases, which can add significantly to the mass and volume of the deposits.
- The **physical properties of the ash deposits** depend largely on the ash chemistry and on the flue gas temperature at the deposition site.
- **On-line cleaning techniques** tend to be relatively ineffective if the deposition is extensive and, off-line, the deposits cool to a hard dense solid, which can be very difficult to remove.
- The deposits formed on boiler surfaces in contact with flue gases at **lower temperatures**, i.e. below about 600-700°C, depending on the chemistry, tend to be relatively weakly bonded. They are more friable in nature and are usually easier to remove both on and off-line.



Deposit shedding mechanisms

- The principal means of on-line control of deposition is the use of the **installed sootblowers**. These devices direct a high velocity jet of steam, water or compressed air at the deposits, and employ a combination of mechanical impact and thermal shock to break up and remove the deposits.
- The deposit material removed in this way may be carried forward with the flue gases, but can also accumulate elsewhere in the furnace or in the convective pass of the boiler.
- The **natural shedding or detachment of deposits** also occurs. This can occur when deposits grow too large for the adhesive forces to support them, or due to the effect of thermal expansion differences between the ash deposit and the boiler tube, during shutdowns and boiler load changes.
- The **detachment of large accumulations of slag** can result in damage to components or in troublesome accumulations of ash lower in the furnace.
- **Heavily fused** deposits of low viscosity can drip on to surfaces lower down in the furnace or boiler.
- In the boiler convective section, **fly ash particle impact erosion wear** can result in the reduction of the thickness of fouling deposits, particularly on the sides of tubes.



The control of ash deposition

- The careful design of the furnace and boiler convective section, which recognises properly the characteristics and behaviour of the fuel ash, is of prime importance. The incorporation of specific furnace and boiler design features to minimise ash deposition, and to aid the removal of ash and the avoidance of ash accumulation.
- The correct design, operation and maintenance of the combustion equipment and of the on-line cleaning systems are important issues.
- Intensive cleaning of the furnace and boiler surfaces during outages can be very effective in increasing the operating times between outages.
- There are **specialised on-line deposition monitoring and sootblowing control systems** that are commercially available and that can assist significantly with the optimisation of the sootblower operations and the control of ash deposition.



Biomass ash erosion

- Particle impact erosive wear processes are associated with hard ash particles,
- The erosion rate is a function of the erosive particle flux and the velocity, viz:

Erosion Rate = kmv^{2.5}

- Biomass materials generally have much lower ash contents than conventional solid fuels,
- Biomass ashes, in general, tend to be less erosive in nature than most solid fuels – lower quartz and pyrite levels,
- The only exceptions are high quartz ashes, e.g. rice husks, which can be erosive in nature.



Boiler tube corrosion factors

- The tube material higher chrome alloys are more resistant.
- High flue gas and metal temperatures generally superheater outlet elements are at high risk.
- The chemical composition of the ash deposit material at the metal-deposit interface. High alkali metal and chloride contents are undesirable.
- The chemical composition of the flue gases high chloride contents are undesirable.
- The operating regime of the plant large numbers of start-ups and shutdowns are undesirable.



Conclusions

- Ash deposition and boiler tube corrosion processes are key issues in the design and operation of biomass combustors and boilers.
- In the main, biomass materials and their ashes tend to be less erosive and abrasive than more conventional solid fuels.
- The key to avoidance of serious deposition and corrosion in biomass combustion plant is in the design phase. It can be very difficult to compensate for poor design after the plant is built.
- The designer of the combustion equipment and boiler plant must have the appropriate fuel assessment and design tools.



Annex 5. Ash related problems in wood fired boilers and effect of additives - Håkan Kassman, Vattenfall Power Consultant AB, Sweden

Workshop on Ash deposition and corrosion, Glasgow September 2006

Ash related problems in wood fired boilers and effect of additives

Håkan Kassman and Magnus Berg Vattenfall AB



Content of the presentation

Introduction

- Co-combustion and additives
- The strategy of Vattenfall
- IACM (In-situ alkali chloride monitor)
- The ChlorOut concept
- Examples from full-scale boilers



INTRODUCTION

- Most bio-fuels fuels have a high content of alkali metals (mainly K) and chlorine, and very little sulphur
- K released during combustion can condense as chlorides (KCl) or sulphates (K_2SO_4) . KCl in deposits may cause accelerated corrosion





Additives and co-combustion

- Superheater corrosion and deposit formation can be reduced by co-combustion (peat, coal) or by additives
- Additives can either prevent the release of gaseous KCl or react with KCl in the gas phase and form less corrosive components
- The additives can be added with the fuel or to the flue gases



Additives and co-combustion

- Reaction with K resulting in K-alumino silicates and consequently decrease the levels of KCl (g) in the flue gas The main constituents of them are Al_2O_3 and SiO_2
- Kaolin, sludge, peat, coal ash
- Sulphation of gaseous alkali chlorides to less corrosive alkali sulphates Elemental sulphur, or other sulphur containing
 - additives





The strategy of Vattenfall

- On-line control of the in-coming fuel-mix by measuring KCl
- Reduction of alkali chlorides by a sulphur containing additive
- Measurements by means of deposit and corrosion probes, characterisation of the flue gas environment at the super heaters
- Reduced of deposit formation and super heater corrosion



The strategy of Vattenfall

- Vattenfall has developed and patented:
- a sulphate containing additive called ChlorOut (normally ammonium sulphate) ;
- \bullet an instrument that measures KCl(g) on-line called IACM (in-situ alkali chloride monitor)
- This presentation will describe some aspects on IACM and the ChlorOut concept.
- Results from a research campaign in a typical application of the concept.



IACM

- In-situ Alkali Chloride Monitor
- Measures KCl, NaCl and SO₂ online at 600-1500 °C
- 3 15 m measuring length
- 5 sec measurement time
- ~1 ppm detection limit












Helsingborg - On-line control of the fuel quality

Conversion of a PF burner from cocombustion of coal to 100% bio-fuel

IACM mätningar vecka 51 2003







Munksund – Previous results







The ChlorOut concept

 ChlorOut (ammonia sulphate) is sprayed into the flue gases and converts chlorides to sulphates, which reduces corrosion and fouling. It also reduces NOx and CO. Main chemical reactions: $(NH_{4})_{2}SO_{4} \rightarrow 2NH_{3} + SO_{3} + H_{2}O$

 $SO_3 + H_2O + 2KCI \rightarrow 2HCI + K_2SO_4$



Idbäcken CHP ~ 100 MWtot BFB







Lövholmen – Reduction of NOx and CO

16 MW grate. Biofuel from a saw mill







The research campaign in Munksund

98 MWth CFB boiler Fuel: Mainly bark>80%, sawdust, wood chips, 6% plastic waste (comes from cardboard recycling)

Steam data : 420°C after SH2 480°C 60 bar after an Intrex.

Two separate cyclones, the flue gases mix again prior to SH2





The research campaign in Munksund

- A short term-measurement campaign: Normal fuel mix, Normal + ChlorOut, 20% Peat + Normal, IACM, deposit probes, DLPI impactor, FTIR
- Right side injection of ChlorOut: Normal fuel mix, Normal + ChlorOut, IACM, deposit and corrosion probes,
 - Long-term measurements: IACM, ChlorOut, Corrosion probes, data recording from the plant including stack emissions





The Munksund boiler



Corrosion/ deposit probes



Short-term – Reduction of alkali chlorides





Short-term – Reduction of alkali chlorides







Short-term – Deposit growth







Short-term – Wet chemistry, 500°C







Right sided injection – Deposit growth

Deposit growth - right sided injection of ChlorOut







Right sided injection – wet chemistry, $500^{\circ}C$









Right sided injection – the corrosion probe





A corrosion probe exposed during 4 weeks Left side: Normal fuel mix Right side: Normal fuel mix + ChlorOut







Long-term measurements – KCl vs load







Long-term measurements – NOx vs load







Conclusions – the research campaign

- It was possible to measure KCl (g) on-line with IACM. It was also possible to distinguish between normal fuel-mix with and without an additive
- The deposit growth decreased during ChlorOut
- The deposits content of Cl decreased during both ChlorOut and co-combustion with peat NOx was significantly reduced during ChlorOut





Annex 6. Experience with ash deposition in poultry litter boilers - David Bowie, Mitsui Babcock, UK

Operational Experience with a High Fouling Biomass Fuel

David Bowie Mitsui Babcock Energy Services

ThermalNet Workshop Glasgow 21-09-06



Supported by the European Commission under the Intelligent Energy - Europe Programme



Design Fuel – Poultry Litter



Gross Calorific Value	12.12 kJ/kg	(7.59 – 13.6
Total Moisture	30%	(20 – 45) %
Ash	14.9%	(11 – 17) %
Carbon	42.4%	(38 – 44) %
Sulphur	0.6%	(0.2 – 0.8) %
Chlorine	0.5%	(0.4 – 0.6) %



63) kJ/kg



Atmospheric Fluidised Bed Combustor (AFBC)



Maximum Continuous Rating Design Steam Flow Steam Pressure Steam Temperature Feedwater Temperature Boiler Efficiency

Fuel Mass Flow Rate Annual Fuel Consumption Bed Temperature Freeboard Temperature



40.6 MW_{TH} 46.6 te/h 62 bar(a) 460^oC 110^oC 89.5%

13.83 te/h 110,000 te/yr 650 - 850°C 850 - 950°C

Boiler Design Basis



- **Bottom Supported construction**
- Membrane Wall Furnace
- Integral Refractory-Lined Fluidised Bed
- **Open pattern Air Distributor**
- Sub-Stoichiometric bed combustion
- **Two-Pass Radiant Zone**
- **Counter Flow Primary Superheater**
- Parallel Flow Secondary Superheater
- Inter-stage Spraywater Attemporation
- **Steaming Economiser**
- **Balanced Draught**
- Flue Gas Recirculation



Furnace Refractory Fouling

- 3.04 x 6.04 metre Bubbling Fluidised Bed
- 90mm thick Silicon Carbide refractory lining
- 480 Bubble Caps in open pattern Air Distributor
- 750°C routine Bed Temperature aim

Fuel ash agglomeration experienced under sustained high power







Furnace Wall Fouling

- 6.3 x 7.5 metre x 17.0 metre high furnace •
- 278°C operating temperature

Progressively fouling under-load









57mm O.D. tubes on 100mm pitch

Secondary Superheater Fouling

Elevated furnace exit temperatures quickly become critical at the flue gas inlet to the Secondary Superheater





Secondary Superheater Fouling

High Superheater gas inlet temperatures lead to fused alkali metal deposits:

 Potassium Sulphate Potassium Chloride



38mm O.D. tubes on 100mm pitch





Superheated Steam Temperatures



Superheater-II Steam Outlet Temperature 465.0 455 H 450.0 445.0 448.8 24.Hours

Increasing surface temperatures subsequently lead to downstream migration of fouling from the Secondary to the Primary **Superheaters**

S/H-I steam outlet temp > S/H-II

A useful indicator of the extent of surface fouling



Convective Surface Fouling High Power

In the extreme, water-cooled surfaces are equally likely to be affected



Boiler exit screen – 76mm O.D. tubes





Economiser Fouling

Again, this is principally dictated by surface temperature

With the Economisers operating between 110°C – 278°C, friable deposits generally continue to be easily removed by steam sootblowers on a 6-hourly cleaning cycle



38mm O.D. tubes on 80mm pitch





Superheater Support Fouling

Surface geometry is equally important:

- Saturated steam cooled superheater hangers
- 278°C operating temperature
- But exposed to maximum flue gas temperature

Susceptible to heavy fouling only at temperature concentrators









Superheater Fouling Trend

The pattern of fouling is entirely predictable:



The duration of the operating cycle is dictated wholly by the rate of deposition versus the efficiency of on-load cleaning systems

Ultimately this is controlled by boiler operating power, hence peak furnace exit temperature



Secondary Superheater Fouling Low Power

Low power and reduced flue gas temperatures lead to deposits that can be more readily controlled by on-load cleaning





Sootblowing Erosion



Repeated sootblowing leads to rapid tube surface erosion





Sootblower Corrosion

Un-cooled surfaces are exposed to rapid corrosion:

Hastelloy C22 Sootblower lance at S/H-II gas inlet Severe corrosion after < 12-months service life




Superheater Draught Loss

Even at reduced power, on-load cleaning is not entirely successful in mitigating fouling

Flue gas path blockage inevitably occurs, accelerated by any nuisance trip event







Cumulative Plant Performance



Cumulative Time Availability 100.0 90.0 80.0 70.0 All Time Availability - 79.8% 60.0 Availability (%) 50. 40.1 30.0 20.0 10.0 0.0 August 2000 - September 2004

Load Factor: 67.8% versus >90% design

Availability: 79.8% versus >95% design



Proposed Design Changes



- Elimination of refractory slopes
- Extended support firing at start-up
- **On-load water washing of Furnace**
- Large Platen superheating surface
- Increased tube pitch
- Fully retractable sootblowers



Annex 7. Experiences with wood/sludge cofiring in Sweden -Claes Tullin, SP, Sweden



Experiences with waste wood/sludge co-firing in Sweden

Claes Tullin and David Eskilsson SP Swedish National Testing and Research Institute

Lars-Erik Åmand and Bo Leckner Chalmers, Department of Energy technology

Financial support from the Swedish Energy Agency





1) Waste wood is contaminated with Zn and Cl

=> increased problems with deposits

- 2) The deposit formation can be radically decreased by co-combustion with sewage sludge
- 3) What are the underlying mechanisms?

Experiments have been performed in Chalmers 12 MW CFB





- Wood pellets
- Waste wood
- Sewage sludge

Three different waste wood qualities were simulated:

- 1) "Clean" waste wood
- 2) "Normally" contaminated waste wood: Added ZnO (pigment in old paint)
- 3) Painted waste wood with high chlorine content: Added ZnO and HCI



Fuel Analysis



	Wood pellets	Waste wood	Sewage sludge
Proximate analysis			
Moisture (mass %, raw)	8.6	33.1	72.8
Ash (mass %, dry)	0.6	0.8	46.9
Ultimate analysis (mass %, daf)			\smile
C	50.3	50.0	51.7
Н	6.1	6.1	7.2
0	43.5	43.7	32.9
S	0.01	0.01 (1.8
Ν	0.09	0.17	6.2
CI	0.01	0.02 (0.1
Heating value (MJ/kg daf)	18.6	18.0	20.5
Ash analysis (g/kg dry ash)			
Κ	87	70	13
Na	5.9 (26	7.8
AI	11	14	73
Si	64	65	130
Fe	16	57	170
Са	190	152	42
Mg	33	26	10
P	13	7.2	(66)

Test programme



WP: Wood Pellets MS: Municipal Sewage sludge Number: mass dry fuel / mass total dry fuel)%) (balance = waste wood) Molar ratio S/Zn CI / 2S / 2S/CI Runs CI/Zn (K+Na) (K+Na) 0.11 0.3 **WP38** 4.4 6.0 2.7 WP33+MS13 3.0 18 **80.0** 1.02 (12.8) WP56+ZnO 0.91 0.64 0.27 0.4 1.5 **88.0** 7.5 WP48+ZnO+MS5 3.2 0.16 1.2 5.9 WP47+ZnO+MS9 0.97 1.9 0.16 11.9 WP51+ZnO+HCI 0.63 0.6 0.3 4.0 1.9 WP44+ZnO+HCI+MS6 2.0 3.9 3.8 0.80 1.6 WP43+ZnO+HCI+MS10 3.5 5.9 0.51 1.7 3.4

The particle size distribution of the fly ash in the convection pass has been measured:

- Number size distribution: ELPI
- Mass size distribution: DLPI and pre-cyclones

A simulated super heater probe (500 °C) has been used to collect and study the deposit formation in the super heater region

The samples from the DLPI and from the simulated super heater have been analysed chemically



Some of the collected particle fractions have been characterized by using chemical analysis:

- The elemental concentrations have been analysed by ICP- OES, ICP- MS and ion chromatography (27 different elements)
- Different critical compounds have been analysed using TOF-SIMS (NaCl, KCl, K₂SO₄, K₂CO₃, CaSO₄ Ca₃(PO₄)2, ZnO, ZnCl₂ and ZnSO₄)

All deposit samples have been analysed as following:
1) Surface analysis on the wind side using TOF-SIMS
2) Elemental concentration of the complete deposit

TOF-SIMS - Time-of-Flight Secondary Ion Mass Spectrometry



Schematic picture of the SIMS process.

A high energy ion hits the surface and gives rise to a cascade of secondary ions from the outermost 1-2 atomic layers of the sample surface. The secondary ions are detected by a mass spectrometer.



Results – Deposit formation





Results – Chemical analysis of the deposits



Results – Mass size distribution





Results – Number size distribution





Results - Sum of elements related to fouling (K, Na, Zn, Cl and S)





Results - Mass concentration of some critical elements in case: WP56+ZnO





Observations during sludge combustion:

- The deposit formation decreases radically
- The fouling related elements (mainly KCI and K2SO4) in the submicron particles are transported to the larger particles (Dp>1 µm)

Three explanations are going to be discussed for the reduction of the formation of solid deposits on tubes during addition of sludge

2 KCI + SO2 + ¹/₂O2 + H2O => K2SO4 + 2 HCI

Test	S/Cl
WP38	1,35
WP33+MS13	<mark>6,4</mark>
WP56+ZnO	0,75
WP48+ZnO+MS5	<mark>3,75</mark>
WP47+ZnO+MS9	<mark>6,0</mark>
WP51+ZnO+HCl	<mark>0,15</mark>
WP44+ZnO+HCl+MS6	1
WP43+ZnO+HCl+MS10	<mark>2,52</mark>

It has been stated¹ that when the fuel's molar ratio of S/Cl > 4, corrosion caused by chlorine will be avoided

Previous measurements have shown that these reactions cause a high mass concentration of submicron particles containing K2SO4

¹ Krause, 1986, Robinsson et al., 2002



Discussion – Explanation 3: Chemical reaction

- The third possibility is a chemical reaction between the components of the sludge ash, particularly aluminium-silicon compounds, and potassium, liberating chlorine in the gaseous form (HCI).
- A suggestion in this direction has been advocated by Aho in connection to co-combustion of coal and biomass¹

¹ Aho and Silvennoinen, 2004, Aho and Ferrer, 2005





Conclusions



The deposit formation decreases radically when sludge is added to the combustion

The fouling related elements (mainly KCI) in the submicron particles are transported to the larger particles (Dp>1 μm)

During high S/CI ratios, the potassium is sulphated

Some of the potassium is found on the larger particles as KCI and K2SO4 which indicates heterogeneous condensation

>Looking at the results from the elemental concentration of the larger particles during sludge combustion indicates that a major part of the potassium could have reacted with aluminum-silica compounds

For more info: Åmand et al, Fuel 85 (2006) 1313-1322