Data to Allaska, which and which quality?

Quantitative data on the properties of combustion residues, on their origin and their production are collected in Allaska. The purpose of this memo is an overview over the information registered in Allaska and of the test methods that have been used and that should be used when producing the information. The memo is an update of Appendix A to the report number 857, January 2004, to Värmeforsk.

Review of the data registered in Allaska

In the table below are presented the main types of information registered in Allaska. Tests and analyses shall be standard methods. Please note that if space has been reserved for a parameter, it does not necessarily follow that there are such data in Allaska.

	Type of information, method of analysis or testing
Fuel	According to SS 18 71 10, with additional details
Combustion plant	Grate or fluidised bed
Combustion residue	Bottom ash, bed ash (FB), fly ash
Extraction of residue	Wet or dry
Chemical composition	Loss on ignition, TOC,
	Total composition as in SKS meddelande 2001:4
Leaching properties	Percolation test, EN 14405
	Batch test, EN 12457-3 och 12457-4
	Availability test, NT Envir 003 och 006
	pH-static test
Technical properties	Particle size distribution, EN 933-1
	Density, EN 1097-3, appendix D, loose density, SS 02 71 09
	Water absorption EN 1097-6, Bilaga C
	Capilary rise, modified EN 1097-10
	Freeze resistance, prEN 13055-1
	Thaw sensitivity, VVMB 301:2001
	Thermal conductivity, EN 12664:2001
	Permeability, Nordtest TR 254
	Compacting, SS-EN 13286-2:2004
	Dynamic tri-axial test, EN 13286-7:2000
	Compressibility, SP-method 2670

This information is described in more details below.

Which information?

Obviously, all information on the properties of combustion residues belongs in Allaska, provided it satisfies a few criteria on quality. For the information on the properties of the residues to be useful, a first requirement is that the data have been obtained using a standardised test method and that the information is sufficiently wide. Standardised tests are a prerequisite for comparison between different materials.

Data have been grouped together in the database Allaska the following way:

- Chemical composition (primarily inorganic, i.e. total composition or elements, but also organic substances
- Leaching properties
- Geotechnical properties (particle size distribution, density, compressibility etc)

In addition to that, enough information should be had for tracking the possible causes for a property: origin and history, i.e. the fuel yielding the ash and the process and the treatment at the combustion plant. The database contains, therefore, information on:

- The fuel and its properties
- The characteristics of the combustion plant and operating conditions
- Where the ash was extracted and how it was treated after extraction

The parameters which should be recorded in Allaska are described below, following the flow scheme for a combustion plant: fuel first, combustion process next, extraction and possible treatment of ash, and finally the properties of the combustion residue. Striking a reasonable balance between all information which would be nice to have and the quantity of information that may reasonably be had from participants is delicate work.

Fuels

The description of the fuel should be as detailed as possible for an analysis of the influence of different factors on the properties of the residues to be possible, but it should also not be more detailed than the large-scale handling of fuels will allow[1]. The level of detailing that was assessed to be feasible was having two levels: a main level, as in the standard SS 18 71 10, and a sub-level.

Please note that, since Allaska was created, European standards have been developed, which standards should replace SS 18 71 10. Those existing today are:

- For solid biofuels, CEN/TS 14588:2004 for terminology, definitions and descriptions, CEN/TS 14961:2005 for fuel specifications and categories
- For recovered fuels, CEN/TS 15357:2006 for terminology, definitions and descriptions, CEN/TS 14359:2006 for fuel specifications and categories

These standards have not yet been implemented in Allaska, but it is unavoidable that they will be when information is delivered to Allaska according to them.

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[1] The Swedish standard SS 18 71 10 for the classification of combustion residues is rather rough and presntns only one level for the original fuel. The emphasis in foreign databases for solid biofuels and ash (e.g. Phyllis) is on the fuel. In these, up to four levels are used to describe the fuel. Other instances, e.g. the Swedish Energy Agency and the Swedish Forest Agency use another type of categories for woody biofuels.

In the standard SS 18 71 10 definition and in most databases[2] one assumes that 100 % fuel fractions are combusted at one time, but it is much more common to mix several fuels. One Swedish combustion plant is known to use six fuel fractions.

The fuel description is as follows:

- Principal category or level for the fuel (coal, waste, woody fuels, peat, other solid biofuels, other solid fuels as in standard SS 18 71 10)
- A sub-level or sub-category (for woody fuels it could be forest fuel, sawmill residues, etc)
- Shape (pulverised fuel, chips –chopped or crushed -, pellets, etc)
- Percentage in the fuel mix
- Comments

The quality assurance and monitoring of fuel quality at combustion plants could deliver further information. In principle, most of this additional information would be desirable, but obtaining this additional information tends to be a demanding task.

Combustion

The furnace is described as follows:

- Main principle (grate, fluidised bed, pulverised fuel, etc)
- Flue gas dedusting and cleaning (cyclone, ESP, baghouse filter, condensation, scrubber)
- Additives to the flue gas cleaning (lime, activated carbon, ammonia for SCR/SNCR)
- Nominal capacity

The category fluidised bed has been divided into CFB (Circulating Fluidised Bed) and BFB (Bubbling Fluidised Bed) because it was expected that their respective residues should be different. Regarding grate furnaces, there are so many variants of grates that it was decided to lump them into only one category. The space for comments is used to note if it is a vibrating grate, a moving grate, a spreader-stoker, etc..), in order to save that information if this policy needs to be reconsidered in the future. In Sweden, retrofitting an oil furnace or a PF furnace with an external furnace (“förugn”) in order to handle solid biofuels used to be common, but this design is gradually disappearing. More details than a comment would not have been cost-efficient.

If it is needed, a more detailed description of the flue gas treatment could be written as a comment.

The additives used in flue gas treatment should be recorded in the database. Those injected in the flue gas ducts and influencing the composition of the APC residues are lime or sodium bicarbonate for the sulphur oxides and hydrochloric acid as well as activated carbon for mercury and dioxins. Other such as ammonia or urea are not expected to influence the composition of ash, neither are ammonium sulphate or similar additives that counteract corrosion on boiler tubes. However, not including them would have lead to an unnecessary loss of information.

[2] These may have a category ”mixtures”, but it is then mainly a mixed bag where there is no possibility to describe the components of the mixture.

The combustion residue

Only three categories are used today to describe the combustion residue: bottom ash, fly ash and APC residue. There is reason enough to be more detailed, e.g. discerning between cyclone ash, ESP ash and baghouse filter ash. It has often not been possible to obtain such details and consequently a least common denominator approach has been chosen.

Practice complicates the description further as different streams of residues often are mixed together, different fly ashes together, fly ash with bottom ash. Ash may be fed out of a silo common to two or three furnaces.

The description of ash or combustion residue is therefore:

- Main category for the combustion residue (e.g. bottom ash, fly ash or APC residue)
- Percentage in the ash mixture
- Comments

Next group of descriptors refers to sampling. This information is not really important for the properties of combustion residues, but it increases the chances of tracking a residue back into the plant:

- Representative sample (gathered over a longer period of time) or momentaneous sample (date/hour)
- Extraction, wet or dry
- Actual load on the boiler for this sample (an information which is usually very difficult to obtain)
- Sampled at transporter, from a container or from a heap?

However, the last group of information is definitively important for the properties of a combustion residue, as it pertains to treatment after extraction:

- Aged or fresh residue
- For bioashes - hardened, agglomerated, crushed etc
- Mixed with another material, e.g. sewage sludge
- The date of sampling after ageing/treatment (for tracking purposes)

Logically, the material mixed with a combustion residue should be described at least as detailed as the residue. However, it is difficult to foresee all variations.

The properties of ash

The properties that are been asked for are primarily the technical properties and the environmental properties. As only those data which are relevant for an investigation are determined, it is possible to divide them into categories according to use. A reason for not doing so is that this locks the database into certain paths.

Chemical composition

Chemical composition means very often elemental composition. As information on content of chemical substances is scarce, no effort was done to collect it.

Valuable information is:

- Water content determined by drying at 105°C,
- Unburned matter (the method must be stated: loss on ignition and the temperature at which the test was done, TOC[3], etc)
- The total composition, main elements (reported either as weight percent of oxides or as g/kg) and trace elements (mg/kg)
- Organic components (PAH[4], PCDD/F[5] and others) – in 2007 there were no data on content of organic substances, but data will be added as soon as these are delivered

The first step in an analysis is to determine **water content**. In Allaska, this is recorded in weight percent of the sample as received because this is the most common definition in reports. In geotechnical applications, the water ratio[6] is used more frequently but the conversion does not present any difficulties.

Unburned matter is the combustible matter, unburned carbon, which did not burn out during the combustion. There are several methods to determine it:

- As the LOI (loss on ignition) at a temperature according to a standard, of which they are several
- As TOC, according to one of several standards, primarily EN 13137

Determining the loss of mass after ignition at a high temperature is a convenient and popular method to obtain a measure of remaining carbon. One problem with LOI is that the method does not make any difference between organic carbon (unreacted fuel), elementary carbon in char, carbon in inorganic carbonates, structural water in salt hydrates and hydroxides or volatile salts such as potassium chloride. Another problem is that LOI at different temperatures will yield different values and it is, therefore, necessary to state at which temperature the test was carried out. For ash from solid biofuels, the temperature is 550°C (SS 18 71 87), the same as for determining ash content in the solid biofuels (SS 18 71 71 and SIS-CEN/TS 14 775). For ash in cement the temperature is 950°C (EN 196-2) and for ash as ballast material the temperature is 975°C (SS-EN 1744-1).

A method that gives the possibility to distinguish between carbon and hydrogen (consequently between unburned carbon and structural water) is elemental analysis. With the European standard EN 13 137, there is a possibility to distinguish between unburned carbon (TOC) and inorganic carbonate carbon.

The method to determine the **total inorganic composition** that the Swedish Forest Agency specifies in its recommendations in 2001[7] is dissolution of the sample in a strong acid, i.e. a mixture of nitric acid, hydrochloric acid and hydrofluoric acid (ASTM 3683) or, alternatively, in lithium metaborate melt (ASTM 3682) in a closed vessel in order not to loose volatile elements and determine the concentrations using an instrument.

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[3] TOC, Total Organic Carbon in the sample if one carries over the definition from water analyses or flue gas analyses. However, TOC in combustion residues is not organic but mainly elementary carbon. In their case the name Total Oxidisable Carbon would be preferable.

[4] PAH, Polycyclic Aromatic Hydrocarbons

[5] PCDD/F, PolyChlorinated DibenzoDioxins and –Furans, i common language dioxins and furans

[6] Water content is the mass of water divided with the mass of moist material, while the water ratio is the mass of water divided with the mass of dry material.

[7] The English translation published in 2002 is “Recommendations for the extraction of forest fuels and compensation fertilisation”, Swedish Forest Agency, Meddelande 2002:3, Jönköping 2002

The concentrations should actually be stated using the units mg/kg or g/kg, but it is very common to report:

- The main elements, i.e. Ca, Al, Si, Na, K, P, Ti, Fe, Mn as oxides and in weight percents
- Trace elements, a.o. As, B, Cd, Cu, Cr, Hg, Ni, Pb, V and Zn, but also S with the unit mg/kg DM

Please observe that in its recommendations in 2008[8], the Swedish Forest Agency does not specify methods of analysis.

In the Directive 2003/33/EEC on acceptance criteria for waste at landfills, two methods are specified for dissolution of waste:

- EN 13657, in aqua regia, leaving the silicate matrix intact
- EN 13656, in hydrofluoric acid, nitric acid and hydrochloric acid in a microwave oven for the total composition, dissolving the silicates

The number of **organic substances** is very large. In combustion residues, principally PAH and PCDD/F have hitherto been in the focus of attention. Very few analyses of organic substances have hitherto been performed, making it difficult to specify any method.

Leaching properties

An important part of the environmental properties is the leaching properties, i.e. how much is released in contact with water. In addition to the methods described in standard literature, there are, or it is possible to develop leaching tests for any situation. The number of tests accepted in Allaska has been limited to a few, see Table 1, related to waste:

- Percolation test, prEN 14405
- Two-stage batch leaching, EN 12457-3, with L/S[9]=2 och L/S=2-10
- One-stage batch leaching, EN 12457- 4
- Availability test, NT ENVIR 003
- Availability test in oxidised state, NT ENVIR 006
- pH-static leaching

As far as Swedish conditions are concerned, there are additional leaching methods, specific to spreading of ashes to forest soils:

- The availability of nutrients and hazardous substances during one forest generation – the method has been described by the Swedish Forest Agency in its recommendations, Meddelande 2008:2
- IVL's thirty days' test for biomass ash aims at describing the release of nutrients from a treated ash to forest soils in the course of several years. Only main elements are (Ca, Mg, K, P etc). It does not that this method has been used very much..

For the time being, no data are available from these two methods in any Värmeforsk report. When data become available, they will be registered.

[8] "Rekommendationer vid uttag av avverkningsrester och askåterföring", Swedish Forest Agency, Meddelande 2008:2, Jönköping 2008, in Swedish

[9] L/S, Liquid to Solid ratio, i.e. the volume of liquid to the mass of solid material

Tabell 1. Information obtained from the various leaching tests

Test	**Reported as**
Percolation test prEN 14405	Reported at the following L/S-ratios: **L/S = 0,1 in mg/l** L/S = 0,2 in mg/kg DM L/S = 0,5 in mg/kg DM L/S = 1,0 in mg/kg DM **L/S = 2 in mg/kg DM** L/S = 5 in mg/kg DM **L/S = 10 in mg/kg DM** The following parameters are usually analysed: **As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Zn, V,** Al**,** Ca ,Co, Fe, K, Mg, Mn, Na, S, **chloride, fluoride, sulphate, the phenol index, DOC** For the parameters in bold letters there are limit values in directive 2003/33/EEC on criteria for reception at landfills
Two-stage batch leaching EN 12457-3	Reported at L/S 2 and L/S 10 using the unit mg/kg DM. Substances see above
One-stage batch leaching EN 12457- 4	Reported at L/S 10 in mg/kg DM Substances see above
Availability test NT ENVIR 003	Reported in mg/kg DM (not L/S related) Metallic elements as above
Availability in oxidised state NT ENVIR 006	Reported in mg/kg DM (not L/S related) Metallic elements as above
pH-static leaching	Reported at pH (8 pH values according to) in mg/litre Metallic elements as above and DOC[10]
Surface leaching (diffusion test) NEN 7345	Reported with unit mg/m². Metallic elements as above

[10] DOC, Dissolved Organic Carbon

Technical properties

The properties of secondary materials, to be used in civil works, which should be determined have been defined starting from requirements on function in two reports:

- Criteria in quality for bottom ash in civil works; Phase I – inventory of testing methods and requirements on function (B von Bahr, A Ekvall och B Schouenborg), Värmeforsk report number 867, 2004
- Quality criteria on bottom ash to civil works; Phase II – the techniocal åproperties of bottom ash (B von Bahr, H Arvidsson, A Ekvall och K-J Loorents), Värmeforsk report number 952, 2006

The two most common properties are:

- Particle size distribution – EN 933-1. The primary data are reported as percent passing a mesh width in a standard series (see report 952, Appendix B, for a round-robin comparison between laboratories)
- Density – EN 1097-3, Appendix D. The parameter usually reported is the loose density (in kg/m^3) for the material before it is packed. Th term compact density is used for the density of a single particle. The following concepts are used:
  - Loose density without packing
  - Maximal dry loose density, heavy laboratory stamping and light laboratory packing (SS 02 71 09), reported at the optimal water ratio
  - Compact density

Other properties are:

- Water absorption - EN 1097-6, Appendix C, is the first choice but it yields misdirecting results for porous alternative ballast materials. See report 952, Appendix E, for modifications.
- Capillary height (both rise and drainage) – EN 1097-10, modified, see report 952, Appendix F
- Freeze resistance – prEN 13055-1, Appendix C for light ballast (not SS-EN 1367-1, see report 952, Appendix G)
- Thaw sensitivity – Swedish Road Administration method VVMB 301:2001, see report 952, Appendix H, reported at the optimal water ratio
- Thermal conductivity – EN 12664:2001 that builds upon ISO 8301 and ISO 8302, see report 952, Appendix I
- Permeability – with a tube permeametre according to Nordtest TR 254, see report 952, Appendix J
- Packing properties – SS-EN 13286-2:2004, see report 952, Appendix K, at the optimal water ratio, light stamping (standard Proctor) or heavy stamping (modified Proctor)
- Dynamic triaxial compression tests – EN 13286-7:2000, see report 952, Appendix L – the tests yield stiffness (resilience module) and permanent deformation
- Compressibility – SP-method 2670, see report 952, Appendix M – the test yield the E-modulus under strain
- Mechanical resistance, the micro-Deval method is misdirecting for alternative ballast materials as e.g. combustion residues, see report 952, but it is nevertheless used

Please observe that several of these parameters are determined at the optimal water ratio, but it may be so that this cannot be determined for various reasons. In such a case, the actual water ratio is stated.