CLASSIFICATION OF ASH AS HAZARDOUS OR NON-HAZARDOUS WASTE

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SUMMARY: Combustion and incineration are utilized extensively in Sweden for the generation of heat and electricity. Substantial volumes of ash with varying chemical composition are also generated in the process. Classification of such ash as hazardous or non-hazardous under the European union legislation is, in principle, a "mission impossible" since the chemical forms of the inorganic components are very complex. Consequently, a method has been identified according to which reference substances are selected such that they represent the hazards of the actual forms of those trace elements that might influence health and the environment. The reference substances have been selected such that the hazard is not underestimated, that the result becomes reasonable realistic and that the evaluation is feasible to carry out. There are indications, especially with regard to ecotoxicity, that the method is overly cautious, and a potential is identified for combining testing with information from Authority data bases. It is explained and exemplified that ash may be very susceptible to ageing, and that this in many cases, and for most of the elements of interest, may improve the properties considerably. This not only influences the status of an ash with regard to the acceptance criteria for landfilling, but also influences the classification. Leach properties are important when the degree of solid solution is to be assessed. Elements with similar properties, especially regarding their ionic radii, tend to exchange for each other even in solids. The effect is strongest for those elements that are the lowest abundance. Solid solution effects may lead to that trace elements become as inaccessible as the major elements in a certain crystalline phase. Iron(hydr)oxides and other iron rich phases frequently act as sinks for chromium, nickel and zinc, and in many cases this implies that most of these elements may not contribute to a classification as hazardous. The method has been applied to around 30 facilities with typically several ashes at each facility. It is concluded that this approach has lead to that many ashes have been classified in a cautious bur also reasonably realistic manner which at the same time has been practical.

1. BACKGROUND

1.1. Ash management in Sweden

District heating accounts for about half of the domestic heating in Sweden as well as for much of the heating in commercial buildings. According to statistics on the webb site of the Distric

Heating in Sweden (Svensk Fjärrvärme), the district heating facilities generated, in the year 2012, a total of about 50 000 GWh heat and about 7 600 GWh electricity. About two thirds of this energy came from combustion and incineration. Sweden has around 9.5 million inhabitants.

According to the Swedish Waste Management (Avfall Sverige, 2013), a total of 5 042 thousand tonnes of waste was incinerated in the year 2013, 2 771 of which comprised domestic waste. In the process, a total of 1 067 thousand tonnes of ash was generated, 217 of which was air pollution control residues. According to the webb site of Svenska Energiaskor, the total generation of ash, including biofuels and the paper and pulp industry, was 1 709 thousand tonnes in the year 2012.

A brief compilation of the metabolism of the combustion and incineration of renewable fuels in Sweden can be found in (Sjöblom, 2013).

Some of the ashes generated are used in geotechnical constructions or are recycled as a nutrient to the forest. However, most of the ashes are used for constructions at landfills, for stabilization agents for other wastes, or are deposited at landfills.

1.2. Legislation

The destination of an ash is highly dependent on its content of elements that may have the potential to cause detriment to health and the environment. Such elements as well as the corresponding substances are referred to as “contaminants” in the following. Everyone is obligated to comply with all legislation, including the various national implementations of the European Union waste directive and hazardous waste directive and their statements on classification of all waste as hazardous or non-hazardous. Most of the implementation of these directives into the Swedish legislation can be found in the Ordinance of waste (SFS 2011:927). It regulates how waste is to be handled and managed. Moreover, the European Union Directive on the landfill of waste and the associated Council decision have been implemented into the Swedish legislation largely in the form of a regulation (NFS 2004:10). It states that non-hazardous waste may (under certain conditions) be deposited on a landfill for non-hazardous waste without any “basic characterization”(which includes leach testing according to the Council decision).

The classification of waste as hazardous or non-hazardous is to be made based on the content of various substances and their inherent hazardous properties. For many wastes, this is determined, at least in principle, by their labelling in the list of wastes. For other wastes, analyses have to be made based on actual forms of occurrence for the various elements together with the classification of the chemical substances in question in the “old” system for labelling of chemical products, i. e. the hazardous substances directive (DSD) and the dangerous preparations directive (DPD). In the realm of labelling of chemical substances, DSD/DPD is currently being phased out and being replaced by CLP. However, the classification of waste is still based on the “old” system.

Thus, knowledge of the classification of an ash itself under DSD or its constituent substances under DPD is sufficient for the classification of the ash in question as a waste. Such a procedure is relatively straightforward for organic compounds that can be found in the data bases over hazardous substances.

However, for inorganic constituents, the forms of occurrence are very complex and cannot usually be found in the data bases provided by the Authorities. Nonetheless, it is essential that all existing forms of a contaminant element be included, such that the hazard of the ash in question is not to be underestimated.

There is, of course, the option to run all the various tests required on an ash that is to be classified. Bu, unfortunately, ashes from different furnaces as well as point of exit are different, and therefore the task of testing all these varieties is truly insurmountable.

Thus, classification of ash as hazardous or non-hazardous would thus appear to be a “mission impossible”.

1.3. Examples of approaches

Efforts have been made in many of the European Union countries in order to find approaches for the practical implementation of the legislation on waste classification, see e. g. (Hennebert 2013) and the Technical Guidance WM2 issued jointly by the various Authorities in the UK.

However, none of the sources found is intended specifically for the classification of ash from combustion and incineration. As already mentioned in Section 1.1, ash constitutes one of the major waste categories in Sweden, and this has prompted the work presented in this paper.

2. OBJECTIVES AND APPROACH

2.1. Objectives

The objective of the present work is to find a method for classification of ash as hazardous or non-hazardous such that the intent of the legislation can become realized in practice. The hazards should be dealt with in a cautious (precautionary principle) but also reasonably realistic manner. The method should be reasonably easy to apply in practice, and possible for the staff at a utility to carry out by themselves.

2.2. Approach

The approach is based on the identification of hypothetical forms of occurrence (referred to in the following as reference substances) for the various contaminant elements. These substances should have the following properties:

- They should represent the actual forms in a cautious manner
- Initial contact between ash, air and moisture is assumed to have taken place
- The representation should be reasonably realistic
- The hazardous properties should be known, and the substances should be included in the data base of the Authorities
- All contaminant element atoms should be associated with one or more reference substances

The reference substances identified are then used for calculation of the hazardous properties of ashes. The calculations are carried out in the same manner as would have been the case if the actual substances could have been identified.

Some of the rationale for the approach selected will be presented in the following.

Further information on the approach and method used can be found in (Adler et al, 2004; Sjöblom et al, 2006; Sjöblom, 2007; Sjöblom, 2009; Sjöblom, 2011; Sjöblom & Noläng, 2011; Sjöblom, 2012).

3. CALCULATIONS WITH REGARD TO HAZARDOUS PROPERTIES

Whether an ash is hazardous or not can be assessed by means of a calculation that includes the risk phrases associated with the various reference substances, as listed in the Authority data base. Risk phrases are identical to what is referred to as R-values in the waste legislation.

Reference substances have been identified based on various compilations and assessments of the chemistry involved and the result is shown in Table 1.

During a calculation, sums are made over the concentrations in each column H4-H6 and H8, but only the elements labelled “Y” in Table 1 are included. Similarly, the largest concentration is selected for columns H7-H11. The values so obtained are compared with the limits in Table 1. An ash is classified as hazardous if any of the concentrations exceeds a limit.

Table 1 - Relations between reference substances, R-values and the quantified hazardous properties. H4 = Irritant, H5 = Harmful, H6 = Toxic, H7 = Carcinogenic, H8 = Corrosive, H10 = Teratogenic and H11 = Mutagenic. Y = yes.

Property	**H6**	**H6**	**H5**	**H8**	**H8**	**H4**	**H4**	**H7**	**H7**	**H10**	**H10**	**H11**	**H11**
Code	**TT+**	**T**	**Xn**	**C**	**C**	**Xi**	**Xi**	**T**	**Xn**	**T**	**Xn**	**T**	**Xn**
Limit %	**0,1**	**3**	**25**	**1**	**5**	**10**	**20**	**0,1**	**1**	**0,5**	**5**	**0,1**	**1**
S=Sum; L=Largest	**S**	**S**	**S**	**S**	**S**	**S**	**S**	**L**	**L**	**L**	**L**	**L**	**L**
R-values*	**26** **26** **26**	**23** **24** **25**	**20** **21** **22**	**35**	**34**	**41**	**36** **37** **38**	**45** **49**	**40**	**60** **61**	**62** **63**	**46**	**68**
antimony(III) oxide									Y				
arsenic(III) oxide	Y				Y			Y					
barium(II) oxide			Y										
lead(II) oxide			Y							Y	Y		
cadmium(II) chloride	Y	Y						Y		Y		Y	
kobalt(II,III) oxide			Y						Y				
copper(II) oxide			Y										
chromium(VI) oxide	Y	Y		Y				Y			Y	Y	
chromium(III) oxide*													
mercury(II) chloride	Y	Y			Y								
lantanium(III) oxide						Y							
molybdenum(VI) oxide			Y				Y						
nickel(II) oxide								Y					
ferronickel slag*													
vanadium(V) oxide		Y	Y				Y				Y		Y
tungsten(VI) oxide			Y		Y								
zinc(II) oxide													
Franklinite $ZnFe_2O_4$*													

* Represents solid solution with iron(hydr)oxide, see text

The reference substances in Table 1 have been selected based on the prerequisites presented in Section 2.2 together with a comprehensive review of the chemistry involved. For instance, arsenic-III oxide would be a realistic choice as well as arsenic-V oxide, but arsenic-III oxide is selected since it contributes the most in the calculations.

4. ONE OR MORE SUBSTANCES

It was mentioned briefly above that it may be unfeasible to regard an ash as a single substance, since there would be very many ashes to test and since the volume of each ash would be moderate.

It might, however, be considered to utilize tests such that several different ashes are included at the same time. The problem involved with this alternative is illustrated in Figure 1. As can be seen from the Figure, the tests will have to be made on an ash with largest value for all of the contaminants, and as a consequence, the joint classification may be much tougher than warranted as well as for any of the component ashes.

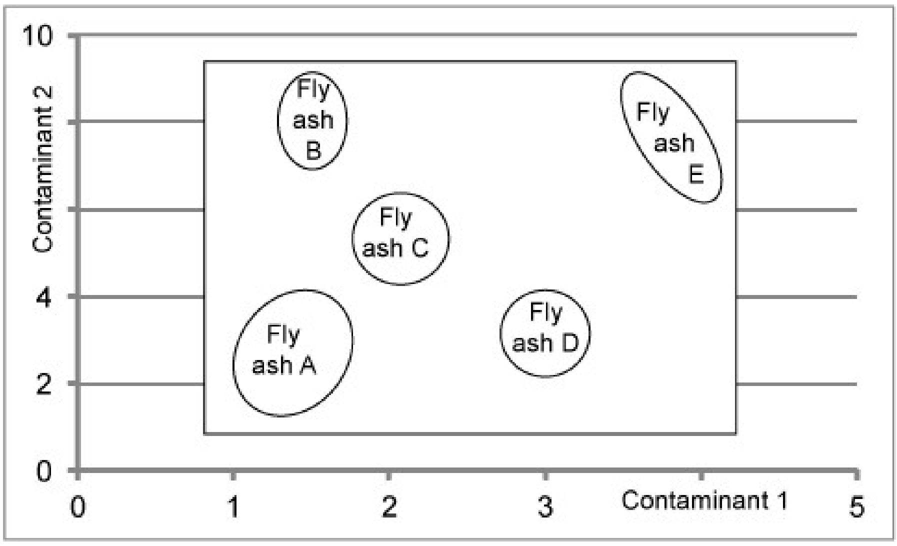

Figure 1 – The figure illustrates the problems involved if several ashes are included in one classification, The case of only two contaminants. Cf. text.

However, there might be some pattern in the variations between the ashes, e g such that the calculations for the classification of a large number of ashes might be possible to describe by a "blending" of only a few ashes. This corresponds mathematically to a linear combination of only a few vectors (chemical composition) or matrices (corresponding to Table 1 with concentrations filled in and excluding H7-H11 for which the highest value applies). This is illustrated by the expression below in which an ash might be regarded as a mixture of ashes with varying contents of reference substances.

$$\text{🝗} = A \times \text{🝗}_0 + B \times \text{🝗}_1 + C \times \text{🝗}_2 + D \times \text{🝗}_3$$

The symbol used in the expression is the chemical symbol for ash according to (Wallerius, 1759) established long before the modern atomic theory and associated symbols was introduced.

The blending may comprise test data, as well as data from the Authority data base, and even other entities, but the procedure used will have to be validated and it needs to be shown that any approach is conservative.

Expressions such as the one above have been used to predict the classification of ash from various fuel mixtures, and might be utilized for efficient use of test data on ecotoxicity. It has been shown that the method described in Section 3 (based on DPD) strongly exaggerates ecotoxicity (Stiernström, 2012), and this may well be the case also for other properties.

Nonetheless, the vast majority of classifications in Sweden have been carried out using the dangerous preparations (DSD) related alternative.

5. FRESH OR AGED ASH

It is well established in the scientific literature that carbonation modifies ash. It is perhaps less well known that ash is substantially altered and aged already on contact with water. It has e g been reported (Bayusenoa & Schmahlb, 2011) that as much as 40 % of an incinerator fly ash might consist of glass that is quite reactive in contact with water, at least at high pH values.

Consequently, the mineralogy of ash may change quite dramatically on ageing after contact with water. This phenomenon can be observed indirectly on the change in the leach rate on ageing, and an example is provided in Figure 2.

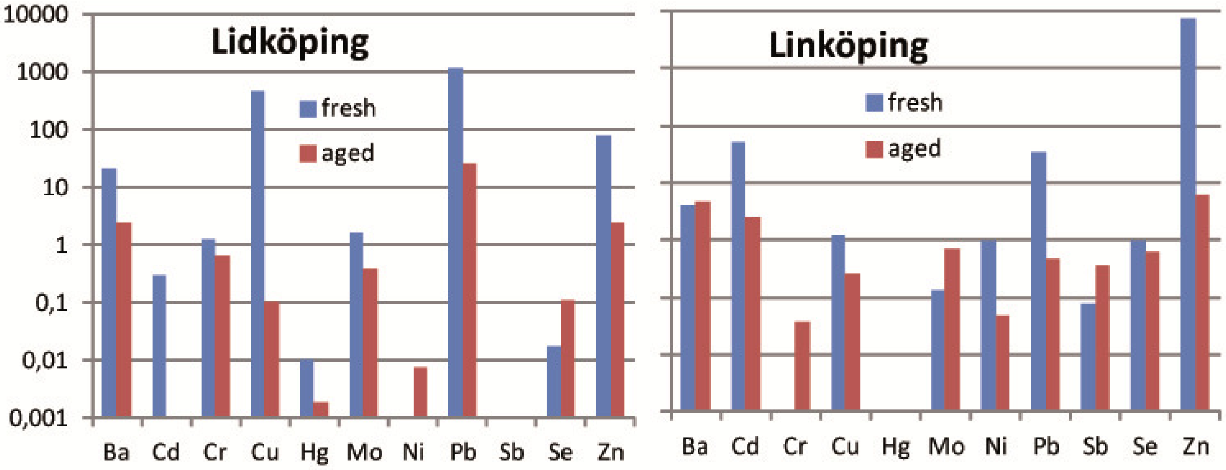

Figure 2 – Two examples of leaching (L/S 10, 24 h, mg/kg dry ash) of fresh fly ash as well as fly ash that has been aged after addition of water for one week in a closed container. Data from (Sjöblom, 2011).

The difference in leaching may be highly important in conjunction with e g disposal of stabilized hazardous waste on a landfill for hazardous or non-hazardous waste. In the relevant Swedish regulation, (FS 2004:10, it is required that attempts are made to establish equilibrium conditions for the leach testing, and the leach to be used is not applicable for cases where the sample reacts with the leachant. Clearly, data for aged ash is preferable in this case.

Leach data may be important also for the classification of waste as hazardous or non-hazardous since they may have an impact on the selection of reference substances. Clearly, one should not select a reference substance that is insoluble for cases in which the leaching of the element in question is high.

According to the legislation on labelling of chemical substances, tests and assessments should be made on the substances according to their initial properties. This clearly contrasts to the approach taken in the acceptance criteria for landfilling. Moreover, much of the practical significance of a classification as hazardous or non-hazardous relates to qualification with regard to landfilling.

The approach taken on this issue in Sweden is a rather pragmatic one. Initial contact with water and air is assumed, and the corresponding leaching rates are used as a support in the selection of pertinent reference substances. This selection also depends on the prerequisites for solid solution, see the next section.

6. SOLID SOLUTION

It is frequently envisaged that minor elements form phases of their own in which they are major elements. This is also sometimes the case, but usually the minor elements in an ash are included in the phases formed by the major elements in the form of solid solution. This phenomenon is very well established in the areas of mineralogy and inorganic chemistry. It means that the atoms of the minor elements are dispersed, typically one by one, in phases containing primarily major elements. Such a dispersion influences and lowers the Gibbs' free energy, and the effect is stronger the lower the concentration of the minor element. The phenomenon can also be regarded as a consequence of the well-known law in chemistry of mass action.

The prerequisites for solid solution vary considerably between elements, oxidation numbers and possible positions in crystal lattices. Solid solution often takes place when the difference in ionic radii is not larger than 20 %. Some data on ionic radii is given in Table 2.

Table 2 – Ionic radii for some major elements and contaminant elements in ash (Wells, 1975).

Valence	**I**	**II**		**III**		**IV**
Spin		**low**	**high**	**low**	**high**	
Na	1,02					
K	1,38					
Mg		0,72				
Ca		1,00				
Al				0,53		
Ti						0,61
Cr		0,73	0,82	0,62		
Mn		0,67	0,82	0,58	0,65	
Fe		0,61	0,77	0,55	0,65	
Co		0,65	0,74	0,53	0,61	
Ni		0,70		0,56	0,60	
Cu		0,73				
Zn		0,75				
Pb		1,19				0,775

It should be noted in particular that the elements Mg, Fe, Cr, Mn, Co, Ni, Cu and Zn frequently substitute for each other, and thus iron oxide and other iron-rich compounds typically constitute a sink for the other elements with similar radii. Even Cr-VI appears to be destabilized in favour of Cr-III even though the pH is often high (Callender, 2005). Accordingly, mixed oxides of Cr, Ni and Zn with Fe are not associated with any R-values in the tables of the Authorities, and do not contribute in any calculations based on Table 1. However, it has to be ensured that such solid solution actually takes place. Indications to the contrary include high leach rates as well as low contents of iron.

Pb exchanges for Ca and may show a high leach rate when Ca occurs in the form of very soluble chloride and perhaps also hydroxide. Consequently, the leaching of Pb is typically decreased to low levels on carbonation, as has been observed by e g (Wang et al, 2010). (Alternative explanations exist, e g that anions are formed at high pH-values.)

7. CONCLUSIONS AND FINAL COMMENTS

A method has been identified by means of which ash can be classified as hazardous or non-hazardous under the European Union legislation. The method is conservative and reasonably realistic, as well as feasible. Since attempts to apply the actual forms of occurrence may be referred to as a “mission impossible”, classification is made by means of reference substances that represent the various elements that may contribute in an evaluation of the hazardous properties.

The chemical form of an ash is substantially altered on contact with air and water. This includes the trace elements which often – but not always – may become much less accessible as well as less hazardous. The minor elements typically go into solid solution with the phases defined by the major elements. This makes their availability comparable to that of the major elements in the phase in question, and the associated contribution to the hazard decreases accordingly.

The method has been applied to around 30 sites, mostly district heating facilities, each typically representing several ashes.

New legislation is underway, and can be expected to come into force on July 1st 2017, at the latest. It is anticipated that the method will prove to be equally applicable also in the future.

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