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Classification of waste according to the European Union Directive

91/689/EEC on hazardous waste from a Swedish application perspective

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Abstract

Substantial volumes of residues of mainly inorganic content are generated in Sweden from incineration, combustion, and the operation of paper mills. The management and future fate of such residues – as well as the possible impact on health and environment - highly depend on an appropriate classification according to the European Union Directive 91/689/EEC on hazardous waste. However, this directive cannot be applied directly to the above mentioned categories of waste, and consequently branch organisations have developed procedures for responsible but practicable classification. The main feature of the method is to identify reference substances which resemble the actual ones, represent them in a conservative way, and can be found in the data bases on dangerous properties.

One major difficulty in classification of the above mentioned substances is the requirements regarding ecotoxic properties where no limits are given. International co-operation is underway within the European Union to investigate how tests on living organisms can be utilized. In might be expected, however, that some time will be required before practical tools are available. In the meantime, feasible and conservative assessments can be carried out based on comparison with other criteria together with the full recognition of any differences in character. A few examples of such comparisons in real cases are presented, and it is hoped that this will promote information exchange and co-operation.

Background and purpose

District heating supplies about 50 % of the heating required in Sweden for domestic and other buildings at a total capacity of 50 TWh/year. Large quantities of heat are also generated at paper mills. The vast majority of such heating comes from wood based fuels, including virgin fuels, recycled fuels, by-products from paper mills and waste. The latter includes about 2 Mtonnes of domestic waste which are incinerated annually and which correspond to

almost half of all domestic waste generated. The total volume of ash generated exceeds 1 Mtonne and constitutes by far the largest category of waste deposited at municipal landfills.

Moreover, comparable quantities of residues of mainly inorganic composition are generated at steel mills and other metal works including various slags from metallurgic operations and sludges from treatment of liquids from pickling.

The management, handling and conceivable future fate of such residues – as well as the possible impact on health and environment - highly depend on an appropriate classification according to the European Union Directive 91/689/EEC on hazardous waste (EUDHW). However, this directive cannot be applied directly to the above mentioned categories of waste, and little further guidance to this end is provided in national Swedish regulations and guidelines.

Two routes can be considered: assessment by testing and by composition (cf the regulations on labelling of chemical products). The "tool-box" for testing has been "imported" from the legislation on chemical products where the properties stay within narrow limits for large volumes of material. It is thus not designed with the variability of residues in mind. Thus, testing is cumbersome, and the present authors know of no case where classification based on testing has been attempted for waste streams. Even for chemical products, most of the assessments are based on composition.

Ideally, the composition of a chemical product corresponds to constant ratios of the well known constituents. For the types of residues mentioned above, the chemical form is very complex, and the various chemical species that can be identified do not appear in the data bases for hazardous substances. It is therefore understandable that the practical implementation of EUDHW in the European Union for such waste is a tedious process. Moreover, it might be tempting, in awaiting for executable guidance, and in accordance with some precautionary principle, to assess all such waste as hazardous which might be suspected of having any of the dangerous properties mentioned in EUDHW. However, such an option is not actually available since the legislation also requires conservation and reuse of material whenever suitable applications can be found. In the case of Sweden such regulation is provided in the *Swedish Environmental Code* where (Chapter 2, Section 5) the following is stated: "Persons who pursue an activity or take a measure shall conserve raw materials and energy and reuse and recycle them wherever possible." (Translation taken from the webb page of the Swedish Environmental Protection Agency.) Thus, there is an obligation by law to classify waste according to EUDHW.

In concordance, the Swedish *Thermal Engineering Research Institute* and *RVF - The Swedish Association of Waste Management* have taken initiative to the development of methodology (Adler et al 1994, Adler et al 2005, Mikaelsson 2004a, Mikaelsson 2004b) that enables practicable as well as responsible classification of waste according to the Swedish implementation of EUDHW, the ordinance of waste (avfallsförordningen, SFS 2001:1063). The analyses and assessments will have to include the variations in properties in actual ashes as well as any ageing phenomena and associated changes of properties over time.

It is apparent from the above that such guidance by necessity will have to rely not only on a compilation of existing legislation and official guidance but also on investigations of the chemical speciation together with the properties from a health and environment point of view of each of the compounds formed. Thus, scientific and technical investigations are necessary,

not only as a basis for the Authorities in their development and formulation of legislative frameworks, but also for the implementers in their actual compliance with the regulations and the practical management of the waste.

It is the purpose of the present paper to present a selection of such work and results, and how they might be utilised for robust classifications according to EUDHW. In particular, the paper focuses on ecotoxic properties.

General approach

According to EUDHW, a substance should be classified as hazardous if it has at least one of the properties explosive, oxidizing, flammable, very toxic, toxic, harmful, corrosive, irritant, carcinogenic, toxic for reproduction, mutagenic and toxic to the environment. Also, substances that might give rise to some other substance that has dangerous properties are included. Limits are given for each of these properties, either as a maximum value for each substance, or as a total concentration of the substances that have the property in question. No limit is given for toxic to the environment, however.

Since the actual substances in the above mentioned types of waste are difficult to characterize (at least in detail), and since they do not appear in the data bases on dangerous properties, reference substances might identified such that they:

- represent the actual substances in a reasonable way
- are represented in the data bases on hazardous properties
- reflect the hazardous properties in a conservative way
- represent the properties over time initial contact with water is assumed

Derivation of reference substances for ash was made in (Adler et al 2004 and Adler et al 2005). Each element having the potential to generate dangerous substances is associated with

a reference substance. Summation is then made for each of the dangerous properties over the amounts of the reference substances. For some properties, the largest value is used instead. Comparison is then made with the limits as stated in EUDHW. As soon as any of the limits is exceeded, the waste in question is classified as hazardous.

The procedure has been applied to residues from Söderenergi AB kept in store at Telge Återvinning AB where a large number of samples were taken from four drillholes and subsequently analysed (Sjöblom et al 2005). At present, the methodology has been applied in classifications of residues at around two dozen plants of different kinds in Sweden.

Toxic to the environment

General

Toxicity to the environment deviates from most other properties in the sense that there is a requirement on compliance in spite of the fact that no statutory limit is provided. In such a case, it might be tempting to look around for similar regulations for other purposes, and to apply them if they are found to be to the liking. Such an approach has no legal significance, however, since regulations are valid only for the purposes specified.

Instead, compliance will have to be looked for against the basic requirements of the law, and in the case of Sweden they are stated in the *Environmental Code*. Thus, assessment of longterm effects on the environment may be evaluated as described for an *Environmental Impact Statement* (EIS). Since the effects of interest are long term, it is only scenarios that might generate such consequences that are of interest (in the present context). In conceivable scenarios identified (e g a lorry accident on a bridge), the immediate effects of the accident are larger than the long-term ones on the environment. The conceivable largest effects on the environment are likely to occur when the ash is at its final destination. For such cases known to the authors, separate analyses are made on a case by case basis and thus provide much more relevant results as compared to any attempt to a generic analysis. In short, in the cases studied, no significant and relevant generic scenarios for long term effects on the environment have been identified. The present authors recommend, nonetheless, that specific environmental hazard identification activities be carried out for each specific case of final destination.

It should be clearly stated, that on the present issue, Swedish subjects are held responsible under Swedish Law. Non-compliance with nonexistent requirements must not lead to any consequences in any legal court (Klingberg 2006).

Comparison with rules for chemical products

The fact that limits set for other purposes should not be applied does not preclude the use of comparison. Actually, a careful analysis of how compliance to environmental requirements can be achieved in similar areas can be most helpful for the identification of cases where residues ought to be classified as hazardous waste. However, any such comparison is warranted only when the differences between the various types of cases are fully realized.

However, the Swedish Thermal Engineering Research Institute work on classification (Adler et al 2004) was based on the strategy that adequate attention should be paid to all requirements in EUDHW and corresponding restrictions were proposed. Thus ecotoxic properties were included in the analyses and a comparison was made based on the levels stated for the quantified properties in EUDHW. They are never stricter than what gives rise to *indications of danger* for a chemical product. It was assessed to be unwarranted to voluntarily impose stricter limits for unquantified criteria as compared to quantified ones. Thus, a limit amounting to weighed sum of 2,5 % was proposed. The above can be illustrated using the case of Söderenergi / Telge Återvinning mentioned above (Sjöblom et al 2005). The content of elements of interest with regard to ecotoxic properties are presented in Table 1, and corresponding leach data are presented in Table 2. The example refers to samples from drill hole one.

A quick look at Table 1 indicates that this limit is more than an order of magnitude higher than sums of elements, and this holds also when it is considered that the reference substances are actually oxides.

Comparison with waste acceptance criteria

Another ground for comparison is the availability, as represented by leach data in Table 2. They might be compared with the criteria for acceptance at a landfill for non-hazardous waste which are also shown in Table 2 for comparison. (Non-hazardous waste may - at least in Sweden - be deposited at a landfill for non-hazardous waste without testing for availability).

Comparison with guidelines for contaminated soil

A further ground for comparison may be some guidelines for contaminated soil published by the Swedish Environmental Protection Agency (SNV 1996, SNV 1997, SNV 2005a). Data on equilibrium constants for soil-water interactions together with the limit values for various types of land use are presented in Table 3.

A comparison between the data for the samples from drill hole one at Telge Återvinning AB and the guideline limits from the Swedish Environmental Protection Agency is presented in Table 4. The values are given in percent. Correction has been made with regard to the difference in equilibrium constants for soil as compared to ash. The equilibrium constants used, $K_d = C / S$, where S = mass sorbed at equilibrium per mass of sorbent (mol/g), and C =sorbate concentration in solution at equilibrium (mol/litre). The methodology for this is described in (Svensson 1995). Equilibrium constants for ash are calculated using the data in Tables 1 and 2. As can be seen from Table 4, the largest value is only 6 % of the limit.

There is a specific point in making the comparison with the Swedish Environmental Protection Agency guideline value for contaminated soil. It is not unreasonable to assume that the Agency has selected her guideline values such that soil left untreated after a cleaning operation would not be comparable in properties to hazardous waste.

Ongoing work and discussions

It has been put forward that a limit of 0,25 % should be applied (SNV 2005b, UK EPA 2003), and that it should refer to the sum of the percentages of substances having ecotoxic properties. However, little or no guidance exist as to how the calculation should be performed for the types of waste mentioned above. If the methodology of (Adler et al 2004) is to be applied with its cautious assumptions on reference substances, then most of the ashes from virgin biofuels must be classified as hazardous waste. This would be in sharp contradiction with the recommendations (SFA 2001) of the Swedish Forest Agency which state that ash should contain between 0,1 and 0,7 % zinc figured as metal. The reason for this is that zinc is an essential element for all living organisms, and that it is necessary that the zinc withdrawn from the forest at harvesting of biofuels (branches and tops) is returned.

It may well be that the interpretation of the branch for 2,5 % together with the (at least in this case) very conservative assumptions on reference substances actually corresponds to the "requirement" of 0,25 %. For instance, the reference substance for zinc is (at present) zinc

oxide. The dissolution behaviour of zinc oxide in a water containing chloride ions is illustrated in Figure 1. The results in the Figure are based on thermodynamic calculations using equilibrium data from (Lindsay 2001). A comparison between the data in Figure 1 and those in Table 2 indicate that the experimentally determined values are 2 - 3 orders of magnitude lower than those expected using zinc oxide as the reference substance. Similar observations have been made also from other ash samples provided that they have been properly aged (but without contact with the carbon dioxide in the atmosphere). Actually, values observed for zinc in such leach water are frequently lower than what the Swedish Environmental Protection Agency states (SNV 1999) as being at or insignificantly above natural levels, i e 0,1 mg/litre. For a liquid to solid ratio of 10 this corresponds to a leach rate of 1 mg/kg which is considerably higher than the values presented in Table 2.

A reference substance that would much better concord with existing data is the zinc mineral Franklinite which might be described by the chemical formula $ZnFe_2O_4$. Iron is abundant in ash and is known to form sinks for transition elements in nature under oxidising conditions. Franklinite has a solubility in water that follows the same pattern as zinc oxide but the level is about three orders of magnitude lower (Lindsay 2001). Work is currently in progress with the aim to find out if it might be warranted to use Franklinite as the reference substance for zinc.

It is generally accepted, see e g (SNV 2005a) and (Van der Sloot 2005), that ecotoxic effects can for the most part be associated with content of harmful chemical species in water. It would therefore seem appropriate to scan the data bases on dangerous substances for ecotoxic test data on readily soluble substances and find correlations between content of various ions and effects on living organisms. Such a survey has been conducted but the results are discouraging since the effects from the same ion may vary by two orders of

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magnitude or so between different substances and tests. At least a partial explanation for this may be found in (Mikaelsson 2004a) where it is concluded that the total content of ionic species as well as the relative content of various species has a great influence on the results.

It must also be realised that the content of ions in general may have a profound effect on certain organisms, the natural habitat of which may be essentially ion-free. Testing of ashes must therefore be carried out using methodology that reflects the hazardousness and not the particular properties of a certain environment. It is also imperative that testing be carried out on samples that are properly aged and which thus are representative for the actual conditions. Ecotoxic testing of waste is planned to be carried out in a project under the auspices of the European Union. Hopefully, this and related work will result in methodology for assessment of environmental hazard based on leach data. It might be wise, however, to be prepared that it might take some time before such results are available.

Conclusions

Methodology is available for the cautious but practicable classification of waste from incineration, combustion, metallurgy and cleaning of metals according to the European Union Directive 91/689/EEC on hazardous waste (EUDHW). The key feature in this methodology is the identification of reference substances, one for each element of interest to health and environment. The reference substances represent the actual ones in a conservative but reasonably realistic manner, and they are represented in the databases on dangerous properties.

Ecotoxicity constitutes a special problem since there are requirements on compliance but no limits. Eventually, such figures can be expected to evolve, but it is pertinent to be prepared that such processes may require some time. In the meantime, assessments will have to rely on comparisons with what is declared by Authorities to be appropriate in similar applications. It is essential that any such comparisons be made with full awareness of the differences in character between the applications. Several examples of such assessments are presented, and it is hoped that they might serve as a basis for exchange of information as well as co-

operation, and perhaps also serve as reference cases in other countries.

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Table 1. Minor elements in ash at the store at the Tveta Recycling Plant in mg/kg (ppm by weight) figured as elements. Samples taken from drill hole A. Selection made based on interest with regard to ecotoxic properties.

Ele-						11-12	13-14	15-16	16-17
ment	0-1 m	2-3 m	4-5 m	6-7 m	8-9 m	m	m	m	m
As	28	30	28	22	10	13	13	19	19
Pb	99	119	97	72	47	81	95	105	105
Cu	114	110	130	95	80	100	91	71	71
Cr	132	150	134	126	112	115	116	80	80
Zn	203	194	179	144	123	204	271	519	519

Table 2. Leached fraction in mg/kg (ppm by weight) figured as elements in mg divided by dry weight of total in kilograms. Liquid to solid rate is 10 ml/g. Method used is SS-EN 12457-3. Statutory limits according to the acceptance criteria for disposal at a landfill for non-hazardous waste is also shown for comparison. Samples taken from drill hole A. Selection made based on interest with regard to ecotoxic properties. pH values of the leach water are also shown in the table.

Ele-						11-12	13-14	15-16	16-17	Legal
ment	0-1 m	2-3 m	4-5 m	6-7 m	8-9 m	m	m	m	m	limit
As	0,013	0,017	0,034	0,035	0,046	0,031	0,07	0,053	0,062	2
Pb	0,003	0,003	0,003	0,003	0,003	0,003	0,003	0,003	0,003	10
Cu	0,03	0,02	0,01	0,01	0,01	0,01	0,01	0,02	0,23	50
Cr	0,019	0,07	0,047	0,018	0,009	0,034	0,01	0,008	0,007	10
Zn	0,01	0,02	0,01	0,01	0,01	0,01	0,01	0,02	0,01	50
pН	9,4	10,3	10,0	9,8	9,7	9,9	10,0	9,7	9,0	

Table 3. Data from the Swedish Environmental protection Agency, cf text, on guideline values for contaminated soil.

Element	Kd = equilibrium constant soil- water (litres / kg)	Sensitive land use (mg/kg)	Less sensitive land use + use of ground water (mg/kg)	Less sensitive land use (mg/kg)
As	100	20	40	40
Pb	1000	150	300	300
Cu	500	100	200	200
Cr	2000	120	250	250
Zn	200	350	700	700

Table 4. Fraction in % of guideline value for less sensitive land use according to the Swedish Environmental Protection Agency, cf text, for ash at the store at the Tveta Recycling Plant. Samples taken from drill hole A. Selection made based on interest with regard to ecotoxic properties.

Ele-						11-12	13-14	15-16	16-17
ment	0-1 m	2-3 m	4-5 m	6-7 m	8-9 m	m	m	m	m
As	0,3	0,4	0,9	0,9	1,2	0,8	1,8	1,3	1,6
Pb	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Cu	0,8	0,5	0,3	0,3	0,3	0,3	0,3	0,5	5,8
Cr	1,5	5,6	3,8	1,4	0,7	2,7	0,8	0,6	0,6
Zn	0,0	0,1	0,0	0,0	0,0	0,0	0,0	0,1	0,0

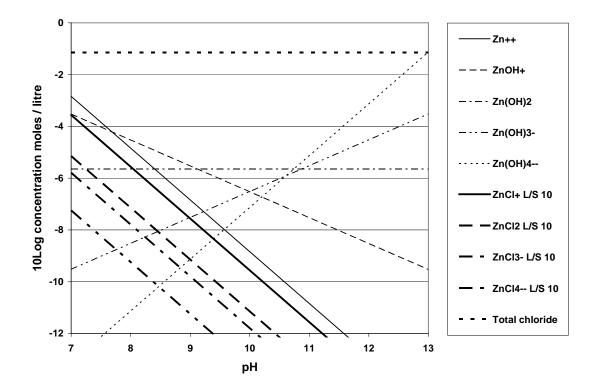


Figure 1. Concentration of various zinc species in water containing chloride as a function of pH. Results of thermodynamic calculations for which it is assumed that the water is in contact with solid zinc oxide.