Hazard evaluation for inorganic oxide materials having complex chemical form with emphasis on waste, recycled materials and by-products.

Rolf Sjöblom, Division of Waste Science and Technology, Luleå University of Technology

ABSTRACT

Before the year 2001, differentiation between hazardous and non-hazardous waste was made by using a checklist called the European Waste Catalogue (EWC). From the end of the year 2001, differentiation was to be achieved largely based on the features of the European Union Dangerous Substances Directive (DSD) and the Dangerous Preparations Directive (DPD).

Many inorganic oxide wastes such as ashes and certain residues from metals beneficiation have complex chemical forms that do not appear in the data bases for hazardous properties of various substances. Of course, the properties of a substance might be determined by testing. However, there are considerable variations in compositions between different industrial plants that generate ash, and often also between different points of exit. Therefore, full testing according to DSD is not feasible in practice.

Instead a method was developed based on the assumption that a residue can be regarded as a mixture of different reference substances where each such substance represents a certain chemical element in a realistic but cautious manner, and where each such substance appears in the data bases on hazardous properties. The method has successfully been applied to a large number of wastes from combustion, incineration and metals beneficiation.

It is expected that the legislation on classification of waste will soon be based on the new regulation for labelling of chemical substances, CLP. It is found that the method is applicable also in this case, but after some adjustment.

New national Swedish legislation under the recent EU Waste Framework Directive may imply that much of what has previously been regarded as waste will in the future instead be considered as recycled material and as by-products. Thus, the EU regulation REACH may apply in some cases, and it was found that the methodology developed for waste classification might be utilised also under REACH.

INTRODUCTION

Classification of waste into hazardous and non-hazardous governs how the waste will have to be managed. It is imperative that all waste that actually is hazardous also becomes classified as such so that adequate measures can be taken in order to protect health and the environment. However, waste that can be shown to be non-hazardous should also be classified as such in order to conserve resources through recycling.

For many categories of waste, classification is simple and easy. For other categories, e. g. combustion residues, classification is far from trivial. Actual forms of occurrence are very complicated, and the actual chemical species do not occur in the data bases for hazardous properties of various substances.

This issue is far from negligible for the companies and Authorities involved as well as for society. Over a million tonnes of ashes from wood-based fuel are generated each year in Sweden. For this ash, classification is essential not only for the appropriate handling but also for the proper utilisation as well as the safe disposal.

This has prompted Värmeforsk (the Swedish Thermal Engineering Research Association)[1-4] and others [5-6] to develop a method for classification of ashes into hazardous and non-hazardous under the ordinance of waste[I] which is part of the Swedish implementation of the European Union waste directive[II].

In addition, new legislation (CLP) is being introduced regarding labelling of chemical products. It is expected that CLP will constitute the basis for classification in the near future.

Moreover, the definition of waste has been clarified, and it is possible that much of what we regard as waste today might be considered as non-waste in the future. The basic requirements in the Swedish Environmental Code [III] applies to either case, but other legislation may be somewhat different. Much of the basis can still be found in the legislation related to labelling of chemical products.

OBJECTIVE AND SCOPE

The primary objective of the present paper is to briefly summarise the legal as well as the scientific basis for the Värmeforsk waste classification method, and to communicate some of the experiences made.

The objective is also to identify and discuss some issues to consider for the future in view of the new and anticipated legislation.

LEGAL BASIS

Many of the residues from combustion and incineration have double entries (mirror entries) in the European Waste Catalogue (EWC) [I,IV], and thus classification is mandatory.

There exists two alternatives for the classification.

According to alternative A, it is to be investigated whether the waste in question may possess certain properties that render it hazardous. The properties in question are as follows[I-II]:

H 1	Explosive
H 2	Oxidizing
H 3-A	Highly flammable
H 3-B	Flammable
H 4	Irritant
H 5	Harmful
H 6	Toxic
H 7	Carcinogenic
H 8	Corrosive
H 9	Infectious
H 10	Toxic for reproduction
H 11	Mutagenic
H 12	Waste which releases toxic or very toxic gases in contact with water, air or an acid.
H 13	Sensitizing (As far as testing methods are available)
H 14 ‘	Ecotoxic
H 15	Waste capable by any means, after disposal, of yielding another substance, e.g. a leachate, which possesses any of the characteristics listed above.

According to alternative B, a specific batch of waste is to be classified as hazardous if it possesses one or more of the following properties[I]:

- flame point ≤ 55 ºC,
- one or more substances that is/are classified as highly toxic at a total concentration ≤ 0,1 %,
- one or more substances that is/are classified as toxic at a total concentration ≤ 3 %,
- one or more substances that is/are classified as harmful at a total concentration ≤ 25 %,
- one or more corrosive substances that is/are classified as R35 at a total concentration ≤ 1 %,
- one or more corrosive substances that is/are classified as R34 at a total concentration ≤ 5 %,
- one or more irritant substances that is/are classified as R41 at a total concentration ≤ 10 %,
- one or more irritant substances that is/are classified as R36, R37 or R38 at a total concentration ≤ 20 %,
- a substance that is known to be carcinogenic (category 1 or 2) at a concentration ≤ 0,1 %,
- a substance that is known to be carcinogenic (category 3) at a concentration ≤ 1 %,

- a substance that is tetratogenic (category 1 or 2) and that is classified as R60 or R61 at a concentration ≤ 0,5 %,
- a substance that is tetratogenic (category3) and that is classified as R62 or R63 at a concentration ≤ 5 %,
- a substance that is mutagenic (category 1 or 2) and that is classified as R46 at a concentration ≤ 0,1 %,
- a substance that is mutagenic (category 3) and that is classified as R40 at a concentration ≤ 1 %,

Reference is made to the Dangerous Substances Directive (DSD)[V] and to the Dangerous Preparations Directive (DPD)[VI] as well as to their implementations into Swedish legislation through our rules for labelling of chemical products, primarily Reference [VII]. It is mentioned that the so-called "*R-values*" above as quoted from the ordinance of waste have the same meaning as the so-called "*risk phrases*" in Reference [VII]. The words toxic, highly toxic and harmful also have the same meanings in the ordinance of waste[I] and in the Swedish Chemicals Agency's classification and labelling regulations[VII]. The test methods to be used are the same as for assessments of the hazards of chemical substances.[VIII]

METHOD

Analysis of the alternatives A and B above soon resulted in the conclusion that alternative A is impossible to pursue in practice, since testing is cumbersome, and since ash is generated in moderate volumes at many exit points, and since its properties may vary over time. This would have been an enormous task.

Alternative B presupposes that the ash has been prepared by mixing various substances with known classifications. This alternative can be applied in a quite straightforwardly manner for organic molecules. However, the complex chemical forms of the inorganic constituents do not appear in the data bases for hazardous substances.

If the inorganic chemistry is not known, or the actual chemical species are not listed in the data bases, the possibility remains to make an analysis of the elementary composition and to make worst case assumptions. Knowledge of the chemistry involved may contribute such that hypothetical and unrealistic alternatives can be excluded.

This was essentially the route taken. In addition, it was found that it is reasonable to consider the conditions after initial contact with air and water. The forms chosen for reference were called reference substances. The relations between the reference substances and the various hazard properties are summarised in Table 1.

Table 1. The relation between the reference substances, R-values and 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**
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 $ZnFe_2O_4$													

Detailed analysis of the chemistry involved showed[1-6] that although several elements may initially form chlorides in the furnace system, such chlorides are for the most part rapidly hydrolysed as soon as the ash is contacted with water. It was also found that several elements, and especially those having ionic radii similar to those of iron, have a clear tendency to become strongly incorporated by solid solution in the iron-rich phases formed. Such mechanisms strongly stabilise the oxidation number +III for chromium.

These conclusions are reflected in Table 1 in which mixed oxides with iron are listed for chromium, nickel and zinc. However, caution must be applied in the assignments of such phases, and details of what ought to be considered can be found in References [1-6], see also [7].

CLASSIFICATION EXPERIENCE

It is apparent from the references on the domestic Swedish method development work[1-7] that there has been a continuous calling in question (by the author) of whether or not the method is sufficiently conservative and robust. The experience is that in no case has it been found that previous work (that has been challenged) has been found to be insufficiently conservative. Instead, it has in several cases been found warranted to reduce the caution applied.

In at least a few cases, the method has been discussed in conjunction with court cases on permits for district heating facilities as well as landfills / recycling stations. In such a court case (M 4182-02), the highest environmental court in Sweden accepted the use of the present method.

The method has (with the involvement of the author) been applied successfully to ash and slag from more than 30 sites, and typically there have been several types of ashes from each site. The facilities and activities in question include district heating, recycling/landfilling, steel mills, paper mills, and remediation of contaminated soil.

It can be concluded that the method is conservative, and yet reasonably precise. It is also efficient, and generally accepted. Its use has implied that large volumes of ash have been managed with appropriate caution with regard to health and the environment. The application of the method has also facilitated utilisation of ashes for geotechnical construction purposes, and has enabled for various ashes to be deposited at landfills of the appropriate classes.

There is also some international support for the method. For instance, the Technical Guidance M2[IX], issued by the competent environmental Authorities and appropriate for use in England, Northern Ireland, Scotland and Wales, put forward a scheme in its latter versions that is similar to the one described above. It should be added, however, that this is a general document that does not focus specifically on complex inorganic waste forms such as is the case for [1-7].

OUTLOOK FOR THE FUTURE

Conversion to CLP as the basis for hazard assessment

Until recent years, the labelling of chemical substances has been based on the dangerous substances directive (DSD)[V] first issued in 1967, and the dangerous preparations directive (DPD)[VI], first issued in 1999. The word "preparations" is to be understood as a mixture of substances, and DPD contains formulae by means of which calculations can be made on the dangerous properties of a mixture based on the relative proportions of different ingredients having different known classifications.

At present (January 2011) the rules for labelling are being changed from DSD/DPD to the new CLP regulation[X]. CLP stands for Classification, Labelling and Packaging of chemical substances. It is based on largely the same tests as DSD/DPD, but there are many more alternatives for labels. Also, the intervals in test results associated with the various labels are different. One important reason for this is that CLP is very similar to the rules for labelling issued by the United Nations, which are called GHS Globally Harmonized System).

At present, substances must be labelled according to CLP, but preparations (called mixtures under CLP) can be labelled with either of CLP and DPD until mid-2015 when all substances and mixtures of substances must be labelled according to CLP.

It intended that CLP will provide the basis also for classification of waste. In principle, accommodating for this change is straightforward since the underlying testing is similar. Conversions will be needed, however, since the relations between the test results and the labels they give rise to are different.

It should be noted that there are some difference in how the summations are made under the ordinance of waste[I] and according to DPD[VI]. There may also be differences between a revised ordinance and CLP.

Nonetheless, it is possible to conclude at this stage that the method for managing complex inorganic substances and mixtures described above appear to be equally applicable after the shift to CLP as the basis for classification of waste.

Definition of waste

The new waste directive[IIb] as well as its implementation in Swedish legislation[III] define when a production residue is not waste but a by-product, as well as when waste has been recycled and become a product.

According to Article 5 in [IIb], a residue should be regarded as a by-product if

(a) further use of the substance or object is certain;

(b) the substance or object can be used directly without any further processing other than normal industrial practice;

(c) the substance or object is produced as an integral part of a production process; and

(d) further use is lawful.
See the exact formulation in the Directive.[IIb]

According to Article 6 in [IIb], "certain specific waste" shall cease to be waste when it has undergone a recovery, and complies with specific criteria to be developed in accordance with the following conditions:

(a) the substance or object is commonly used for specific purposes;
(b) a market or demand exists for such a substance or object;
(c) the substance or object fulfils the technical requirements for the specific purposes and meets the existing legislation and standards applicable to products; and
(d) the use of the substance or object will not lead to overall adverse environmental or human health impacts.

Criteria (cf. above) are presently being developed at the Joint Research Centre of the European Commission. So far, one regulation has been issued and it deals with when certain types of scrap metal cease to be waste.[XI]

It should be noted, in particular, that the present waste directive[IIb] mentions "certain specific waste" while the previous version[IIa] mentions category of waste.

It can be expected that these new rules will lead to that much of what has previously been regarded as waste will in the future be considered as non-waste.

Non-waste, CLP and REACH

By-products as well as recycled material will not have the waste legislation as a shield to protect health and the environment. General requirements such as [III] still apply regardless of whether a substance is waste or not waste, but there is also legislation that applies specifically to non-waste, e. g. CLP[XI] and REACH[XII].

REACH stands for Registration, Evaluation, Authorisation and restriction of CHemicals, and applies to substances and their use. REACH is complex and will not be described here. The reader is instead referred to a separate report in English issued by Värmeforsk that deals with REACH and ash[8]. It is concluded that the method for classification of ash according to the ordinance of waste is feasible also under REACH and CLP. In particular, it offers the feature of lowering the threshold for registrations in cases where there are many moderately large batches of mutually varying composition.

Comments on testing

It should be realised that the European Union legislation not only implies coherence in the legislations between the various European Union Countries. There is also a requirement in the treaty of the European Union[XIII] to the end that different pieces of legislation must be coherent (see Articles 11:3 and 17:2).

The consequences of this requirement are obvious in the legislation related to chemical hazards. Contrary to the situation some years ago when each laboratory with any self-respect had its own sets of tests that it tried to promote, there are now standard tests that are pretty much accepted not only within the European Union but also more or less world-wide.[VIII]

On their internet site, the Swedish Chemicals Inspectorate puts forward that the classification according to CLP forms the basis for REACH, environmental protection, consumer products, hazardous waste, transport and storage, working environment, cosmetics and authorisation, see (http://www.kemi.se/en/Content/Rules-and-regulations/Classification-labelling-and-safety-data-sheets/).

The Swedish Government, in its preparations for the implementation of the new waste framework directive, has recurrently referred to CLP.

It can thus be anticipated that gaining acceptance for test methods specific to waste classification may prove to be an uphill battle. Of course, there may be good reasons for waste-specific tests. For instance, testing of ash for ecotoxicity has shown that ions of calcium and potassium may influence fresh water organisms, thereby concealing any conceivable effects of ions of heavy metals.

If waste-specific testing is considered, it must also be made very clear whether any such testing is to be performed on each batch, or on some reference substance. Ecotoxic testing is tens of times more expensive than testing for elemental chemical composition.

Alternatively, there are features in CLP as well as in REACH that enable a certain input within their frameworks. In the example just given, the ecotoxic testing under realistic saline conditions, using appropriate salt water organisms, may be used to select appropriate reference substances, similarly to what has been described above for other properties.

More specifically, CLP maintains the weighed averaging over various ingredients introduced by DPD, but in a more elaborate way. This is called bridging in CLP. Bridging is not possible in REACH since REACH deals almost exclusively with substances, not mixtures/preparations.

Instead, REACH offers the feature of read across, meaning that similar chemical compounds can be compared for assessments of hazards. This is described in [8], see also[XIV].

CONCLUDING REMARKS

The method for classification of ash described in this report has been successfully applied to a large number of ashes and similar, primarily in Sweden. The method has been found to be robust and conservative, and at the same time somewhat realistic such that recycling and landfilling are facilitated. It is designed to be suitable for ash that is generated in many qualities and in moderate volumes for each quality.

The method is equally applicable under CLP which is expected to replace DSD/DPD as the basis for classification in the near future. This will require some adaptation, however.

It can be expected that much of the ash generated will be regarded as non-waste in the future. For such ashes, compliance with CLP and REACH may be required. The present method is applicable also in such cases although adaptation is needed.

It is pointed out that CLP and REACH contain the features of bridging and read across, respectively, and that the potential advantages of working under the auspices of the legislation as it is should be considered.

So far, considerable efforts have been spent on assuring the reliability and quality of the method by recurrently calling the results in question, and by continual research. The material compiled and the results obtained would benefit from international peer review, which would either unveil deficiencies or validate conclusions (or both). Such publications may also influence other investigators to start related work, the results of which may be useful to us in Sweden. Publications can also be expected to improve acceptance, abroad as well as in Sweden. All this will support further and improved use of the method by those who are responsible for the ash.

REFERENCES, LEGISLATION

[Ia] *Ordinance of waste* (Avfallsförordningen). Swedish Government SFS 2001:1063. (In force during 2001-01-01 -- 2011-08-08)

[Ib] *Ordinance of waste* (Avfallsförordningen). Swedish Government SFS 2001:1063. (In force from 2011-08-09).

[IIa] *European Union Council Directive 91/689/EEC of 12 December 1991 on hazardous waste.*

[IIb] *Directive 2008/98/EC of 19 November 2008 on waste and repealing certain directives.*

[III] *Miljöbalken*. (The Swedish environmental code; in Swedish). SFS 1998:808.

[IV] *Commission decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision*

94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.

[V] *Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances as amended taking account of changes up to 1/08/2008.* It is commonly called the Dangerous Substances Directive, or DSD.

[VI] *Directive 1999/45/EC of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations* It is commonly called the Dangerous Preparations Directive, or DPD.

[VII] *Kemikalieinspektionens föreskrifter om klassificering och märkning av kemiska produkter.* (The Swedish Chemicals Agency's Classification and Labelling Regulations, in Swedish). KIFS 2005:7.

[VIII] *Council Regulation (EC) No 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).*

[IX] *Technical Guide WM2. Hazardous waste. Interpretation of the definition and classification of hazardous waste.* Published by the environmental agencies in England, Northern Ireland and Scotland.

[X] Regulation *(EC) No 1272/2008 of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.* This regulation is commonly referred to as CLP.

[XI] *Council regulation (EU) No 333/2011 of 31 March 2011 establishing criteria determining when certain types of scrap metal cease to be waste under Directive 2008/98/EC of the European Parliament and of the Council.*

[XII] *Regulation (EC) No 1907/2006 of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. This regulation is commonly referred to as REACH.*

[XIII] Consolidated version of the treaty of the European Union. Official Journal of the European Union C 83/15. 30.3.2010.

[XIV] How to report read-across and categories. European Chemicals Agency, Practical guide 6, 2009.

REFERENCES, OTHER

[1] Adler, P., Haglund, J.-E.,. and Sjöblom, R. *Guidance for classification of incineration residues according to the Ordinance of waste.* Värmeforsk (the Swedish Thermal Engineering Research Association), Miljöriktig användning av askor (The Swedish Programme on Environmentally Friendly Use of Non-Coal Ashes), Report 866, January, 2004.

[2] Sjöblom, R., Tham, G., Haglund, J.-E. and Ribbing, C. *Classification of waste according to the European Union Directive 91/689/EEC on hazardous waste from a Swedish application perspective.* CIWM Conference 12th – 16th June 2006, Paignton, Torbay, UK.

[3] Sjöblom, R. *Tillämpning av avfallsförordningen SFS 2001:1063; Bidrag till kunskapsbasen avseende förbränningsrester.* Värmeforsk (the Swedish Thermal Engineering Research Association). Miljöriktig användning av askor (The Swedish Programme on Environmentally Friendly Use of Non-Coal Ashes). Rapport nummer 1103, mars 2009.

[4] Sjöblom, R. and Noläng, B. *The significance of solid solution in iron (hydr)oxides for stabilization of elements potentially harmful to health and environment.* (Betydelsen av fast löslighet i järn(hydr)oxider för fastläggning av potentiellt miljöstörande ämnen i askor, in Swedish). Värmeforsk (the Swedish Thermal Engineering Research Association), Miljöriktig användning av askor (The Swedish Programme on Environmentally Friendly Use of Non-Coal Ashes) 1198, November, 2011.

[5] Sjöblom, R., Tham, G., Haglund, J.-E. and Sjöö, C. *Environmental qualification of ash from wood-based recycled fuels for utilization in covers for landfills*. Kalmar ECO-TECH ´05 and The Second Baltic Symposium on Environmental Chemistry. Kalmar, Sweden November 28-29, 2005.

[6] Sjöblom, R. *Basis for selection of reference substance for zinc for classification of ash under the ordinance of waste.* (Underlag för val av referenssubstans för zink inför klassning enligt Avfallsförordningen, in Swedish.) Avfall Sverige - Swedish Waste Management, Report F2007:03, 2007.

[7] Sjöblom, R. and Noläng, B. *On the significance of solid solution in iron (hydr)oxides for immobilisation of potentially polluting elements in ashes.* Proceedings of Ash Utilisation 2012, Ashes in a Sustainable Society. Värmeforsk, January 25-27, 2012, Stockholm, Sweden.

[8] Sjöblom, R. and Tivegård, A.-M. *Methodology for qualification of wood-based ash according to REACH - prestudy.* Värmeforsk, Miljöriktig användning av askor, Rapport 1127. Februari, 2010.