Validation of a European Standard or the Determination of Acid Potential and Neutralization Potential of Sulphidic Waste

Tommi Kaartinen and Margareta Wahlström

VTT Technical Research Centre of Finland, Biologinkuja 7, 02150Espoo, FINLAND,Tommi.Kaartinen@vtt.fi, Margareta.Wahlstrom@vtt.fi, tel. +358 20 722 111

Abstract
This paper describes the development stages of the European static test method prEN 15875 "Static test for determination of acid potential and neutralization potential of sulphidic waste" developed for waste sulphide bearing materials which may generate sulphuric acid when subjected to weathering. In the test procedure specified methods for determining both the acid potential and the neutralization potential of the material are presented.

Robustness testing is the first step in validation of a European test method. The objective is to assess the sensitivity of the test with respect to variations in parameters that are potentially critical to the result of the test. We studied 8 test conditions, with one condition being a combination of the two acid addition steps into one atthe beginning of the test. According to the results, this modification gave no significant differences in results.

The second step in the development of a European standard is an inter-laboratory comparison study. For development of this standard we used5 waste samples and 18 participating laboratories. Generally, the results show good reproducibility. One sample exhibited larger variations than the other samples. Here possibly the pH sensitivity of the sample may have caused the difference.

Key Words: static test, robustness testing, inter-laboratory comparison, reproducibility

Introduction
European Directive (2006/21/EC) on the management of waste from the extractive industries lays down requirements for the safe management of extractive waste including proper characterization of the waste. The directive covers wastes arising from prospecting, extraction, treatment and storage of mineral resources and from the working of quarries.

The waste characterization includes both physical and chemical properties. The Directive states that the waste to be deposited in a facility shall be characterized in such a way as to guarantee the long-term physical and chemical stability of the structure of the facility and to prevent major accidents. Harmonized test methods are to be used in waste sampling and analysis. European Commission Decisions on "definition of inert waste" and "technical requirements for waste characterization" give further guidance for the implementation of the Directive and set requirements on testing or evaluation of specific properties in waste characterization.

In 2006, the European Commission gave a mandate to the European Committee for Standardization(CEN) for the development of standardized methods relating to the characterization of wastes from the extractive industries. The mandate specifies particularly the following tasks:

- guidance on characterization of extractive waste
- guidance on sampling
- test methods for determination of acid generation behavior (including both static and kinetic testing)
- sampling and analysis of weak acid dissociable (WAD) cyanide discharged into tailings ponds

In CEN the practical work is done in working groups. For this work Working Group 8 (WG8)called "Wastes from the extractive industry" was established in 2005 under CEN's Technical Committee 292. WG8 has active members representing 14 national standardization bodies.

As deliverables of these work tasks CEN will publish documents with different status in CEN document hierarchy. Static tests will be published as an European Norm (EN) which has the highest status. Deliverables from the work task on WAD cyanide will be published as a Technical Specification (TS), which is not avalidated method and hasa limited existence time of 6 years. Other deliverables will be published asTechnical Reports (TR), which arenon-normative documents. However, the status of the Technical reports may be for a specific purpose raised by a decision of the European Commission.

European Norms developed by the CEN are to be reviewed at least every five years to ensure that an EN is still current. Development of an EN takes about three years and includes two enquiries (the first seeks comments from all CEN standardization bodies and the second is a formal vote for the approval of the final draft). The CEN procedure for development of EN documents also sets requirements for the validation of the test methods before methods are accepted for publication and use.

The mandated work started in April 2009 and all work tasks will be completed during 2012. The starting point for all tasks was the evaluation of existing standards and assessment of their applicability to extractive waste, and the identification of needs for modifications.

This paper concentrates on describing the steps in the validation of the static test EN 15875. Background and rationales for the choice of the static test method to be standardized have been described only briefly here. They have been discussed in detail earlier (Kaartinen and Wahlström 2009).

Background for the Choice of the Method

Static tests are designed for the single purpose of measuring an extractive waste's capacity toproduceacidity and its acid neutralization capacity. Accordingly, static tests are commonly used for screening purposes and to provide an answer to whether the mine waste material has a potential to be an acid producer or an acid neutralizer using a finely ground sample. These tests do not consider parameters such as the actual availability of acid-producing and acid-neutralizing minerals in coarse materials and differences between the respective dissolution rates of acid-producing and acid-neutralizing minerals.

As discussed in detail in a previous document (Kaartinen & Wahlström 2009), Working Group 8 (WG8) chose the method developed by Lawrence and Wang (1996) to form the basis of the static test to be standardized. Calculation of acid potential (AP) as described in the modified acid-base accounting (ABA) by Lawrence and Wang is done based on the sulphide-sulphur content of the material. Determination of neutralization potential according to Lawrence & Wang is performed on a pulverized sample by adding water and pre-determined amounts of acid to the suspension. The so called Fizz-test is used as a preliminary test to roughly estimate the amount of calcium carbonate in the sample and thus the amount of acid added to the test suspension in the early stages of the test. In the Fizz-test a few drops of strong hydrochloric acid are added to a small amount of pulverized sample. The intensity of bubbling caused by the acid is evaluated on a sensory basis and the acid amount to be added is chosen from four alternative categories based on the intensity. The suspension is mixed throughout the test. Acid is added at the beginningand after two hours of mixing. After 22 hours the pH of the suspension is measured and, if needed, adjusted to between 2.0 and 2.5.After 24 hours the test is terminated and the suspension is back-titrated with base to pH 8.3. The acid consumed in the test is converted to neutralization potential (NP) in calcium carbonate equivalents (kg $CaCO_3$/t of waste).

Validation of Static Test EN 15875

According to CEN rules,validation of standardized environmental test methods usually begins by creating the first draft standard based on experts' opinions (CEN 2008). The second step is robustness testing to assess the sensitivity of the test with respect to variations in parameters that are potentially critical to the result of the test. After robustness testing the draft standard is revised based on the findings.The final step of the validationisan inter-laboratory comparison study, which is performed to evaluate the repeatability and reproducibility of the method and to produce the performance characteristics thatare then incorporated into the final draft standard.The first of the two previously mentioned enquiries takes places after the first draft of the standard is created. Latter enquiry, the formal vote, is arranged with the final draft standard.

It is to be noted that in a validation protocol not all waste types and ranges of properties can be covered. Samples used to produce the data described in the following sections were chosen by experts in WG8 to represent as well as possible the different operations and sulphidic waste types that are common in the extractive industries.

Robustness testing

WG8 experts drafted the first version of the static test standard in 2008 for CEN enquiry. Main differences betweenthe first draft of EN 15875 andthe Lawrence and Wang method are:

- the Fizz test was replaced by the determination of carbonate-carbon content and thus the carbonate rating (CR) to pre-determine the volume of acid added in the early stages of the test
- EN 15875 had 10 categories for acid volumes instead of the 4 categories of the Lawrence and Wang method
- an upper limit for the volume of acid added at 22 hours was set to be 50% of the total volume
- the results were to be expressed in mol H^+/kg in parallel with kg/$CaCO_3$.

After the CEN enquiry the robustness testing of the method could be started. In the robustness testing the sensitivity of some of the most critical test parameters wastested.

Determination of neutralization potential

Neutralization potential parameters studied in the robustness testing includedthe timing of the acid additions in the test, test temperature, end-point of back-titration and the means of mixing the suspension during the test. The results from the robustness testing were evaluated statistically and some of the testing conditions were further adjusted.

An interesting, and perhaps the most important, finding from the robustness testing was the observation that combining the two acid addition steps at t=0 and at t=2 into one acid addition step at t=0 h made no significant difference in the results on a wide range of NPs with tailings and waste rock samples from different operations and origins. This combination of acid addition steps was thus introduced to the standard draft in order to bring more flexibility to the execution time of the test within working hours and reduce possible sources of errors in the procedure. Figure 1 shows the comparison between the original 2-stage acid adding procedure and the adopted 1-stage acid adding procedure.

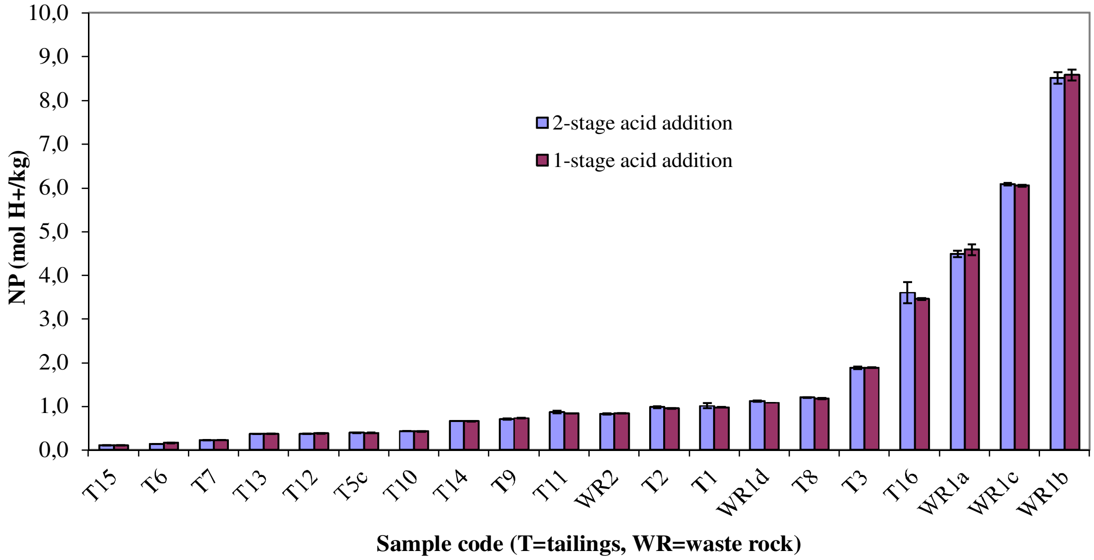

Figure 1. Comparison of NP values with 1-stage and 2-stage acid additions in the static test. Error bars show the standard deviations based on two replicates.

Determination of acid potential

Analysis of total sulphur to determine acid potential is a well-established method with a high potential of automatization. Total sulphur determination is therefore the default methodin EN 15875for the calculation of acid potential.

For the analysis of sulphur species no international standards are available. Speciation of sulphur compounds is a difficult task and varies with the material to be analyzed. A number of different methods have been developed and are used in the mining industry worldwide.

As part of the robustness study for standard EN 15875 nine waste samples were analyzed for sulphur species by 7 laboratories withcoal or metal mining background using different methods to produce informative guidance on the determination of sulphur species. Sulphur species have different thermal stabilitiesupon combustion andsulphides, especially pyrite, requirelower combustion temperatures than do sulphates, which typically have low or no acid potential. This fact is used for direct determination of pyrite at a temperature of about 800°C in an automated sulphur analyzer. Alternatively in standard ASTM E-1915the sulphide-sulphur is determined by roasting (pyrolysis) the sample in an oven at a temperature of 550°C or 650°C. After roasting the sulphur content of the pyrolysis residue is determined. Sulphide-sulphur is calculated by subtracting sulphur in the roasted sample from sulphur in the untreated sample (= total sulphur).

Another speciation method for coal is given in standard ISO 157. Samples are treated with HCl for sulphides and with HCl plus Cr^{3+} for disulphide (pyrite) to form hydrogen sulphide, which is collected and its concentration determined by titration.Other methods (eg,ASTM E-1915) remove sulphates and determine sulphide-sulphur in the leached residue. Sulphate-sulphur is extracted with a hot aqueous carbonate solution; some do an additional extraction with carbon disulphide to remove elemental sulphur. Sulphate-sulphur can also be determined directly by extraction with a carbonate solution and gravimetrical measurement of $BaSO_4$ after addition of barium chloride. Sulphide-sulphur is calculated by subtraction of sulphate-sulphur from sulphur in the untreated sample (= total sulphur).

Another method is described by Sobek et.al (1978). Sulphates are extracted with HCl at about room temperature and the sulphate-sulphur is calculated by subtraction of sulphur in the treated residue from sulphur in the untreated sample (= total sulphur). Pyritic sulphur is removed by treatment with hot HNO_3; pyritic sulphur is sulphur in the HCl-treated residue minus sulphur in the HNO_3 – treated residue. Non-extractable sulphur is the sulphur in the HNO_3 – treated residue. Often a so called “modified Sobek procedure” is applied using hot instead of cold HCl.

The results from this comparison are compiled in an informative annex of EN 15875 and can be summarized as follows:

- When the main constituent of sulphidic minerals is pyrite, all different methods give similar results and may be used.
- When a major part of sulphidic minerals is non-pyritic, the results are variable.
- Higher thermal stabilities are found for minerals that contain other metals (eg,iron); this is the casefor Pentlandite ($(Fe,Ni)_9S_8$) and even more for mono-sulphidesuch asgalena (PbS) and sphalerite(ZnS). Therefore all methods that use low temperature combustion show systematically lower values. If these minerals are present it could be advisable to use carbonate leaching or a direct method. Also the modified Sobek procedure can be applied.

Inter-laboratory comparison on the determination of neutralization potential
In the inter-laboratory comparison organized by CEN/TC 292/WG 8 18 participating laboratories were asked to perform the determination of neutralization potential according to standard draft prEN 15875 for five mining waste samples. Laboratories were given the carbonate carbon content as necessary as preliminary data for the determination of NP.

Samples for inter-laboratory comparison were selected to represent different types of wastes (tailings and waste rock) from different mining operations (coal mining and enrichment of different metal ores). The range of neutralization potential (NP) covered by these samples was selected to represent typical NPs found in extractive wastes.

The number of samples was limited to five since the participating laboratories worked on a voluntary basis andthis was seen as a maximum number to be worked on with without monetary compensation. Samples were tested for homogeneity and stability with regard to neutralization potential.

The inter-laboratory comparison was executed during 2010. Results were evaluated according to standard ISO 5725-2. Table 1 shows an overview of the most important data (relative reproducibility and relative repeatability standard deviation) produced in the comparison. Thesedata form the performance characteristics of static test EN 15875.

Table 1.Summary of performance characteristics for the determination of neutralization potential according to EN 15875.

Material	p	N	O	Mean NP mol H^+/kg	s_r %	s_R %
Waste rock from mining of Zn-, Cu-, Au- and Ag-ore	18	36	2 1)	0,750	1,28	10,5
Coal mining waste	17	34	2 2)	0,653	2,07	16,5
Tailings from enrichment of Zn- and Pb-ore	18	36	2 2)	1,69	1,36	12,9
Tailings from enrichment of Ni-ore	17	34	2 2)	0,870	2,90	40,6
Tailings from enrichment of Au-ore	17	34	0	3,65	1,56	10,8

p is the number of participating laboratories
N is the number of observed values
O is the number of rejected laboratories
s_r is the relative repeatability standard deviation
s_R is the relative reproducibility standard deviation

1) statistical outliers
2) rejections based on non-compliance with the protocol

Working Group 8 experts agreed that generally the results indicated a good repeatability and reproducibility.The high reproducibility standard deviation found for sample “Tailings from enrichment of Ni-ore” was judged to be caused by the presence of serpentine – a silicate mineral - as the main neutralizing mineral of this material. Silicate minerals are, in general,slower to react than carbonates in the conditions of this test method. Therefore, as a result from this comparison it was decided to further emphasize in the test description the importance of proper mixing of the test slurry in order to provide for the reaction of available neutralization potential.

In some cases the laboratories had difficulties completing the tests usingthe pre-determined acid additions. These findings resulted in slight modifications of the test description. After the comparison, the standard has been modified to allow an initial volume of acid to deviate from pre-determined volumes if neither a smaller nor a bigger volume of initial acid addition has led to completion of the test.

Finalization ofStatic Test EN 15875

European standard EN 15875 consists of four steps:

- Determination of total sulphur by bomb (standard EN 14582) or high temperature combustion (standard ISO 15178) and calculation of acid potential (AP). Instead of total sulphur, sulphides may be determined using techniques described above and in an informative annex of EN 15875.
- Determination of carbonate content by dry combustion (standard EN 13137:2001, method A) to give the carbonate rating (CR).
- Determination of the neutralization potential (NP) by hydrochloric acid addition to reach pH=2 to pH=2,5 and back titration with sodium hydroxide to reach pH=8,3 after a reaction time of 24 hours.
- Calculation of the net neutralization potential (NNP) and the neutralization potential ratio (NPR) based on AP and NP.

After the inter-laboratory comparison the performance characteristics were brought to the draft standard along with the other above described “fine tunings” of the method. The final draft of the standard EN

15875 was subject to formal votingamong EU member states during 2011. Theresult was positive meaningthat the standard could be published as a European Norm in October 2011.

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Acronyms

CEN	European Committee for Standardization
CR	Carbonate Rating
EN	European Norm
NPR	Neutralization Potential Ratio
TR	Technical Report
TS	Technical Specification
WAD	Weak acid dissociable
WG8	Working Group 8 under Technical Committee 292 of CEN